

40 YEARS OF  
CATALYSIS  
RESEARCH

RUTGER VAN SANTEN'S Journey  
through *Chemical Complexity*

**40 YEARS OF**  
**CATALYSIS RESEARCH**

Edited by EMIEL J.M. HENSEN

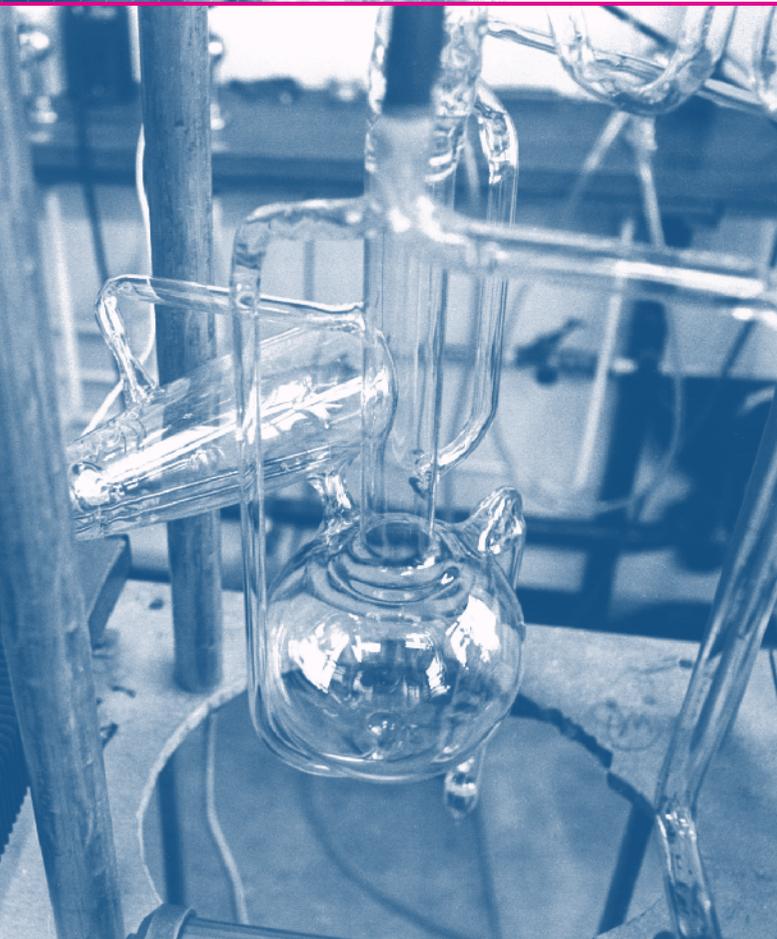
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*To my dear wife, Edith, who is my muse;  
to my children, who are our joy:  
Hanneke, Marieke, Suzanne, and Bas;  
to my grandchildren, whom we adore:  
Niels, Julie, Marius, Lotje, Gavin, Milan,  
Simone, Yordin, and Edwin.*



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# PREFACE

By *Emiel Hensen*

Emiel Hensen is professor of heterogeneous catalysis at TU/e. He researches the development of clean and sustainable processes for the production of fuels and chemicals. His focus is on synthesizing complex catalyst systems that contain well-designed catalytically active ensembles and are structured at various length scales to optimize reaction and diffusion. He has been awarded the prestigious VENI and VIDI grants from the Netherlands Organization for Scientific Research (NWO).

**THIS FESTSCHRIFT** celebrates the achievements of Rutger van Santen throughout his career of forty years in catalysis research. Not only is this a wonderful occasion for Rutger and his colleagues to look back and recount his many successes and advances in understanding catalysis during this time, but it is also an opportunity for this compilation of his life's work to inspire a new generation of researchers in finding solutions to today's and the future's problems. Every scientific field needs driven, farsighted leadership, and catalysis in the Netherlands had the great fortune of securing Rutger in that role during its formative years. His collaborative approach, enquiring mind, strong theoretical background, multidisciplinary style, and adeptness with new technologies—this combination of qualities ensured that Rutger made many inspiring contributions to catalysis research.

Rutger van Santen received his PhD (with *honors*) in 1971 for his thesis, “On the Theory of Resonant Scattering,” under Luut Oosterhoff, his thesis advisor. He then joined Shell Research Amsterdam, where he became interested in catalysis, a love affair that would last a lifetime. In 1986 he became a part-time professor and, two years later, full professor of catalysis at Eindhoven University of Technology (TU/e).

His vast research interests include a wide range of subjects in the field of heterogeneous catalysis: the study of mechanisms, materials synthesis, and computational modeling, to name just a few. Rutger's work has contributed significantly to the present wide and general current acceptance of computational catalysis. He formulated reactivity rules of heterogeneous catalytic reactions on the basis of first-principle quantum mechanical methods. He was also the first to calculate activation-free energies of a surface dissociation reaction.

Rutger's understanding of the Fischer-Tropsch reaction led him to discover the oligomerization of methane. He used this new reaction to make labeled hydrocarbons with positron-emitting atoms and thereby track reaction profiles in zeolites. He also proved that a surface oxide is needed for the epoxidation of ethene and that this oxygen determines selectivity. This counterintuitive result was rewarded with the Golden Medal of the Royal Netherlands Chemical Society (KNCV).

Experimental studies strongly supported his computational work. Highlights are the infrared (IR) spectroscopic study of proton transfer in zeolites and nuclear magnetic resonance (NMR) studies of the siting of hydrocarbons in zeolites. Rutger studied the synthesis of zeolites with small-angle-wide-angle

x-ray scattering (SAXS-WAXS) techniques, solid-state NMR, and simulations. He was the first to recognize that silica agglomerates self-assemble around a template in a solution before crystallization. This work is of great interest for zeolite synthesis and has led to the synthesis of novel, very well-defined hybrid inorganic-organic catalytic systems. A start-up company is now exploiting the new silsesquioxane catalysts he developed. Rutger continues to focus on the theoretical analysis of reaction kinetics, using calculations of transition states, reaction rate constants, and time-dependent Monte Carlo methods. He also studies in situ spectroscopic techniques, biomimicry, and energy systems.

So far, Rutger has supervised more than eighty PhD students. He attracted and inspired PhD students and postdoctoral researchers from all over the world, several of whom became leading experts in their fields. The results of the research of Rutger van Santen and his students and coworkers were presented in more than 630 original papers in international journals, hundreds of oral contributions at international conferences, universities, industrial laboratories, and research centers, six monographs, and forty-six contributions to books. Indeed, this is simply too much science to cover in a one-volume festschrift, but with Rutger's aid (of course) I made an attempt to review his main topics, grouped according to the research highlights he selected himself. Each topic begins with an introduction by a colleague who, at some stage in Rutger's career, became inspired by his enthusiasm for catalysis science and technology and reflects on these initial contacts. Everybody in the catalysis community knows Rutger for his ability to dissect complex issues, which we invariably encounter in catalysis research, into general and basic concepts that often prove invaluable in quite different subfields of catalysis.

Because of his broad research achievements, Rutger has received many honors including the Alwin Mittasch Medal, the Spinoza Award, and an Academy Professorship—to mention just a few. He is a foreign associate of the United States National Academy of Engineering and holds an honorary doctorate from the National Ukrainian Technical University. Moreover, his activities in organizing science deserve special recognition: after having brought together Eindhoven scientists with a warm heart for catalysis research in the Schuit Institute of Catalysis in the early 1990s, he became the founding father of the Dutch catalysis graduate school, NIOK, which has served, and continues to do so, as the organizational model for many catalysis communities abroad. From NIOK and the unprecedented level of cooperation it entailed, many other initiatives sprung up. A direct result of his ability to bring together top scientists from “adjacent” fields has been the National Research School Combination Catalysis (NRSC-C), which had a huge impact on the catalysis landscape in the Netherlands. His creativity and talent lifted catalysis research at Eindhoven to a world-class level.

It has been my extreme pleasure to be involved in the composition of this festschrift as an expression of my esteem for the outstanding contribution of Rutger van Santen to the field of catalysis and for his impact on the Dutch School of Catalysis and our university. I hope it will serve as a source of inspiration to the reader, and also to Rutger himself, to continue his scientific activities in our research group with the same tenacity and perspicacity as ever.

*Eindhoven, June 2012*



## 1.1

# OBSERVING THE PROFESSOR

By *Marcel van Buijtenen*

Written in 2010 as a reflection on a presentation given  
by RUTGER VAN SANTEN (original in Dutch).

### POÈSIS

De professor praat  
praat energie over zijn voetlicht heen  
vult zijn proscenium met zijn geleerdheid  
verpakt zijn kennis in olie als beste  
transportmiddel

middelen zijn onmisbaar soms te laat  
soms op tijd ondervraagt hij de geleerde  
wereld en zoekt continu naar tijd  
juist op tijd

ingenieurs veranderen de wereld  
ze lopen aan de hand van de maatschappij  
welke technologie denken ze  
heb ik nu nodig

dan vraagt hij, vraagt hij zich hardop af  
hoe maak ik dat en tegelijk gelooft hij  
in de maatschappij draait alles om  
als de wetenschapper de basisvragen  
blijft stellen wat ik geloof

### POÈSIS

The professor talks  
talks energy across the footlights  
fills his proscenium with his learning  
knowledge packed in oil as the best  
vehicle

resources are indispensable but too late  
or timely he interrogates the learned  
world and continuously seeks time  
just in time

engineers change the world  
they walk alongside society  
what technologies they think  
do I need now

then he asks, he asks himself aloud  
how do I create that while he believes  
in society all will turn around  
as the scientist continues to ask  
the basic questions of what I believe

# 1

## Chapter 1

# From Computational Science to Catalysis

## RUTGER'S PENDULUM

### *Catalysis between Industry and Academia*

By *Ton van Helvoort*

Ton van Helvoort was educated as a chemist and for a quarter of a century he has been an independent researcher and writer in the history of science. At the moment he is working with the Foundation for the History of Technology affiliated to TU/e.

When, shortly before the dawn of the twenty-first century, the editors of the Dutch science journal *Natuurwetenschap & Techniek* asked Rutger van Santen what he considered to be the most important work of popular science, he surprised them by picking a fifty-year-old book by the Anglo-Irish chemist, crystallographer, and historian of science John Desmond Bernal, *The Social Function of Science*.<sup>[1]</sup> Explaining his choice, Rutger said that the text illustrates “how the exploitation of invention or interest in a given field of science can be closely aligned with societal needs and successful social use.” The development of science is driven by curiosity on the one hand and the potential applications of that science on the other. Rutger had learned through three decades of research that scientific development—and hence the emergence of new disciplines and subdisciplines—does not happen by itself like some force of nature, but is the work of human beings.

Research does not come cheap and those who fund it—whether governments, industry, or philanthropists—have to be persuaded that it makes sense to invest their money in the practice of science. If the scientific community wants to secure that funding, it has to sketch out attractive prospects—the “endless frontier” of the nature of matter, for instance,

or applications of nanotechnology in *Thinking Pills*.<sup>[2,3]</sup> Meanwhile, persuading potential financiers is just one side of the coin: the other is all about getting scientific researchers organized.

The practice of science has become so complex that efforts have to be pooled, taking account all the while of the competition that exists between universities and semipublic research institutes, for instance, or between different countries. A specific branch of chemistry that has taken independent shape in the Netherlands over the past four decades is that of catalysis. The Dutch chemical industry expanded enormously after World War II, with catalysts playing a major part. Scientific research into catalysts contributed immensely to improvements in processes and products alike. That research, however, was also extremely diverse, with contributions from many disciplines of chemistry and physics.

Over the past four decades Dutch scientists have made great efforts to structure and organize catalysis as a field of research. Boundaries between disciplines were dismantled in order to achieve interdisciplinary cooperation, and competition and turf wars between institutions were overcome. The collaborative ties that resulted convinced national, regional, and local government of the importance of catalysis research, and industry was

sounded out about public-private partnerships. These developments did not occur in catalysis alone, but in many more fields besides—the most obvious result being the numerous high-tech campuses now linked to the country's universities.

This deliberate profiling of catalysis research means that it is now practiced in the Netherlands at an international level. All the same, the emergence of catalysis as an integrated, multidisciplinary field reflects considerable work by individual people. This can be illustrated with another example—namely, biochemistry—a hybrid of chemistry and biology that has become so familiar that it now seems more like another “natural” discipline alongside chemistry or physics.

Biochemistry in the strict sense, however, is barely half a century old, even if it has obvious precursors like physiological chemistry, which played a significant role in medicine. It is only half a century or so ago that biochemistry first carved out its place within the Dutch university curriculum, but it was able to establish itself as an autonomous field as practitioners worked hard to distinguish it from medical and other applications. To fund the expensive apparatus that was needed, the government was asked to provide money to advance the boundaries of science without any certainty of direct social utility.

The development of catalysis research in the Netherlands has swung like a pendulum between justification as “science for science's sake” and the prediction of applications capable of boosting the economy, solving environmental problems, and contributing to a more sustainable society. Achieving these goals also meant bringing together researchers active in fields relevant to catalysts, and then keeping them together.

Although the prominent international position now enjoyed by Dutch catalysis research was not the work

of just one man, Rutger was certainly a driving force behind that research, backed by TU/e and its Department of Chemical Engineering and Chemistry. This chapter describes how it all came about, with a particular focus on how scientific catalysis research was justified in terms of both curiosity-driven study and social utility. Rutger does not flinch from the administrative demands made by research of this kind, which meant he was able to exert considerable influence on the field. Even more importantly, he successfully established the framework in which public and corporate (private) interests and expectations could come together. The high level of the research in which he and his group were engaged meant, moreover, that he was able to speak with authority and that his voice was heard. Rutger kept the pendulum of catalysis in constant motion between academia and industry, raising the profile of the field enormously as he did so.

### *Biochemist manqué?*

Rutger van Santen trained as a theoretical chemist at Leiden University, suggesting that he has travelled a long way, given that he is now seeking to orient catalysis research toward man-made biocatalysts and to contribute to a sustainable society in the twenty-first century. The journey does not seem as long, however, when we realize that Rutger had a strong interest in biology in his youth. He belonged to the Dutch Youth Association for Nature Study (NJN), for instance, and he initially chose to study biochemistry at university. However, having attended lectures by Professor Luut Oosterhoff on theoretical organic chemistry, Rutger's imagination was captured by quantum mechanics: theoretical chemistry was generating surprising new insights. This fascination led in due course to his thesis, *On the Theory of Resonant Scattering*, for which he gained his PhD (with *honors*) under Oosterhoff in 1971.

A year later Rutger joined Shell Research Amsterdam, thus making a first swing. There, Oosterhoff held a part-time position. It soon became apparent that Shell did not have much use for a theoretical chemist, and so he was asked to apply his expertise to catalysis. One of the topics Rutger worked on during his sixteen years at Shell was uncovering the mechanism of selective oxidation of hydrocarbons. He also worked at Shell Development Company in Houston, Texas, from 1982 to 1984.

The chemical industry tends to be conservative with respect to applied technology, so it is usual for a particular catalyst technology to have a long half-life stretching to many years, if not decades. Consequently, new technology only filters through gradually into industry. When exploratory research in the chemical industry failed to live up to expectations in the seventies, the multinationals cut back sharply on R & D spending, refocusing their efforts on the development aspect rather than on fundamental research. Rutger van Santen decided in the latter half of the eighties that he wanted to commit himself to scientific research, which therefore meant moving from industry to academia. Thus, Rutger's love of research prompted a switch in 1986 to the Department of Chemical Engineering and Chemistry at TU/e, where he was appointed associate professor of surface chemistry. Two years later he completed his second swing in becoming full professor of catalysis.

### *The TU/e and the Schuit Institute of Catalysis*

Standard practice at his former employer was for working arrangements to be made between the people with overall responsibility for the research and those who actually carried it out. Everybody else was expected to keep their distance. At Eindhoven, Rutger was immediately confronted

with a form of widespread democracy and participation that was totally at odds with what he had been used to at Shell. Although the traditional committee culture within the Dutch universities was already in decline by the late eighties, the best way to deal with it was still to create your own networks and organizations.

Catalysis research had been performed at Eindhoven by people like George Schuit (1961–77), his successor, Roel Prins (since 1978), and Johannes van Hooff (since 1972), but in the context of inorganic chemistry. There were countless informal contacts at the TU/e in the seventies and eighties with industry, which was the breeding ground for chemistry and physics at recently founded universities such as those in Nijmegen, Eindhoven, and Twente (and others that underwent a growth spurt in the same period).

This, then, was the situation Rutger van Santen encountered at Eindhoven in 1988 when he succeeded Roel Prins: a chemical engineering department with good contacts in the chemical industry. The department even had an Industrial Advisory Council. Catalysis was not really an academic specialization at all, and industrial catalysis was seeing little in the way of technological innovation and certainly very few radical breakthroughs. Academic heterogeneous catalysis research was biased toward inorganic, physical, and surface chemistry. In the meantime, however, a great many new scientific specializations had arisen, holding out great promise for the improvement, renewal, and optimization of catalytic reactions. With the help of ancillary sciences like spectroscopy and other analytical techniques, mathematics and computerization, new theoretical insights, and materials science, it now became possible to build a bridge between the empirical manner in which many traditional catalysts were developed and new possibilities, such as molecular design, the creation

of microscopic, kinetic models, and the development of catalytic reactor engineering. Groundbreaking innovations occurred: fluid dynamics, catalyst design, reactor design, and numerous types of spectroscopy.

It was evident by the late eighties that catalysis research would necessarily have to be interdisciplinary in character and that it was vital for fundamental research in chemistry and chemical engineering—that is, the process aspects, to be pursued side by side. An interdisciplinary organization was needed to enable this collaboration to occur, to facilitate cooperation with industry, and to attract funding. Rutger van Santen was one of the prime movers behind the achievement of that collaboration, thanks to his willingness to take on the administrative work (as witnessed by several chairmanships) and the clarity of his analysis.

The Schuit Institute of Catalysis, for instance, was set up at TU/e in 1989, focusing primarily on heterogeneous catalysis. The key aspects of catalysis research comprised the triangle of catalyst synthesis, spectroscopic research, and the study of reaction mechanisms. Rutger represented his vision of cooperation between these fields using the polyhedron shown in figure 1.1.

The active site of the catalyst, where the acceleration of the reaction occurs, is located in the middle of the figure. However, it cannot be viewed in isolation from its underpinning in theoretical chemistry: the knowledge axis. The top of the figure also highlights the importance of controlling the process conditions and the end products and byproducts: the engineering axis.

The Schuit Institute of Catalysis (SKI) also entailed the introduction at Eindhoven of a new management structure for key parts of the university's research activities. Rutger van Santen was appointed director of the institute, which meant in practice that

an increasingly threadbare committee culture could be circumvented.

The Schuit Institute's objectives were as follows: (1) to strengthen fundamental, innovative and multi-disciplinary research geared toward long-term needs in the field of industrial catalysis; (2) to create postgraduate two- and four-year educational programs for research assistants; and (3) to create a high-quality infrastructure for contract research in the field of catalysts.

This reordering of catalysis research placed the development and synthesis of homogeneous catalysts on a significantly more scientific footing. It now became possible to replace the traditional trial-and-error approach toward the design of industrial catalysts with a much more scientific and technological method. This allowed greater control over molecular transformations, which in turn saved energy, reduced the environmental impact, and used raw materials more sustainably. In other words, significant societal benefits could be achieved.

### Netherlands Catalysis Foundation 1988

One side effect of the Schuit Institute was the creation of enhanced opportunities for contact with industry. Although that had not been one of the main considerations behind its foundation, it was certainly a key objective when the Ministry of Economic Affairs set up its Innovative Catalyst Research Program in 1986. The program's focus was on promoting homogeneous rather than heterogeneous catalysis. It included strengthening organic chemistry, and it was also geared more to the short than to the long term. What's more, the program was intended first and foremost for smaller businesses that could not perform their own exploratory research.

The Netherlands Catalysis Foundation (SKN), founded in 1988, was an initiative concerned more with university-industry links in the area of

Figure 1.1. The key aspects of catalysis research comprise the triangle of catalyst synthesis, spectroscopic research, and the study of reaction mechanisms. These aspects are held between the apexes of basic understanding (bottom) and engineering (top).

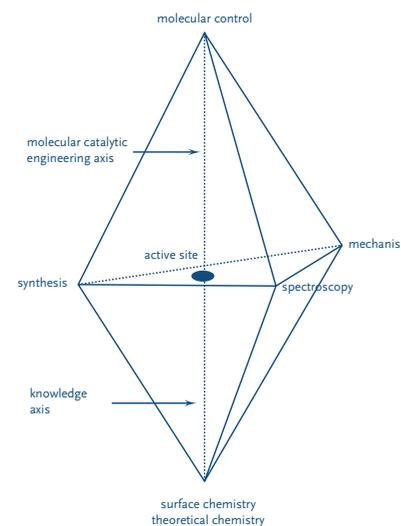
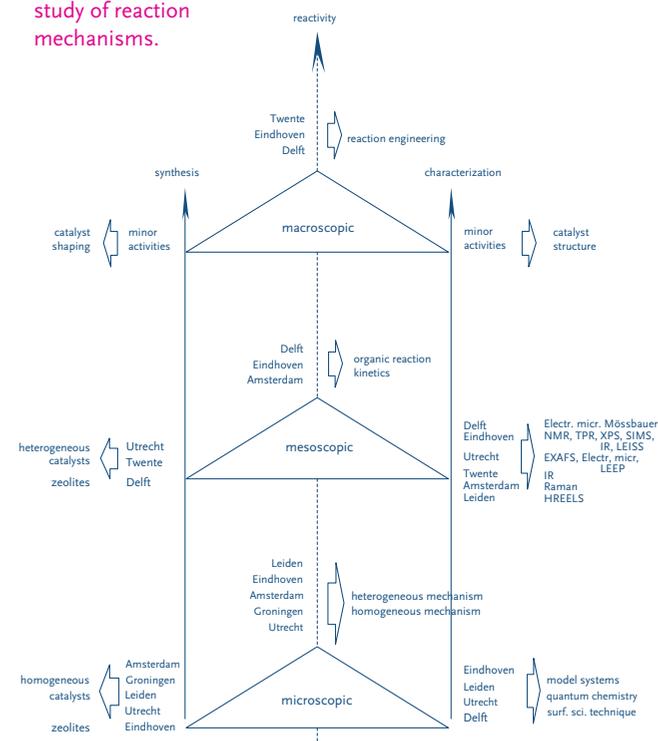


Figure 1.2. At all levels of scale, research is based on the triangle of catalyst synthesis, spectroscopic research, and the study of reaction mechanisms.



heterogeneous catalysts. The SKN had several industrial research directors on its board, together with an Advisory Panel, which functioned as a regular sounding board for the foundation's catalysis experts.

The documents once again reveal the important part played by Rutger van Santen. Used to producing analyses at Shell, Rutger used the first SKN report to provide a compelling visual breakdown of the strengths of academic catalysis (see the "catalysis prism" in figure 1.2)

This showed once again that university-based research in this area was based on synthesis, observation (chiefly spectroscopic), and reactivity (kinetics). These three disciplinary fields were applied at three different levels: microscopic (molecular), mesoscopic (nanoscale), and macroscopic (reactors, apparatus). The latter was the traditional field of catalytic reactor engineering, while catalysis research at the mesoscopic level was the customary stratum at which the work was carried out in the sixties and seventies. The microscopic level was added in the eighties. Van Santen's analysis set out the division of labor between Amsterdam, Groningen, Leiden, Delft, Utrecht, Twente, and Eindhoven, illustrating where collaboration and complementarity were possible. The diagram also shows that little work was being carried out at the macroscopic level, which was still considered to be the preserve of industry.

### Netherlands Institute for Catalysis Research

Organizational developments came thick and fast in the period around 1990. A clear rapprochement occurred in the eighties between academia and industry—very much in line with what the Ministry of Education and Science wanted to see. The Ministry was eager to stimulate science education in the broadest sense, and so in 1991 it published a plan to create research

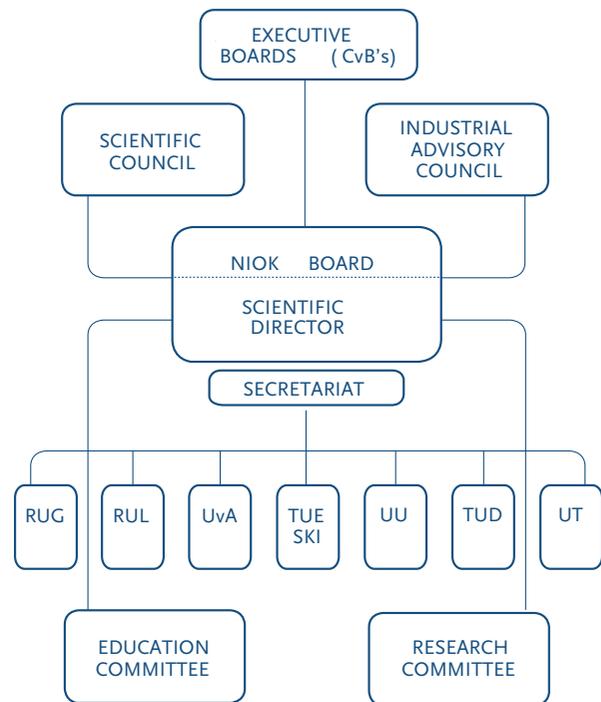


Figure 1.3. Seven universities cooperate in NIOK. Research and education are an integral part of it.

schools. The Netherlands Catalysis Foundation (SKN) recognized the importance of this ambition and immediately began to explore the creation of a research school of its own that would be aligned to as great an extent as possible with its own thinking.

The chemical industry had been sponsoring research assistants since the mideighties, due in part to the spin-off or closure of many corporate R & D departments. The concept of a research school dovetailed perfectly with this development. The creation of a virtual, intrauniversity institute for catalysis was considered, the quality of which would be monitored via a peer review process. Experience with the Schuit Institute of Catalysis at Eindhoven served as a guide for the planned Netherlands Institute for Catalysis Research (NIOK). Contacts between the universities, which until then had been largely informal, were now formalized via NIOK. Seven uni-

versities were to take part. The organization chart in figure 1.3 shows that the universities' executive boards were formally involved and that research and education both formed part of NIOK. The input of the Industrial Advisory Council was also particularly important.

TU/e—more specifically, its Department of Chemical Engineering and Chemistry—acted as coordinator on the universities' side. Management of NIOK was duly placed with the Schuit Institute, which had been given intrauniversity status under the 1986 Science Education Act. The post of NIOK director coincided with that of administrator of the Schuit Institute—namely, Rutger van Santen. The purpose of NIOK was to pool skills and talent in organized groups, focused on both research and education. Catalysis was conceived as an integrated science, bringing together multidisciplinary approaches, all of which was given direct expression in the drafting and publication of the textbook *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*.<sup>[4]</sup> NIOK also functioned as a vehicle for securing European Commission funding.

One of NIOK's founding principles was that catalysis research and education were of national importance and that a degree of supervision by industry was desirable, hence the institute's seventeen-member Industrial Advisory Council. As previously noted, research into the engineering aspects of catalysis was not getting the attention it deserved in academia. This was addressed by a focus on new reactors and modes of operation (particularly in the oil industry). The effect of NIOK was thus to tackle gaps in Dutch catalysis research, while achieving greater critical mass and raising the international profile of Dutch researchers. There were inevitably a few setbacks along the way, while the influence of industry fueled concerns that academic

freedom could be jeopardized: the universities were not willing merely to follow industry's lead.

The next stage of development at NIOK was the spin-off of its Industrial Advisory Council to the VIRAN association in 1996. In the early nineties, the Council consisted of seventeen members, including AkzoNobel, Dow Chemicals, DSM, Shell Engelfhard, Norit, Philips, and Solvay Duphar, which held out the prospect of a new foundation for public-private cooperation in the field of catalysis.

In the meantime, Rutger van Santen kept up his contribution to fundamental science, earning him the Netherlands Organization for Scientific Research's (NWO) Spinoza Award in 1997.

### NIOK: Continuation 1996

Research schools were accredited for periods of five years at a time, and so a first extension was requested in 1996. NIOK had not achieved one of the goals set in its first application for accreditation in 1991—namely, to narrow the gap between university and industry. All the same, the institute believed that it had made good progress. Instead of purely fundamental (“observational”) catalysis research, a transition was being made toward the *prediction* of catalytic reactions. Moreover, the field of research had expanded. Heterogeneous catalysis was useful to oil refineries and the chemical and food industries, while homogeneous catalysis was primarily important to the synthesis of fine chemicals, although it was not limited to that activity. As the twentieth century approached its close, the catalysis community increasingly began to adopt biocatalysis—a discipline that had long been overlooked because of a lack of interest on the part of industry (Gist-Brocades was the only company to focus on it). All the same, biological catalysts drawn from nature were increasingly entering the research of traditional catalyst scientists. Given

Rutger's background as a biochemist *manqué*, it comes as little surprise to learn that he now turned to biocatalysis too.

### The National Research Center: National Research School Combination Catalysis

Catalysis experts were not the only scientists to successfully create intrauniversity research schools in which collaboration with industry was institutionalized. A hundred schools of this kind had sprung up in the Netherlands by around the year 2000. However, this enormous success in curriculum reform made it harder to differentiate between the quality of the schools—something the Dutch government considered very important. A select number of Technological Top Institutes (TTIs) were therefore set up with the support of the Ministry of Economic Affairs. Catalysis experts campaigned for a TTI Catalysis, but to no avail (one of the few occasions when they failed to get their way).

Another option for them to raise their profile was to set up a top research school of their own: a school engaged in fundamental research of exceptionally high quality. So it was that Rutger's pendulum swung back once again toward pure scientific research. As director of the National Research School Combination Catalysis, he launched a new initiative on June 23, 1999 to bring together the three existing research schools: Catalysis (NIOK), Molecular Chemistry (HRSMC), and Polymers (PTN/EPL). It was high time, he believed, to integrate heterogeneous and homogeneous catalysis together with biocatalysis. It was good for catalysts to take their example from nature, and he identified the objective of creating a new generation of catalytic processes based on bio-inspired, man-made catalysts. As usual, Rutger set the bar very high: there would have to be “top master” programs and industry would have to recognize that genuine innovation

takes time, which meant abandoning its short-term policy and beginning to plan for the long term.

True to form, Rutger did not shy away from the administrative work. And he was also a driver of change once again when university chemistry courses began to suffer around the beginning of the new millennium from falling student numbers. In 2001 he accepted the presidency of the Royal Netherlands Chemical Society (KNCV), his motto being that you cannot simply stand by and watch the ship sink when you might be able to help rescue it.

### *Advanced Catalytic Technologies for Sustainability (ACTS)*

Rutger's principle has always been that the practice of science—catalysis research included—needs a push to get it rolling. Financiers, whether governments, industry, or philanthropists, will only part with their money if you have a convincing story to tell and a solid educational and research track record to back it up.

Falling numbers of chemistry students also threatened to push the quantity and quality of university chemical research into the danger zone. The government would not provide the funding, thus another swing had to be made. The support of industry would have to be sought instead. So it was that in 2002 the Advanced Catalytic Technologies for Sustainability (ACTS) consortium was launched, with NIOK once again acting as the prime mover. This was an innovative form of organization, in which contributions were provided by both NWO and the Ministry of Economic Affairs. NWO, who also did the administration, contributed funds for public-private partnerships in the field of precompetitive catalyst research. The usual suspects—NIOK and VIRAN—were involved in the ACTS, as were the Netherlands Research School in Process Technology (OSPT) and the Association of Biotechnological Research Schools in

the Netherlands (ABON). ACTS hopes that this multidisciplinary approach involving chemistry, engineering, and biotechnology will produce radically new technological concepts capable of contributing to a more sustainable society.

Within TU/e itself, developments were not limited to the Schuit Institute and NIOK (the coordination of which later transferred to Utrecht). Rutger van Santen, Jaap Schouten, and Bert Meijer also founded the Institute for Complex Molecular Systems (ICMS) at TU/e to pursue self-organizing catalysts, inspired by autocatalytic enzymes in biology. It has long been understood within industrial catalysis that the academic definition of a catalyst as a chemical substance that comes through the reaction intact is, in practice, far from accurate. Industrial catalyst preparation is a lucrative business precisely because catalysts are consumed. However, contaminated or “poisoned” catalysts can sometimes take on unusual and sought-after characteristics, which actually make them very valuable, as the catalyst can adjust to the reaction conditions. The future will teach us whether biocatalysis science will have similar unexpected turns.

### *Epilogue*

Rutger van Santen is fond of using analytical techniques in his administrative work, explaining his ideas through three-dimensional drawings like the “catalysis prism” in figure 1.2. Catalysis has however also proved to be the prism that reveals the rainbow of Rutger's own immense versatility and commitment. We know him as a lover of nature, a biochemist, a theoretician, a catalysis expert, and an administrator, whose four decades of scientific practice have very definitely had a multiplier effect on Dutch chemistry.

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## 1.3

# KEY MILESTONES

## *Rutger's Biography*

1945

Born on 28 May as RUTGER ANTHONY VAN SANTEN in Langedijk, Netherlands

1957–1961

Drachtster Lyceum, Drachten, Netherlands

1961–1963

Gymnasium B, Middelburg, Netherlands

1963–1966

BS (kandidaatsexamen) in Biochemistry, *Leiden University*, Netherlands

1966–1967

MS (doctoraal examen) in Theoretical Organic Chemistry, with *honors*, *Leiden University*

1967–1971

Assistant research scientist, Theoretical Chemistry Department, *Leiden University*

1971

PhD (promotie), with *honors*, supervised by Prof. Dr. L. J. Oosterhoff, *Leiden University*

1971–1972

Postdoctoral fellowship, Molecular Physics Department, headed by DR. F.T. SMITH, *SRI, Menlo Park, California*; funded by the *Netherlands Organization for Scientific Research (NWO)*

1972–1978

Research chemist, *Shell Research Amsterdam*

1976–1977

Visiting professor in Theoretical Chemistry (part-time), *VU University, Amsterdam*

December 1978–June 1979

Special assignment, Group Planning, *Shell International Petroleum Company*, London, United Kingdom

June 1979–July 1982

Section head, Solid State Chemistry, *Shell Research Amsterdam*

1982–1984

Supervisor of exploratory catalysis, *Westhollow Research Center, Shell Development Company*, Houston, Texas

1984

Section head, Physical Chemistry and Catalysis, *Shell Research Amsterdam*

1986

Part-time Professor of surface chemistry, *TU/e*

1988–present

Full professor of catalysis, *Department of Chemistry and Chemical Engineering, TU/e*

1989–2001

Scientific director, *Schuit Institute of Catalysis, TU/e*

1992–2000

Founding director, *Netherlands Institute for Catalysis Research (NIOK), TU/e*

1998–2001

Director, *National Research School Combination Catalysis (NRSC-C)*

2001–2005

Rector magnificus, *TU/e*

2002–2005

Vice president, *TU/e*

2005–2010

Full professor of catalysis, *TU/e*; Director, *NRSC-C*

2010–present

Honorary professor emeritus, *TU/e*; Director, *NRSC-C*

## 1.4

# AWARDS AND LECTURESHIPS

- 1981 Golden Medal, *Royal Netherlands Chemical Society (KNCV)*
- 1987 Shell Research Best Publication Award
- 1991 Shell Research Best publication Award
- 1992 F. G. Chiapetta Lectureship in Catalysis, *North American Catalysis Society*
- 1992 Schuit Lecture, *Delaware University*
- 1992 Berzelius Lecture, *Scandinavian Catalysis Society*
- 1992 Arch T. Colwell Merit Award, *Society of Automotive Engineers, Detroit, Michigan*
- 1994 Ipatieff Lectureship, *Northwestern University, Evanston, Illinois*
- 1994 Japanese Society for the Promotion of Science Fellowship, *Hokkaido University*
- 1994 Shell Research Best Publication Award
- 1994 Prêtre Lecture, *IRC, Lyon*
- 1995 Frontiers in Chemistry Lectures, *College Station, Texas A & M University*
- 1996 Daresbury Lecture, *Daresbury Laboratory*
- 1997 Bourke Lecturer, *Royal Society of Chemistry, United Kingdom*
- 1997 Spinoza Award, *Netherlands Organization for Scientific Research (NWO)*
- 1998 Honorary doctorate, *National Ukrainian Technical University (Poly Technical Institute), Kiev*
- 1999 Gwathmey Distinguished Lecturer, *University of Virginia*
- 2000 Karl Ziegler Visiting Professor, *Max-Planck-Institut für Kohlenforschung, Mülheim*
- 2000 Visiting lecturer, *National Science Foundation Taiwan*
- 2001 Visiting professor, *Sapporo, Japan*
- 2001 Alwin Mittasch Medal, *DECHEMA, Germany*
- 2001 Foreign member, *National Academy of Sciences of Ukraine*
- 2001 Member, *Royal Dutch Academy of Sciences and Arts*
- 2004 Visiting Miller Professorship, *Berkeley University, California*
- 2004 Academy Professor Award, *Royal Netherlands Academy of Arts and Sciences*
- 2005 Knighted in the Order of the Dutch Lion
- 2008 Foreign associate of the *United States National Academy of Engineering (NAE)*
- 2009 Fellow of the *Royal Society of Chemistry (RSC)*
- 2010 Francois-Gault Lecturer, *European Federation of Catalysis Societies*
- 2011 Visiting fellow, *Institute for Advanced Studies, Technische Universität München (TUM)*

## FIELD TRIP LEADER

*From Frisian Meadows to Quantum Mechanics*By *Bram Vermeer*

Bram Vermeer is a science writer with a background in physics who has been publishing about technology for an international audience for twenty-five years. He has written several books and reports together with Rutger van Santen. Vermeer is based in Amsterdam and Berlin.

There's more going on in the meadows of Friesland than you might think. As a boy, Rutger van Santen liked to study the strange interaction of the plants in those fields. Pegging out a square meter of pasture, he would spend hours cataloguing the different grasses, orchids, and daffodils—a love of nature he inherited from his mother. But it wasn't so much the individual varieties that fascinated him, as the way the community of plants developed. Rutger was drawn to the complexity of the ecosystem, even though he wouldn't have used that term back then. "The nutrient-poor, wet pastures of south-eastern Friesland are a link in the evolution of peat," he says now. "The plants change the soil. They bind the sand and add nutrients as they digest. They alter their own biotope, making a different plant community possible. That was an exciting realization: the dynamics of it all fascinated me."

Rutger's passion for complex mechanisms and his desire to explore interconnections was, in other words, present from an early age, as was the remarkable ease with which he seems to move through organizations. He joined the Dutch Youth Association for Nature Study (NJV) at the age of eleven, simply because a friend told him it was fun. Participation was what mattered at the Association rather than authority,

with the youngsters running their respective sections themselves. By the age of twelve, Rutger had become an *excursieleider* or field trip leader. "We taught each other, using whatever books we had. When I was fourteen, I invited a moss specialist—a professor from Groningen—to our house. My parents must have been a bit startled, but they always supported me."

Collecting plants and bird-watching weren't particularly attractive prospects employment-wise. "There's more future in biochemistry," advised a cousin with a degree in chemistry, which is how Rutger came to enroll at Leiden University. "But I couldn't summon up enough enthusiasm for biochemistry, the way it was taught in those days. We spent the whole time working with Petri dishes, measuring nitrogen and oxygen. It was all based on nineteenth-century microbiology—focusing more on the phenomena than on the mechanisms. My interest was only really sparked when I took a course on "chemical bonds," which gave me my first exposure to quantum mechanics, and to Luut Oosterhoff, my future supervisor. After my *kandidaats* examination I opted for theoretical organic chemistry, which meant studying under Oosterhoff."

It was natural, therefore, that he should subsequently take his doctorate under Oosterhoff's supervision

too. "He left it entirely up to me. It was supposed to be about the excitation of molecules by electron scattering, but the precise topic only crystallized a year or so later. He let me approach it in my own way and encouraged me to seek out information all over the place. He sent me to Sweden and Norway, for instance, to get a better grounding in quantum chemistry." Oosterhoff's group was half-experimental, half-theoretical. Rutger was the only one who didn't do any experiments himself. But he was given the task of performing the quantum chemical calculations needed by the experimenters in Leiden and by other groups as well. "Quantum chemistry was on the rise at that time," Rutger says. "As illustrated by the Nobel Prize that had just been awarded to Roald Hoffmann. The first semiempirical methods for calculating the electron structure of organic molecules were extremely useful in understanding experiments. That work really helped me to think in terms of mechanisms."

Rutger prepared the computer programs himself, writing them in Fortran on punch cards. None of these calculations ultimately found its way into his thesis, which turned out to be an algebraic study in which Rutger integrated scattering theories from different fields into one single abstract framework. It did, therefore, deal with a quite different phenomenon. The thesis ranged from nuclear physics to spectroscopy, from molecules to quantum chemical processes—a variety made possible by Rutger's minors: theoretical physics and mathematics. He enjoyed following his curiosity: "I was able to dig deep and to find new things." The work turned out very well indeed and was rewarded with an *honors*. Quite unexpectedly, these theoretical insights would later prove extremely valuable to theoretical catalysis. The computer programming he had mastered so thoroughly during his doctoral studies would also come in very handy.

Rutger didn't think too much about his future at that time. When he mused once about possible jobs, Oosterhoff told him to do what he enjoyed doing and that everything else would then fall into place. "I've followed that principle throughout my life: if you enjoy something, you do it well. The abstract, theoretical work I was doing at that time didn't contribute directly to society, but it was felt in those days that it would contribute indirectly," Rutger says. Not that he was impervious to social issues. He was involved with the students' union and was an activist during the turbulent period of the late sixties student revolution, spending his evenings putting up posters calling for protest. He was also the first student to sit on the faculty council.

Oosterhoff's speech at Rutger's doctoral ceremony reiterated the importance of pursuing your own curiosity. Rutger isn't afraid of the new, he told the audience. "I've never forgotten that," Rutger says. "A lot of things came together at that time. I'd just got married and there was a baby on the way. And three months later we were due to leave for America." At one stage, Rutger thought he would become a chemistry teacher—as did most chemistry students. Although he had the necessary teaching qualification, his *honors* now opened up a different world to him.

*Crossing the Atlantic*

Rutger began with a year at Stanford, California, where he continued to research scattering theory. Scientifically, it was an inspiring continuation of his work in Leiden. It was on the cultural side that things were genuinely new for him: "Everyone is extremely open to you. It was my first time in the United States and it was a real revelation." The young family—Rutger and his wife now had a daughter—lived on an apricot orchard in Mountain View, in the heart of what is now Silicon Valley. Rutger travelled

widely, visiting the Grand Canyon, Death Valley, and the Painted Desert in Arizona. Here too, he was fascinated by the plant life per square meter. “Nature is overwhelming there—a totally different climate. That was very new for me as well.”

It was also during this period that Rutger developed closer ties with his faith. As the son of a Protestant minister, he naturally knew the church very well. His father was a liberal preacher who always emphasized the good in other people. Individuals should be free to develop in their own way, his father believed—an attitude toward faith that Rutger also encountered in his student period. In the United States, however, on Baptist territory, the connection was more direct and also brought Rutger a close-knit social network.

### *Entering Catalysis*

Dutch industry in that period was falling over itself to recruit brilliant students. Anyone who was doing well would be snapped up, regardless of their precise field of research. Philips and Shell both courted Rutger. “I chose Shell: The focus on chemical reactions appealed to me. I was interested in new problems, and it was also a challenge to go and work alongside the best chemists in a broader environment than you find in the university. The work also had a more obvious social importance. Plus I already had a contract with Shell before we left for Stanford.” However, by the time Rutger returned to the Netherlands, there had been a change of course at Shell, with a new emphasis on applied research. Fundamental research into quantum chemistry was no longer considered relevant to the company’s future, which Wolfgang Sachtler, Rutger’s new boss, made very clear on his first day at work. As a theoretical chemist, Rutger had little knowledge of the catalytic processes that are central to the oil industry. “What overlap is there between theoretical chemistry

and catalysis?,” Sachtler asked him. “That was a hard one to answer,” Rutger recalls. “Catalysis was more of an art than a science back then. Theory didn’t get you very far. But I went away and thought about it.” Rutger spent days wandering around the lab, badgering everyone with questions about their research. “I soon discovered something that would interest my boss and made a proposal concerning the theory of alloy catalysis. I knew nothing about it, but it seemed relevant and was duly approved.”

It turned out to be a traditional, mechanical study with no reference to quantum mechanics. When Rutger later began to study surface reactions, he discovered that the quantum mechanical techniques used to calculate reactivity displayed major similarities with the scattering theory he had formulated for his doctoral thesis. The framework that Rutger had developed for radiationless transitions dovetailed perfectly with the methods used by other scientists to describe the electron structure of simple atoms adsorbed onto metallic surfaces. “That was pretty mind-blowing. But it meant I could dive straight into the algebraic theory being developed at that time. It was all obviously far too imprecise to apply to industrial catalysts, and it was only indirectly important at best to Shell.” The relevance of this work to Shell was raised again three years later during a new conversation with Sachtler, who suggested carrying out a series of experiments. Rutger was to study catalysts consisting of an alloy of silver with alkali metals in an ultra-high vacuum. He collaborated closely with an excellent technical expert, as he did not have sufficient experience himself with practical experimental work. It gave him a flying start. For the experimental work dealing with ethylene epoxidation that followed, he earned the Golden Medal of the Royal Netherlands Chemical Society (KNCV).

So it was that Rutger gained a thorough knowledge of different

aspects of the oil company. He later went to London to consider Shell’s future strategy before being appointed section head in Amsterdam with a dozen people under him. His new position put him in charge of a team of academic researchers each with their own technicians. “Taking a leadership role was an entirely new discovery for me. You can only do it if you have a clear insight into the way you function yourself. You learn to think on the basis of a strategy: Where is this leading? What can you do with it?”

Rutger’s section researched catalysts in existing industrial processes. “We dealt with highly practical questions. I also came into contact for the first time with the production of catalysts. I always stressed the importance of fundamental chemistry issues in that sort of practical work, which occasionally caused tension with people who were more directly engaged with implementing processes. I later realized that different time horizons play an important part in that respect. I came into contact with typical engineers and hence with the tension between design and science, which is something I hadn’t really experienced in Leiden. That tension wasn’t always pleasant, but I understood that it had to be overcome if we were to progress. I realized that it was important to give my work value in the eyes of an engineer because that’s who will ultimately make it valuable for society. How do you do that while maintaining your own values and continuing to follow your own scientific interests? In later years I always made a point of seeking out that tension, which I also discovered as a source of creativity.”

### *Theory amid Engineers*

Rutger continued his theoretical exploration in that period, chiefly during the evenings. This work was inspired by all the new questions raised by heterogeneous catalysis—especially as the techniques for performing experiments were becoming increasingly

refined. Surface science emerged with techniques for observing individual molecules on a catalyst. Sachtler was among the pioneers who applied those techniques at Shell too. Rutger didn’t leave the calculations to the computer experts who formed a separate department at that time. “I was keen to keep it close by. I wanted a programmer who knew exactly what we were talking about. That’s how you shift boundaries, which is precisely what we did. Fortunately, we were able to disclose some of what we were doing, enabling us to publish some great scientific results.” Actual catalysts were also being produced, which meant that the research generated patents as well, underscoring its industrial relevance.

Travel was on the agenda again. It was a normal part of career development at Shell to spend time working abroad, and so Rutger now transferred to the Shell Development Company in Houston, Texas, for two years. He was appointed supervisor of exploratory catalysis at Westhollow Research Center, where he was responsible for developing a new catalyst line. Shell Houston had close ties at that time with Caltech in Los Angeles, where theoretical research was being carried out into silver epoxidation—the topic that Rutger had already studied so effectively in Amsterdam. He became a close friend of Bill Goddard, the two theoretical chemists hitting it off immediately. “We spent a lot of time together in that period, and later as well.”

Rutger didn’t want to stay though. “I was offered another job there, but I felt I had to return to Europe. I wanted my children to be settled in the Netherlands. And I also didn’t want to remain with a part of Shell that had such a strong orientation toward applied science.” A professor’s post came up around then at Eindhoven. “It was very attractive to me, especially because George Schuit had initiated important catalysis research at Eindhoven, pursuing a vision that was very familiar

to me. He had been linking quantum chemistry to catalytic processes and systems since 1958. Schuit's first two doctoral candidates went on to become important professors of theoretical chemistry—Ad van der Avoirt in Nijmegen and Piet Ros at VU University in Amsterdam. Roel Prins took that work further by introducing new spectroscopic techniques. I was keen to continue in that direction, but in a period in which theoretical chemistry was becoming much more precise and hence usable.”

### *Building Coalitions*

Rutger knew what he was letting himself in for at the university. He had lectured for one day a week at the VU University Amsterdam and was familiar with the bickering that was part and parcel of the democratic administrative structure of Dutch academia. He therefore secured an agreement that he would be spared all that for the first two years. “Most of the research funding didn't come from the university itself,” he explains, “but from NWO and the European Union. Even so, everything changed the day after I made that agreement. I really had to wonder what kind of world I'd gotten myself into.” For the first six months, Rutger considered returning to Shell, where everything happened via clear lines of decision, and where the youngest technicians didn't get to vote on the company's research program. But it was too late to go back. “That's when I turned the corner. I realized that I had to make it at Eindhoven. I read management books to understand why it was all so crazy. I gradually began to understand how political mechanisms work and realized that I had to take part in them. I joined the faculty council and began to build coalitions. It was also around that time that I set up the Schuit Institute, in which we brought together the different groups needed to take catalysis forward, while also enabling us to raise our external profile. The

university had a nice program in which it gave each postdoc I appointed an extra year. That was innovative and had a very positive impact in bringing fresh knowledge into the group.”

In substantive terms, Rutger wanted to work on spectroscopy and theoretical chemistry as a means of unraveling the mechanisms of catalysis. He also wanted to bring in the production of catalysts so that ideas arising from theory could be used to synthesize new catalytic systems. Together these formed the three pillars: spectroscopy, theory, and synthesis. “I've always been aware that you have to develop new methods, otherwise you don't advance fundamental science. So I've consistently had to choose which methods to adopt from other researchers and which to develop ourselves. We developed two important methods in that period: Monte Carlo methods to predict the kinetics of a reaction and a spectroscopic technique for displaying radiochemically labeled molecules during the reaction, which enables you to see how they are distributed over the catalyst surface. At the same time, we brought methods into our lab from all over the world, all with a view to understanding what is happening in a catalyst at molecular level. We consistently tied that to catalysts that were currently relevant to industry and society.” It began with the removal of sulfur from crude oil, followed by Fischer-Tropsch for producing liquid fuel from natural gas, hydrogen storage, and a great deal of research into improving the environment, such as removing nitrogen compounds from water and exhaust gases.

“An important question throughout has been, how do I maintain the confrontation between theory and application? That kind of tension had been important at Shell, and I wanted to go on seeking it out.” This was also an important reason for him to found the Netherlands Institute for Catalysis Research (NIOK) research school,

which brought together all the key researchers in the Netherlands. “In the early stages I interacted most at NIOK with Ulrick, an engineer from Delft, who was a director at Shell Research. Our relationship embodied that tension. He saw me as an exponent of the fundamental side, but he also understood that I wanted to keep theory and practice in alignment.”

For the first time, Rutger was able to shape his own surroundings. He had followed his own path at Shell, led by his curiosity, while during his studies he had been sufficiently headstrong only to take on interesting assignments. Now, however, he managed to win people over to his vision and to build up an infrastructure that matched his ambitions. “That might be why I made my breakthrough at Eindhoven,” Rutger thinks. “That's where it first happened.”

The ties with Shell remained strong. For the first five years Rutger con-

tinued to manage two researchers at Shell, even though he was already based at Eindhoven. One of them was Gert Jan Kramer (see section 4.1). Other links with industry were also forged. Rutger began to work as a consultant, for instance, for Solvay and DuPont. Other companies later joined the list, such as Sasol, which has a plant in Qatar where the Fischer-Tropsch process is applied on a large scale to manufacture liquid fuel from natural gas.

Rutger enjoyed a long series of successes at Eindhoven. If you talk to him about it, you'll hear the names of scientists from all over the world, some of which crop up time and again. Rutger is faithful in his scientific relationships. “That initial click keeps repeating itself,” he explains. The resultant network constantly inspired him to take new steps. Several of those colleagues look back in this book over their remarkable collaborations with Rutger van Santen.

## AN ANALYSIS OF THE ACADEMIC PORTFOLIO

By *Edwin Horlings*

Edwin Horlings is coordinator in the Science System Assessment Department of the Rathenau Institute in The Hague. His team of researchers study knowledge infrastructure, including projects on innovation networks in the water sector, transdisciplinary climate programs, science parks, and research coordination. In addition, his team is developing new methods of scientometric analysis and visualization to improve understanding of the cognitive, social, and institutional development of scientific fields. Edwin studied Economic and Social History at VU University Amsterdam and has held various positions at universities in Utrecht, Leuven, and Amsterdam.

Figure 1.4 on page 38 shows beautifully the long and distinguished scientific career of Rutger van Santen. It is a map of his complete academic work, drawn up by a new method developed by the Rathenau Institute. Each dot is a publication, plotted through time on the horizontal axis and categorized into research topics on the vertical axis. The size of the dots is determined by the number of citations that the publication has received on average per year.

Rutger van Santen started his career, as most scientists do, with a single topic during his PhD study. But after Rutger's postdoctoral fellowship the portfolio expanded to cover several different areas, and he often worked on several topics simultaneously. Both the magnitude and breadth of his research portfolio had increased dramatically by the end of the eighties when he was full professor of catalysis at TU/e. Throughout his career Rutger has been active in twenty-three areas, sometimes only passingly, but in certain areas his work has spanned decades and has been very intense in its nature. At his peak, Rutger van Santen was active in eight to ten different areas simultaneously.

The graph shows how important

PhD students have been for Rutger. Since 1988 his PhD students have been involved in more than half of his publications. In 2005 and 2006 the number of publications was lower than in previous years. This may have been due to the demands of his position as rector magnificus at that time. Fortunately, the work of his PhD students continued in those years.

Changes in Rutger's career can be recognized in the development of his portfolio. After the establishment of NIOK, the Netherlands Institute for Catalysis Research, a number of new topics in catalysis arose, such as immobilization or silsesquioxane-based catalysis. When he took on the position of rector, he left a number of areas, such as zeolite catalysis and positron emission profiling (PEP) in situ transient kinetic technique, but after the resumption of his academic work in 2005, he became active in some new areas like the study of vesicles and hydrogen storage. He also returned to some of his earlier research programs, such as the density functional theory (DFT) study of zeolites.

Rutger's career path gives us valuable insights into how research areas

come to maturity. After zeolites had been explored as solid acids, zeolite research continued with cationic complexes and iron. In the case of Rutger, an area of study reaches its fruition in approximately ten years.

The shift in the chemisorption timeline to metal catalysis is a clear jump to a more complex level of studying surface chemical reactivity. Initially the work mainly focused on understanding the relationship between surface chemical reactivity and chemical bonding features of adsorbates; at a later stage Rutger's research was able to address the actual formation and breaking of chemical bonds between reacting molecules. This illustrates progress in methodology. At a particular moment chemisorption is better understood, and this knowledge can then be used to study reactivity at different length and time scales.

New research lines sometimes reflect a change in the field of application. Research in ammonia oxidation relates to the importance of environmental research by the end of the nineties. The graph shows two main research areas with very long timelines: the mechanism of catalytic reactions (in different systems over time) and of zeolite synthesis.

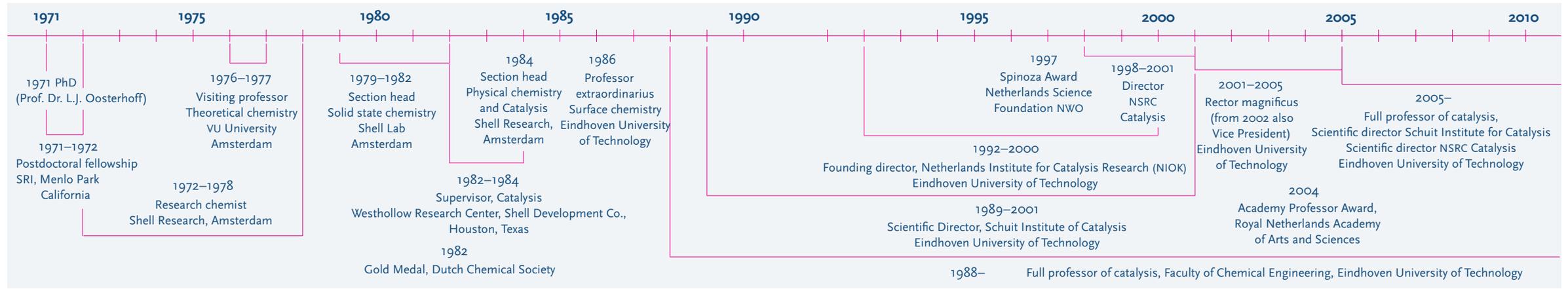
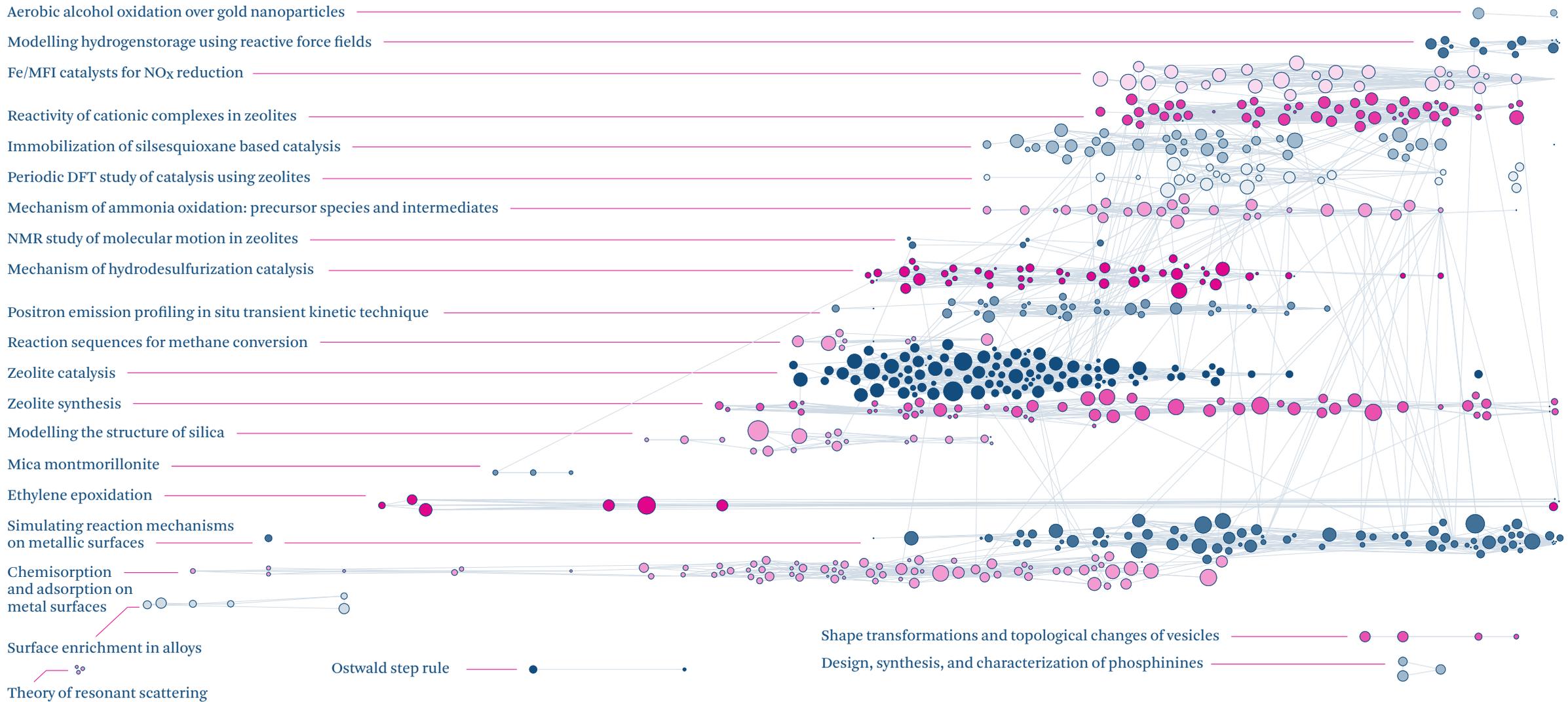
The mapping method, developed by the Rathenau Institute [1], uses data on publications from Thomson

Reuters' *Web of Science*. This is a comprehensive index of publications in academic journals and conference proceedings with very good coverage of the natural sciences, such as chemistry and physics. We calculated how similar the publications of Rutger van Santen are by comparing words in the titles and references to other publications. If the same words feature in the title of two publications, this indicates that they explore a similar topic. When two publications refer to the same literature, they have a similar cognitive or technical background. The result is a correlation matrix that shows the degree of similarity for each pair of publications. The community detection algorithm of Blondel et al. has been used to identify clusters of highly similar publications within the matrix. [2] Blondel's method rapidly identifies sets of highly interconnected nodes within very large networks. The result is a clustering with a high density of links within clusters and a low density of links between clusters. Each publication cluster represents a research area.

**REFERENCES** / 1. Horlings, Edwin and Gurney, Guillaume, J.L., et al., (2012). *Search Strategies along the Academic Lifecycle*, (forthcoming) / 2. Blondel, V.D., J.L. Guillaume et al., (2008). Fast Unfolding of Communities in Large Networks. *Journal of Statistical Mechanics: Theory and Experiment* P10008.

# FORTY YEARS OF CATALYSIS RESEARCH

Figure 1.4: The research portfolio and career of Rutger van Santen.



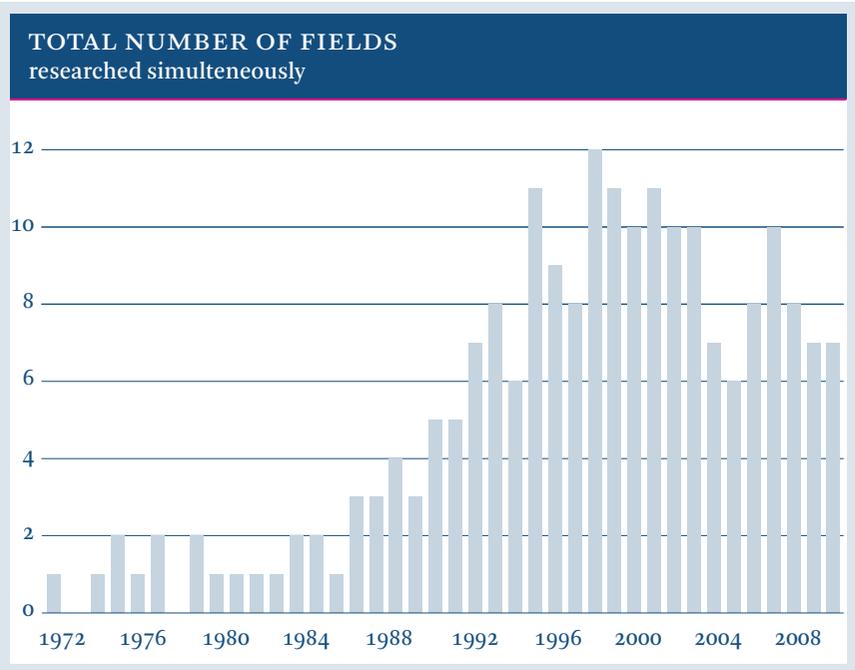
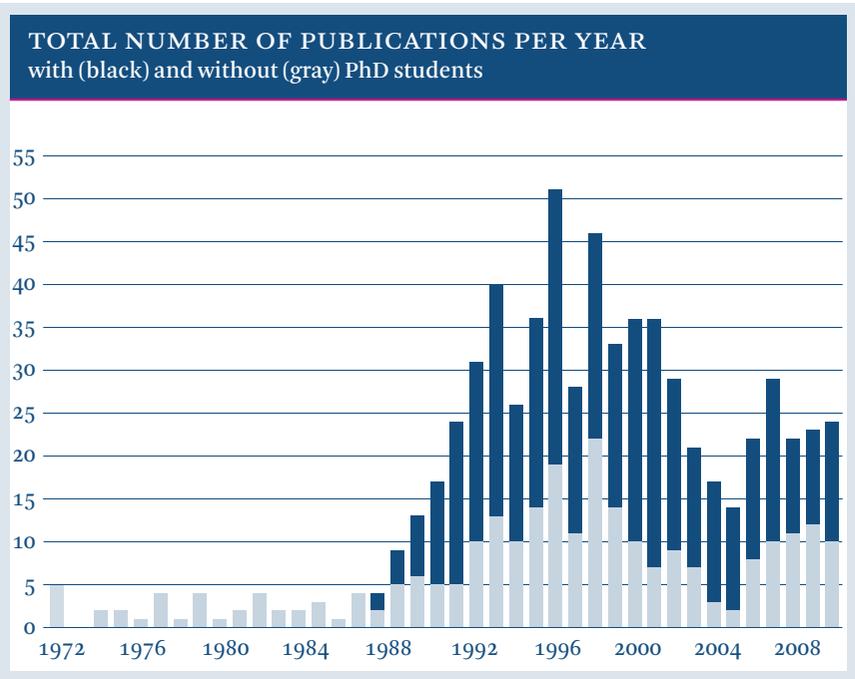
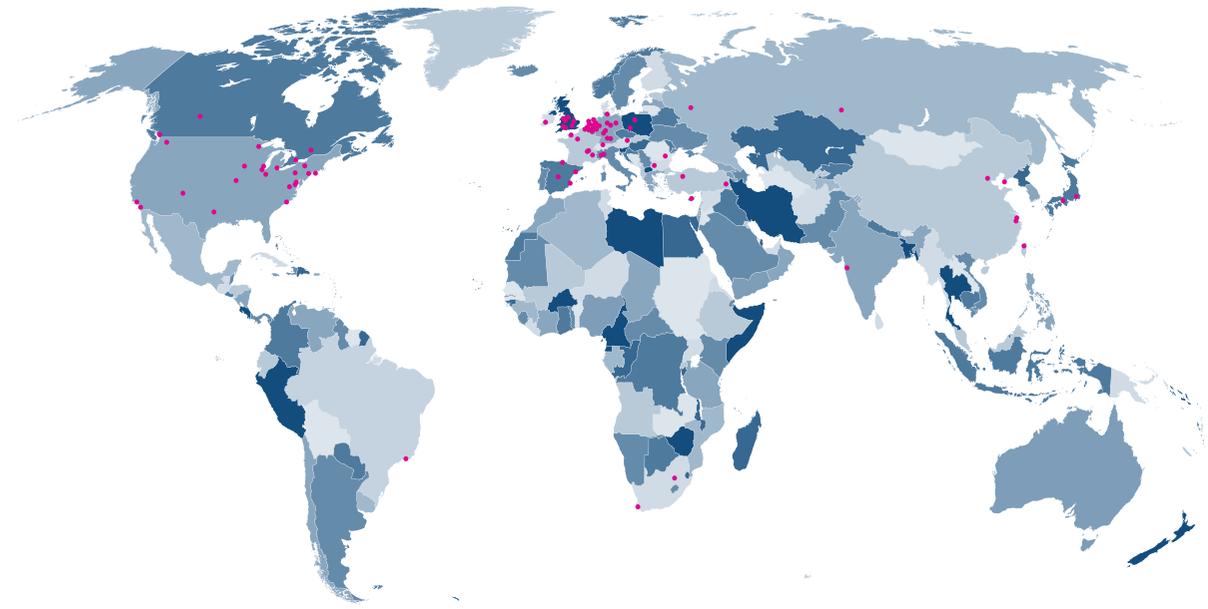


Figure 1.5: Rutgers' co-authors come from all over the world.



## 2.1

# MY WAY THROUGH CATALYSIS

By *Rutger van Santen*

In my early days at Shell awoke in me an interest in catalysis that has sustained my intellectual curiosity ever since. It was also at Shell where my long-term interest in the reaction mechanism of heterogeneous catalysis began. The work within the industrial environment brought me into contact with many catalytic systems. I look at those systems essentially through the eyes of an organic chemist, who has a natural inclination toward thinking in terms of the rearrangement of atoms within molecules. I became more and more focused on the discovery of new catalytic systems, but possibilities for exploring these systems fully within an industrial context remained limited. At the university in Eindhoven it became possible to implement this research interest at full scale.

It turned out to be a very fruitful research theme. In the last decade of the twentieth century computational possibilities increased dramatically with increasing hardware resources. It became possible to calculate molecular models of the reacting system with improved atomic accuracy and increased similarity between experiments. At the same time, experimental facilities for studying surfaces made the experimental results increasingly more detailed and relevant. Theory and experiment became complementary, and experimental validation of theory at the atomic level became possible in a way that had been unheard of in previous decades!

In the early nineties the Schuit Institute of Catalysis program at Eindhoven became targeted toward a paradigm change: “from correlation to

prediction.” Most research in heterogeneous catalysis at the time was aimed at finding out experimentally how to improve catalyst performance by changing the catalyst parameters. But we believed that a mechanistic understanding of catalytic reactivity would convert this into a predictive science, with the possibility of bypassing much trial and error. We started a program for molecularization of heterogeneous catalysis, which integrated the three big questions we have in catalysis: how to make, how to measure, and how to predict catalytic processes. I tried to use state-of-the-art computational methods as much as possible to uncover the mechanisms of catalytic reactions. In the Eindhoven laboratory we introduced experimental techniques to probe the catalysts on a level that would validate the theory by refining spectroscopy so that we could actually see what happened on a catalyst. In parallel, I tried to introduce catalyst synthesis approaches that would enable us to implement some of the new insights we obtained.

I am mentally more focused on creating a conceptual framework of understanding, but I was very conscious that this only could be obtained by developing new approaches and techniques. I think that this awareness originated especially from my stays in the United States. In contrast to my theoretical education in Leiden, which focused strongly on in-depth, complete descriptions of physical phenomena, there I came into contact with a culture more oriented toward the new and unexpected. New instruments or new chemistry were

considered key to the success of such research. A characteristic of frontier research is the introduction and development of new techniques on which new discoveries are based, as well as the development of new theories. I was very conscious of making research project choices that would relate to each other. In this way, the teams with different disciplinary backgrounds in the laboratory would interact and the different research programs would become truly integrated.

One of the reasons why I had accepted the chair at Eindhoven was its tradition in relating quantum chemistry with catalysis. When George Schuit became the first full professor in catalysis in the Netherlands fifty years ago, he had already initiated quantum chemistry research at Eindhoven. He was also interested in introducing new physical techniques, such as electron spin resonance (ESR), in an environment strongly oriented toward the inorganic chemistry of catalyst development. His successor, Roel Prins, who also came to Eindhoven after a career at Shell, introduced advanced x-ray scattering techniques among other things. Hence, Eindhoven research was very receptive to further expansion of work along these lines.

### *The development of research at Eindhoven*

Upon my arrival at Eindhoven, collaborations with Hans Niemantsverdriet, Tonek Jansen, and Joop van Grondelle were key to the initial success in implementing new program directions. There existed already a large research group in the Inorganic Laboratory at Eindhoven. I was able to recruit Hans Niemantsverdriet in a tenured position, and we decided to invest substantially in modern spectroscopic tools of surface science and to build a unique laboratory to study model catalysts. Hans was uniquely suited to this because he had just finished a postdoctoral fellowship with the future Nobel laureate Gerhard

Ertl, who pioneered the application of surface science to catalysis. Later he also spent a year with another pioneer in this field, Gábor Somorjai. I was very concerned with attracting the necessary funding for the expensive equipment we needed. Hans and I were able to get one of the first Pioneer grants from the Dutch science funding organization NWO, which made the catalysis research facilities possible.

Tonek, who had graduated with the theoretical chemist Ad van der Avoirt from Nijmegen (a former student of Schuit at Eindhoven), helped us introduce computational chemistry into the laboratory. He was the second person I was able to hire in a tenured position when I started at Eindhoven. Tonek introduced state-of-the-art computational chemical techniques to the laboratory. We also decided to develop new computational techniques to bridge the divide between quantum chemistry and kinetics. He developed new computational tools, such as dynamic Monte Carlo (DMC) techniques, to simulate the kinetics of surface phenomena. He based these new tools on molecular computed or measured data and new methods to simulate complex vibrational spectra with anharmonic couplings, as well as other phenomena. Tonek's stay with Risto Nieminen in Finland helped this new development significantly.

We also put considerable effort into developing new force fields for inorganic materials. Part of it was in collaboration with Gert Jan Kramer, who was at Shell at that time. Together we set out to predict the structure, stability, and vibrational properties of new zeolitic materials that didn't even exist yet. Zeolites are complex microporous, siliceous materials. Back then, they were too complex to be studied by quantum chemical means. We used molecular dynamics and related methods based on classical force fields derived from smaller-scale quantum chemical calculations. In spectroscopy we decided to focus on

developing positron emission profiling (PEP). This was a technique that we had developed earlier with Gert Jonkers and Kurt Vonkeman at Shell as a tool for in situ observation of chemical reactivity. With Theo Beelen and Peter-Paul de Moor we developed integrated wide-angle, small-angle, and ultra-small-angle x-ray scattering techniques with corresponding cells to study zeolite synthesis in situ. Joop van Grondelle played a crucial role in supporting all these activities with his technical skills.

Ultimately, we realized that we needed to develop new materials and catalysts to make a real impact on the application of catalysts. The synthetic work by Eric Abbenhuis and Rob Duchateau on silsesquioxanes and by Nico Sommerdijk on siliceous materials belongs to this part of the story. The silsesquioxanes are unique molecular siliceous clusters that we used to explore the synthesis of new catalysts for selective oxidation and polymerization. In collaboration with Nico, we developed interesting catalytic materials structured on different length scales.

The financing of all these activities was made possible by many grants. I already mentioned the Pioneer grant. Among others, the Spinoza grant we were awarded in 1997 was also very essential, as well as a large infrastructure grant from the Netherlands Organization for Scientific Research (NWO), the so-called NWO Groot grant. The Top Research School Award spurred us on to form the National Research School Combination Catalysis (NRSC-C). The chemical division of the NWO and the Technology Foundation STW grant system funded many other small projects. Wilfried Mortier at Exxon helped us to get into the innovation-oriented program (IOP) from the Dutch Ministry of Economic Affairs to develop our zeolite synthesis research further.

The Huygens program of the Royal Netherlands Academy of Arts and

Sciences (KNAW) helped to finance several key postdoctoral fellows in my group, including Eric Abbenhuis and Marc Koper. They helped me to develop new initiatives in the fields of catalyst synthesis and electrocatalysis, respectively. The National Computer Federation made available the extensive computational resources necessary for our research with supercomputer facilities at SARA, Amsterdam, for which I am very grateful.

Also important for my research were the decades of long-term international collaborations with China and Russia, funded by KNAW and NWO. It enabled me to have very beneficial interactions with Can Li from Dalian, China, and Vladimir Kazansky from Moscow. Can Li and I had first met in 1993 when I was the Ipatieff Lecturer at Northwestern University in Evanston, Illinois. I had been invited by Wolfgang Sachtler, who had moved to that university ten years earlier. This created an opportunity for joint research. Can Li and I appeared to have very similar ambitions. After several years he, then research director of catalysis at the Institute of Catalysis in Dalian, invited me to visit him and give some lectures. It was the beginning of a long and fruitful collaboration. Vladimir Kazansky organized for me to visit Moscow for the first time at the end of the eighties. This started a collaboration of more than fifteen years, which was a great inspiration to my work on zeolites. We spent many hours debating science and other topics.

The approach of our group's computational catalysis research was initially very similar to that in Leiden, which I had learned to appreciate during my PhD there. My participation in the Marie Curie networks and the French theoretical catalysis initiative, led by Hervé Toulhoat from the French research institute IFP Energies Nouvelles, inspired the development of computational catalysis in our group further. This was a structural collaboration spanning more than ten years.

It brought me into contact with Jürgen Hafner, the developer of the Vienna ab initio simulation package (VASP) code. Very early on in his and my career, we decided to collaborate so that I had early access to this important code. This French connection also strengthened my contacts with Philippe Sautet from Lyon, France (see also his contribution in section 5.1). This started with Bernard Bigot, Philippe's thesis advisor, and continued for many years, leading to several collaborations and numerous inspired discussions.

European collaboration grants also helped us to collaborate with Richard Catlow, now at the University of London. This contact was essential in building up our theoretical basis in zeolite catalysis. The European Network of Excellence for catalysis, called Integrated Design of Catalytic Nanomaterials for a Sustainable Production or IDECAT, helped to intensify contacts with Gabriele Centi from Messina, Italy, and Jean-Marie Basset from Lyon. We organized several joint conferences and summer schools. I benefited also from many long-term industrial contacts and grants, initially from Shell, and also later especially from DuPont, Solvay Hannover, and Sasol South Africa.

With the establishment of the Netherlands Institute for Catalysis Research (NIOK), the Schuit Institute of Catalysis (SKI) program became part of a national program. The research school NIOK was established in 1992. I was its scientific director until the National Research School Combination Catalysis (NRSC-C) started in 1999, when I became the scientific director of NRSC-C. When NIOK started, the research program was expanded to include homogeneous catalysis, biocatalysis, and reactor engineering. The increasing molecular depth of the science of catalysis made the interaction between heterogeneous catalysis, homogeneous catalysis, and biocatalysis fruitful. Essential to turning chemi-

cal catalytic materials into operational catalytic processes, we also added reactor engineering to the program.

I was the one who took the initiative in establishing NIOK. I felt strongly that it would be beneficial to be part of a national platform for catalysis, which would meet on a regular basis with industrial research management and government agencies. By 1990 several strong catalysis centers had started at different universities. A strategic interchange would be to everyone's mutual benefit.

The nineties were a period of substantial extra funding in catalysis and flourishing university catalysis research. We found a need for a new textbook that would create a multidisciplinary science of catalysis, integrating knowledge from the broad spectrum of sciences within NIOK. Jacob Moulijn, Piet van Leeuwen, and I started writing and editing the NIOK textbook *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*. This was a great success and was reprinted three times. An important activity within NIOK was the organization of a national catalysis course, which was based on this book. We also organized theme-based summer courses. The course materials from some of these also appeared as books. A successful book that I edited with Frans Jansen, originally from KEMA, was titled *Environmental Catalysis*, and later when IDECAT was established, Gabriele Centi and I edited the book *Sustainable Catalysis*. Philip Sautet from Lyon and I taught a summer course entitled "Computational Methods in Materials Science and Catalysis" several times. The lecture material also appeared as a book (see the bibliography in section 10).

In the first ten years of NIOK's existence, I became good friends with Gerard van Koten, who then was chairman while I, myself, was scientific director. It still gives me great pleasure to think back on the many ventures we undertook jointly on behalf of NIOK.

## 2.2

# CATALYSIS FOR A NEW MILLENNIUM

## *Visions at the Turn of the Century*

By *Rutger van Santen*

Reprinted from: RUTGER A. VAN SANTEN (1998). *Catalysis, Quo Vadis? Progress from Sixteenth Century Alchemy to the Molecular Design of the Twenty-First Century*. *CATTECH* 2 (2), 161-168. The article is based on the address he delivered when he received the Spinoza Award in Amsterdam in 1998. The original figures have been redrawn and renumbered.

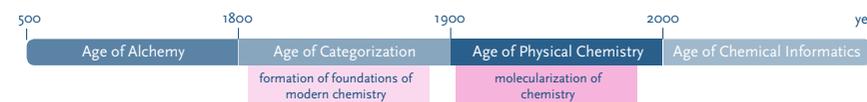
Catalytic technology now holds a key position in industrial manufacturing processes that support current Western civilization. Although its history dates back to the Middle Ages, catalysis only reached this position around the middle of the twentieth century. As we look forward into the next century, being aware of the major organizational restructuring currently taking place in the chemical industry, it is natural to speculate on the role that catalytic processes will play in the future. There is a need to establish whether catalytic processes will continue to play such a dominant role in society, with continued development of new processes, or whether another stage will be reached in which these processes will be considered to be part of a mature technology. Rather than to extrapolate from our current state of the art to the future, an attempt will be made here to analyze the dynamics of the processes that generated chemical science and technology. The perspective thus created may be helpful in order to assess the relative importance of future developments. The history of catalysis

is intimately intertwined with that of chemistry. Therefore, we will start our analysis with a discussion of the history of chemistry, highlighting in particular the events essential to progress in catalysis. After having set the scene, we will describe the development and current status of molecular heterogeneous catalysis, emphasizing understanding of the mechanistic aspects of the working of the catalyst. A more extensive exposition on catalysis as a science has been presented elsewhere.[1] It will become apparent that we view the prediction of overall catalytic behavior at a macroscopic level, based on molecular mechanistic understanding as one of the main factors driving innovation in catalytic science. Secondly, we view chemistry as a scientific bridge between knowledge of the properties of materials, the processes of life, and technology.

### *A bird's eye view of the history of chemistry*

We wish to highlight here several major historical chemical events, dating back to the centuries just before

Figure 2.1. Timeline showing the four ages in the evolution of modern-day chemistry.



the beginning of modern chemistry. As is shown in figure 2.1, we start our investigation in the sixteenth century with the alchemists and have divided the period after the year 1500 into four periods. We will discuss the crucial questions—namely, the mission of the research, the key ideas (the scientific paradigms), and the status of technology (utilization) within each period.

### The Age of Alchemy

The period from 1500 (this year being more or less arbitrarily chosen) to 1800 is considered to be the “Age of Alchemy.” The nineteenth century is the age in which modern chemistry as we know it today was created, it is the “Age of Categorization.” For reasons that we will explain later, we have chosen to call the twentieth century the “Age of Physical Chemistry.” The beginning of the next century has been named the “Age of Chemical Informatics.”

The Age of Alchemy is illustrated in figure 2.2. During this period the Aristotelian worldview was dominant. The all important goal of the alchemists was to discover the “stone of wisdom” or the “elixir of life” that would prolong life. This idea came via the Arabs

from the Chinese. Since it was believed that gold had the ability to extend life (*vis vitalis*), their main task was to find ways to convert nonnoble metals into gold (transmutation). In hindsight, the “stone of wisdom” was nothing other than a miracle catalyst that, when added to the reaction mixture, would affect the desired transmutation reaction.

The alchemists were the metallurgists of the Middle Ages. They possessed the technology to distinguish minerals that contained metals of potential utility and the knowledge of how to extract these metals. These valuable abilities meant that they were highly regarded by contemporary rulers. This period also saw the use of inorganic compounds—for example, mercury compounds as drugs or paints (vermillion). Sulfuric acid was (catalytically) produced on a large scale and was essential for the treatment of wool and for the manufacture of candles.

The view of the alchemists illustrates a few important points. Chemists, as we will see, are involved in wide-ranging and very fundamental questions that are of broad relevance to mankind. Their activities may have considerable economic value, however, this value is not always in the areas immediately related to the fundamental questions that are considered most important in a particular period.

### Nineteenth century: The Age of Categorization

Chemists such as Lavoisier and Priestley initiated the age of modern chemistry by properly formulating the laws of conservation of mass and by discovering chemical compound formation. As is shown in figure 2.3, we have identified three crucial research topics for this age, the nineteenth century: biogenesis, electrochemistry, and chemical reactivity.

Biogenesis, the search for the origins of biological life, was an area of fundamental importance in the re-

Figure 2.4. Important concepts in the early development of molecular catalysis science.

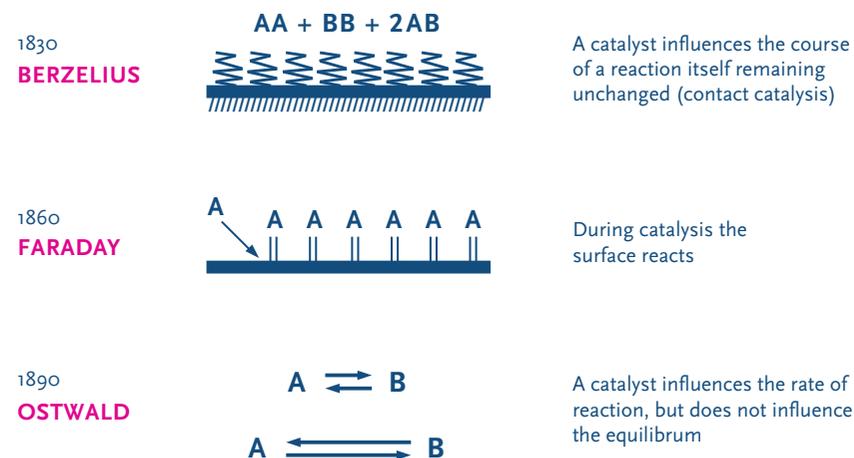


Figure 2.2. The Age of Alchemy. Figure 2.3. The Age of Categorization.

ALCHEMY (1500–1800)		
THE CRUCIAL QUESTION	THE KEY ANSWER	TECHNOLOGY
vis vitalis	elixir of life	sulfuric acid production
transmutation	stone of wisdom	inorganic pigments
		inorganic drugs
		metallurgy

CATEGORIZATION (1800–1900)		
THE CRUCIAL QUESTION	THE KEY ANSWER	TECHNOLOGY
biogenesis	organic chemistry	synthetic organic pigments and drugs
electrochemistry	periodic system	large-scale inorganic industry (soda, $Cl_2$ )
chemical reactivity	catalysis	Davy's mine lamp

search of the early nineteenth century. Scientists wished to determine whether life could originate from lifeless material. Louis Pasteur's research into the origin of living microorganisms, germs, showed this to be impossible. Pasteur demonstrated that germs were introduced from the environment and were not “spontaneously produced” in substances themselves. However, at the same time, chemists discovered that the molecules of life (organic molecules) could be synthesized from nonliving (inorganic) materials. In 1828 this was proven conclusively by Wöhler's laboratory synthesis of urea, a compound known to exist in the urine of many animals from the inorganic substance ammonium cyanate. Prior to this discovery it was widely believed that a so-called life force must also be involved in the synthesis of organic compounds. Organic chemistry was thus established as a branch of chemistry, and at the end of last century this resulted in the creation of organic chemistry-based paint and pharmaceuticals. Previously rare natural materials (e.g., purple dyes extracted from snails to tint paints) were replaced by readily available and cheap synthetic substrates. In the same century soda, previously scarce because its ingredients had to

be isolated from plants, was produced on a large scale by the infant inorganic chemistry industry. This search for synthetic materials to replace natural ones still occupies much of chemists' attention today.

Inorganic chemistry was the first to become a highly developed discipline. In the early part of the century, catalysis as a phenomenon obtained its famous definition from Berzelius: a catalytically active material enhances or suppresses the rate of a reaction but does not alter itself by the reaction. The catalyst reappears unchanged after reaction. How catalysts worked remained a mystery (contact catalysis). Examples of early catalytic systems developed during this time are Döbereiner's tinder box (which made use of the platinum-catalyzed combustion of hydrogen) and Davy's mine lamp.

Electrochemistry led to the discovery of many new elements, in turn, aiding the formulation of the periodic system by Mendeleev. The nineteenth century can be best described as the “Age of Categorization.”

The development of the fundamental principles of catalysis science is illustrated in figure 2.4. After Berzelius' formulation of catalysis as a phenomenon, Faraday noted that the nature of the catalyst may change due to a

reaction. A surface reaction seemed to occur. The next major contribution came when the founding father of physical chemistry, Ostwald, gave the physical chemical definition of the action of a catalyst: a catalyst cannot change the thermodynamics between reactant and product but affects the rate of a chemical transformation. It was Ostwald's definition that led to the idea of continuous catalytic chemical processes that are the basis of the modern chemical industry.

ture: the molecular basis of heredity and evolution, the need to replace natural materials, and radioactivity. The last topic appears to resolve the old alchemists' question. Transmutation of elements appears possible, but in a completely unexpected way. The discovery of radium and the nature of radioactivity by Pierre and Marie Curie led to nuclear medicine and to nuclear energy. Transmutation is a good example of a phenomenon that is frequently observed in scientific development. The desired result may indeed prove attainable, but it often occurs in a very different manner than was originally expected. Further, applications are often found in totally unrelated areas (or perhaps even in previously unknown areas).

At the beginning of this century "guano," a material basic to the production of dynamite, was imported by the Europeans from Chile. However, the imperialistic politics of European nations led to a need to replace this material by man-made nitrates. This led to the discovery and development of the ammonia synthesis and the ammonia-to-nitrate oxidation processes. Both are continuous processes based on heterogeneous catalysis. Their invention has been awarded with several Nobel prizes. The formulation of chemical thermodynamics by van 't Hoff together with Ostwald's definition of catalysis were crucial to these industrial developments. It was now possible to determine the operating conditions under which reaction was possible. The discovery of proper catalyst composition, however, remained completely empirical. Throughout its history the science of catalysis developed as a basis upon which catalyst performance could be predicted. This will be discussed in the next section when we deal with the molecular basis of heterogeneous catalysis.

The development of performance prediction ran parallel to the discovery of numerous new catalytic processes, the driving force for which was often

societal need.[1,2] Among these, the development of the automotive exhaust catalyst is recognized as one of the most significant of recent discoveries. Whereas this development was driven by the need to reduce environmental pollution, many earlier processes continued the trend to replace scarce natural materials with man-made materials (e.g., synthetic rubber, polymers, gasoline, etc.).

The molecularization of chemistry culminated in the second half of the twentieth century with the discovery of DNA as the molecular carrier of hereditary information. The molecular information contained in DNA is transferred to the developing organism by autocatalytic processes. These discoveries were basic to the development of the biogenetic industries.

### Chemistry and industry

The relationship between industry and modern chemistry cannot be neglected. The modern roots of chemistry were in separation and purification. Classical examples are the refinement of sugar from sugarcane and the purification of kitchen salt. Chemistry is concerned with the use of developed methods to produce new materials to meet specific needs. Sometimes these materials can be made by different routes. Sometimes these materials are unknown in nature. Chemistry transforms the role of people from that of passive observers of nature to that of creators of an artificial world. This, of course, may have positive or negative effects. Three important industrial developments from the end of the last century and from the beginning of this one will now be discussed.

One of the first successes of synthetic organic chemistry was Perkin's accidental discovery of a procedure by which purple dyes could be produced. Earlier such dyes were extracted, at a much greater cost, from plants such as madder. This is an example of the substitution of a scarce, naturally occurring material for a readily ac-

cessible, synthetic equivalent. This scenario is again being played out in this century in the use of genetic manipulation of biological systems by efficient and clean production of scarce, but highly desired products. Another example from the last century is the development of the soda process by Solvay, which was also an accidental discovery. He discovered that ammonia, which was liberated in an environmentally friendly manner during coal gasification, could be used to produce soda. The effects on the working conditions of laborers involved were enormous as it replaced the previously used Leblanc process, which exposed workers to harmful emissions of hydrochloric acid and sulfides. The Leblanc process, the first synthetic method for soda production, had replaced the costly extraction from seaweed. Solvay himself recognized the importance of independent research to boundary-broadening discoveries. This is evident from his request that the Nobel laureate Lorentz organize the first Solvay conference, which brought together the crème de la crème of the scientists of the period. The third example is the industrial preparation of ammonia from nitrogen (present in air) and hydrogen (produced by steam reforming of coal) by Fritz Haber. Plants produce ammonia by using sunlight and their biocatalytic systems. They thus anticipate our need for this useful material. The discovery that inorganic materials, such as iron, working as catalysts could produce ammonia on an industrial scale had an enormous effect on agriculture, as the production of artificial fertilizer was now possible. The scientific knowledge gained earlier during the development of the Solvay process was essential to the discovery and development of this and similar heterogeneous catalytic processes.

We recognize in these three examples the motive of the replacement of scarce natural materials and natural

PHYSICAL CHEMISTRY (20th century)		
THE CRUCIAL QUESTION	THE KEY ANSWER	TECHNOLOGY
molecular basis of heredity / evolution	DNA / RNA (autocatalysis)	genetic manipulation
substitution of natural scarce materials	polymer chemistry	polymer industry
radioactivity	homogeneous catalysis	large-scale, continuous chemical processes
	heterogeneous catalysis	
	transformation of nuclei	nuclear energy, medicine

Figure 2.5. The Age of Physical Chemistry.

### The Age of Physical Chemistry

We have called the twentieth century the "Age of Physical Chemistry." Classical physical chemistry gave birth to heterogeneous catalytic processes. The development of these processes required the development of complex chemical engineering. In addition, colloid chemistry and polymer science were other branches that played important roles. The discovery of quantum mechanics by physicists was also revolutionary to chemistry. It led to the understanding of the nature of the chemical bond and to completely new spectroscopies (using lasers, nuclear magnetic resonance) and materials (semiconductors). It established chemistry as a molecular science. The molecularization of chemistry is the essential contribution of this century.

As shown in figure 2.5, three crucial research topics characterize our cen-

processes by man-made materials and processes. These are often of higher quality and result in a more livable world. The extension of the early discoveries of this century has resulted in many other scientific and industrial developments. These include the large-scale production of new and useful materials, some of which are unknown in nature—for example, margarine, biodegradable detergents, gasoline and diesel fuel, polymers, and weedkillers. Clean, energy-efficient processes, such as modern petroleum refining, electricity generation, solar energy conversion, and exhaust emission control catalysts, have been developed.

There is a continuous cycle of wishes and discoveries in which the successful production of the desired molecule is often a matter of discovering the “right chemistry.” Modern developments include materials that possess unexpected chemical and physical properties. Nobel prizes have been given for the discovery of high temperature superconductors and for “buckyballs” and for acid catalysts. The development of modern computer technology is unthinkable without the very special properties of new materials, sometimes developed or discovered simply because the need for them existed.

### Molecular heterogeneous catalysis

The conceptual development of molecular heterogeneous catalysis that occurred in this century is illustrated in figure 2.6. Several discoveries essential to the development of a mechanistic understanding of heterogeneous catalytic kinetics are shown. Of course, these discoveries were not possible without the impressive progress in instrumentation, computational advances, and perhaps even more importantly, the detailed study of model systems. Most important and revolutionary to kinetics is the ability to predict the activation energy of

elementary surface reaction steps by computational means.[3] Fundamental to catalytic kinetics is the Sabatier principle. It explains the volcano curves obtained by Balandin and by Sachtler that appeared when the rate of a reaction was plotted as a function of a material-reactivity parameter—for example, the heat of formation of bulk oxides.[2a,4] When the interaction between reactant and catalyst is weak, the rate of the reaction increases with increasing catalyst reactivity. A maximum in the rate appears at optimum interaction strength. When the interaction with reactant or product becomes too large, the rate slows down because desorption now becomes rate limiting. The surface changes from its initial nearly empty state, when the interaction strength is small, to one in which it is highly covered with reaction intermediates, when the interaction strength becomes large. Sabatier’s principle indicates that optimum catalytic performance does not relate to a particular surface electronic property, but is due to the balance in rates of activating and desorbing elementary reaction steps that are part of the catalytic reaction cycle.

Another very important step in the development of an understanding of the molecular events occurring on catalyst surfaces was the discovery of corrosive chemisorption, which was first reported by Holscher and Sachtler.[5] It was observed that the positions of atoms on the surface of tungsten metal were altered during the dissociative adsorption of molecular nitrogen. This phenomenon revealed two important concepts fundamental to modern molecular heterogeneous catalysis: the concept of a surface complex as a unique entity and the concept of surface reconstruction.[6] The surface complex formed by adsorbing atoms or molecules usually has a local structure very similar to that of molecular coordination complexes. Indeed, very often the vibrational spectrum of adsorbed

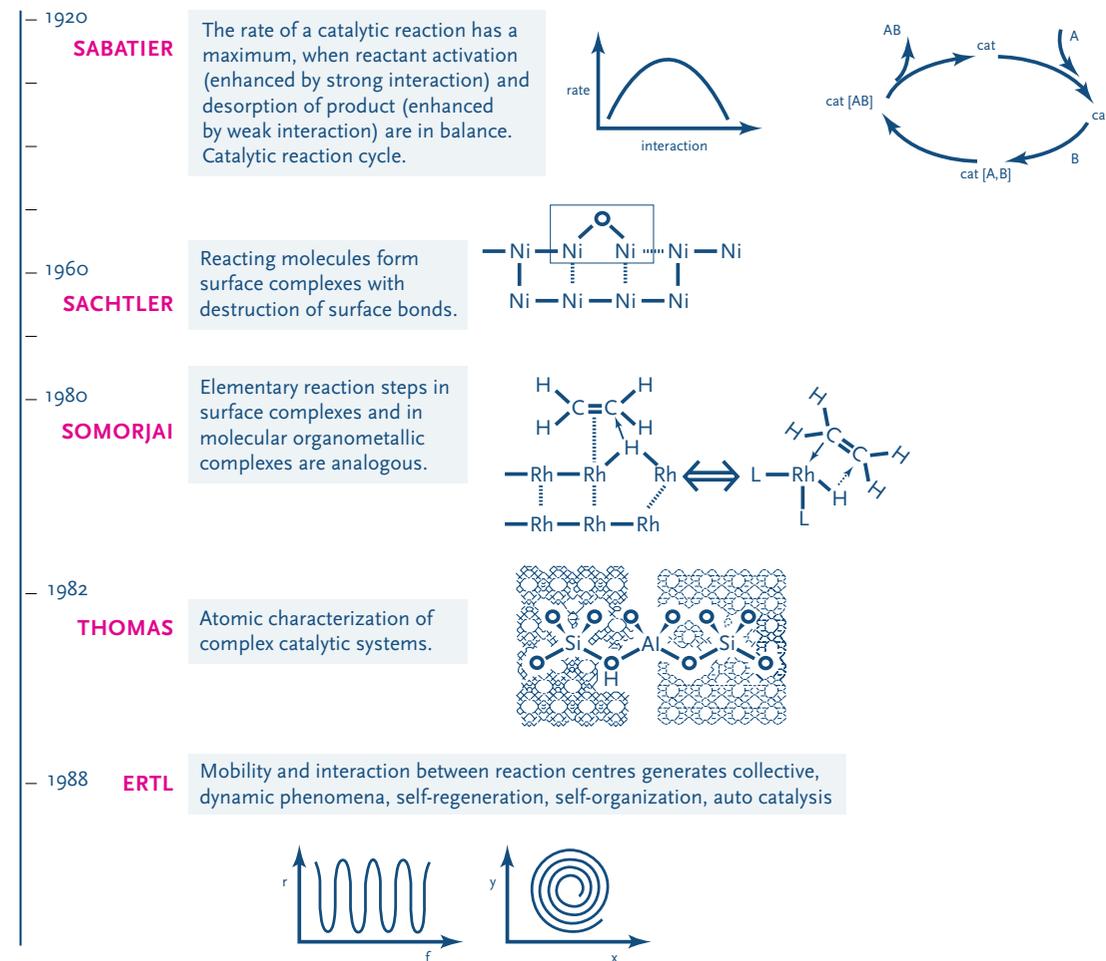


Figure 2.6. Several important discoveries essential to the conceptual development of molecular heterogeneous catalysis.

molecules compares very closely to that produced by analogous molecular organometallic compounds. The only major difference is in the interaction energy that differs as a result of the weakening of surface atom—atom bonds upon adsorption. This electronic response costs energy and depends strongly on surface state or type of complex.

The concept of the adsorbed state as a surface complex brought chemisorption within the realm of molecular chemistry. Surface corrosion and surface reconstruction are closely related features since both result from the weakening of the surface bonds upon chemisorption. Surface reconstruction also requires strong lateral interac-

tions between adatoms or molecules. Such lateral interactions may lead to island overlayer formation and demixing of adlayers containing different adsorbed species. Surface reconstruction with transport of metal atoms occurs when the corresponding energy cost is overcome by the more favorable adatom or admolecule bonding energies in the reconstructed phase. Since catalysis is cyclic, however, any changes due to surface reconstruction must be undone during each repetition of the sequence (self-repair).

The three key features of a catalytic reaction—activation, desorption, and self-repair—have been shown in certain instances to couple in such a manner as to produce nonlinear

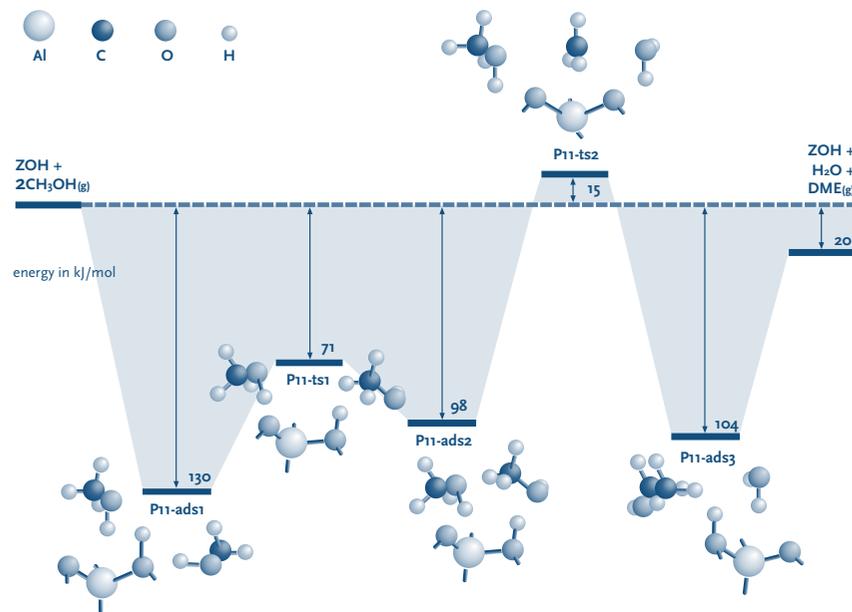


Figure 2.7. Calculated reaction energy diagram for the conversion of an adsorbed methanol complex to dimethyl ether and water under the influence of the acidic zeolite proton.[15]

feedback effects that result in self-organization of reactants and intermediates. Oscillatory reactions and spatiotemporal overlay structures may then be observed.[7] Surface reactions have also been shown to possess strong autocatalytic behavior. Whereas lateral effects and island formation lead to short-range synchronization of the catalytic cycles, surface diffusion synchronizes over larger distances and gives rise to macroscopic oscillatory kinetics. The intimate coupling of diffusional phenomena and localized reactions is also quite apparent for reactions that occur in the micropores of zeolites.[8] The micropore filling with reactants or products is strongly dependent on micropore size as this largely affects the interaction energies of molecules adsorbed in zeolites.[9] Diffusion, of course, becomes more difficult as the micropores become full. Hence, to predict and understand the catalytic differences between zeolites, this intimate relationship will have to be unraveled.

Detailed molecular understanding makes bridges between several

important catalytic subdisciplines possible. One important consequence is the reformulation of the modeling approach in chemical engineering. Instead of the use of parameterized kinetic equations with parameters fitted to experimental data, the new approach attempts to predict these parameters using statistical methods such as Monte Carlo methods and molecular data.[10,11] An example of the latter are quantum chemical studies of the activation of methanol by solid acid zeolitic protons.[12] A representation of the zeolitic proton and the zeolite lattice is found in figure 2.6 (Thomas' atomic characterization). One of the most interesting results is that the zeolite protons behave in a totally different manner than the protons found in solutions of strong acids. The interaction of the protonated, positively charged reactant with the negatively charged zeolite wall has an essential influence on the course of solid-acid-catalyzed reactions. The structure of an adsorbed cluster, consisting of two methanol molecules surrounding an acidic proton, and the changes in energy that it undergoes

during reaction is shown in figure 2.7. Here the methanol molecules are shown to interact with a protonic site of the zeolite lattice. The reaction energy diagram is given for the conversion of methanol into dimethyl ether and water. The reactive intermediates in contact with the zeolite atoms are drawn at the minima and maxima of the energy diagram. We recognize that these activated cation complexes are similar in structure to the stable, cationic intermediates found in liquid superacids.

Chemistry is concerned with the synthesis of new compounds and with the development of new processes. Knowledge serves synthesis. Modern catalytic systems are developed by using a combination of molecular insight and modern synthetic techniques. The development of a catalyst requires insight into the mechanisms of self-regeneration. This is enormously important for industrial catalysis. For many catalytic systems the overall economics of process are determined by the lifetime of the catalyst. Many catalysts lose their ability to regenerate themselves after a certain time, thereby losing their activity. A great deal of research is carried out by industry to solve this problem.

The above can be illustrated by the use of titanium-containing catalysts to affect the industrially important production of propylene oxide, a precursor of polyurethane. The selective liquid-phase oxidation of propylene to propylene oxide appears to be limited by the slow rate of dissolution of the necessary titanium complexes in the reaction medium. Titanium gels,

however, dissolve rapidly. The Ti-O bond that must be broken during the catalytic reaction cannot reform in the titanium gel. This does not permit the formation of many diagonal bonds and circular rigidity. However, in the discrete complex, reconstruction is possible. The practical problem now focuses on the creating the soluble complex itself.

The solution to the above problem can be found using the dimensions of the reactive complex and our knowledge of microporous systems. A stable heterogeneous system can be devised, in which the complex is encaged in a microporous material whose pores are of the same order of magnitude as the diameter of the catalytically active complex. The tight fit of the complex within the pore results in a strong interaction between the two. In fact, the complex remains bound to the micropore even during reaction. Refinement of synthetic structures makes artificial catalytic systems possible. This can be accomplished as well and sometimes better than by using natural biocatalysts—that is to say, enzymes.

### The twenty-first century: The Age of Chemical Informatics

Possibly the twenty-first century will become the "Age of Chemical Informatics." Not only will molecular manipulation lead to molecular recognition for highly specific design of (catalytic) materials, but it may also make new molecular-based information processes possible. Major challenges, as we see them now, are renewable energy and the question of whether self-reproducing man-made systems can be designed. This could be referred to as the quest for the generation of artificial life. As we see it now, ideas such as self-organization, autocatalysis, and complex catalytic networks are concepts that will belong to the answers to such a search in the next century.[14]

As we begin the twenty-first century, new developments in catalysis will

Figure 2.8. The Age of Chemical Informatics.

CHEMICAL INFORMATICS (21st century)		
THE CRUCIAL QUESTION	THE KEY ANSWER	TECHNOLOGY
artificial life	self-organization	biogenetic industry
renewable energy	biomimicry	catalytic systems

be strongly driven by environmental needs. Processes are required to clean both effluent gas and water streams. In addition, there is an increasing interest in selective catalytic processes that reduce waste by eliminating undesired byproducts. The increasing understanding of the molecular basis of catalytic processes combined with the need for stereo- and enantioselective catalysis will provide a fruitful application area for organometallic and coordination catalysis. Molecular control is then possible by the synthesis and use of organic ligands. Supramolecular approaches directed toward molecular recognition and organized systems may be useful to biomimetic catalysis.

The revolution in our molecular understanding of the gas-solid interphase has been mainly due to the application of model catalytic systems, such as single crystal surfaces and the use of advanced spectroscopies. A similar approach toward the deepening of our understanding of the liquid-surface interphase should be undertaken. This is even more desirable with the increasing interest in liquid-phase processes.

Electrochemistry may provide the key to bridging heterogeneous and biocatalysis. For example, the oxidation of ammonia to nitrogen in waste streams is a highly desirable reaction. In the gas phase, this low-temperature process catalyzed by noble metals is becoming reasonably understood. Ammonia is activated by preadsorbed atomic or molecular oxygen on a platinum surface to give adsorbed NH and OH intermediates.[15] Nitrogen formation takes place by consecutive NH activation and nitrogen atom recombination. Oxygen adatoms are needed to activate the NH bond in NH<sub>3</sub>. The high exothermicity of OH formation overcomes the relatively weak hydrogen-platinum surface interaction. Interestingly, by contrast, no adsorbed oxygen is involved in the activation of the NH bond in the electrocatalytic

oxidation of NH<sub>3</sub>[16]. The overall stoichiometry for the half-reaction is:



In the electrochemical system, the necessary activation of NH<sub>3</sub> on the platinum surface is accomplished by the solvation of the protons generated; water molecules participate directly in the ammonia activation step performing the same role that preadsorbed oxygen plays in the gas-phase reaction.

It is also quite interesting to compare the electrocatalytic conversion of ammonia to nitrogen with its reverse reaction, nitrogen activation, which is accomplished biocatalytically at room temperature by the enzyme nitrogenase. The iron-sulfide cluster active in this reaction initiates nitrogen activation by electrochemical reduction with formation of N<sub>2</sub><sup>-</sup>. [17] Ammonia production occurs consecutively by protonation of N<sub>2</sub><sup>-</sup> and continued electron transfer:



### Conclusions

We have argued through the use of historical examples that the progress made in catalysis science and technology from the age of the alchemists to the present day has been intimately linked to the search for answers to a broad range of fundamental questions relevant to mankind. Often the desired result has proven to be achievable, however, the manner in which it is finally accomplished may be quite different than that originally conceived. In addition, developments resulting from research activities have often been of value in areas that were totally unrelated to those intended at the time, often producing entirely new areas previously unknown. Chemistry in general and catalysis science in particular has developed as a result of our need to bridge the gap between the properties of materials and of life, as well as technology. Technology has been driven by the needs of society. One continuing, recurring need is the need to replace rare or expensive

materials with more readily available, cheaper materials. Environmental concerns have been an important driving factor in the past and are expected to be even more important in the future. The progress achieved in the last 400 years has resulted in our current molecular mechanistic understanding of catalytic processes occurring at a macroscopic level. This will allow us to predict the performance of materials as catalysts under various reaction conditions and aids us in developing new catalytic processes. The continued development of this molecular understanding and its continued application into the twenty-first century to problems arising due to the needs of society will almost certainly ensure that catalysis will continue to be an important and dynamic field of endeavor for many years to come.

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# 3

## Chapter 3

### Theory of Metal Catalysis

## 3.1

# BEYOND THE THEORY OF METAL CATALYSIS

By *Matthew Neurock*

Matthew Neurock is the Alice M. and Guy A. Wilson Professor of Chemical Engineering and Professor of Chemistry at the University of Virginia. He specializes in the areas of computational catalysis, computational chemistry, and molecular reaction engineering. His work is focused on understanding the mechanisms and active sites that control catalysis and electrocatalysis over a wide range of materials, including supported metals, metal alloys, oxides, sulfides, carbides and zeolites, the development of structure-property relationships, and the design of new materials.

Rutger has provided a wealth of insight, guidance, and direction to the field of catalysis over the past forty years and is considered the leading founder of theoretical and computational catalysis. This stems from his outstanding ability to couple theoretical chemistry and experimental catalysis to provide novel insights into the electronic and structural factors that control surface chemistry, as well as the influence of the complex reaction environment. The tremendous advances in spectroscopy and characterization that have occurred over the past few decades have led to the development of novel insights into the atomic scale features that control the molecular transformations in catalytic systems.

In addition to these experimental advances, novel developments in theory and exponential increases in computing have allowed for the simulation of complex material systems. Rutger has been the leading figure in integrating these advances and developments in experiment and theory, as they have occurred, into breakthroughs in understanding catalysis. I will try to outline here a personal account of the developments in the field along with my interactions with Rutger over the past twenty years.

Most of the work in theory applied to catalysis up until the early nineties was focused on the development of models to understand surface adsorbate bonding. Pioneering developments by Hoffmann, van Santen, and Anderson in applying simple electronic structure theory (extended Hückel theory, or EHT) to predict how changes in the metals and conditions would come to influence catalysis. They used such ideas to predict periodic trends. Their predictions were based on their strong understanding of the chemical bonding and reactivity and were thus able to demonstrate the controlling phenomena, even with very simple models of reactivity. As such, many of their predictions have held true. Professor van Santen's work in the areas of Fischer-Tropsch synthesis, ethylene epoxidation, acid-catalyzed hydrocarbon conversions, and hydrodesulfurization have been pivotal, as they have set a strong foundation for understanding these mechanisms.

I first met Rutger at the plenary talk he gave at the 1992 International Symposium on Chemical Reaction Engineering (ISCRE) in Toronto. I had some experience in carrying out simple theoretical calculations on small molecules and had an interest into extending this to model-

ing catalytic materials. His talk was eye-opening as it showed what was currently possible and how far he had advanced the field. Density functional theory (DFT) was just beginning to emerge as a novel technique to solve the electron structure of molecular and solid-state systems. Rutger had already begun to advance its use in the analysis of surface chemistry. He was now able to build on many of the important, simple ideas that he gained from qualitative EHT calculations to carry out more quantitative analyses of the reaction kinetics and mechanisms through the use of DFT. Some of his first efforts were aimed at ammonia oxidation.

I'm greatly indebted to Rutger as my time spent working with him as a post-doc changed my life forever. He has an enthusiastic passion for science, which I, and no doubt others too, found highly contagious. I learned from him the importance of how bonding influences reactivity and to search not only for the answers to specific mechanistic questions, but also to search deeper for the underlying foundations that control other reactions, the changes that occur in changing catalysts, and the influence of the working catalytic environment. In addition, he was a wonderful and generous host, who taught me as well as my wife a great deal about the Netherlands, its history, and the Dutch culture.

I was learning so much working with Rutger and having so much fun that I extended my stay in the Netherlands by six months. By this point in time, Rutger had demonstrated the tremendous impact that DFT had on providing not only qualitative guidance but also near quantitative energetics, for predicting adsorption energies and activation energies over different metal compositions and surface structures. We then began to develop some of the first quantitative structure-reactivity relationships to guide the reactivity of ideal metal surfaces.

Rutger knew that I was interested in teaching and strongly advised me to spend some time in industry before moving on to academia. He was instrumental in helping me land a position as a visiting scientist at the DuPont Experimental Station in their Corporate Catalysis group. My supervisor at DuPont, Dr. Jan Lerou, had been following Rutger's work over the years and recognized the tremendous synergy between theory and experiment. He brought Rutger in as a consultant to support a collaborative effort between the two of us on vinyl acetate synthesis and, in addition, to support other efforts at DuPont.

By this point in time, in 1993, DFT had reached the stage where it could be used to predict the adsorption and reactivity of small molecules on ideal surfaces. The necessity to solve actual industrial problems, such as vinyl acetate monomer (VAM) synthesis, forced us to extend these ideas to more realistic environmental conditions. In order to properly describe the chemistry under operating conditions, we had to fully explore the effects of surface coverage, alloying, and alloy segregation. These effects could not be explored with cluster models, which had been used throughout the computational catalysis community, but instead required the adoption of periodic DFT methods that had been developed in the solid-state physics community. In addition, he guided parallel experimental efforts at DuPont, which carried out in situ Raman studies to fully establish the mechanism over homogeneous palladium acetate clusters.

Our friendship and scientific interactions have continued and have grown stronger over the past two decades. We have collaborated closely and have published numerous papers together since my move to Virginia in 1995. We extended many of the fundamental concepts for surface reactivity to other catalytic systems.

Rutger was instrumental in guiding much of our initial efforts on the hydrogenation of olefins. In particular, we published a joint paper on the formation of transient intermediates that form in the hydrogenation of ethylene. [1] This earlier work has been the basis for much of our efforts on the selective hydrogenation of oxygenates derived from biomass and used in the synthesis of fine chemical and pharmaceutical intermediates.

In 2006 we embarked on a remarkable journey together to coauthor the first book on computational catalysis entitled *Molecular Heterogeneous Catalysis: A Conceptual and Computational Approach*. [2] We set out to describe the remarkable advances that occurred in theoretical catalysis and its application to catalytic systems over the previous two decades. The work provided a detailed account of the principles that govern the theory of chemisorption and molecular bond-making and bond-breaking processes

elementary processes and establishing the electronic factors and underlying principles that control these steps. In addition, we attempted to provide an integrative framework by which it would be possible to extend such ideas and draw clear analogies with more complex catalysts found in nature that drive similar biochemical transformations. The latter came solely from Rutger, who had long contemplated the chemical theories on the evolution and adaptation of protocellular systems, the biocatalytic design principles that exploit immunoresponse, cell growth, self-assembly, and their analogy and potential adaptation to heterogeneous catalysis. This provided a new foundation for understanding and interpreting catalysis and has been a major focus of much of Rutger's present research.

Writing the book was a rich and invaluable learning experience for which I am forever grateful to Rutger, as it allowed us to work together

Table 3.1: Top coauthors in this theme, with the number of papers together with Rutger van Santen and their affiliation. Source: TU/e Library

113 PUBLICATIONS		
40	JANSEN, A.P.J.	TU/e
13	KOPER, M.T.M.	Leiden University
11	LUKKIEN, J.J.	TU/e
9	SHETTY, S.G.	Sabic, Bangalore
8	NEUROCK, M.	University of Virginia, Charlottesville
7	BAVEL, A.P. VAN	Topsoe, Denmark
7	HILBERS, P.A.J.	TU/e
6	HERMSE, C.G.M.	TNO, Eindhoven
5	BIEMOLT, W.	TU/e
5	BURGHGRAEF, H.	TU/e

that occur on metal, metal oxide, metal sulfide surfaces, and within microporous systems. It described the application of these principles to the kinetics of complex catalytic processes and extended these concepts and their analogy to complex biological transformations that occur in nature. As such, we attempted to provide a reductionist approach to analyzing the complex catalytic systems in terms of their

to clearly connect the concepts of formal chemisorption and reactivity theory to actual catalytic systems. His excitement and enthusiasm made this the most exciting and educational endeavor that I've ever been involved in. We spent countless hours together in Eindhoven, Charlottesville, and Georgetown discussing principles that control catalysis. I'm also greatly indebted to his wife, Edith, who would

join us on most occasions and make sure that we would take time to eat, monitor what we ate, and occasionally take us shopping. This remarkable experience brought our families much closer together, as Rutger and Edith would spend many weekends with my wife and young children in Charlottesville. This forged a remarkable friendship.

Rutger is a superb scientist, teacher, mentor, and a wonderful individual who has inspired and made an impact on the lives of so many in our field. I am forever grateful to him for the tre-

mendous impact that he has had on my life and my career and for his enduring friendship.

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## 3.2

# THEORY OF CHEMISORPTION

By *Rutger van Santen*

When I was working at Shell Research on the formal theory of chemisorption in the context of catalysis in the late 1970s, I was highly surprised to discover that there is a great similarity with the theory of scattering. The formal theory of chemisorption had been adapted from the impurity theory of solid-state physics to be able to handle the chemisorption of atoms to metal surfaces. The formal theory of chemisorption and scattering theory are both quantum mechanical resonance theories based on this resolvent method, originally developed for nuclear physics by F. Dyson using Green's functions. I was fortunate enough to meet T. B. Grimley from Liverpool, one of the founders of this theory, at a conference. He introduced me to this field.

I had studied the formal theory of scattering as the subject of my PhD thesis with Luut Oosterhoff, my PhD advisor, at Leiden University. But it was not until I had seen the parallels with chemisorption that I realized how advances in one field could be translated into another. I had close contact at that time with Cesare Pisani, who was collaborating with Grimley at Liverpool University. Later Cesare became a leading computational chemist in Turin, Italy. Through my contact with Cesare, I also became interested in formal embedding methods of clusters into extended lattices. This is an interesting theoretical method because it enables a theoretical comparison of cluster studies with those of surfaces from which the cluster is a part. I extended the molecular-orbital-type approaches based on the tight

binding approximation with effective one center repulsion integrals on the adsorbate and metal. These integrals depend on the repulsion with electrons on neighboring atoms, which proved relevant to later developments in chemisorption theory. It makes it possible to estimate the change in electrostatic interactions of electrons at a surface compared to the bulk of a metal. It results in an upward shift of the d valence electrons on a surface compared to the bulk and hence is a signature of the increased reactivity of surface atoms. This has been pointed out later especially by Jens Nørskov, who was then at Nordita in Copenhagen.

Jens and I met for the first time when we both had a poster in the same booth at the 8<sup>th</sup> International Congress on Catalysis in Berlin in 1984. At that time we both were very interested in the theories described above, also known as the Newns-Anderson models, which still play a central role in formal chemisorption theories. Jens is one of the leading theoretical physicists in computational catalysis in the world. We shared an early interest in applying quantum chemical theories to catalysis. In the pioneering period of the early nineties I was invited to Denmark several times to discuss our work and, in turn, I have invited him many times to Eindhoven. He has been one of my great scientific colleagues in computational catalysis through the years. TU/e awarded Jens an honorary doctorate in 2006.

Through discussions with colleagues at Shell Research and with Wolfgang

Sachtler especially, who was also professor of catalysis at Leiden and who became my managing boss at Shell Research, I started to formulate fundamental questions on chemisorption. I developed simple quantum mechanical models to address the following questions:

- How does the adatom bond of a hydrogen atom depend on d-band width and d-band occupation? How does this relate to the metal surface coordination number?
- What determines the preference of carbon monoxide or hydrogen to be adsorbed at particular surface metal atom sites?
- Do surface symmetry orbitals play a role in answering these questions?

These were the main themes that stayed with me for the rest of my career. It began in the seventies with the use of the extended Hückel method and formal chemisorption theory. Ten years later I collaborated with Marja Zonnevylle, who had joined us at Shell Research from Cornell. We analyzed chemisorption with Marja and her supervisor from Cornell, Roald Hoffmann, in terms of the interaction of surface group orbitals of surface electrons. Later I continued this type of analysis through first-principle cluster studies for chemisorption. These resulted in the first density functional theory (DFT) papers I coauthored with Evert-Jan Baerends from the VU University Amsterdam and Tonek Jansen at Eindhoven.

R.A. VAN SANTEN (1982). *Chemical-Bonding Aspects of Heterogeneous Catalysis. I. Chemisorption by Metals and Alloys. Recueil des Travaux Chimiques des Pays-Bas, 101 (4), 121–136.*

### Chemical-Bonding Aspects of Heterogeneous Catalysis. I. Chemisorption by Metals and Alloys

**ABSTRACT** We discuss chemisorption to metals and alloys using an elementary tight-binding-type of approach. Calculated results are interpreted in terms of model parameters, which have a chemical meaning. We conclude that the structure of the surface around the adsorption site has to be included properly in any model used. Since the interaction with the Group VIII metals

is for a large part taking place via the *d*-electron band and these electrons are highly delocalized, differences in site geometry between adsorbed molecules have to be studied on models that properly take into consideration the delocalized nature of the electrons. This means that interactions over at least several atomic distances have to be accounted for.

#### The Preference of Adsorption Site

**COMMENT** The two figures above show a model cluster (figure 3.1) and its binding energy (figure 3.2) as a function of  $\mu$ . The model cluster simulates the interaction of a hydrogen atom with a metal surface. Figure 3.2 shows the results of a tight-binding-type calculation. The hydrogen atom (white) interacts with *Z* metal atoms (black) of the surface, which have *Z'* neighbor metal atoms. The paper shows that the hydro-

gen atom's preference for being adsorbed to a single surface metal atom or in a higher coordination site depends on the valence electron band filling of the metal atoms. The model compares results between a half-occupied (1 electron per atom) and completely occupied (2 electrons per atom) metal valence band. The parameter  $\mu$  increases with an increasing ratio of  $\beta'/\beta$ . The interaction energy

between the hydrogen atom and metal atom is  $\beta'$  and between two metal atoms is  $\beta$ . Adsorption in high coordination sites is preferred for all values of  $\mu$  when the metal valence band is only half occupied. For large values of  $\mu$  this difference is proportional to the square root of the number of binding surface atoms *Z*. This is the surface molecule limit. It changes when the valence band is completely occupied. Then low co-

ordination is preferred. The repulsive interaction that causes this difference is proportional to *Z*. It clarifies the experimental finding that for many transition metals, preference for adsorption is sometimes on top of the metal atom. This is a purely quantum mechanical effect that relates to the dominance of Pauli repulsion. It is a topic I often returned to when quantum chemical methods improved.

Figure 3.1

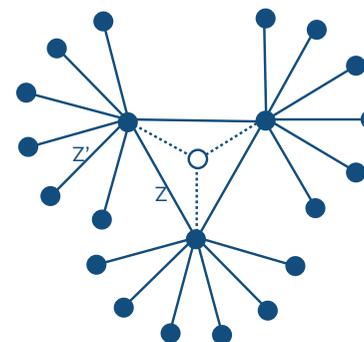
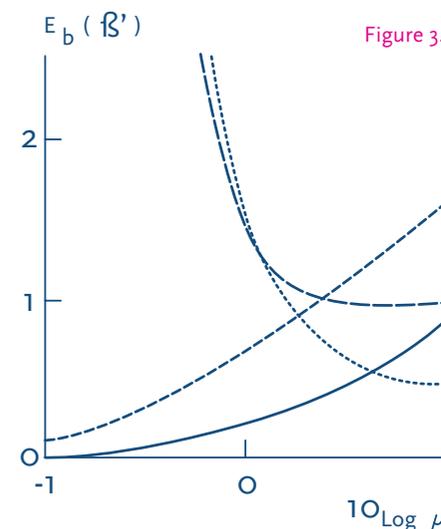


Figure 3.2



#### RESEARCH HIGHLIGHT

#### RESEARCH HIGHLIGHT

RUTGER A. VAN SANTEN (1987). *Coordination of Carbon Monoxide to Transition Metal Surfaces. Chem. Soc., Faraday Trans., 1, 1987, 83*

### Coordination of Carbon Monoxide to Transition Metal Surfaces

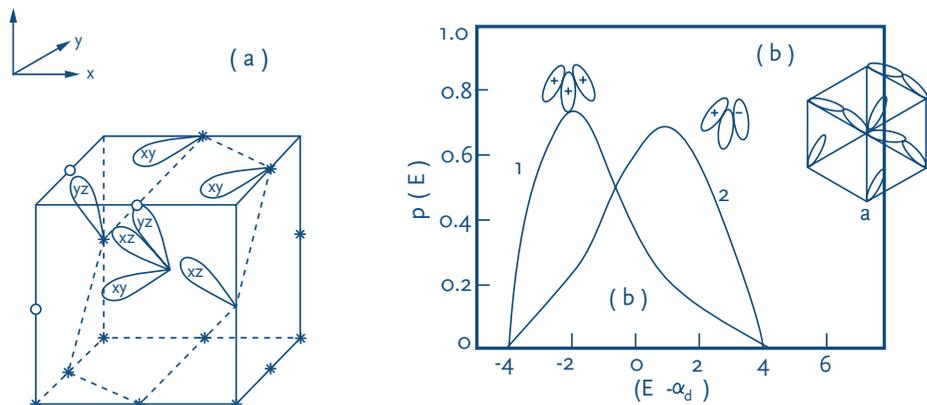
**ABSTRACT** The coordination of CO chemisorbed on a transition metal surface is a sensitive function of the electronic structure of the surface metal atoms. The group orbital concept appears to provide a key to the understanding of the fundamental electronic features that determine the stability of adsorption complexes. This will be demonstrated using a simple quantum chemical approach, which is the surface analog of the Hückel molecular orbital method. Analysis of chemisorption on the surface of an *s*-band lattice as a function of band occupation shows the following: multiatom coordi-

nation is favored at low electron band occupation and single-atom coordination at high electron band occupation for adsorbate orbitals of *s*-symmetry; interaction with orbitals of *p*-symmetry is only possible at bridging positions and increases with band filling; the effect of changes in surface geometry on chemisorption is a function of band occupation.

Chemisorption of CO on platinum is discussed in detail. It is shown that CO prefers coordination to a single atom because of the relative large interaction of the CO-5 $\sigma$  orbital with the highly occupied *d* valence electron band.

The increase in  $2\pi^*$  occupation, deduced from infrared studies, for CO adsorbed on a single-atom position with increased Pt surface atom unsaturation is found to depend critically on the occupation of the Pt surface d valence electron band. Coadsorption effects of potassium and sulfur are discussed. Sulfur coadsorption induces changes in the electronic structure that can be understood on the basis of changes in covalence. Low-coverage alkali-metal coadsorption has two effects on CO chemisorption. Direct interaction with adsorbed alkali metal occurs, resulting in very large decreases in CO frequency and indirect long-range effects occur, resulting in the case of Pt in a shift of CO from a single-atom to a bridge position. The latter effect is calculated to be due to the changed electrostatic potential at the metal surface.

Figure 3.3



### Orbital Symmetry Effects on Surfaces: Surface Group Orbital Interactions

**COMMENT** This paper was my first lengthy paper on the chemisorption of carbon monoxide to a transition metal surface. It analyzed differences in preferred adsorption sites in terms of the symmetry of interacting orbitals. It investigated for carbon monoxide the driving force for adsorption in high and low coordination sites. Scattering-theory-type Newns-Anderson expressions have been solved as a function of d valence bond occupation. The main conclusion is that the interaction between CO- $5\sigma$  orbital and doubly occupied metal d valence electrons forces carbon monoxide to be adsorbed into the on-top adsorption site. The paper implies a significant modification of the Blyholder model, which was current

at that time. 3.3 figure gives a surface d-electron density of state, showing that the surface group orbital local density of states that interacts with the different carbon monoxide orbitals is very different. Curve 1 shows the surface group orbital local density of states for the dxz, dyz, and dxy lobes of surface atomic orbitals interacting with a CO- $5\sigma$  orbital. Curve 2 shows the surface group orbital local density of states that interacts with the CO- $2\pi^*$  orbital. The deep location of the group orbital local density of states (LDOS) that interconnects with the CO- $5\sigma$  orbital implies a large repulsive interaction in a high coordination site. The repulsive interaction is converted into an attractive interaction for the  $2\pi^*$  orbital.

## 3.3

# THEORY OF METAL CATALYSIS

By *Rutger van Santen*

My first theoretical study at Shell Research, when I started there in 1972, concerned the statistical thermodynamics of the surface composition of alloys. Heterogeneous catalysis was completely new to me. Wolfgang Sachtler, who at that time was the department head at Shell Research as well as a part-time professor at Leiden University, had a major interest in heterogeneous catalysis. He had been making the scientific argument that the reactivity of transition metal surfaces should be related to the surface composition and reactivity of exposed surface atoms, rather than to overall bulk physical properties like magnetic properties or electric conductivity. This molecular view of catalytic reactivity was one of the theories that made the “Dutch School of Catalysis” famous.

As my boss at Shell, Wolfgang strongly encouraged me to study the surface composition of alloys that are used as catalysts. Knowledge of this composition was necessary for making useful catalytic studies. Colleagues of mine were highly involved in experimental work. Therefore, I was put in charge of finding the theory to predict surface composition as a function of the properties of their components. After completing this work, I started working on studies that show the relationship between changes in chemical reactivity and chemisorption in metal alloys. Wolfgang had developed notions such as the ensemble effect and ligand effect to rationalize these changes. The ensemble effect assigns the reactivity of a molecule in contact with a metal surface to its contact with several reactive metal atoms. Alloying

with a nonreactive metal atom will reduce ensemble size and hence reduce reactivity. Apart from this geometric effect, electronic changes may alter the reactivity of the surface metal atoms. He called this “the ligand effect.” These two concepts were an important starting point for later theoretical work on chemisorption.

Ad de Koster was my first PhD student at Eindhoven, and we initiated extended Hückel calculations on the dissociation path of carbon monoxide on models of transition metal surfaces. Al Anderson from Cleveland provided the software. The calculations enabled us to approximately calculate interaction energies of molecules with surfaces. Differences could be related with changes in the electronic structure of different surface models studies. We developed a preliminary idea on site dependence of carbon monoxide dissociation.

By the end of the eighties I had met Evgeny Shustorovich at a conference in the United States. Back then he was with Eastman Kodak in Rochester and did his postdoctoral study with Roald Hoffmann, the Nobel laureate from Cornell, after having fled from Russia. He worked on the theory of chemical bonding of molecules to surfaces and had developed a semiempirical theory of chemisorption that could predict adsorption energies as well as transition state energies. Although approximate, it greatly appealed to me because it was one of the first methods capable of predicting transition state energies. For some time we had close contact. Evgeny had developed his so-called bond-order conservation

principle, which he could use to quantify energies. Energies could be expressed as a function of the coordination number of a metal atom. It became one of the leading principles in our work on surface chemical reactivity. It helped us to calculate how low activation energies of molecules at a transition metal surface depend on surface adsorbate coverage.

The work with Evgeny took place at a time when quantitative first-principle quantum chemical studies like those we have now were not available yet. His theories initiated our interest in structure sensitivity and insensitivity of surface chemical reactions. The extensive work that followed using the density function theory-based (DFT) quantum chemical studies has been summarized recently in the 2010 *Chemical Reviews* paper “Reactivity Theory of Transition Metal Surfaces: A Brønsted-Evans-Polanyi Linear Activation Energy-Free-Energy Analysis,” cowritten with Matthew Neurock and Sharan Shetty. For the analysis of surface reactivity, the bond-order conservation principle appears to be essential. In 1995 Matthew and I had published a paper in *Catalysis Reviews* that summarized our understanding of the Sabatier principle and the Brønsted-Evans-Polanyi principle. The ideas presented in that paper on the Sabatier principle stemmed from my early confrontation at Shell Research with Sachtler’s views on the volcano curves of formic acid decomposition.

I carried out the first ever complete first-principle quantum chemical studies of reaction energy diagrams of desulfurization and ammonia oxidation with Matthew. They were cluster studies based on the use of the Amsterdam density functional (ADF) code. These reaction energy diagrams showed how initially interaction between a reactant and a catalyst stabilizes intermediates, and also that to release a reactant from the surface, energy is needed. The more stabilized the intermediates, the less reactive

the catalyst. It was the first time I saw a quantitative analysis of the Sabatier principle that describes an optimum catalyst as one that balances the rates of reactant activation and product desorption.

Matthew was my first postdoctoral fellow at Eindhoven. It was the beginning of a lifelong friendship. I had actually met Matthew for the first time in Toronto at a chemical reaction engineering meeting when he was still a graduate student. I had been invited to deliver a plenary talk on computational catalysis. He had just finished his PhD in chemical engineering at Delaware and was convinced that quantum chemistry would make an important impact on catalysis. At that meeting we decided he would come to Eindhoven.

I published the first quantum chemical study on transition states of methane and carbon monoxide with PhD students Hielke Burggraef and Ton van Daelen. It implied that we could actually compute reaction rate constants of surface reactions. Ton had decided to move to California after his master’s degree at Eindhoven and did his research at the then start-up company Biosym, where I was a consultant. Based on these simulations, we had become aware of the notion of late and tight transition states in surface dissociation and association reactions. This makes it possible to rationalize linear activation energy-reaction energy relations and brings us back to the use of bond-order conservation rules to predict reaction rates.

At the end of the nineties we decided to actually simulate overall catalytic reaction rates. This became possible due to a breakthrough in the work on the dynamic Monte Carlo (DMC) method by Tonek Jansen and Johan Lukkien at Eindhoven. Johan Lukkien is a computer scientist who joined the Schuit Institute of Catalysis for some time. In those days he was collaborating with Peter Hilbers, who then held the chair of information science at Eind-

hoven and had had an earlier career at Shell Research, just as I had. It was the beginning of many joint papers with the Hilbers group. With Johan’s help, Tonek has been able to scale up his kinetic method to systems with large grids so that surface reconstruction can also be incorporated. PhD student Ronald Gelten and I applied this method to the first atomic analysis of excitable catalytic systems—for example, the reconstructing platinum surface during carbon monoxide oxidation—in the way that the later Nobel laureate Gerhard Ertl studied extensively.

I had heard Ertl lecture on this topic many times and felt that a sensitive test of our work would be predicting the self-organization of surface intermediates that he had experimentally demonstrated for a simple reaction like carbon monoxide oxidation. The basis of this phenomenon is the

complex interplay between adsorbed reaction intermediates that the DMC method can capture.

This self-organization leads to interesting patterns of reaction intermediates and surface phases that change with time and are induced to the surface by the catalytic reaction. It is an example of complexity phenomena in catalysis, which more than ten years later became even more important to us when the Institute for Complex Molecular Systems (ICMS) started under the leadership of the organic chemist, my colleague and friend, Bert Meijer (see also his contribution in section 9).

The simulations were a great success. The oscillating and spiraling patterns were recorded in movies that we used on many occasions to illustrate our insights into molecular catalysis and the power of the predictability of the techniques available to us.

## RESEARCH HIGHLIGHT

A. DE KOSTER, A. P. J. JANSEN, R. A. VAN SANTEN AND J. J. C. GEERLINGS (1989). *Reactivity of CO on Stepped and Non-Stepped Surfaces of Transition Metals. Faraday Discuss. Chem. Soc., 87, 263–273.*

### Reactivity of CO on Stepped and Non-Stepped Surfaces of Transition Metals

**ABSTRACT** Results of extended Hückel calculations show that coordination of CO to Group VIII transition metal surfaces depends on a subtle balance of the interaction with the CO-5σ orbital, which tends to direct the CO molecule to the on-top position, and the CO-2π\* orbital, which directs the molecule to higher coordination sites. In the on-top position, the changes in bonding to different surfaces of the same metal can be mainly attributed to differences in the interaction with the CO-5σ molecular orbital. The favored dissociation path is such that carbon and oxygen atoms end in high coordination sites, sharing as few surface metal atoms as possible. The CO bond is activated by the metal atoms that are crossed upon dissociation.

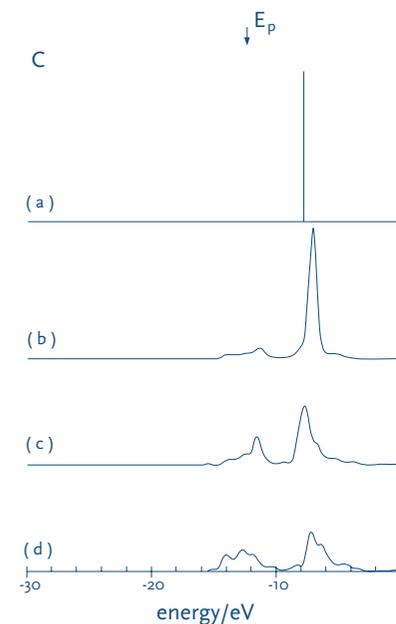


Figure 3.4

## Bonding and Antibonding Admolecule Orbital Interactions: Activation on Stepped Surfaces

**COMMENT** This is our first comparative electronic structure study for carbon monoxide adsorbed to a stepped (figure 3.4d) and nonstepped site (figures 3.4b, 3.4c) of a Rh(111) surface. It shows the lower density of states (LDOS) of the  $2\pi^*$  carbon monoxide molecular orbitals (a) in the gas phase, (b) onefold adsorbed on Rh(111), (c) threefold adsorbed on Rh(111), and (d) threefold adsorbed on stepped Rh(111), the distance of carbon monoxide to step being 1.551 Å. The Fermi level is indicated by EF.

This kind of study is essential for the understanding of structure sensitivity effects in catalysis. It shows an increased electron density of the  $2\pi^*$  orbital projected density states below the Fermi

level for carbon monoxide adsorbed to a step edge, compared to that of carbon monoxide adsorbed to the terrace. The electron density below the Fermi level is to be ascribed to a bonding interaction of the metal  $d$ -orbitals with the CO- $2\pi^*$  orbital; the density above the Fermi level corresponds to the antibonding interaction of CO- $2\pi^*$  orbital with the surface.

The increased energy difference between bonding and antibonding surface metal-adsorbate fragment orbitals indicates a stronger interaction with the metal surface and a larger bond weakening of the carbon monoxide bond adsorbed at step-edge sites than on the Rh(111) terrace.

## RESEARCH HIGHLIGHT

M.A. VAN DAELEN, Y.S. LI, J.-M. NEWSAM, R.A. VAN SANTEN (1994). *Transition States for NO and CO Dissociation on Cu(100) and Cu(111) Surfaces. Chemical Physics Letters, 226, 100–105.*

### Transition States for NO and CO Dissociation on Cu(100) and Cu(111) Surfaces

**ABSTRACT** The transition states for dissociation of NO and CO have been located and optimized for several reaction paths on cluster models of the copper (100) and (111) surfaces using density functional theory. Classical transition state theory was then used to calculate the rates of dissociation and recombination. The partition function of the

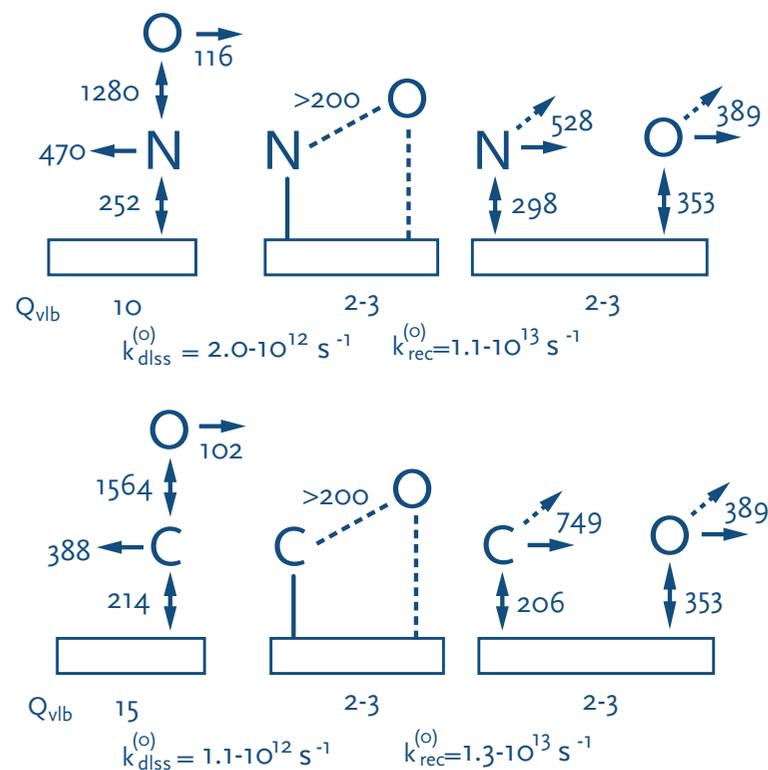
transition state is substantially smaller than that of the reactant state, corresponding to preexponentials for dissociation in the range of  $10^{10}$ – $10^{12}$  s<sup>-1</sup>. The dissociation barrier for NO is significantly lower than that for CO. In addition, the less densely packed Cu(100) surface is more reactive towards dissociation than the close-packed Cu(111) surface.

### First-Principle Transition States

**COMMENT** This was one of our first papers that presented first-principle density functional theory-calculated (DFT) rate constants for a dissociation reaction at a metal surface. We had to use a cluster to approximate the surface. By identifying the transition states and calculating the partition functions, it gives the activation entropy of the transition state. We concluded that the transition state of dissociating carbon monoxide and NO on copper is im-

mobile. Figure 3.5 shows calculated normal mode frequencies (in cm<sup>-1</sup>) for the reactant states, transition states, and dissociated states for NO and carbon monoxide on cluster models of the Cu(100) surface. Modes for the transition state are all above 200 cm<sup>-1</sup> except for the imaginary mode corresponding to the reaction coordinate. The calculated preexponential factors  $k^{(0)}$  for the dissociation and recombination reaction are shown below the figures.

Figure 3.5



## 4.1

# UNDERSTANDING ZEOLITE CATALYSIS

By *Gert Jan Kramer*

Gert Jan Kramer is manager Energy Futures at Shell Global Solutions International B.V., Amsterdam, and professor of sustainable energy at the Institute for Environmental Sciences (CML), Leiden University. He worked part-time from 1998 until 2010 at TU/e, first as professor of fundamentals aspects of heterogeneous catalysis, then later as professor of hydrogen technology.

When I joined Shell Research Amsterdam in 1988 after completing my PhD in solid-state physics at Leiden, Rutger van Santen had just left Shell to become professor of catalysis at Eindhoven. But Rutger remained actively involved with research at Shell as a consultant, and for four years we were the closest of collaborators, working in the area of computational chemistry of zeolites and zeolite catalysis.

The request to contribute to this festschrift for Rutger made me reflect on how he influenced my habits and outlook as a scientist. The above chronology makes clear that in all but the formal sense I did my postdoc with Rutger, and this marks that unique time in a scientist's career when scientific habits are still susceptible to change before inevitably settling into permanency—one's own scientific style. The one thing that I learned from Rutger during this period was that it is all right to err. This was in many ways a liberating experience. Coming from the Leiden Physics Department and having worked in the field of organic (super)conductors, I had come to understand science as an activity whose ultimate purpose was "being right." This may have been the rigor of the Physics Department, it may have been the people I worked with or the leading figures in the field, or it may have been my personal mental makeup, but on entering Shell and

at the start of my collaboration with Rutger, I was afraid to err.

The four years that followed liberated me once and for all from that fear. There is no doubt that the enterprise of science generally benefits from intellectual courage, from the use of intuition next to formal argumentation, and the willingness to adapt hypotheses to new experimental facts. This is especially true in the field of theoretical catalysis.

In retrospect then, catalysis was in no way an obvious choice for a physicist obsessed with finding scientific truth. But then again, postgraduate career decisions are often the greatest gambles of our lives. And Rutger proved to be my ideal intellectual mentor, helping me to settle into the strange world of theoretical catalysis.

For me, that was equally important to settling into a role in industrial research. Because while in academia the touchstone for the relevance of a hypothesis is in its veracity, in industry the value of hypotheses is first and foremost for their utility to inspire the next experiment. Agility is more important than rigor. A memory, whose details have become blurred over the years but whose central message I still remember, has me mentioning to Rutger that I had read a paper that implied that a conclusion of one of our early papers was wrong, and Rutger shrugging and saying, "That is

how science progresses.” (And that was it.)

The late eighties marked a time at Shell when its senior research management had decided to reinvigorate its capabilities in the basic sciences. Shell had a proud tradition of doing fundamental research to inform and “feed” its applied research. In the sixties Shell’s Amsterdam laboratory was known as Amsterdam’s third university. Nobody has properly kept track of the professors that have come out of this lab over the decades, but Tony Farragher, one of its department heads, has listed about one hundred from his own memory. Rutger’s PhD supervisor at Leiden, Professor Oosterhoff, also came from Shell; Rutger’s longtime boss at Shell and head of the Catalysis and General Processes Department, Wolfgang Sachtler, was a professor at Leiden, and Rutger’s predecessor as Eindhoven, Professor Roel Prins, was also a Shell alumnus.[1]

But over time, through periods of expansion and contraction or research not unrelated to oil price and outlook, basic research was slowly but inexorably on its way out of industry labs. This is also reflected in the name of Shell’s Amsterdam laboratory. When I came there, it was called KSLA, short for Koninklijke-Shell Laboratorium Amsterdam (Royal Shell Laboratory Amsterdam). It was later rechristened Shell Research and Technology Centre Amsterdam (SRTCA) and is presently called Shell Technology Centre Amsterdam (STCA). This sequence of names is a short summary of the diminishing role of (pure) research in industry in the past decades, a trend which has been both global and affecting virtually all industries. Research moved into universities and government laboratories, which had grown in the long postwar boom to a size that could ultimately only be sustained by industrial support as a source of income, as well as being necessary proof of the “societal relevance” of government-funded research.

But, as said, the time of my joining Shell saw—what proved to be—the last flaring up of fundamental research. I joined a small group led by Gijs Ooms, who had just returned from Delft University to head up the Engineering Physics Department in which Rutger’s and my fundamental work on catalysis was embedded. (“Engineering physics” was a misnomer for a group of a dozen theoretical physicists and chemists, but the more accurate “fundamental research” was apparently ruled out because a department of that name had existed, but had fallen victim to a wave of “rationalization.”) The topic of our joint research was the theoretical basis of acid catalytic conversion of hydrocarbons in zeolites. The business motivation was for Shell to establish an advantaged position in the application of novel zeolite structures to oil-conversion processes. At the time there was a burst of new activity following the discovery of a new class of zeolites—the aluminophosphates, or AlPOs. As zeolites are less amenable to being studied by the techniques of surface science and—in contrast to metallic catalysts—their reactive sites are well defined, it was natural to look to theory for help.

But soon they were to produce work that changed Shell business forever...



With this motivation in mind, it was natural to ask: what makes one zeolite more catalytically active than another? If this was understood, then supposedly one could design in silica a zeolite with superior properties and—if this was a theoretical rather than an already existing structure—it led to the follow-on question: is the theoretically identified zeolite framework thermodynamically stable? If yes, the logical third question became: can one design a template molecule that will direct its synthesis?

These three questions have been, I believe, the drivers for Rutger’s work in the area of zeolites throughout his long career, and one of the highlights of which are reproduced in this chapter. My involvement in this was on the first two questions. The two of us, together with Shell researcher Bertwim van Beest and Rutger’s PhD student Andries de Man, set out to determine molecular potentials for silicas and AlPOs based on ab initio calculations. We modeled small zeolite clusters, stretched and bended their bonds, and thus derived an energy hypersurface that was used as the training set for fitting the parameters of intermolecular potentials. These potentials were published in *Physical Review Letters* in 1991, a paper that has received over 700 citations.[2]

We first employed these potentials for the study of the stability of zeolites, exploring the mixed covalent/ionic character of zeolites by varying the balance between the two and studying the effect thereof on crystal structure.[3] But we also applied the methodology to acid zeolites by extending the set of potentials to describe the acid OH site as a pseudoatom. This allowed us for the first time to study the lattice relaxation around acid sites (as compared to the all silica lattice) and estimate the differences in “intrinsic acidity” between crystallographically different sites. We found that the significant distortion of the lattice to accommodate the bulkier Al–OH substituent in

the silica lattice was essentially locally accommodated, and that acidity differences due to differences in relaxation are 50–100 kJ/mol, which makes them chemically significant.[4,5] Having taken the description of zeolite catalysts this far, we felt ready to look at catalysis.

We had a go at the simplest hydrocarbon reaction conceivable, the acid proton exchange of methane, and tried to see if we could observe and calculate activities in zeolites FAU and mordenite framework introverted (MFI). In order to do this, we used all the work we had done up to this point: the potential modeling of zeolites and their acid sites, as well as the deprotonation energy of all individual sites in the frameworks that were calculated with these. But because we felt that potential modeling would be inadequate for reaction modeling, we wanted to simulate the actual reaction quantum chemically. We used the argument of the validity of the local description to study the reaction in a small aluminosilicate cluster whose terminal hydrogen bonds were constrained so as to mimic the lattice stress-induced acidity differences in the real zeolites.[3] As it turned out, the rate of this particular reaction is not dependent on acidity, but on the *difference* in deprotonation energy between the donating and receiving oxygen atom. Because FAU has but a single crystallographically unique T-site (where silicon or aluminum can reside), it is only modestly active, whereas MFI is more active by virtue of the fact that some of its twelve different T-sites have very small deprotonation energies of their coordinating oxygen atoms. This prediction was corroborated in an elegant experiment of Andreas Nowak and Cees Emeis, who measured the (slow) D–H exchange between the zeolites and deuteromethane and followed it through in situ infrared spectroscopy. The results were published in a Letter to *Nature*. [6] This gave us great pride, not least because the letter received

mention in the News & Views section, where Joachim Sauer put our results in a wider context.[7]

This paper was the apotheosis of our work together. All new science and methodology that we developed in our collaboration was brought to bear in this comparison of theory and experiment of a true zeolite-catalyzed hydrocarbon reaction. As Joachim Sauer put it in his comment: “The design of efficient and selective catalysts is still largely empirical, despite the substantial efforts made to elucidate the mechanisms of heterogeneous catalysis. For acidic zeolites Kramer et al. now show [...] that reliable predictions can be made by combining the power of quantum chemical techniques, with classical methods of lattice-energy minimization.”[7] Of course, it was that hope, the dream, to move beyond empiricism to “design” that motivated the work at Shell. For a few years—that I was lucky enough to be part of—this seemed possible; progress in computational science, propelled by Moore’s law of ever-faster, ever-cheaper computing, was so swift that many R & D leaders saw that the design of novel catalysts in silico would soon replace the cumbersome trial-and-error practice of the “wet” laboratory.

Looking back today on what computation has done for practical catalysis, in particular also for invention in industry and the design of novel catalysts and catalytic processes, I think we must conclude with some irony that the greatest impact of computation—of computers—has been on experimental catalysis rather than theoretical or computational catalysis. Developments such as high-throughput experimentation, made possible by lab automation and robotization, have made it possible to scan vast swaths of catalytic parameter space without having much of an idea as to how or why certain reactions take place on specific catalysts. Just give it a shot; failure is cheap. It is the

ultimate triumph of the romantic “black art” school of catalysis—namely, those in the field who, implicitly or explicitly, work on the assumption that the topic is too difficult to understand properly, so it is best done on the basis of intuition formed by many years of accumulated practical experience.

This was the conclusion that, in my observation, the world of catalysis seemed to be slowly converging on in the midnineties. I have not followed the field of catalysis much after the first few years of the twenty-first century, but I do not believe that the situation has changed (i.e., the occasional claim to success notwithstanding, nobody ever drew my attention to series of ex silico inventions or a trend in that direction). It has been my view that theoretical chemistry, helped by computational chemistry, is a tool that improves our *general understanding* of chemistry and catalysis. But it is generally not a sufficiently precise instrument and too cumbersome in its use to be used for specific predictions in aid of experimental improvements or inventions. Thus, it helps the chemist by improving his general understanding of his art, but it doesn’t remove the ultimately “artisan” nature of it. I would therefore argue that theoretical/computational chemistry has a natural and rightful place in academia, but that it will find it difficult to make inroads into industry in a decisive way. As I learned only slowly in over twenty years in industrial research: what matters for success is not being clever, but being relevant.

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Table 4.1: Top coauthors in this theme, with the number of papers together with Rutger van Santen and their affiliation.

Source: TU/e Library

133 PUBLICATIONS		
19	PIDKO, E.A.	TU/e
15	HENSEN, E.J.M.	TU/e
14	KAZANSKY, V.B.	Russian Academy of Sciences, Moscow
14	ZHIDOMIROV, G.M.	Moscow Physical Engineering Institute
13	JANSEN, A.P.J.	TU/e
13	ROZANSKA, X.	Materials Design, Paris
11	BARBOSA, L.A.M.M.	Covidien, Petten
11	HUTSCHKA, F.	Institute for Materials Physics, Vienna
10	KRAMER, G.J.	Shell Amsterdam, TU/e
9	FRASH, M.V.	University of Toronto

## THEORY OF ZEOLITES

By *Rutger van Santen*

The theoretical work on zeolites and zeolite catalysis started in the mid-eighties on my return from Houston to Shell Research in Amsterdam. Then director of Shell Research, Alan Abbott, decided that supercomputers, such as Shell's Cray machines, should be deployed more in applied research that is directly related to manufacturing.

Gijs Ooms, a theoretical physicist who had returned from a professorship at Delft, started a new theoretical physics group at Shell Research, and he approached me about a project in catalysis. We decided to take zeolites as our subject—namely, catalytic systems that from a quantum chemical point of view were not too complex, but for Shell were highly relevant.

Zeolites are microporous aluminosilicates that are used as solid acid catalysts in several important refinery processes. They are simple in terms of quantum chemistry because they do not contain electron-rich atoms in the way that the transition metals do. We studied the stability of zeolite structures to figure out which structures, in principle, can be synthesized and which structures would not be within reach of zeolite synthesis. As catalytic reactivity relates to the reactivity of zeolitic protons, we also studied the proton acidity of the zeolites. We invoked the help of Richard Catlow, then at Keele University, and later also became engaged in joint activities with John Thomas at Cambridge University. The paper on force field parameters of siliceous and  $\text{AlPO}_4$  structures, which has been well cited by colleagues interested in zeolite simulation, written together with Gert Jan Kramer and Bertwim van Beest, is also from that period, as well as studies on zeolite

framework vibrational spectra. We initiated the latter studies because experimentally they are easy to obtain. Their interpretation, however, is difficult. We looked for the relation between particular spectral features and particular ring structures within the zeolites.

The preliminary work at Shell Research in the early nineties on zeolites initiated a long friendship and collaboration with Gert Jan Kramer, who at that time joined Shell Research after his PhD at Leiden. We both had a strong theoretical physics background and had come to catalysis at a later stage in our scientific development. We were both interested in new scientific questions. The molecular catalysis interest of fundamental catalysis research at Shell Research turned out to be the ideal environment to apply the rapidly developing molecular computational approaches at that point in time. Later Gert Jan became a part-time professor at the Schuit Institute at Eindhoven, which offered further possibilities to explore our mutual interests.

My first serious quantum chemical probe into zeolite acidity was together with Frans van Duijneveldt at Utrecht University. He had developed the high-quality quantum chemical methods that enabled the first quantum chemical studies of ammonia adsorbing to a zeolitic proton and its transformation to ammonium. At that time, such a study had to be limited to ammonia interacting with a small cluster.

My lifelong contact with the Russian scientist Vladimir Kazansky started in the early eighties when he visited Sachtler at Shell Research. Kazansky was the leading quantum

chemist in Russia at that time, who made pioneering studies on the reactivity of protons in zeolites. I have been able to invite Kazansky many times to Eindhoven for longer periods. We enjoyed discussing proton activation and the nature of proton-activated transition states in hydrocarbons. He initiated our thinking on carbonium ions and carbonium ions as transition states of proton-activated reactions and alcoxy intermediates as stable adsorbed species.

Another important early contact was with the quantum chemist Joachim Sauer, then in East Berlin. I met him for the first time in 1988 at an early computational catalysis meeting in Krakow, organized by the great Polish catalytic chemist Jerzy Haber. Joachim's sharp insight into the limitations of the methods available and hence the limited accuracy of the results obtained has made him an important contact ever since.

The ideas generated through these contacts were fundamental to the work I did with Solange Blaszowski on methanol conversion and our discovery of associated and direct reaction intermediates. Solange was the first of several PhD students who joined our group from Brazil. Marco Nascimento invited me to an early computational catalysis meeting in Rio de Janeiro, which was the beginning of a long exchange with him and his colleagues. Solange and I demonstrated that proton-activated processes proceed through different transition states for each different reaction channel. The calculations showed that this is due to the large electrostatic interactions that develop between protonated intermediates and negatively charged zeolite frameworks when charge separates with the movement of proton to reactant. This was very different from ideas derived from work with stable carbonium ions in mass spectrometers, which used statistical theories such as the Rice-Ramsperger-Kassel-Marcus (RRKM) theory.

In the middle of the nineties Johannes Lercher, who at that time occupied a chair at the University of Twente (our collaboration on zeolite catalysis still continues to this day), and I began work on adsorption and activation of longer hydrocarbons in zeolites. He had convincingly demonstrated that the reactivity of hydrocarbons with zeolites sensitively depends on hydrocarbon chain length. The forces responsible for their interaction with zeolites are the dispersive van der Waals forces that cannot be captured by the usual quantum chemical techniques. Berend Smit, who by that time had moved from Shell Research to the University of Amsterdam, had developed an interesting method for computing the free energy of adsorbates dominated by van der Waals interactions using coarse-grained dynamic Monte Carlo (DMC) methods based on fitted force fields. In joint papers with postdoc Simon Bates and PhD student Willy van Well, we studied the differences in site occupation of hydrocarbons dependent on their size both experimentally, using nuclear magnetic resonance (NMR), and computationally. We studied competitive adsorption effects experimentally, as Berend had predicted, using the positron emission profiling (PEP) technique. Catalytic measurements on hydroisomerization with PhD students Frank de Gauw and Annemiek van Runstraat showed the importance of the entropy of adsorbed molecules to explain differences in the reactivity of zeolites.

The contact with Jürgen Hafner from Vienna gave me the opportunity very early on to use his software for proton activation studies in zeolites, including the full periodic structure of the lattice. One of the highlights of that period was the paper on the alkylation of toluene by methanol in mordenite with Robert Schoonheijdt from Leuven and PhD student Xavier Rozanska. We used Hafner's Vienna ab initio simulation package (VASP)

method but corrected it empirically for the required van der Waals interactions. It gave us another occasion to highlight the importance of pre-transition state rearrangements for obtaining the proper activation energies of a reaction.

A new period began when we started to explore Lewis acidity, such as that promoted by zinc and gallium in zeolites. Again, it was Kazansky who inspired this new line of research. He was our key research partner. By contrasting homolytic with heterolytic CH bond activation, we were able to demonstrate the essential role of extra-framework oxygen atoms in the low energy of CH bond activation. The second PhD student from Brazil who joined our group, Luis Barbosa, followed this up with detailed studies on hydrating nitriles in chabazite. Again we noted the collaborative role of several water molecules, as in the work with Blaszkowski, on the activation with methanol.

Through our contact with Kazansky, in 2003 one of his best students, Evgeny Pidko, became interested in joining our group, and an intensive period started where we studied activation of molecules using hard and soft Lewis acids. Pidko and Emiel Hensen, my current successor in the chair of Catalysis at Eindhoven, discovered the self-assembly of GaO<sub>2</sub> oxycations in the mordenite zeolite with unique activity in CH activation. This was the first example in our work that demonstrated that dual-site oxycations can be more reactive than single-site cations in zeolites. They also discovered a similar effect in biomass conversion. The homogeneous catalytic reaction of glucose to HMF by chromium ions in ionic liquid proceeds with high reactivity. The reaction proceeds through a transition state in which two chromium cations participate. Later we discovered that iron cations—for example, single cations in zeolites—have high selectivity for converting

benzene to phenol with N<sub>2</sub>O. The dimeric oxycation activates the phenol for nonselective deactivating reactions.

Visits from Zhdimirov in Novosibirsk, funded by the same international collaboration contract with Russia that funded Kazansky's visits, had initiated interest in this reaction, known as the Panov reaction. A similar collaboration with Isik Onal from Ankara ensued. With his PhD student Ferdi Fellah we were able to calculate the first transition state of the reaction diagram for the Panov reaction on zeolitic cluster models. In 2011 a final paper appeared in collaboration with the group of Can Li from Dalian, China (another long-term collaboration funded by international collaboration programs), in which his PhD student Ganna Li and Evgeny demonstrated the same for periodic zeolite models.

The very innovative photocatalytic work of Heinz Frey of Berkeley and Leon Lefferts at the University of Twente inspired me to explore the orienting effects of alkaline-earth cations on the interaction of adsorbed olefins in zeolites with Evgeny in that period. I had met Heinz during my stay as Miller Professor at Berkeley in 2004. He had demonstrated photon-induced selective oxidation of olefins in zeolites activated by alkali cations. It is based on a molecular recognition effect analogous to that found in enzymes. It led me to further explore molecular recognition in cationic zeolites in studies dealing with NO decomposition with Robert Schoonheydt again.

More recently, also in collaboration with the Dalian group, we restarted the computational work on zeolite synthesis. Through our contacts with Krakow we were able to attract Bartek Szyja. With him on board, an interesting period emerged where we started to model silicalite synthesis supported by molecular dynamics simulations. This work benefited largely from joint meetings with Michael Waroquier and Veronique van Speybroeck's group in Ghent.

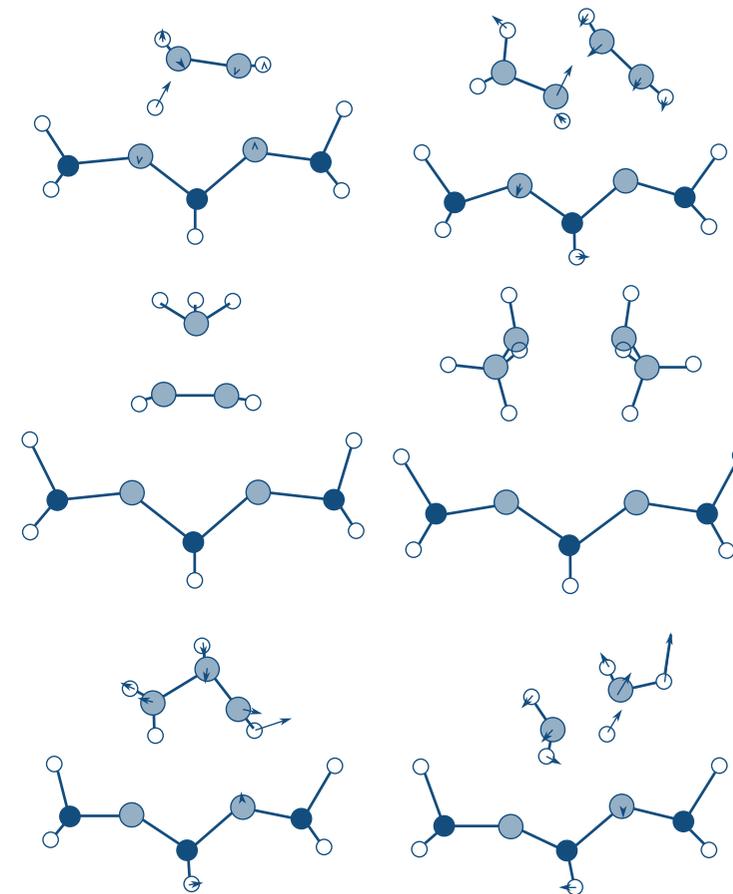


Figure 4.1

## RESEARCH HIGHLIGHT

A. M. RIGBY, G. J. KRAMER AND R. A. VAN SANTEN (1997).

*Mechanisms of Hydrocarbon Conversion in Zeolites: A Quantum Mechanical Study. Journal of Catalysis, 170, 1–10.*

### Mechanisms of Hydrocarbon Conversion in Zeolites: A Quantum Mechanical Study

**ABSTRACT** Ab initio quantum chemical methods have been used to study the mechanisms for the hydrocarbon conversion in zeolites (cracking, isomerization, alkylation, etc.). It is found that the intermediates are covalent alkoxide species and indicate that there is no energy ordering of these alkoxides according to their primary, secondary, or tertiary nature. Transition states have been located for the most important conversion reaction steps for

hydrocarbons up to C<sub>6</sub>. The reactions are concerted and the transition states are ionic and ring-like. Due to charge delocalization in the transition state the activation energies depend on the nature of the initial and final alkoxides. These calculations are the foundation for a new model of the hydrocarbon conversion, which can better describe the influence of the zeolite as will be illustrated with calculations on acid sites with varying acid strength.

## Transition States in Zeolites

**COMMENT** This is an early ab initio quantum chemical study of the transition state of proton-activated hydrocarbon reactions in zeolites. The relevance of these results lies in the observation of the striking difference in the structure of a transition state for

different reaction channels of the activated hydrocarbon. Figure 4.1 shows the structure and reaction coordinate of small hydrocarbons activated by a proton from the small zeolitic cluster that we then had to use to simulate the zeolite protonic site.

SOLANGE R. BLASZKOWSKI AND RUTGER A. VAN SANTEN (1997).

*Theoretical Study of C–C Bond Formation in the Methanol-to-Gasoline Process.* *J. Am. Chem. Soc.*, 119, 5020–5027

## Theoretical Study of C–C Bond Formation in the Methanol-to-Gasoline Process

**ABSTRACT** Density functional theory is used to study one of the most successful routes to the production of synthetic fuels, the conversion of methanol to gasoline (MTG process) with an acidic zeolite. With our calculations we have determined transition states and adsorption complexes of reactants, intermediates, and products, as well as the corresponding activation barriers and adsorption energies of the numerous reactions involved in such a process. Brønsted acid-catalyzed methanol dehydration to dimethylether is the first step of the MTG process. Two different mechanisms are possible. One proceeds via an associative interaction between two methanol molecules, generating directly dimethylether, while the other proceeds via a methoxy surface species intermediate. The presence of water lowers the activation barrier of the last mechanism by more than 50 kJ/mol. Our calculations suggest that ethanol and ethyl methyl ether

are the first formed species with a C–C bond. Several different mechanisms for those reactions have been studied. The activation barriers involved in such reactions are of the order of 300 kJ/mol for both ethanol and ethyl methyl ether. Without coadsorbed water, the activation barriers are 60 kJ/mol higher. In a following step ethylene is formed from alcohol or ether. Those reactions are very fast due to a very low activation barrier. Trimethyloxonium, proposed to be an intermediate in the formation of ethyl methyl ether, can be excluded as an intermediate for the C–C bond formation. Although it can be formed, its further reaction to ethanol or ethyl methyl ether involves activation barriers that are over 80–150 kJ/mol higher than their formation directly from dimethyl ether and methanol. Reaction paths for the formation of methane and formaldehyde, which are observed in reactions for very low methanol coverages, have also been studied.

## Direct C–C Bond Formation in Zeolites Has High Barriers

**COMMENT** The methanol-to-olefin conversion by solid acids is one of the first reactions we studied with density functional theory-based (DFT) cluster models. We investigated the several mechanistic models proposed for this reaction and concluded that C–C

bond formation occurs preferentially through a water-assisted reaction between adsorbed methoxy and methanol. We found in a cluster calculation that the activation energy for this reaction is 250 kJ/mol. We found this barrier is reduced because coadsorbed

water makes proton transfer geometrically more convenient. Cluster calculations usually overestimate activation energies. For ethanol dehydration the comparable activation energy was

171 kJ/mol. We concluded that direct C–C bond formation will occur at a very slow rate. Figure 4.2 shows ethanol formation via a methoxy/water-mediated mechanism. Energies in kJ/mol.

## RESEARCH HIGHLIGHT

Figure 4.2

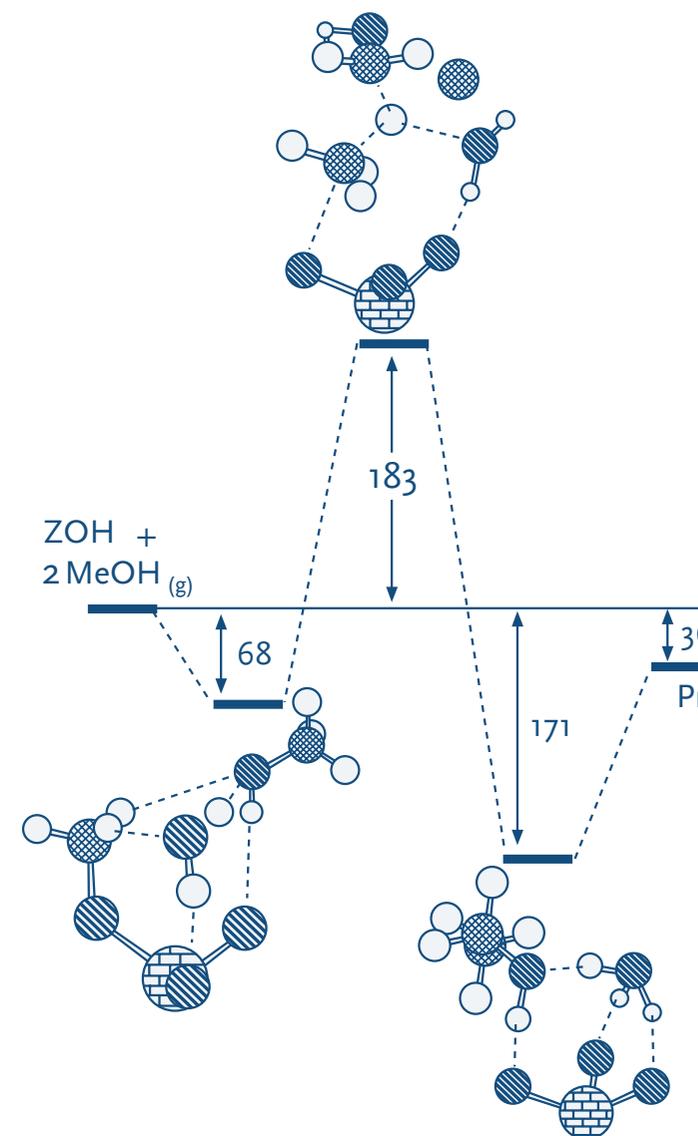
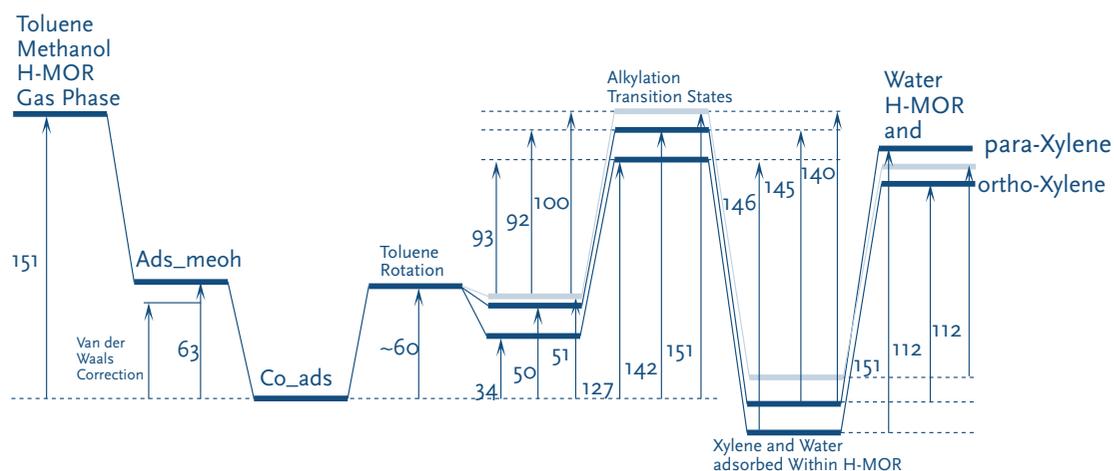


Figure 4.3



different stability of the pretransition state intermediate in the linear microchannel of mordenite. The linear para-arrangement of the methanol-toluene complex has the lower energy. With respect to the pretransition state, the activation energies of different stereoisomers are quite comparable.

The figure shows a dispersive energy corrected reaction energy diagram of the reactions of alkylation of toluene with methanol catalyzed by acidic mordenite that leads to the formation of p-xylene, m-xylene, or o-xylene and water (all values in kJ/mol). The values correspond to energies at 0 K.

## RESEARCH HIGHLIGHT

ANN M. VOS, XAVIER ROZANSKA, ROBERT A. SCHOONHEYDT, RUTGER A. VAN SANTEN, FRANCOIS HUTSCHKA AND JÜRGEN HAFNER (2001).

*A Theoretical Study of the Alkylation Reaction of Toluene with Methanol Catalyzed by Acidic Mordenite. J. Am. Chem. Soc., 123, 2799–2809.*

### A Theoretical Study of the Alkylation Reaction of Toluene with Methanol Catalyzed by Acidic Mordenite

**ABSTRACT** A theoretical study of the alkylation reaction of toluene with methanol catalyzed by the acidic mordenite (Si/Al = 23) is reported. Cluster DFT as well as periodical structure DFT calculations have been performed. Full reaction energy diagrams of the elementary reaction steps that lead to the formation of the three xylene isomers are given. The use of periodical structure calculations allows one to account for zeolite framework electrostatic contributions and steric constraints that take place in zeolitic catalysts.

Especially the steric constraint energy contribution has a significant effect on the energies and bond formation paths. The activation energy barrier of *p*-xylene formation is found to be ~20 kJ/mol lower than the corresponding values for the formation of its isomers. Computed host-guest binding energies according to the DFT method need a correction due to the absence of the dispersive interaction with the zeolite wall. Apparent activation energies obtained with this correction are in good agreement with experimental data.

### COMMENT The Pretransition State Concept

The complete reaction energy diagram of toluene alkylation by methanol in mordenite shows clearly that stereoselectivity of the reaction does not relate to the different reactivity of the

carbon atoms in the aromatic ring of toluene. The calculation is one of the first that includes van der Waals corrections to the adsorption energy. The reason for stereoselective catalysis is the

# 5

## Chapter 5

### Mechanisms in Transition Metal Catalysis

## 5.1

# UNRAVELING TRANSITION METAL CATALYSIS

By *Philippe Sautet*

Philippe Sautet is research director at the Centre National de la Recherche Scientifique (CNRS) and the École Normale Supérieure (ENS) de Lyon in France. He is a member of the French Academy of Sciences and is the director of the Institute of Chemistry of Lyon. As a theoretical chemist he applies modeling to the understanding of the fundamental aspects of heterogeneous catalysis.

My first encounter with Rutger van Santen was in Zakopane, Poland, in October 1988 at the Second International Symposium Mechanism of Heterogeneous Catalysis: Quantum Chemical Approach. The topic of that conference could not be more appropriate for the subject of this chapter. At that time I was finishing my PhD in theoretical chemistry in Paris and initiating research into heterogeneous catalysis mechanisms as a freshly appointed research associate at CNRS in the famous *Institut de Recherches sur la Catalyse* (now IRCELYON) in Villeurbanne, France. Still a novice in heterogeneous catalysis, I was not planning to attend this meeting and, even less, to give a lecture. A couple of weeks before the conference, however, Professor Bernard Bigot popped into my office and asked me on the spot to replace him in Zakopane and give the lecture. This was a fantastic but terrifying occasion on which to enter the catalysis community, although I do have to admit that my lecture (adapted from my PhD work) had little to do with heterogeneous catalysis. Rutger was already a renowned expert on catalysis modeling by then, and our meeting and discussions in Zakopane had a great impact on the course of my research.

In those days computational methods were rustic but already very powerful for extracting qualitative concepts.

Rutger and I were both using extended Hückel molecular orbital theory, only with the difference that my experience in its application to heterogeneous catalysis was incommensurate with Rutger's. This was a great time for us because only a few groups were approaching the topic from calculations and only a handful were daring to tackle reactivity and mechanisms, the major names being R. Hoffmann, A. B. Anderson, E. Shustorovich, and R. C. Baetzold, and Rutger. Indeed, most of the studies at that time were dealing with the electronic structure of clusters and surfaces and the chemisorption of simple molecules.

Rutger had a key advantage when it came to modeling catalytic reactivity. He had been exploring the field as an experimentalist for fifteen years, and hence his knowledge of the nature of catalysts and of reaction kinetics was more advanced than that of the pure theoretical chemists approaching the subject. This “chemical feeling” for catalysis has been a strong asset to Rutger's work over the years.

After Zakopane we met regularly at conferences. Our contact intensified some ten years later when I had the honor of receiving the Descartes-Huygens Prize in 1998, awarded by the Royal Netherlands Academy of Arts and Sciences. I am convinced that Rutger was not entirely innocent in the conferral of this prestigious award

that allowed me to visit Eindhoven on several occasions. At that point in time, density functional theory (DFT) was evolving as an accurate predictive tool, and in 1993 Rutger had already pioneered the use of that method for molecular reactivity at transition metal catalysts. The cluster models that had to be used at that time, however, led to size effects, and it was only in the late 1990s that periodic DFT calculations made it possible to study molecular reactivity at transition metal surfaces efficiently—for example, studying polyatomic molecules and surface relaxation effects. In those days Rutger and I belonged to the same network,

Applications in Catalysis and Materials Science,” held in Porquerolles in September 2007, and for the editing of the method-oriented textbook that followed that event. This was a great occasion to converse again with Rutger and review the key theoretical methods applied in catalysis, from electronic structure and DFT to ab initio molecular dynamics, force fields, and statistical and kinetic Monte Carlo approaches.

How has the field of transition metal catalysis evolved in recent years? We are increasingly able to simulate (or characterize from in situ spectroscopy) the catalytic reactions in con-

model study from 1989 (these subsurface oxygen atoms are present in the surface oxide). In his most recent studies of 2011 Rutger considers a silver oxide, and not a silver metal, as the active and selective phase for ethene epoxidation, opening new model reactivities.

It is clear from this brief introduction, and from the rest of this chapter, that Rutger’s ideas and his ability to bridge experiment with theory have been very influential to our understanding of the mechanisms of transition metal catalysis. I am convinced that they will remain so for many, many years.

Table 5.1: Top coauthors in this theme, with the number of papers together with Rutger van Santen and their affiliation.

109 PUBLICATIONS		
12	HENSEN, E.J.M.	TU/e
12	NIEMANTSVERDRIET, J.W.	TU/e
11	KOERTS, T.	Koerts PSM Consultancy
9	GRONDELLE, J. VAN	deceased
9	KOPER, M.T.M.	University Leiden
8	JANSEN, A.P.J.	TU/e
7	CIOBÎCĂ, I.M.	Sasol, TU/e
7	VEEN, J.A.R. VAN	Shell, retired
6	HARDEVELD, R.M. VAN	Shell
6	PIDKO, E.A.	TU/e

which aimed at promoting these methods for heterogeneous mechanisms, including Jürgen Hafner in Vienna and Hervé Toulhoat at IFP in Paris. Detailed multistep mechanisms for polyatomic molecules on transition metal surfaces with well-characterized transition states and accurate barriers appeared around the year 2000 in multiple places: Eindhoven (C–H activation), Lyon (hydrogenation), Copenhagen, and the University of Virginia. This initiated an active field of research on the detailed determination of mechanisms in connection with reaction kinetics.

After roughly ten years recurred a period of close interaction with Rutger for the organization of the summer school “Computational Methods and

ditions close to the experiment and describe the influence of the reaction environment in terms of gas pressure, temperature, or for the presence of a solvent. We still encounter many surprises, for example, in the calculations that we have performed in Lyon since 2000. It appears that under pressure surface compounds, such as oxides, are formed in the conditions of ethene epoxidation, or as carbides for Fischer-Tropsch or hydrogenation catalysis.

So, does transition metal catalysis really occur on a transition metal, or is it a transition metal oxide or transition metal carbide catalysis? In the case of ethene epoxidation on silver, Rutger had foreseen well in advance the role of subsurface oxygen species in his

## UNDERSTANDING MECHANISMS

By *Rutger van Santen*

The great physical organic chemist Egbert Havinga was professor of organic chemistry at Leiden when I was an undergraduate student. His lectures were a great inspiration to me in a long quest that still has not come to an end. Physical organic chemists in the sixties were able to describe reactivity in organic chemistry in molecular detail, often supported by what was then considered to be state-of-the-art quantum chemistry. This is very difficult to do in catalysis. A catalytic reaction consists of a cycle of reaction steps. A decisive factor is the state of the catalyst surface during reactions. Both are difficult to probe experimentally. Only in the past decade with the advances in computational catalysis were we finally able to give conclusive mechanistic descriptions. The key development that made this possible was the implementation of quantum chemical density functional theory (DFT) in computer programs, which makes it possible to predict ground states and, even more importantly, transition state configurations, as well as (free) energies. Hardware possibilities have since increased impressively so that catalytic reactive centers on surfaces are now accessible for realistic simulation.

The early work with Wolfgang Sachtler led to a joint chapter in *Advances in Catalysis* (26, 1977) dealing with the mechanism of hydrocarbon activation by transition metal alloys. Essential was the realization that the mechanism of a catalytic reaction, surface structure, and composition are intricately related. This gave rise to Sachtler's idea of the ensemble effect. My very first experimental papers dealt with the surface composition

of alloys. After I had been working at Shell Research for three years, Wolfgang proposed that we also start doing some experimental work. In this period I bumped into Hidde Brongersma again, who had also graduated with Oosterhoff at Leiden and whose apartment I took over in Leiden when he moved to Philips Research. At that time Hidde also started to apply his unique atom ion scattering techniques to the problem of surface composition of alloys. The issue is that the surface composition of an alloy is often dissimilar to the bulk composition. It is difficult to measure because you only want to probe the outer surface layer of the alloy. Years later, when Hidde—like me—had joined TU/e, in 1990 we organized a joint NATO summer school in Alicante, Spain, on the fundamental aspects of heterogeneous catalysis using particle beams.

I didn't have any hands-on experimental experience, but Wolfgang suggested working with Jan Moolhuysen, who was an accomplished technician. We started with high-vacuum studies of  $H_2-D_2$  exchange via alkali-promoted silver. It marked the beginning of a long interaction with Masaru Ichikawa from Hokkaido, Japan, who first suggested this promotional effect, which arose from an oxygen impurity in the alkali.

We finally met at Northwestern University during the same period in which I met Can Li there. I later invited Masaru several times to Eindhoven. In the nineties he invited me for several longer stays in Japan and Hokkaido, where he became a professor at the Institute of Catalysis. We mainly collaborated on methane activation and zeolite catalysis.

In 1999 I was able to convince Gert Jan Kramer from Shell Research to join Eindhoven for one day a week as a part-time professor. It enabled us to continue our ever so fruitful collaborations for many years, until as recently as 2009. With him at Eindhoven we started to work on adsorbate-induced surface reconstruction effects.

Continued close contact, at first with Bernard Bigot at the Institute of Catalysis in Lyon and later with Philippe Sautet when their group moved to the École Normale Supéri-

eure (ENS) in Lyon, led to several joint research activities. We were all quantum chemists by training and hence spoke the same language. Our initial contact mainly dealt with interpreting adsorption and chemical reactivity in Hoffmann's molecular orbital language. We have published joint papers with Philippe, exploiting his contributions to the theory of scanning tunneling microscopy and Tonek's method of simulating surface structures of adsorbate overlayers using the dynamic Monte Carlo (DMC) method.

## RESEARCH HIGHLIGHT

MATTHEW NEUROCK, VENKATARAMAN PALLASSANA AND RUTGER A. VAN SANTEN (2000). *The Importance of Transient States at Higher Coverages in Catalytic Reactions*. *J. Am. Chem. Soc.*, 122, 1150–1153

## The Importance of Transient States at Higher Coverages in Catalytic Reactions

**ABSTRACT** DFT-GGA periodic slab calculations were used to examine the adsorption and hydrogenation of ethylene to a surface ethyl intermediate on the Pd(111) surface. The reaction was examined for two different surface coverages, corresponding to  $(2 \times 3)$  [low coverage] and  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  [high coverage] unit cells. For the low coverage, the di- $\sigma$  adsorption of ethylene (-62 kJ/mol) is 32 kJ/mol stronger than the  $\pi$ -adsorption mode. The intrinsic activation barrier for hydrogenation of di- $\sigma$  bonded ethylene to ethyl, for a  $(2 \times 3)$  unit cell, was found to be +88 kJ/mol with a reaction energy of +25 kJ/mol. There appeared to be no direct pathway for hydrogenation of  $\pi$ -bonded ethylene to ethyl for low surface coverages. At higher coverages, however, lateral repulsive interactions between adsorbates de-

stabilize the di- $\sigma$  adsorption of ethylene to a binding energy of -23 kJ/mol. A favorable surface geometry for the  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  coverage is achieved when ethylene is  $\pi$ -bound and hydrogen is bound to a neighboring bridge site. At high coverage, the hydrogenation of di- $\sigma$  bound ethylene to ethyl has an intrinsic barrier of +82 kJ/mol and a reaction energy of -5 kJ/mol, which is only slightly reduced from the low coverage case. For a  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  unit cell, however, the more favorable reaction pathway is via hydrogenation of  $\pi$ -bonded ethylene, with an intrinsic barrier of +36 kJ/mol and an energy of reaction of -18 kJ/mol. This pathway is inaccessible at low coverage. This paper illustrates the importance of weakly bound intermediates and surface coverage effects in reaction pathway analysis.

## Reactivity Affected by Surface Concentration

**COMMENT** This was one of the first papers that illustrated the dramatic consequences of high surface coverage of reacting molecules to surface reaction transition state energies. Comparing the results in the two figures

shows that adding hydrogen to ethylene behaves very differently at low or high hydrogen coverage. For low hydrogen coverage, ethylene is strongly adsorbed and a high activation barrier results. When the hydrogen coverage is

high, ethylene is forced to an on-top adsorption site, where it only weakly interacts with the surface. As a result, the hydrogen addition activation energy becomes substantially lower.

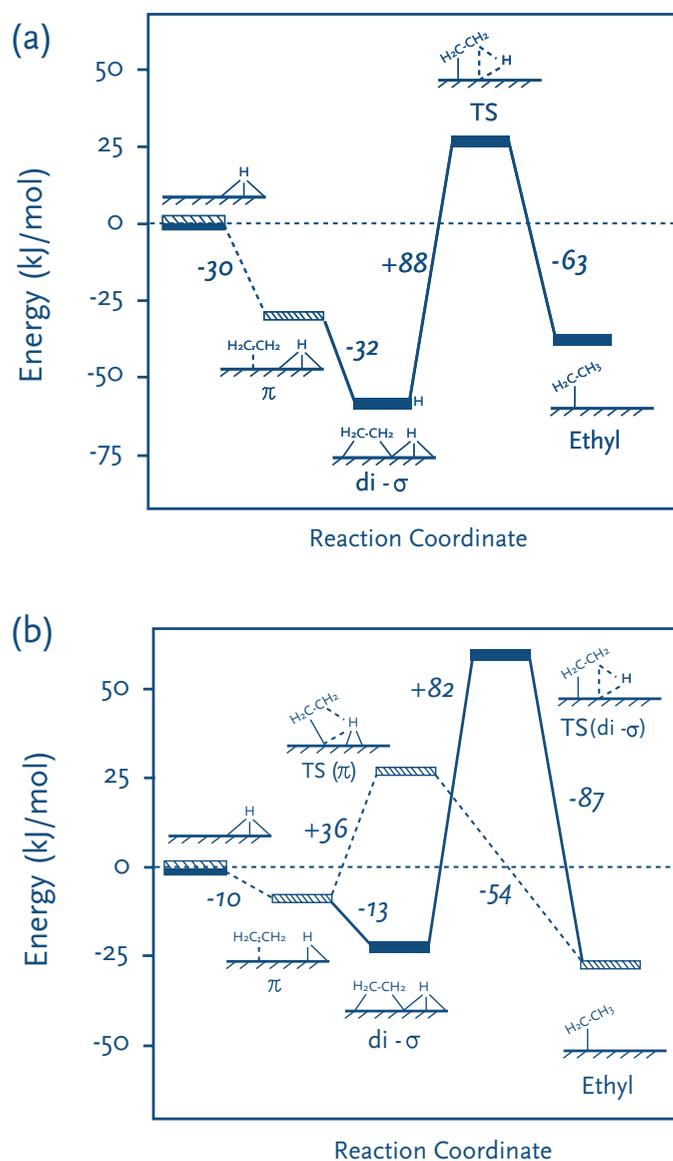
Figure 5.1 shows DFT-computed reaction energy profiles for ethylene hydrogenation to a surface ethyl intermediate on Pd(111): (a) (2×3) periodic

adsorption of ethylene and atomic hydrogen (low coverage) and (b) (√3×√3) periodic adsorption of ethylene and hydrogen (high coverage).

The solid lines depict the pathway via di-σ bonded ethylene.

The dashed lines correspond to ethylene hydrogenation via the π-bonded intermediate.

Figure 5.1



## RESEARCH HIGHLIGHT

MATTHEW NEUROCK AND RUTGER A. VAN SANTEN (1994). *Theory of Carbon-Sulfur Bond Activation by Small Metal Sulfide Particles*. *J. Am. Chem. Soc.*, 116, 4427-4439.

### Theory of Carbon-Sulfur Bond Activation by Small Metal Sulfide Particles

**ABSTRACT** Elementary reaction steps for the catalytic cycle of thiophene desulfurization on Ni<sub>3</sub>S<sub>y</sub> and Ni<sub>4</sub>S<sub>y</sub> clusters are investigated using density functional quantum chemical calculations. The Ni<sub>3</sub>S<sub>y</sub> cluster is active while the Ni<sub>4</sub>S<sub>y</sub> cluster is relatively inactive for HDS catalysis.

Adsorption and overall reaction energies are computed on complete geometry-optimized cluster-adsorbate systems. The nickel-sulfide cluster is found to significantly reorganize upon interaction with adsorbates. Sulfur readily rearranges between 3-fold and 2-fold binding sites. Hydrogen adsorbs molecularly and dissociates heterolytically over Ni<sub>3</sub>S<sub>2</sub> to form both adsorbed sulfhydryl (SH) and hydryl (MH) species. The presence of coadsorbed hydrogen affects both the heat of adsorption and the coordination of thio-

phene. On the “bare” Ni<sub>3</sub>S<sub>2</sub> cluster thiophene binds η<sub>4</sub>-coordinated, while in the presence of coadsorbed hydrogen thiophene prefers the η<sub>1</sub> site. 2,5-dihydrothiophene (DHT) adsorbs somewhat stronger than thiophene on the Ni<sub>3</sub>S<sub>2</sub> cluster. In the preferred η<sub>3</sub> configuration, the ethylene moiety of the DHT adsorbs at one nickel atom site while its sulfur adsorbs at the neighboring nickel atom site. For the HDS cycles initiated by η<sub>1</sub> or η<sub>4</sub> thiophene adsorption, the energy change associated with the carbon-sulfur bond scission step of adsorbed dihydrothiophene and that for the removal of sulfur via H<sub>2</sub>S are the most endothermic steps and are speculated to be rate limiting. Their comparable values indicate that the two steps compete. The cycle that is initiated by the removal of sulfur from Ni<sub>3</sub>S<sub>2</sub> is energetically unfavorable.

### The Reaction Energy Diagram

**COMMENT** One of the first reaction energy diagrams we computed for a complete reaction cycle is for the desulfurization of thiophene. We used Ni<sub>3</sub>S<sub>2</sub> clusters for this study. At that time activation barriers could not yet be included. The reaction energy diagram beautifully illustrates the exothermicity of the bond activation process, which is driven by interaction with the catalyst. To release product from the cluster surface out of the energy valley,

it has to overcome an endothermic process. For an optimum catalyst, the minimum energy of the reaction energy valley should be shallow.

Figure 5.2 shows the proposed catalytic hydrodesulfurization (HDS) cycle 2 for the η<sup>1</sup>-adsorbed thiophene and 2,5-dihydrothiophene intermediates on Ni<sub>3</sub>S<sub>2</sub> (H<sub>2</sub> adsorption initiated): (a) optimized structures for each step of the catalytic reaction path and (b) corresponding energies for each step.

## 5.3

# SURFACE SCIENCE

By *Rutger van Santen*

Surface science at Eindhoven started with the arrival of Hans Niemantsverdriet after a postdoctoral stay with Gerhard Ertl in Berlin. Soon after we both arrived at Eindhoven in 1988, a substantial so-called Pioneer grant was obtained specifically to build the laboratory for Niemantsverdriet's group. This not only enabled him to start a project on model catalysts, initially with the assistance of Shell Research, but it was also very important to our work on heterogeneous catalysis generally.

Niemantsverdriet's group, including Peter Thüne and Tiny Verhoeven, were generally very supportive in assisting the characterization work using their advanced x-ray photoelectron spectroscopy (XPS) and other spectroscopies. We made significant progress in our understanding of surface reactivity as a function of structure. The interpretation of temperature-programmed spectroscopy data is one of Hans' specialties, helped by the use of secondary ion mass spectrometry (SIMS) data. It led at the end of the nineties to a so-called Netherlands Organization for Scien-

tific Research (NWO) Groot grant, based on a proposal that Hans mainly wrote, which gave a further boost to our experimental facilities. The joint work with Hans mainly concerned the experimental determination of surface rate constants of elementary surface reactions. We decided to focus on the decomposition of NO on single crystal surfaces of rhodium. Together with Herman Borg, for the first time Hans determined surface structure dependence of rates of desorption and decomposition of NO as well the elementary reaction rate constants for N<sub>2</sub> formation. On the one hand, a more reactive surface will more strongly adsorb NO and have lower activation energy for dissociation. On the other hand, recombination will be slower on the more reactive surface. Later this work could be refined and rates could be determined as a function of coverage, thereby implying the deduction of the influence of lateral interactions using dynamic Monte Carlo (DMC) simulations. Chretien Hermse carried out this work in combination with experimental studies by Sander van Bavel.

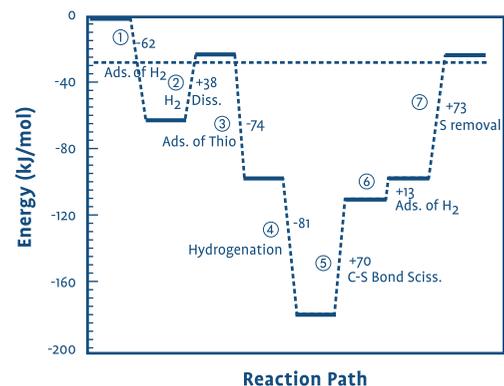
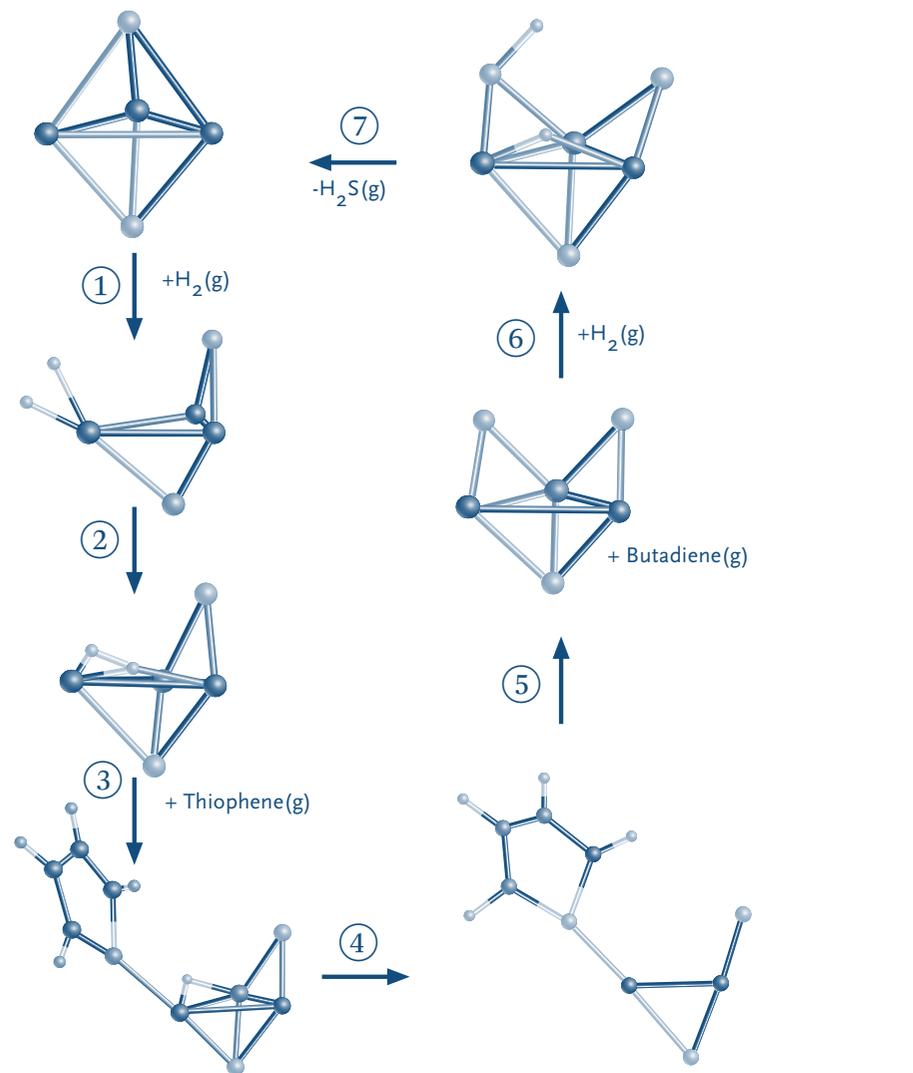


Figure 5.2

### RESEARCH HIGHLIGHT

F. FRECHARD, R. A. VAN SANTEN, A. SIOKOU AND J.W. NIEMANTSVERDRIET (1999). *Adsorption of Ammonia on the Rhodium (111), (100), and Stepped (100) Surfaces: An ab initio and Experimental Study. Journal of Chemical Physics, 111, 8124-8130.*

### Adsorption of Ammonia on the Rhodium (111), (100), and Stepped (100) Surfaces: An ab initio and Experimental Study.

**ABSTRACT** The adsorption of ammonia on the two low index (111) and (100) surfaces of rhodium has been studied by periodic calculations with density

experimental results. The geometries of the adsorbates and the surfaces are completely optimized. For both surfaces the top site is found to be the most functional theory and compared to stable while the adsorption energy of

ammonia is  $8\text{--}10\text{ kJ}\cdot\text{mol}^{-1}$  larger on the (100) surface.

The presence of steps on the (100) surface has a minor effect on the heat of adsorption. The theoretical predictions of the adsorption energies and the changes in work function by  $\text{NH}_3$  are in good agreement with experimental data. Moreover, the prediction of the

on-top adsorption as well as the weak interactions between the adsorbates is confirmed. The broadening of the temperature programmed desorption spectra and the two desorption peaks for the first adlayer are mainly due to an entropy effect which affects the pre-exponential factor of the desorption rate constant.

#### Energetics of Ammonia Adsorption as a Function of Site

**COMMENT** The combination of computational surface chemistry and experimental surface science has become very powerful because well-defined surfaces are accessible to both methods. We initiated this approach with Hans Niemantsverdriet in a study of ammonia interacting with two rhodium surfaces. Theory provides insights into the atomistic details of the process,

whereas experiment can be used to validate computed energies. In later studies the temperature-programmed desorption spectra were simulated with kinetic Monte Carlo methods. Figure 5.3 gives on-top and side views of nine cells (black arrows indicate the unit cell) for the stepped (100) surface with  $\text{NH}_3$  adsorbed tilted on the step.

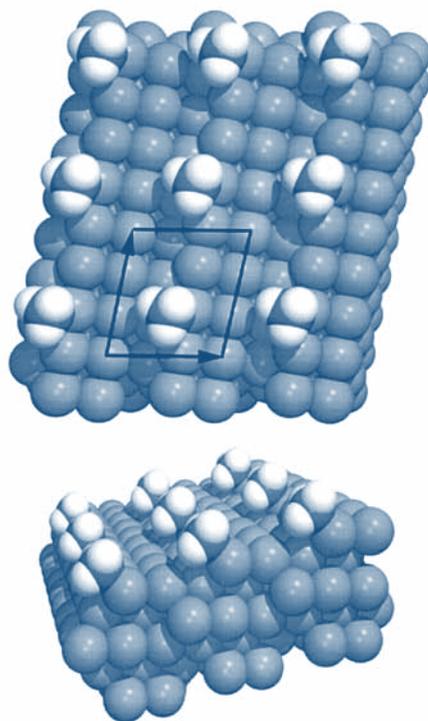


Figure 5.3

## 5.4

# MECHANISMS IN HETEROGENEOUS CATALYSIS

By *Rutger van Santen*

The early work at Shell Research Amsterdam was connected to the high interest in catalytic platforming at that time. In this process, which is essential for producing gasoline in a refinery, a bifunctional catalyst is used that isomerizes linear alkanes and converts them into aromatics. The catalyst consists of highly dispersed platinum particles on a support with high surface acidity. Work at Exxon had demonstrated the benefit of the use of alloys of platinum that increase stability.

The work with Wolfgang Sachtler generated the idea that this beneficial effect is related to the suppression of hydrogenolysis reactions that cleave the C–C bonds in the hydrocarbon, which generates undesirable light gas. The ensemble effect prescribes the need for large ensembles of the reactive surface atoms. Alloying with a nonreactive metal decreases the ensemble size of the reactive surface atoms, which results in a reduction of this hydrogenolysis reaction. This explanation fits with the Langmuirian idea of a checkerboard surface. Within this model, diluting surface atoms with inert metal atoms, such as gold or tin, will reduce the ensemble size of reactive surface atoms.

It is now well understood that the hydrogenolysis reaction—that is to say, initiated by CH activation—is very sensitive to the reactivity of the surface atoms. It preferentially occurs therefore at surface step edges. However, because of their lower surface energy, they are preferentially decorated by the alloying nonreactive atoms. Activity is suppressed because the nonreactive

surface atoms replace the most reactive surface atoms. The Taylor “unique surface” site theory on catalytic reactivity is in line with the idea that preferred reaction centers exist on surfaces that are not only planar but also contain corner atoms or step edges. Our recent work on the Fischer-Tropsch reaction, which converts carbon monoxide into longer hydrocarbons, favors Taylor’s point of view.

With Matthew Neurock we discovered that strong adsorption of the  $\pi$ -bond of the molecule with the catalyst inhibits olefin hydrogenation reactions. High coverage or coadsorption of carbon will shift the molecule from di- $\sigma$  to the weaker  $\pi$  adsorption site with a substantial reduction in hydrogenation energy.

After the first oil crisis in the seventies, interest in the Fischer-Tropsch process reawakened at Shell Research as well. My first paper on this topic was with Frits Dautzenberg on transient kinetics. He had been my supervisor at Shell for a short time—the beginning of another lifelong friendship. He later moved to Canada and the United States. Much later, when he was a research director at Lummus in New Jersey, we even embarked on a joint research project again. I had the pleasure of giving him a doctorate degree from TU/e (he was an Eindhoven alumnus) for his research when he was over fifty years old. Later he became a visiting professor at Eindhoven to assist with courses in applied catalysis.

These early years were also the time of Paul Biloen and Wolfgang Sachtler’s very inspiring work that conclusively

established that a carbon monoxide dissociation step initiates the Fischer-Tropsch reaction. This is called the carbide mechanism. This inspired me later at Eindhoven to start studies with Thijs Koerts on C–C bond formation from C<sub>1</sub> surface species generated by the decomposition of methane. To our great delight we discovered preferential higher hydrocarbon formation on metals such as cobalt and ruthenium. The recombination probability of CH<sub>x</sub> species to give chain growth is hence unrelated to the presence of carbon monoxide. It also became the topic of my first quantum chemical paper on the Fischer-Tropsch reaction. A later important paper on the chain-growth reaction was based on Ciobîcă's PhD thesis, in which he studied the full complexity of hydrogen atom transfer in combination with C–C bond formation. Around the turn of the century, we were approached by the South African oil company Sasol about a joint research program. This led to very intensive contact with Sasolburg and Capetown, South Africa. We had several visitors in our group from Sasol.

Shetty, Ciobîcă, and De Koster confirmed early ideas on the variation

in topological relation with d valence electron occupation between CH<sub>x</sub>, with varying x, and the surface adsorption site. The high stability of a carbon atom adsorbed at a fourfold coordination site and the preference of CH or CH<sub>2</sub> for being adsorbed at a twofold or threefold coordination site appears to be essential to shift the growing hydrocarbon chain away from the preferred site of carbon monoxide dissociation. This suggests an optimum “Taylor” site for the Fischer-Tropsch reaction and explains why the catalyst is not poisoned at sites of highest carbon monoxide dissociation reactivity by growing hydrocarbon chains.

The focus of our recent interest is the particle size dependence of this reaction, which brought us into contact with the interesting experimental work of Krijn de Jong on this topic. Recent dynamic Monte Carlo (DMC) studies by Minhaj Ghouri, who is a postdoc in our laboratory, indicated that their experiments and our theoretical studies show that carbon monoxide dissociation has to be fast, intermediate CH<sub>x</sub> species have to be rather stable, and the reaction that terminates the reaction should be slow.

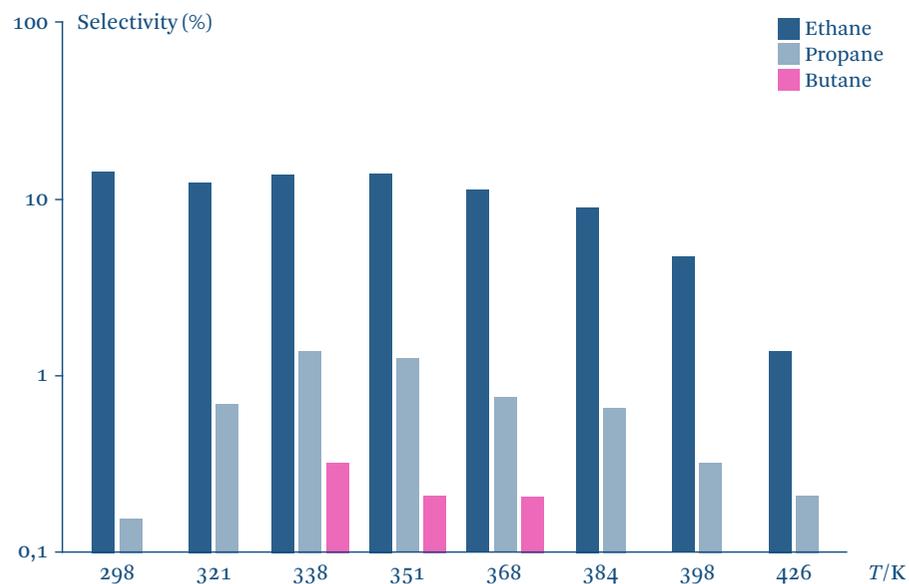


Figure 5.4

## RESEARCH HIGHLIGHT

TIJS KOERTS AND RUTGER A. VAN SANTEN (1991). *A Low Temperature Reaction Sequence for Methane Conversion*. *J. Chem. Soc. Chem. Commun.*, 70 (1), 119–127.

### A Low Temperature Reaction Sequence for Methane Conversion

**ABSTRACT** Surface carbonaceous intermediates produced from methane are shown to produce small alkanes upon hydrogenation below 400 K.

#### C–C Bond Formation from Methane

**COMMENT** This paper demonstrates that carbon atoms deposited on a transition metal by means of decomposing methane can be induced to recombine to give alkane oligomers. The idea for this reaction originated from the mechanistic proposal in Fischer-Tropsch catalysis that carbon monoxide has to dissociate and that hydrocarbon chain growth occurs through recombining the carbon atoms. If this is true, carbon atoms generated from methane should be able to do the same. Figure 5.4 gives the product distribution dependence on the hydrogenation temperature of C<sub>α</sub> deposited from methane at 763 K on a 5% Ru/SiO<sub>2</sub> catalyst.

## RESEARCH HIGHLIGHT

I.M. CIOBÎCĂ, G.J. KRAMER, Q. GE, M. NEUROCK AND R.A. VAN SANTEN (2002). *Mechanisms for Chain Growth in Fischer-Tropsch Synthesis over Ru(0001)*. *Journal of Catalysis*, 212, 136–144  
DOI:10.1006/JCAT.2002.3742

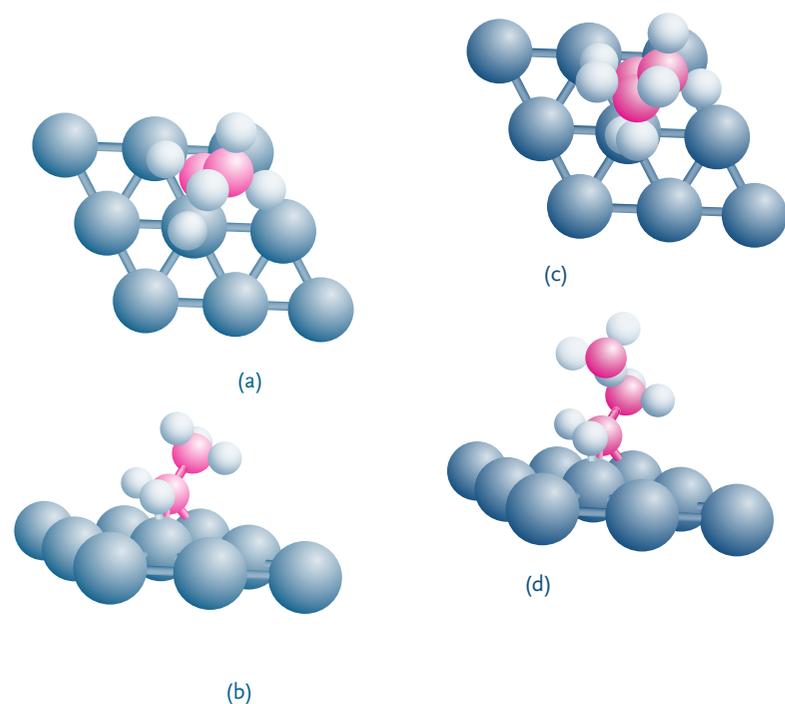
### Mechanisms for Chain Growth in Fischer-Tropsch Synthesis over Ru(0001)

**ABSTRACT** Two reaction pathways for hydrocarbon chain-growth mechanisms over Ru(0001) in Fischer-Tropsch synthesis have been analyzed using periodic ab initio calculations for 25% coverage. Adsorption energies for the intermediates for the first two catalytic cycles for each mechanism as well as the transition states are reported. Both mechanisms are carbene-type mechanisms. Adsorbed CH species are used as the building unit, rather than adsorbed CH<sub>2</sub> intermediates. The resulting intermediate hydrocarbon chains at the surface are alkyl- and alkylidene-like, respectively.

#### Theory of C–C Bond Formation

**COMMENT** This paper studies the energetics (including activation energies) of the chain-growth reaction in the Fischer-Tropsch process. Adsorbed CH species insert into the growing chain. The processes are subsequent C–C bond formation and hydrogen addition steps. Theory is able to discriminate between different possible reaction paths. Figure 5.5 shows the transition states for R–CH<sub>2</sub>–CH hydrogenation, R=H (a, b), CH<sub>3</sub> (c, d), and top (a, c) and side (b, d) views. The hydrogen atom in shadow (a) is the one attacking the vinyl group. In (c) the hydrogen atom that is attacking is under one of the hydrogen atoms from CH<sub>3</sub>.

Figure 5.5



## 5.5

## ETHYLENE EPOXIDATION

By *Rutger van Santen*

My first managing director at Shell Amsterdam was Wolfgang Sachtler; my first supervisor was Peter Kilty. Just before I arrived in Amsterdam, they had published several important papers on silver-catalyzed ethylene epoxidation. Their interest was based on the corresponding Shell catalyst and process. They proposed that molecular oxygen was stabilized on the silver surface, which according to their view was due to coadsorbed chlorine, added as a promotor. The molecular idea corresponded to a decrease in the ensemble size of the silver surface necessary for  $O_2$  dissociation. It suggested a maximum ethylene selectivity of the reaction of 6/7. As my first experimental task, Wolfgang asked me to study the role of promoting cesium on silver. That is why I did the initial experiments on the silver/potassium system with Jan Moolhuysen. Using deuterated ethylene on Cs/Cl doped model silver systems, we found that higher selectivities than 6/7 are possible, which challenged the Kilty-Sachtler proposal. With Cor de Groot having succeeded Jan Moolhuysen as technical assistant, he and I were able to prove experimentally that molecular oxygen adsorbed on the oxidized silver surface does not cause high selectivity to epoxide, but atomic oxygen. The reaction is a Mars-van Krevelen-type oxidation, in which the site of oxygen dissociation is separate from that of reaction with the hydrocarbon. The Royal Netherlands Chemical Society (KNCV) decided to award me the Golden Medal for this finding.

After this success, I went to Shell Development Company in Houston, Texas, where I stayed from 1982 to 1984. To my delight, I was put in charge

of managing the extramural contract that Shell had with Caltech on the topic of ethylene epoxidation. Bill Goddard, whose quantum chemical work I knew well but had never met, turned out to be professor of chemistry and applied physics at Caltech. He hired Emily Carter as a PhD student on that project, and together the three of us spent many pleasant hours discussing science in both Los Angeles and Houston. Nearly thirty years later, Bill and I ran a joint program on the topic of hydrogen storage.

While at Northwestern, Wolfgang decided to organize a Gordon Research Conference on Catalysis where he invited Charles Campbell, then of Sandia laboratories, Richard Lambert of Cambridge, and I to present lectures on the mechanism of the epoxidation of silver catalyzed by silver. He anticipated that we would have opposing views, which would stimulate further discussions on the topic.

By that time I had finished the oxygen isotope studies, which convinced me that oxygen was the key species and that a highly oxidized or chlorinated surface was needed to generate the adatom with the right reactivity. I convinced Evert-Jan Baerends of VU University Amsterdam to study this reaction quantum chemically. Based on this work, we were able to propose a chemical bonding argument as to why the oxidized silver surface is highly selective. I had already become very familiar with Evert-Jan's work when in 1975 Piet Ros, the quantum chemist who introduced density functional theory (DFT) methods to the Netherlands and a former student of Schuit, invited me to be a part-time visiting scientist in his laboratory.

In the early years of the twenty-first century the work of Marc Barteau at the University of Delaware identified for the first time the surface oxametallacycle (OMC) intermediate that produces, in parallel with the epoxide acetaldehyde, the intermediate for nonselective combustion. In 2011 we copublished a computational paper with Isik Onus and his graduate student Olus Ozbek of Middle Eastern Technical University (METU), Ankara, where we showed conclusively that instead of the OMC intermediate, an Eley-Rideal-type intermediate forms that selectively produces the epoxide. The reactive oxygen necessary for this reaction path only forms on highly oxidized surfaces or in the presence of chlorine, exactly as we had proposed nearly twenty years earlier.

This and other stories illustrate the importance of there being a free flow of ideas between scientists working on problems of common interest. They also reveal the long-term lines of

investigation that search for definitive physicochemical answers to the complex problems relating to practical catalytic chemistry. Often the material being investigated is complex and sometimes only a fraction of the surface is actually responsible for the key reaction. Instruments for studying the reactivity directly at a molecular level have to be designed and adapted to the specific system of study. Often only definitive answers are obtained through the proper choice of well-defined model systems. Research into the unknown is an iterative process with a succession of hypotheses and falsification experiments or calculations, often with interference from the unsuspected and rarely validating the original hypothesis. A now well-known example is the work of Gerhard Ertl, who slightly less than one hundred years after the invention of the ammonia catalyst unraveled the molecular action of the catalyst at the atomic level. It earned him the Nobel Prize.

R.A. VAN SANTEN AND C.P.M. DE GROOT (1986). *The Mechanism of Ethylene Epoxidation*. *Journal of Catalysis*, 98, 530–539.

### The Mechanism of Ethylene Epoxidation

**ABSTRACT** The mechanism of the epoxidation of ethylene with oxygen over silver catalysts has been examined. This study was prompted by the notion that if one wishes to increase the selectivity of epoxide formation, one should know the phase of adsorbed oxygen that reacts to give epoxide. Experiments were undertaken (a) to determine whether adsorbed atomic oxygen is incorporated into ethylene to give epoxide, and (b) to establish the relative rates of reaction of molecular oxygen impinging from the gas phase and of preadsorbed atomic oxygen. Experiments were performed in a high-vacuum recirculation system designed to allow volumetric absorption studies as well as kinetic studies using a mass spectrometer to be made. The catalyst

consisted of silver powder precovered with chemisorbed  $^{16}\text{O}$  such that it gave epoxide upon reaction with ethylene. It was contacted with ethylene/ $^{18}\text{O}_2$  as mixtures of different ratios. It is shown that under conditions where oxygen isotope equilibration in the gas phase is slow, ethylene initially reacts more rapidly with preadsorbed oxygen atoms than with molecular oxygen adsorbed in the precursor state ( $p\text{O}_2 < 20$  Torr;  $1 \text{ Torr} = 133.3 \text{ N m}^{-2}$ ) if  $\text{O}_{\text{ads}}/\text{Ag}_s \sim 1$ . If in the beginning only subsurface oxygen atoms are present, this subsurface oxygen and gas-phase oxygen are incorporated into ethylene at about equal rates. It is concluded that ethylene reacts with atomic oxygen to give epoxide either directly, or indirectly, after recombination of the oxygen atoms.

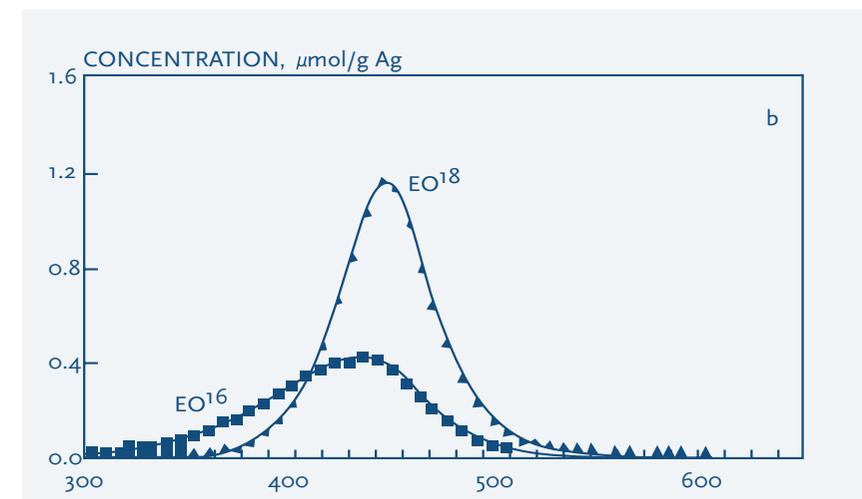
### Atomic versus Molecular Oxygen Conversion of Ethylene to the Epoxide

**COMMENT** This was a paper that demonstrated that epoxidation of ethylene by silver occurs via a Mars-van Krevelen mechanism.

Figure 5.6 shows the appearance of  $\text{E}^{16}\text{O}$  from a silver powder which contains oxygen ( $^{16}\text{O}$ ) at the surface and subsurface. Reaction with a gas-phase mixture of ethylene and  $^{18}\text{O}_2$  demonstrates that the surface oxygen preferentially gives epoxide production from

ethylene. This experiment also demonstrated that molecular  $\text{O}_2$  does not react with ethylene to epoxide, as was widely believed at that time. It demonstrates that a surface oxide gives epoxide selectively. The figure gives the  $\text{E}^{16}\text{O}$  and  $\text{E}^{18}\text{O}$  production as a function of temperature in an experiment with an initial gas-phase  $^{18}\text{O}_2$  pressure of 20.4 Torr, an initial ethylene pressure of 13 Torr,  $^{16}\text{O}_2$  preadsorbed:  $1.08 \mu\text{mol/g Ag}$ .

Figure 5.6



P.J. VAN DEN HOEK, E.J. BAERENDS AND R.A. VAN SANTEN (1989). *Ethylene Epoxidation on Ag(110): The Role of Subsurface Oxygen*. *J. Phys. Chem.*, 93, 6469–6475.

### Ethylene Epoxidation on Ag(110): The Role of Subsurface Oxygen

**ABSTRACT** We have performed electronic structure calculations on the chemisorption of atomic oxygen on Ag(110) and on the subsequent reaction of this chemisorbed oxygen with ethylene. These calculations show that the presence of subsurface oxygen (i) reduces the bond energy between silver and adsorbed oxygen and (ii) converts the repulsive interaction between adsorbed oxygen and (gas-phase) ethylene into an attractive one, thus making possible the epoxidation re-

action. The presence of subsurface oxygen diminishes an important four-electron destabilizing interaction (Pauli repulsion) between the occupied ethylene  $\pi$  orbital and a surface oxygen lone-pair orbital by shifting the band of ethylene  $\pi$ -oxygen lone-pair antibonding orbitals largely above the Fermi level. As for total combustion of ethylene, we do not find any C–H bond activation for several different geometries in which ethylene approaches the adsorbed oxygen atom.

**COMMENT** This was an early DFT cluster study of the ethylene epoxidation reaction. It supports the thesis that the reaction will only selectively occur on an oxidized surface. This is clearly seen from the energy curves plotted as a function of approaching ethylene for an oxidized silver cluster and non-oxidized silver cluster, respectively.

Figure 5.7 shows one of the orbitals in the structure when subsurface oxygen is present. In (a) the orbital is in the

plane of the chemisorbed oxygen atom (*center*) and the surface silver atoms, that is, the (110) plane. In (b) the orbital is in the plane of the chemisorbed (*center*) and subsurface oxygen atoms. In figure 5.10 the interaction energy is shown as a function of adsorbed oxygen–ethylene distance for the geometry of figure 5.7 without (solid) and with (dashed) subsurface oxygen. The curves are based on calculations with  $Ag_4$ .

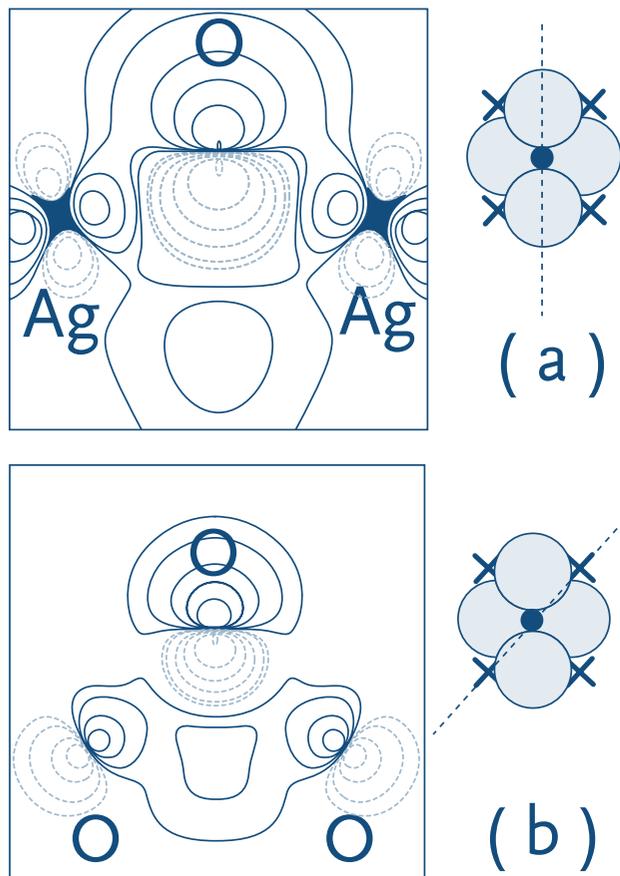


Figure 5.7

Figure 5.8

## 5.6

# AMMONIA OXIDATION

By *Rutger van Santen*

Contact with Wynn Roberts from Cardiff at a meeting in Tokyo inspired the initial work on ammonia oxidation. They had proposed that so-called hot atoms were responsible for ammonia oxidation on magnesium or copper.

It led to the important paper with Matthew Neurock on the oxidation of ammonia by copper clusters. We actually found that the lowest activation barrier for activating ammonia was not the direct interaction with atomic hydrogen, but with molecular oxygen.

In the late eighties Solvay Hannover became interested in quantum chemical modeling of catalysis. Within this context I made biannual visits and worked closely with Armin Klesing for some years. He is a theoretical chemist, who back then had just been hired from the University of Kiel. He was to have an impressive industrial career in Solvay. Armin and I published together my first paper about water on metal surfaces. Through these visits I became familiar with the need to remove ammonia from water without producing nitrates. It became the first reaction that I started to study electrochemically at Eindhoven (see section 5.7).

I also decided to study this reaction in the gas phase. There are main emission streams that contain ammonia in air, from which it needs to be removed. Experimental work with Lu Gang and Nout van den Broek on silver and silver/copper alloys, as well as low-temperature oxidation studies on platinum demonstrated that, indeed, coadsorbed oxygen activates ammonia oxidation, as we found for copper in the computational study with Matthew Neurock. The mechanism of the reaction is very different for the group VIII

metals compared to the IB metals. For the former,  $N_2$  formation is dominated by nitrogen atom recombination; for the latter, the Fogel reaction dominates, in which nitrite is reduced with ammonia.

Participation in a German Research Foundation (Deutsche Forschungsgemeinschaft) research program with Manfred Baerns from Berlin and Ronald Imbihl from Hannover enabled us to continue these studies further on a theoretical level. The main result was the discovery of significant structure sensitivity of the selectivity of this reaction to produce nitrogen. It enabled us to develop a theory of surface reactivity and activation by coadsorbed oxygen that explained surface topology effects in terms of bond-order conservation. This was inspired by early collaborative work with Cynthia Friend, then at Harvard, on the activation of methanol by coadsorbed oxygen. Whereas on platinum O–H bond cleavage preferentially proceeds through reaction with oxygen, on more reactive rhodium adsorbed oxygen is poisonous to this reaction. Experimental confirmation of the necessity of coadsorbed oxygen being present as well as surface topology dependence of overall oxidation of ammonia on platinum came from in situ oxidation experiments using positron emission profiling (PEP) with PhD student Derek Sobzjek. He demonstrated that on the dense (111) surfaces of platinum powder, the oxygen also has to be present as hydroxyls. Adsorbed  $NH_x$  generated by dissociative adsorption of ammonia to platinum by reaction of ammonia with oxygen is only removed as  $N_2$  when some of the coadsorbed oxygen is converted into surface hydroxyls.

## Atomic and Molecular Oxygen as Chemical Precursors in the Oxidation of Ammonia

**ABSTRACT** The role of atomic and molecular oxygen precursors in the overall catalytic cycle for ammonia dissociation is analyzed using first-principle density functional calculations. Adsorption energies for ammonia, molecular oxygen,  $\text{NH}_x$ , NO, and various intermediates and adatoms were computed from geometry-optimized calculations on the model Cu(8,3) cluster of the Cu(111) surface. Reported values systematically underpredict experimental adsorption energies by 30 kJ/mol due to the finite cluster size. Attractive and repulsive lateral interactions were important in accessing accurate adsorption energies. Atomic oxygen enhances N–H bond activation; however, it also acts to poison active surface sites and inhibit ammonia dissociation kinetics. Transient molecular oxygen adsorbs weakly in both parallel (-17 kJ/mol) and perpendicular orientations (-10 kJ/mol) to the surface. Parallel adsorption appears to be a precursor for oxygen dissociation,

## Atomic versus Molecular Oxygen Activation of Ammonia

**COMMENT** This was an early paper with a complete DFT-computed reaction energy diagram containing some (approximate) transition state energies. At that time we were only able to use cluster models of surfaces. The reaction studied is ammonia oxidation by copper. The figures compare activating ammonia by atomic or molecular oxygen. In this case, activation by molecular oxygen has a substantially lower activation energy than activation by oxygen. Figure 5.9 shows reaction coordinate calculations for the path two dissociation of ammonia over the Cu(6) cluster. Oxygen abstracts two hy-

drogens from the coadsorbed ammonia which ultimately results in  $\text{NH}^*$  and the formation of gaseous water. Figure 5.10 shows the same for the path three dissociation. Molecular oxygen acts to abstract a single hydrogen from the coadsorbed ammonia to form  $\text{NH}_2^*$  and  $\text{OOH}^*$  intermediates. In both figures, the N–H stretch is taken as the reaction coordinate and  $E$  refers to total electronic energies (in atomic units) at particular points along the coordinate.  $\Delta E$  is the change in energy with respect to the initial adsorbed state and is reported in kJ/mol. Bond lengths are reported in Å.

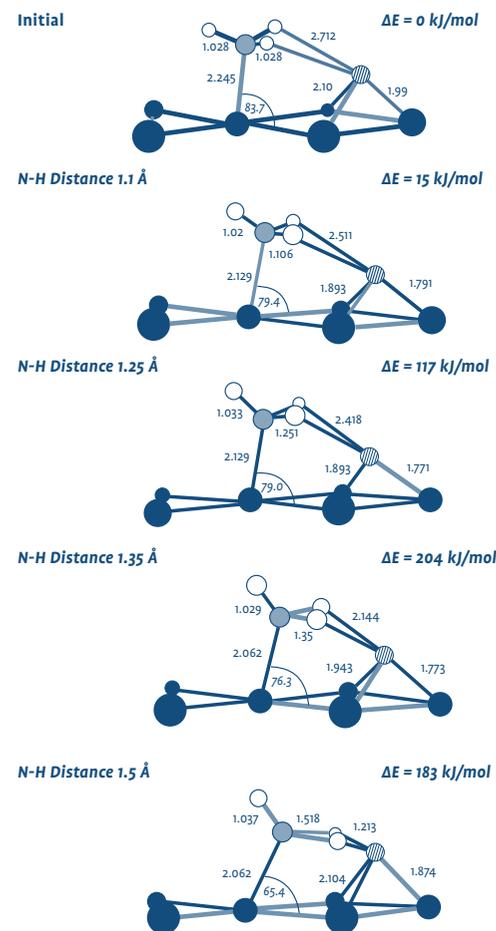


Figure 5.9

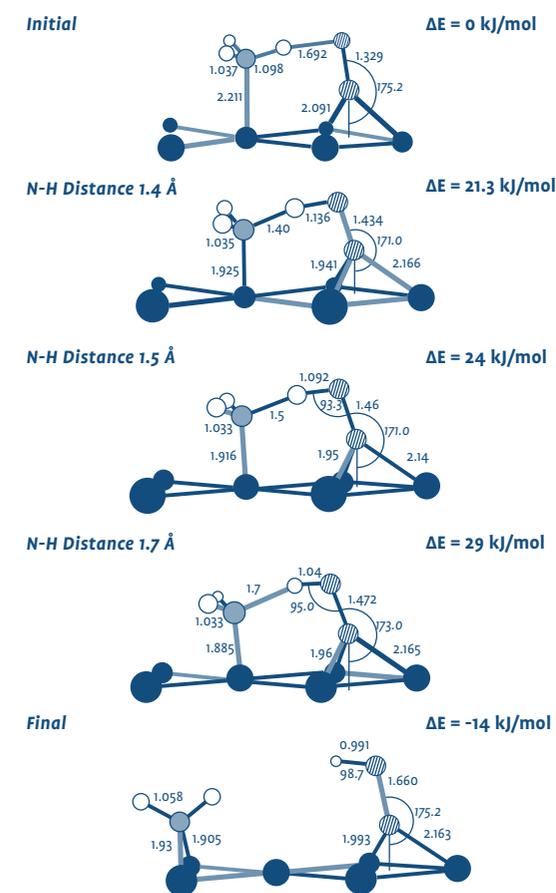


Figure 5.10

## Why Silver Is the Unique Catalyst for Ethylene Epoxidation

**ABSTRACT** The activities of  $\text{Cu}_2\text{O}(001)$ ,  $\text{Ag}_2\text{O}(001)$ , and  $\text{Au}_2\text{O}(001)$  surfaces for direct ethylene epoxidation and alternative paths for EO isomerization are studied. Among these three oxide surfaces, only  $\text{Ag}_2\text{O}(001)$  surfaces enables direct path without a barrier.  $\text{Au}_2\text{O}$  cannot regenerate surface oxygen, and overall reaction on  $\text{Cu}_2\text{O}$  is endothermic. Furthermore, ring opening of ethylene

oxide (EO) and subsequent acetaldehyde (AA) formation on  $\text{Cu}_2\text{O}$  is more favorable than EO desorption. Ethylene adsorption on an oxygen vacancy results in the oxametallacycle (OMC) formation, which causes AA formation and reduces EO selectivity. Chlorine adsorption removes these surface vacant sites and hence prevents the formation of the OMC intermediate.

## Direct Epoxide Formation versus the Oxametallacycle Route

**COMMENT** This paper concludes earlier experimental and theoretical work on the epoxidation of ethylene. The mechanism of the reaction depends sensitively on the state of the silver metal surface. Only on oxidized silver surfaces does the direct mechanism of epoxide formation operate and produce epoxide selectively. Copper cannot be used because the selectivity to acetaldehyde is dominant. Gold is also unsuitable

because the surface will remain metallic. Figure 5.11 shows relative energies of direct epoxidation paths on  $\text{M}_2\text{O}(001)$  surfaces. Initial points correspond to the oxygen adsorption energies at a vacant surface site that saturate the surface. Figure 5.12 compares the energy changes of reaction paths following EO formation. Adsorbed EO may (i) desorb, (ii) isomerize to ethyleneoxy intermediate, or (iii) isomerize to AA.

Figure 5.11

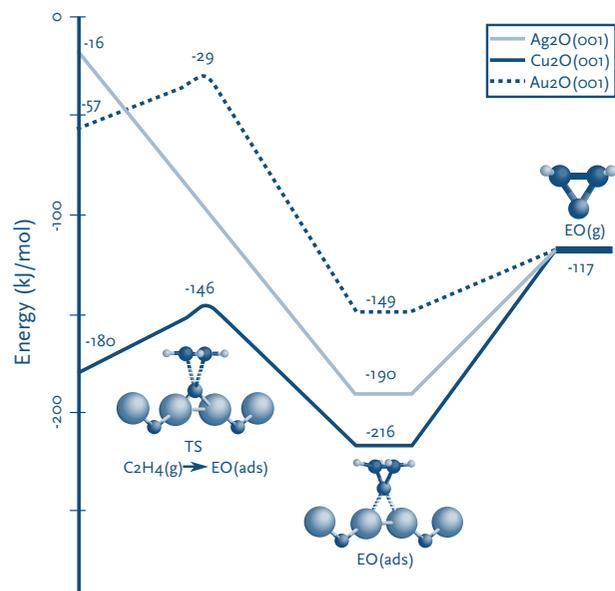
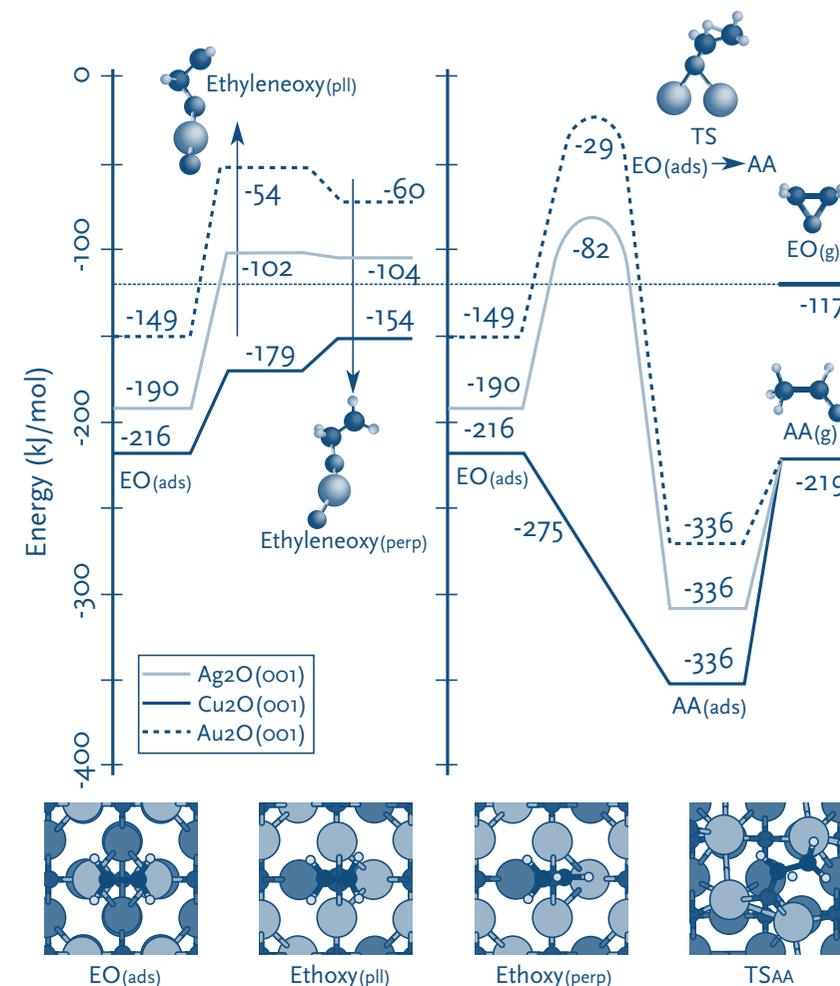


Figure 5.12



## RESEARCH HIGHLIGHT

R.A. VAN SANTEN, W.K. OFFERMANS, J.M. RICART, G. NOVELL-LERUTH AND J. PÉREZ-RAMÍREZ (2008). *Structure Dependence of Pt Surface Activated Ammonia Oxidation. Journal of Physics: Conference Series, 117, 012028.*

## Structure Dependence of Pt Surface Activated Ammonia Oxidation

**ABSTRACT** Computational advances that enable the prediction of the structures and the energies of surface reaction intermediates are providing essential information to the formulation of theories of surface chemical reactivity. In this contribution this is illustrated for the activation of ammonia by co-adsorbed oxygen and hydroxyl on the Pt(111), Pt(100), and Pt(211) surfaces.

Figure 5.13

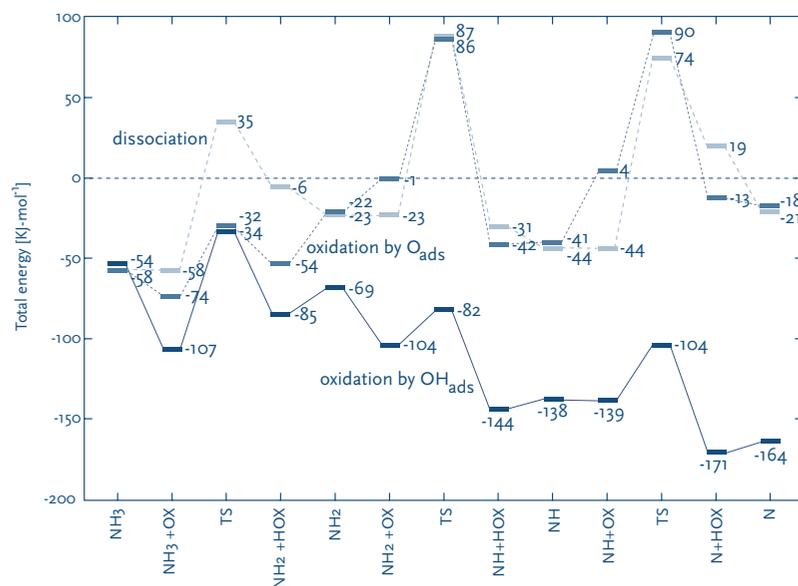
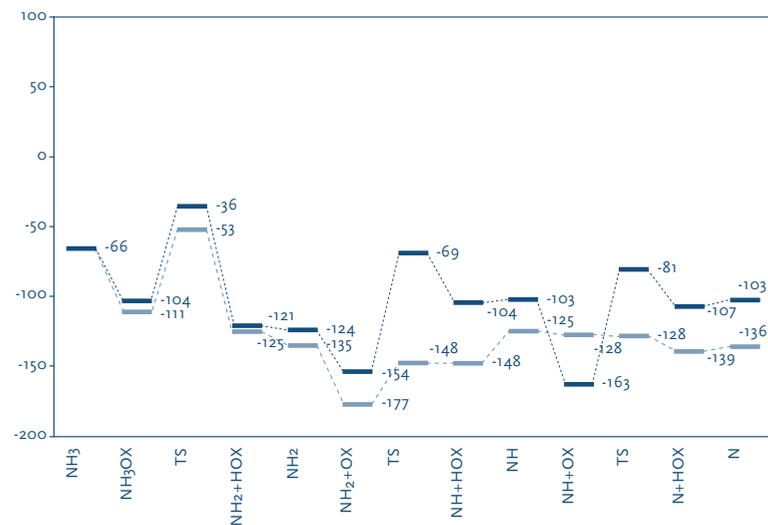


Figure 5.14



### Structure Sensitivity: No Sharing of a Surface Metal Atom in the Transition State

**COMMENT** This is one of a series of papers we wrote on the structure dependence of ammonia activation by platinum. The reactivity of a (111) or (100) surface is very different. On both surfaces activation of the N–H bond occurs through activation by oxygen or OH. On the Pt(111) surface OH<sub>ads</sub> is substantially more reactive than O<sub>ads</sub>.

On Pt(100) the reactivities are comparable. This study illustrates the importance of analyzing the surface topologies of reaction intermediates in detail. The difference in O<sub>ads</sub> reactivity on the two surfaces relates to differences in the transition state structure. The high activation energy on the (111) surface is because surface topology forces O<sub>ads</sub>

and ammonia to share bonding with the same metal surface atom. This can be prevented on the (100) surface.

Figure 5.13 gives the reaction energy diagram of the dehydrogenation reactions of ammonia on Pt(111). All total energies are with respect to NH<sub>3,gas</sub>, Pt(111), 3 O<sub>ads</sub> and 3 H<sub>ads</sub> and are zero point energy corrected. OX or HOX on the abscissa mean oxidator or hydro-

genated oxidator and can be OH, oxygen, an empty site, or their hydrogenated forms. All NH<sub>x</sub>+(H)OX states are coadsorbate states with lateral interactions. In all other adsorbate states, we assume there to be no lateral interactions. Figure 5.14 is the reaction energy diagram for oxygen-assisted (red) and OH-assisted (black) ammonia dehydrogenation on Pt(100).

## VINYL ACETATE

By Rutger van Santen

After his postdoctoral stay at Eindhoven and before moving to the University of Virginia, Matthew Neurock spent some years at the DuPont Experimental Station in Delaware. In that period Matthew asked me to act as a consultant for DuPont. During my many visits to the DuPont laboratories I became well acquainted with Jan Lerou and Leo Manzer, who were then managers of the Chemical Engineering Department. They were very important to me because they strongly believed in the relevance of the molecular approach to catalysis for advancing chemical engineering and publicized this view through many lectures and scientific conferences. This was at a time (in the midnineties) when the relevance of quantum chemical modeling of catalytic reactivity was yet to be generally accepted in the chemical engineering community.

To encourage further cooperation and maintain our close ties, DuPont decided to sponsor our research group at Eindhoven by funding a PhD student. With David Kragten on board, we began computational studies on the oxidation of ethylene with acetic acid to produce vinyl acetate, an important process to Dupont. One issue was to understand the effect of alloying and

promoting the supported palladium catalyst; the other and more important issue was to bring clarity to the mechanism. The essential question regarding the mechanism was whether ethylene is inserted into acetate, followed by  $\beta$ -CH cleavage, or whether a surface vinyl species formed first that subsequently would insert into acetate. Based on computed results, we decided in favor of the first route.

At that time we organized a summer school with the Netherlands Institute for Catalysis Research (NIOK) (Sheldon, R.A. and Santen, R.A. van (eds.) (1995). *Catalytic Oxidation: Principles and Applications*. Singapore: World Scientific.) where we discussed such topics. We also invited the very charming Russian chemist Ilya Moiseev, who made important mechanistic experimental contributions to this topic. To our benefit he introduced us to these studies in great detail during his visits to Eindhoven. This work was, computationally speaking, very challenging because solvent effects are very important. Matthew later published a fine paper on the alloying of gold, in which he explained that it would provide sites for ethylene to adsorb to the metal surface otherwise highly covered with acetate.

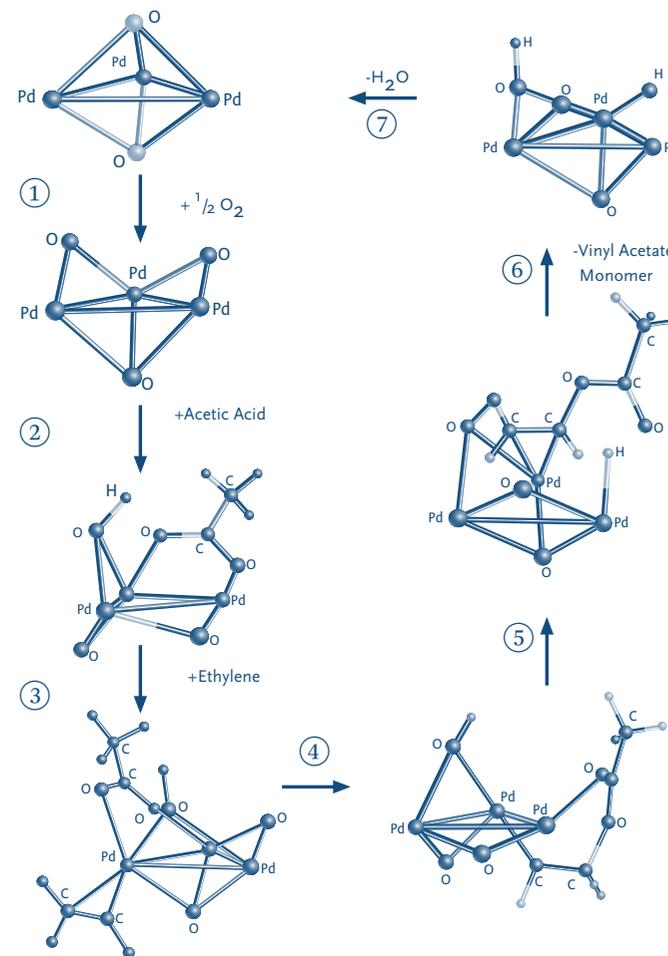


Figure 5.15

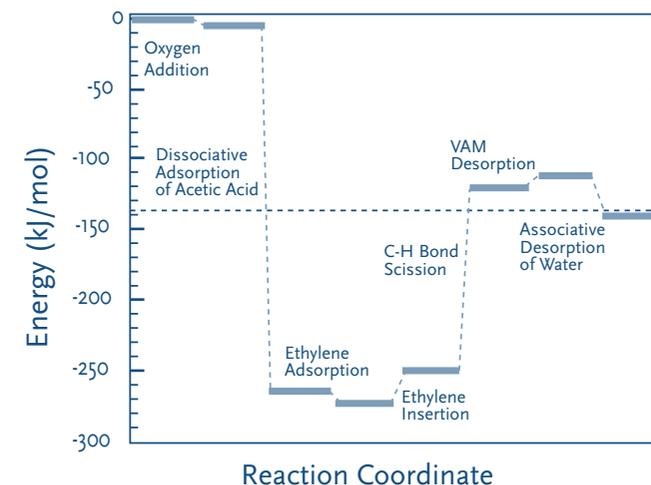


Figure 5.16

### First-Principle Analysis of the Catalytic Reaction Pathways in the Synthesis of Vinyl Acetate

**ABSTRACT** Acetoxylation of ethylene over supported palladium and palladium/gold is a well-established commercial route for the formation of vinyl acetate. While the overall reaction chemistry for the synthesis of vinyl acetate was uncovered some thirty years ago (Eur. Chem. News 1967; World Pet. Cong. Proc. 1968, U.S. Patent 1967 & 1977), the active catalytic surface ensembles, key reaction intermediates, and mechanism are still poorly understood. Issues such as the oxidation state of the active centers ( $\text{Pd}^0$  vs  $\text{Pd}^{2+}$ ), particle ensemble size (small clusters versus large particles, rate-determining

elementary steps, secondary decomposition routes, and the structural and/or electronic role of Au, have yet to be resolved.

Herein, we employ first-principle quantum chemical techniques to model a series of proposed elementary steps representative of vinyl acetate synthesis.

Calculations using palladium and oxidized palladium particles of varying size provide a fundamental understanding of the elementary physico-chemical steps in the oxidative coupling of ethylene and acetic acid in route to the formation of vinyl acetate.

#### In Which Stage of the Catalytic Reaction Cycle Is CH Activated?

**COMMENT** This was a computational study of vinyl acetate formation by oxidation of ethylene and acetic acid. A reaction cycle involving an oxidized  $\text{Pd}_3$  cluster is designed. Oxygen activates acidic OH of acetic acid, ethylene inserts, and product forms by  $\beta\text{-C-H}$  cleavage.

Many joint papers with Dupont followed this work, where we compared inner-shell and outer-shell mechanisms, as well as alternative ways to in-

sert ethylene. We have been able to exclude the alternative reaction path via initial vinyl formation.

Figure 5.15 shows the density functional theory-optimized (DFT) reactant, intermediate, and product structures for an inner-sphere Wacker-like catalytic reaction path for the synthesis of vinyl acetate over  $\text{Pd}_3\text{O}_3$ . The DFT-predicted energies for the steps involved in the inner-sphere mechanism in this figure are depicted in figure 5.16.

## 5.8

# ELECTROCATALYSIS

By *Rutger van Santen*

Around 1990 the Chemical Engineering Faculty at Eindhoven decided to discontinue the chair of electrochemistry, at that time a large research group at the university. They asked me whether I was willing to take over the part of the group that dealt with electrocatalysis. Obviously electrocatalysis has become very relevant again in view of our current search for alternative energy generation, so I am glad I decided at that time to accommodate this group in our institute. Wil Visscher and Ad Wonders were the main group members. Since I am not an electrochemist, I approached Rob van Veen, whom I knew well from my Shell period and who is an expert in electrocatalysis related to energy conversion, to join our laboratory part-time as professor of electrocatalysis. This worked out well, not only for electrocatalysis but also because of Rob's main interest then at Shell Research Amsterdam. He is a leading expert in catalyst preparation and many joint projects on this topic developed in our laboratory. Later Rob's research field at Eindhoven changed to catalyst preparation.

One of the most interesting techniques that Rob decided to develop was the OLEMS (on-line electrochemical mass spectrometry) technique, with the assistance of Ad Wonders as his very competent technician. This is a mass spectrometric technique applicable to liquid-phase reactions. It became a great success in the mechanistic study of several electrocatalytic reactions. Its main advantage is that it makes it possible to probe the evolving products near the electrode. Because of the success of this OLEMS technique, a second apparatus was

constructed at Leiden when Marc Koper moved there as a full professor.

Inspired by my consultancy with Solvay, I also suggested to start work on ammonia oxidation and nitrate reduction. The question was how to selectively convert these molecules into harmless nitrogen. This program gained much strength when Marc Koper joined the Electrocatalysis Department as the Royal Netherlands Academy of Arts and Sciences (KNAW) Huygens Fellow. Using some of the Spinoza funds, we decided to start a program where we would study experimentally and computationally structure sensitivity in electrocatalysis using single crystals.

Especially due to experimental skills of PhD student Natalia Lebedeva, who joined the group from Novosibirsk, Russia, and the help of J.M. Feliu in Alicante, Spain, successful single-crystal experiments were initially done on carbon monoxide oxidation, which were later extended to ammonia oxidation and NO decomposition. The (100) surface of platinum turned out to be uniquely selective for  $\text{N}_2$  formation. NO decomposition structural dependence is very different from that in the gas phase because protons from the water phase can directly react with the oxygen atom of NO.

When Peter Vassilev joined our group as a PhD student from Bulgaria, we started the first computational studies at Eindhoven of the interaction of water with platinum surfaces. Tonek Jansen, PhD student Chretien Hermse, and Marc Koper made very elegant dynamic Monte Carlo (DMC) simulations of current-voltage diagrams of some of these reactions. These studies demonstrated the usefulness of the DMC

method in predicting surface overlayer ordering of adsorbates.

Around the year 2000 Peter Notten from Philips Research approached me to start a battery and hydrogen storage program at Eindhoven. Soon after he ended up accepting our offer to appoint him as a part-time professor. His applied electrochemistry program turned out to be very relevant to current renewable energy programs. It was through our discussions that I became interested in the theory of hydrogen absorption in metal alloys. We started an experimental project on this topic together with Pieter Magusin, who was recruited to Eindhoven to replace Jan de Haan for

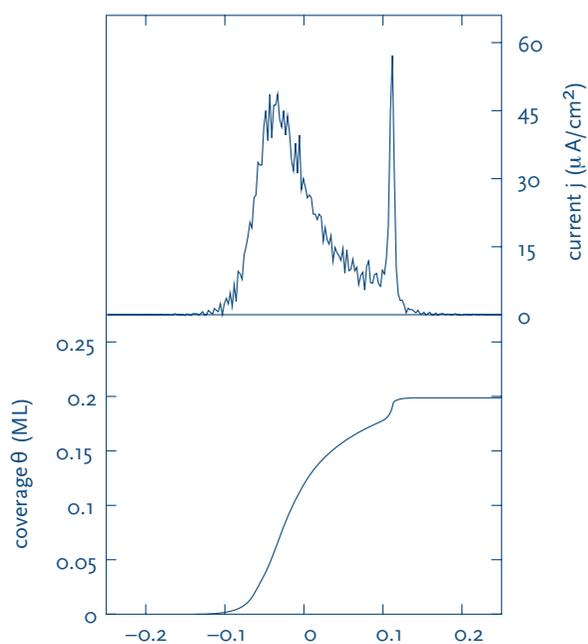
solid-state nuclear magnetic resonance (NMR) research. We developed the theory of hydrogen storage systems with PhD student Shuxi Tao. We found interesting particle size-dependent phenomena that relate to the increasing importance of difference in surface energy of the hydride compared to the metal. We also found this in related studies with J.G.O. Ojwang, a PhD student that Gert Jan Kramer and I advised jointly. We made molecular dynamics studies on the decomposition of alkali hydrides using the reactive force fields developed by Adrie van Duijn, who at that time was a research fellow in Bill Goddard's group at CalTech.

## RESEARCH HIGHLIGHT

C.G.M. HERMSE, A.P. VAN BAVEL, M.T.M. KOPER, J.J. LUKKIEN, R.A. VAN SANTEN AND A.P.J. JANSEN (2004). *Modelling the Butterfly: ( $\sqrt{3} \times \sqrt{7}$ ) Ordering on Fcc(111) Surfaces. Surface Science, 572, 247–260.*

Figure 5.17

### Modeling the Butterfly: ( $\sqrt{3} \times \sqrt{7}$ ) Ordering on Fcc(111) Surfaces



**ABSTRACT** The adsorption of a bridge-bonded anion onto an Fcc(111) surface is studied using kinetic Monte Carlo simulations. Different models with first-neighbor shell exclusion and finite second-neighbor shell lateral interactions are considered. All simulated voltammograms show one peak associated with anion adsorption in a disordered phase, and one peak related to a disorder-order transition in the adlayer. The disorder-order transition transforms the adlayer with a coverage of 0.18 ML into a ( $\sqrt{3} \times \sqrt{7}$ ) ordered structure with a coverage of 0.20 ML. The shape of the adsorption isotherm and the simulated voltammogram is strongly influenced by attractive or repulsive lateral interactions, as well as by the sweep rate and the presence of steps in the surface.

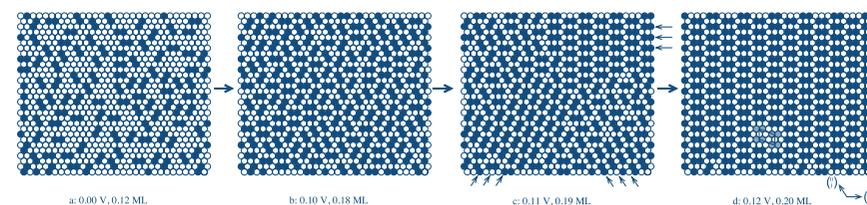


Figure 5.18

### Order-Disorder Transition in Catalysis

**COMMENT** The DMC simulation method that Tonek Jansen and Johan Lukkien developed is very powerful when the ordering of adsorbates controls chemical reactivity.

The simulated “butterfly” voltammogram of sulfate adsorption to a transition metal illustrates this beautifully. Figure 5.17 shows the simulated voltammogram (*top*) and adsorption isotherm (*bottom*) for the model with first-neighbor shell exclusion. Before the disorder-order transition (panel (a) and (b)) there is no ordering; during the disorder-order transition ( $\sqrt{3} \times \sqrt{7}$ ) islands grow ((c) the three different domain orientations are indicated by the small arrows); after the disorder-order transition large islands dominate (d). The ( $\sqrt{3} \times \sqrt{7}$ ) unit cell is indicated in (d). The succession of different

overlayer structures with increased surface coverage and the disorder-order transition is shown in figure 5.18 as a function of electrode potential. Figure 5.18 gives snapshots of the surface during anion adsorption for the model with first-neighbor shell exclusion. Before the disorder-order transition (panel (a) and (b)) there is no ordering; during the disorder-order transition ( $\sqrt{3} \times \sqrt{7}$ ) islands grow ((c) the three different domain orientations are indicated by the small arrows); after the disorder-order transition large islands dominate (d). The ( $\sqrt{3} \times \sqrt{7}$ ) unit cell is indicated in (d).

## 6.1

# USING SPECTROSCOPY AND CALORIMETRY

By *Johannes Lercher*

Johannes Lercher is professor of chemical technology at the Technische Universität München (TUM), Germany, and director of the Institute for Integrated Catalysis at the Pacific Northwest National Laboratory, USA. Between 1993 and 1998 he was professor of catalytic materials and processes at the University of Twente, Netherlands. His research focuses on fundamental aspects of sorption and catalysis, the design of complex multifunctional catalysts, in situ characterization of catalytic processes, and developing new routes to functionalize and defunctionalize organic molecules.

When I look back, what drew me into the field of catalysis was the physical chemistry of mixed oxide surfaces of main group oxides. Viktor Gutmann and Heinrich Noller's approach at the Vienna University of Technology inspired me and guided me to understand the catalytic properties of oxide surfaces by combining electron density redistribution principles and the generation of surface defects. A strong belief that Lewis acid–base pairs were the driving forces in catalytic chemistry complemented this approach, which is indeed true on oxide surfaces if the materials are basic to moderately acidic. My task was to show the variations in properties of such mixed oxides by characterizing their surfaces with probe molecules and predicting acid–base properties on the basis of general rules. After defending my thesis and a year at Yale University, I decided to move on to materials in which Brønsted acidity was crucial for catalysis—namely, acidic zeolites. I stayed on at Vienna and worked there building up a research group for the next ten years.

During this time I met Rutger at meetings as a theoretician working for Shell Research Amsterdam and as a colleague who had an unusually broad

interest in spectroscopy and catalysis. This was a completely new experience for me. I had met impressive theoretical chemists, but they were all interested in problems far from what I was trying to solve. Together with Joachim Sauer and Wilfried Mortier, Rutger was the colleague at that time who stimulated the thinking of our group in the attempt to understand the sorption structures of molecules in zeolite pores. My interactions with Rutger intensified around 1989 with the International Zeolite Conference in Amsterdam, where we presented for the first time the infrared (IR) spectroscopy of polar molecules such as water and methanol and our interpretation of the surface chemistry. Rutger had just moved from Shell to become a professor at TU/e. There, he started to work on the theory of zeolites and the sorption and catalytic conversion of molecules in their micropores.

Because my group in Vienna worked on the spectral and calorimetric characterizations of the interaction of such small molecules with the zeolite pores, we were looking for an exchange of ideas with a physical chemist such as Rutger. Although he was more interested in the stability of zeolite lattices in that period, he never-

theless was always a great partner in discussions. These discussions were intense and, in hindsight, enormously important to us, helping us to probe experimentally into a much larger space than we originally intended.

Discussions became more frequent when I was asked to follow Julian Ross as a professor at the University of Twente. Rutger was a member of the selection committee, and it was a bit difficult to convince him that I would leave Vienna and move to the Netherlands, but I guess I did convince him in the end. The move was attractive largely due to the Netherlands Institute for Catalysis Research, NIOK, which Rutger had played an integral role in setting up. This network allowed catalysis scientists in the Netherlands to closely integrate into a much larger community, and it has revitalized existing interactions and initiated new contacts. The framework brought about unique collaborations across disciplines and across the country, leading also to many friendships over time. I knew little, for example, about molecular catalysis and organic synthesis aspects when our group moved to the Netherlands, and the exposure to this field of catalysis as well as the exposure to the chemical engineering aspects, combined with the incentive to collaborate, broadened my personal horizon enormously. This was only possible because key players in the field, such as Gerard van Koten, Jacob Moulijn, Piet van Leeuwen, and Vladimir Ponc, saw a critical element in the cross-fertilization of catalysis according to the different disciplines. However, at least from the perspective of a newcomer, Rutger was the person that not only facilitated and catalyzed the existing close interactions between key catalysis researchers, but he also kept the catalysis group together, always pushing for new programs.

I had much closer contact with Rutger at this time, and our discussions focused on the interactions and catalysis of small molecules in zeolite

pores, a theme that he had begun to develop at Eindhoven. Our discussions led to a joint paper, laying the basis for understanding the protolytic cleavage of C–H and C–C bonds by zeolites.[1] It was only a note, but it had much impact on our way of thinking. For the first time, we had clear atomistic trajectories and transition states of the generation of carbonium ions that led to protolytic cracking and dehydrogenation. Despite all the constraints of the emerging theory of reactive sorption at that time, we were able to rationalize that the barriers should be higher for cracking than for dehydrogenation, in line with the more stable secondary carbonium ion formed in the latter process. Much to our own surprise, this chemistry is still under intense debate, and while we had understood the potential energy of the reaction pathways at that time, entropy turned out later to be much more important than we had then anticipated.

Our common interest quickly developed toward understanding the adsorption of hydrocarbons, of alkanes, in particular, as a critical element in catalytic chemistry. Using calorimetry and IR spectroscopy, we could show that the dominating fraction of the heat of adsorption resulted from dispersive interactions. Modeling these interactions was beyond the possibilities of computational chemistry at that time, but in collaboration with Jan van Hooff, Rutger initiated a complementary nuclear magnetic resonance (NMR) study to also understand the configurational aspects of hydrocarbon sorption. [3] These configurational aspects are especially important because the reduction of configurational entropy critically determines the relative differences of the adsorption entropy of alkanes in zeolites.

During that time we were also both most interested in the reactive sorption of polar molecules, such as methanol. This led to a joint paper on IR light-induced activation of metha-

108 PUBLICATIONS		
28	BEELLEN, T.P.M.	retired
17	HAAN, J.W. DE	retired
12	VEN, L.J.M. VAN DE	retired
11	JACOBS, W.P.J.H..	TU/e
11	JONG, A.M. DE	TU/e
10	BAKKER, H.J.	AMOLF, Amsterdam
10	GARDEREN, H.F. VAN	Canon, Venlo
10	KLEYN, A.W.	University of Amsterdam
9	BONN, M.	Max-Planck Institute Mainz
9	MOOR, P.-P.E.A. DE	Exxon, Machelen

Table 6.1: Top coauthors in this theme, with the number of papers together with Rutger van Santen and their affiliation. Source: TU/e Library

nol.[2] We were also involved in intense discussions on whether zeolites were able to protonate methanol and water. Rutger's calculations helped us to understand that protons would not transfer with 1:1 complexes and that only larger clusters would provide sufficient delocalization for the proton to be stabilized in the protonated form.

Our scientific dialogue and exchanges maintained their intensity after I left for Technische Universität München (TUM). For several years we worked together in the European Network of Excellence in Catalysis, IDECAT (Integrated Design of Catalytic Nanomaterials for a Sustainable Production), on several ongoing European projects, and in the joint Graduate School for Sustainable Energy. Rutger is one of the visiting fellows at the TUM Institute for Advanced Studies. One of our latest continuing joint efforts is to explain the unusual effects that large cations, such as  $\text{La}^{3+}$ , exert on alkanes—for example, in zeolite X but not in zeolite Y.[4] In this case, theory could show that only the higher concentration of aluminum in zeolite X leads to exposed Lewis acidic  $\text{La}^{3+}$ , which is able to polarize C–H bonds of alkanes so that carbonium ions can be formed at ambient temperatures.

Rapid developments in both spectroscopy and catalysis theory have characterized the period of our collaboration. The combination of methods in spectroscopy and the emerging

computational methods, in particular, density functional theory, allowed us to address increasingly complex problems for catalytic reactions at the gas-solid interface. From a methodological approach, the new frontier will now be to understand the catalytic chemistry at the liquid-solid interface and the stabilization of the interacting reactants and products, as well as the stabilization of the intermediates and transition states. New approaches to experiment and theory are necessary to reach the rigor and insight that were achieved for gas-solid reactions. From the societal point of view, the conversion of carbon dioxide by light into carbon-based fuels and the generation of hydrogen from water will be the dominating themes.

I expect that Rutger will make important contributions to these themes. He has a unique approach to science. In fact, theoretical chemistry and computational catalysis are not the only fields you would associate with Rutger, and probably not even the principle ones. He is a rare and brilliant physical chemist and conceptual thinker, who likes logical chains of arguments and sticks at a particular problem for a long time. He believes in computational models as a way to test arguments, hypotheses, and (the validity of) experiments. Using theory as a *Gedanken* experiment, theory exceeds its function as a tool to explain and goes on to be useful in predicting,

making it fun and inspiring to engage in discussion with Rutger.

Having said all this, I now feel uneasy. The text sounds a bit like a farewell, and that is the last thing I would want. I am neither willing nor prepared to reduce the intensity of our discussions, to give up the pleasure of disagreement, nor to forgo the excitement of beginning to put together small pieces of the huge puzzle that is catalysis science. Fortunately, I was able to convince myself that my worries are unfounded; there are still many years to come for Rutger and I, and the fun has just begun.

**REFERENCES** / 1. Lercher, J.A., Santen, R.A. van & Vinek, H. (1994). Carbonium Ion Formation in Zeolite Catalysis. *Catalysis Letters*, 27 (1-2), 91-96. / 2. Bonn, M., Santen, R.A. van, Lercher, J.A., Kleyn, A.W. & Bakker, H.J. (1997). Picosecond Infrared Activation of Methanol in Acid Zeolites. *Chemical Physics Letters*, 278 (4-6), 213-219. / 3. Well, W.J.M. van, Cottin, X.S.J., Haan, J.W. de, Smit, B., Nivarthi, G., Lercher, J.A., Hooff, J.H.C. van & Santen, R.A. van (1998). Chain Length Effects in the Adsorption Properties of N-Alkanes in Zeolite Ferrierite. Part 1: Sorption and  $^{13}\text{C}$  NMR Measurements. *Journal of Physical Chemistry*, B, 102 (20), 3945-3951. / 4. In press.

## 6.2

# INFRARED SPECTROSCOPY OF ZEOLITES

By *Rutger van Santen*

One of the most intriguing early questions in solid acid catalysis was the determination of the intrinsic strength of the protons. One might expect dependence on the composition of the zeolite lattice framework, but would it also be dependent on the structure? Initial calculations by Erik Theunissen, a PhD student who had obtained his master's degree at Utrecht with Frans van Duyneveldt, indicated that even to molecules such as ammonia, proton transfer would only occur when the ammonia molecule would have an optimum interaction with several negatively charged oxygen atoms of the zeolite framework. Strongly influenced by discussions with Johannes Lercher, then at Twente, we decided to focus the experimental work mainly on methanol, in which we also had a computational interest. The fundamental question became whether the molecule in the adsorbed state would be protonated or not. It was the beginning of a very pleasant, lifelong scientific exchange and friendship with Johannes Lercher.

With EU funding and a small grant from TU/e, I had been able to purchase a new infrared (IR) Brooker spectrometer, which was suitable for in situ studies from 50 to 4500  $\text{cm}^{-1}$ . Jos van Wolput was the very capable spectroscopist who did the experiments. In parallel, Jochem Janchen, a postdoc from Berlin, was doing calorimetric measurements where he discovered the weakening of the proton bonds with increasing exchange of alkali cations by protons, approximating that high intrinsic acidity of low aluminum zeolites. An interesting debate

emerged with John Meurig Thomas of Cambridge, who together with Fransesco Marchese initially proposed that methanol would be protonated, based on the complex spectra with several proton-related bands. I also thought the same initially for adsorbed water in a collaboration with the spectroscopist Hervé Jobic from Lyon.

We studied the (A,B,C) triplet bands that are induced by the strong non-linear vibrational coupling of hydrogen bonds between these adsorbates and the zeolitic proton. We managed to understand these phenomena, due to van Wolput's elegant IR studies, which we could interpret thanks to the insights of Alexej Pelmenchikov, who came to Eindhoven from Novosibirsk as a postdoc. Tonek Jansen, with PhD student Eric Meijer, and later Velicka Mihaleva, who joined the group from Bulgaria, developed the computational method to actually simulate these nonlinear coupling effects in great detail.

At the same time in Japan, Kazunari Domen was doing related work that led him to visit Eindhoven several times, and me, Yokohama. After a stay of Mischa Bonn in Yokohama, it later led to a joint review paper.

At AMOLF I was able to interest Mischa Bonn, Huib Bakker, and Aart Kleyn in studying related systems with IR picosecond transient spectroscopy. Because of their parallel studies in the liquid phase, they made me aware of the essential similarity between hydrogen bonding and proton transfer in a zeolite regarding the reactivity of protons in the gas phase rather than

the liquid phase. It implies much more subtle and different energetics for protonation in zeolites, which makes them intrinsically less reactive than liquid superacids. We concluded together with Mischa that the best way to probe the intrinsic acidity of a zeolitic proton would be to measure its change in frequency and intensity on contact with a weakly disturbing molecule such as  $N_2$ .

Due to the unique Bruker instrument we had purchased at Eindhoven, we were also able to study the vibrational frequencies in the far and intermediate IR, in particular, detailed studies of the lattice vibrations and their changes when molecules would interact with the zeolite. In a joint EU project with Herman Gies, Richard Catlow, and also Gert Jan Kramer at Shell Research Amsterdam, we used force fields to simulate the lattice spectra. The interpretation of these spectra requires group theoretical arguments. Loek Vogel, with whom I collaborated very briefly when I arrived at Eindhoven, and I cowrote a review paper that shed light on this

method. We also showed that embedding zeolitic ring systems in the extended zeolite lattice leads to spectral changes that can be computed using similar techniques, which are related to Green's function, as we had used previously in the theory of chemisorption. Beautiful spectra obtained by Jan van Hooff's group, my colleague as then professor of inorganic chemistry at Eindhoven, were the motivation for this study. Jan was one of the first graduate students from Schuit. After he returned from AkzoNobel, he initiated zeolite research at Eindhoven.

Andries de Man did computational simulations with classical force fields for his PhD, as did Wim Jacobs in complementary experimental work. The question we addressed was generated in contact with Mark Davis, who then was still at Virginia Tech. We were interested in how to create and stabilize zeolites with micropores wider than were available in zeolites at that time. We decided to study the spectroscopy and relative stability of structures built from three-ring structures not present in known zeolites.

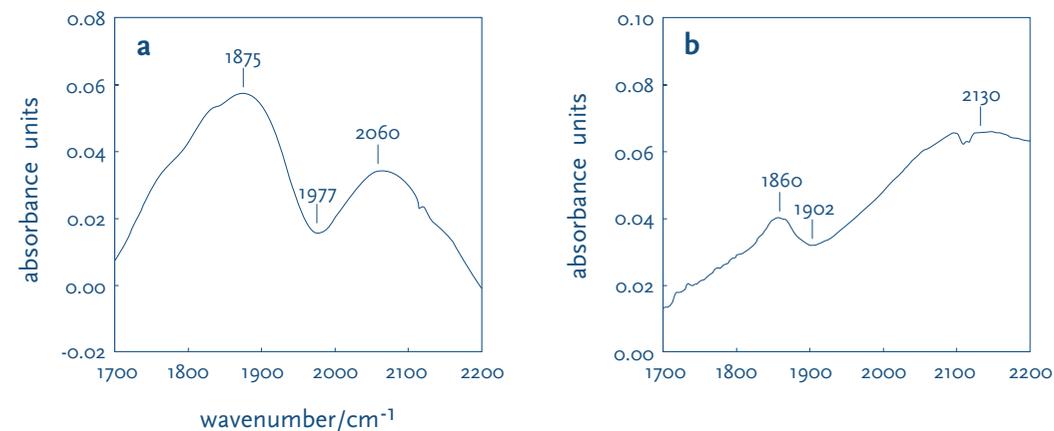
## Hydrogen Bonding versus Proton Transfer

**COMMENT** Interaction of a zeolitic proton with water,  $CH_3OH$  or  $CH_3CN$ , weakens the zeolitic O–H bond. This should result in a zeolite OH adsorption feature with a frequency that is shifted downward and broadened. Experimentally one observes the appearance not of a single band, but a two-peaked and sometimes three-peaked feature. We discovered that this is a signature of hydrogen-bonded adsorbates. The expected broadband feature is altered because of resonance with low intensity overtones, with the two bending vibrations of the zeolitic O–H bonds.

For deuterated OD, the figure shows the resulting dip in the broadened OD stretch adsorption bond due to Fermi resonance with the overtone of the in-plane OD mode.

Figure 6.1 shows OD stretching frequency spectra of (a) OD-ZSM5 with  $CD_3CN$  at 295 K and 0.05 mbar and (b) OD-FeSil with  $CD_3CN$  at 295 K and 0.05 mbar. The practical importance of this is that spectroscopy can discriminate between protonation and hydrogen bonding. Interesting to me was the return of resonant scattering theory in one of our scientific investigations.

Figure 6.1



## RESEARCH HIGHLIGHT

A.G. PELMENSCHIKOV, J.H.M.C. VAN WOLPUT, J. JÄCHEN, AND R.A. VAN SANTEN (1995). *(A,B,C) Triplet of Infrared OH Bands of Zeolitic H-Complexes. J. Phys. Chem., 99, 3612-3617.*

### (A,B,C) Triplet of Infrared OH Bands of Zeolitic H-Complexes

**ABSTRACT** The phenomenon of the (A,B,C) triplet of infrared OH bands at  $\sim 2800$ ,  $\sim 2400$ , and  $\sim 1700$   $cm^{-1}$ , well-known for strong X–OH $\cdots$ Y molecular H-complexes in solutions, liquids, and solids, is studied for the first time for surface H-complexes using  $CD_3CN$  and  $CCl_3CN$  adsorption on deuterated H-ZSM5 and H-FeSil zeolites. A direct experimental proof is given that the minimum between the A and B bands of D-complexes occurs at nearly exactly the  $2\delta(OD)$  in-plane bending overtone

frequency of the perturbed OD group. This verifies the resonance theory of the (A,B) doublet by Claydon and Sheppard. In reference to zeolites this means that the  $\sim 2800$  and  $\sim 2400$   $cm^{-1}$  OH bands recently found in adsorption of many basic molecules on zeolitic OH groups are actually pseudobands, caused by the subdivision of the very broad  $\nu(OH) \pm k\nu(OH\cdots Y)$  superposition band of the perturbed OH groups by Evans transmission window at the  $2\delta(OH) \sim 2600$   $cm^{-1}$  frequency.

## SOLID-STATE NMR

By Rutger van Santen

In the early nineties Jan de Haan joined our group and with him came the solid-state nuclear magnetic resonance (NMR) equipment. Until then it had been in Karel Cramer's analytical chemistry laboratories at Eindhoven. They were a very welcome addition because this technique is essential for characterizing zeolites. Many joint programs made important contributions to the development of this technique.

Initially with Gert Vorbeck as a postdoc we applied the technique extensively to study changes in micropore volume as well as the state of sulfided cations in zeolites. For the study of dynamics in zeolites it provides unique opportunities, as Hubert Koller, who joined us as a postdoc from Mark Davis' group, demonstra-

ted with the study of the location and dynamics of Mo(CO)<sub>6</sub> and ferrocene in contact with sodium ions in zeolite Y.

With PhD student Willy van Well from our side, we were able to successfully use C-13 spectroscopy in a joint program with Simon Bates, Berend Smit, and Johannes Lercher on differences in adsorption siting of hydrocarbons when the zeolite structure varies. Due to a National Research School Combination Catalysis (NRSC-C) grant we were able to upgrade the NMR facilities and continue its use in zeolite-related systems. We were able to continue our research on dynamics using Pieter Magusin's unique skills in relaxation theory and correlation spectroscopy. We exploited these skills specifically in our research on zeolite synthesis.

WILLY J.M. VAN WELL, XAVIER COTTIN, JAN W. DE HAAN, BEREND SMIT, GAUTAM NIVARTHY, JOHANNES A. LERCHER, JAN H.C. VAN HOOFF AND RUTGER A. VAN SANTEN (1998). *Chain Length Effects of Linear Alkanes in Zeolite Ferrierite. 1. Sorption and <sup>13</sup>C NMR Experiments.* *J. Phys. Chem., B* 102, 3945–3951.

### Chain Length Effects of Linear Alkanes in Zeolite Ferrierite. 1. Sorption and <sup>13</sup>C NMR Experiments

**ABSTRACT** Temperature-programmed desorption, heat of adsorption, adsorption isotherm, and <sup>13</sup>C NMR measurements are used to study the sorption properties of linear alkanes in ferrierite. Some remarkable chain length effects are found in these properties. While propane, *n*-butane, and *n*-pentane fill the ferrierite pore structure completely, *n*-hexane and *n*-heptane can only access a part of the pore structure. It is shown by <sup>13</sup>C NMR that *n*-hexane adsorbs only in the 10-ring

channels of ferrierite and not in the ferrierite 8-ring cages. Adsorption of *n*-pentane in this cage is possible but only at relatively high pressures. At low pressures, only the 10-ring channels are filled by *n*-pentane.

This remarkable sorption behavior is caused by the much lower heat of adsorption of *n*-pentane in the ferrierite 8-ring cage compared to the 10-ring channels and results in a two-stage desorption profile. In contrast to *n*-pentane, propane and *n*-butane

adsorb easily into the complete pore structure, which is reflected in the normal single-stage desorption profile. The <sup>13</sup>C NMR measurements show furthermore that propane is preferentially adsorbed in the ferrierite 8-ring cage, while no clear preference is found for *n*-butane.

### COMMENT Site Selection of Hydrocarbons in Zeolites

Solid-state NMR is a very useful technique for studying the siting of molecules in small zeolite crystallites. Figures 6.2 to 6.5 compare NMR spectra as a function of hydrocarbon chain length for a zeolite with a linear ten-ring pore system turn (TON) with that in a system with ten- and eight-ring pores (ferrierite, or FER). For hexane, there is no difference. One concludes that hexane can only adsorb in the ten-ring pore. However, the smaller molecules show an increasingly larger occupation of the eight-ring channel in FER. Simulations by Berend Smit and adsorption

studies by Johannes Lercher indicate significant differences in the packing of hydrocarbons in the zeolite micropore when studied as a function of chain length. Such siting effects are relevant for understanding differences in the reactivity of zeolites as a function of structure.

The figures give the <sup>13</sup>C NMR spectra in H-FER and NaZSM-22 (TON) at different loadings, indicated in units of mmol/g in the spectra. The spectra are from *n*-hexane (figure 6.2), *n*-pentane (figure 6.3), *n*-butane (figure 6.4), and propane (figure 6.5) respectively.

Figure 6.2

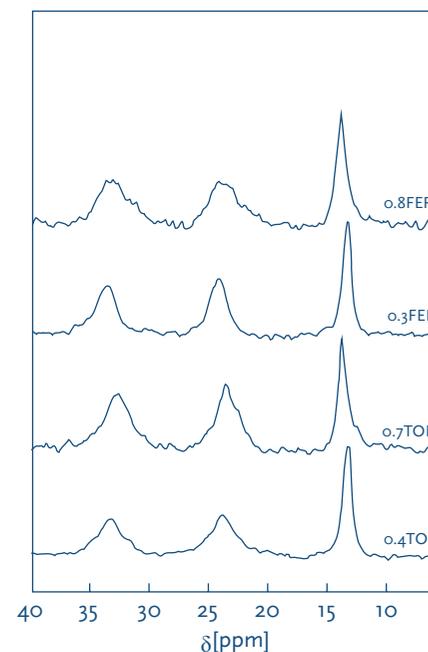


Figure 6.3

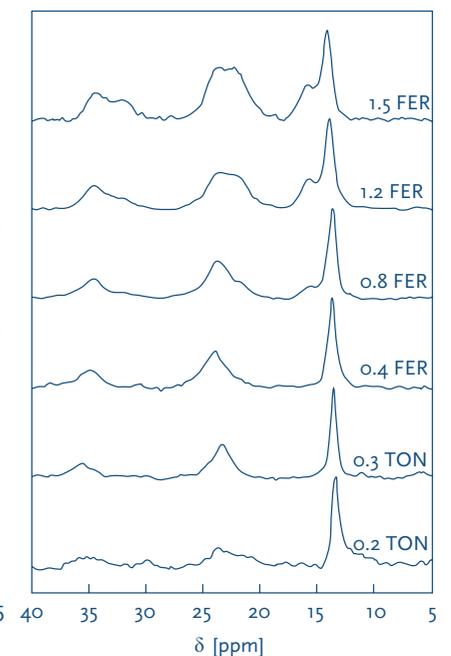


Figure 6.4

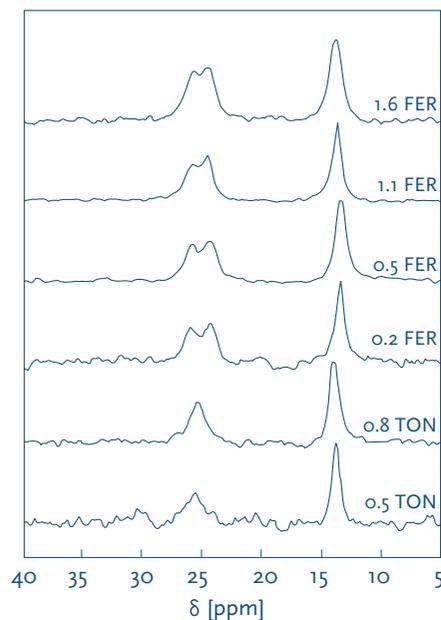
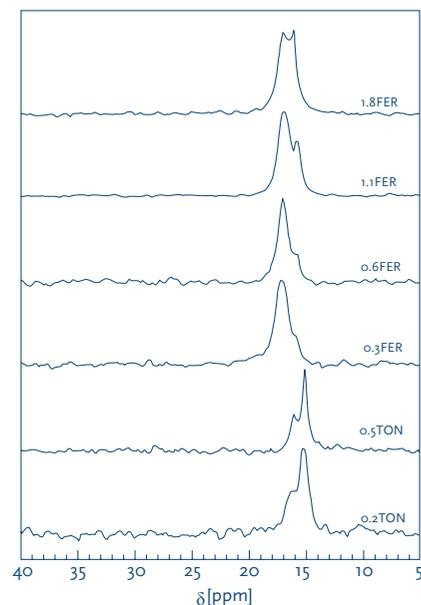


Figure 6.5



## 6.4

# SAXS-WAXS-USAXS STUDIES OF ZEOLITE SYNTHESIS

By *Rutger van Santen*

The innovation-oriented program (IOP) research program in applied catalysis, which started in the early nineties, created the opportunity to study silica gel synthesis as well as zeolite synthesis in close contact with several companies. The IOP program sponsored joint research projects, which industrial scientists monitored carefully. This benefited us greatly because they helped us with their probing questions and rich expertise. Research was directed toward the truly unexpected, which brought significant new expertise to our group. Participating companies later hired many PhD students who worked on this project.

AkzoNobel, Unilever, and Dutch scientists from DuPont followed our initial work with PhD students Henk Dokter and Peter Wijnen closely. Wilfried Mortier, then at Exxon, heavily inspired and helped the later work of PhD student Peter-Paul de Moor by providing us with the silicalite recipes to prepare them from homogeneous solutions. We also started simulation studies of silica gel aggregation with Harold van Garderen in close collaboration with computer scientist Peter Hilbers and theoretical physicist Thijs Michels. They had both recently been professors at Eindhoven who also came from Shell.

Also in this period we started to gain interest in the unique silica microstructure of diatomaceous algae. Initially we tried to grow them in our laboratory, but with no success. We approached the biologists Engel Vrieling and Winfried Gieskes in Groningen, with whom a continued collaboration started in attempting to understand

the role of templating peptides in biological silica-growing algae.

Theo Beelen was in charge of directing the IOP projects mentioned above in our laboratory for over ten years. We shared an enthusiasm for the topic and both had to learn light scattering simulation techniques. Interestingly, through the gel studies I made my first contact with fractals, which was my initiation into the complexity theory. It taught me how different pore densities are generated depending on the ratio of diffusion rate and sticking coefficient of the aggregating species.

The work with algae initiated my current interest in the origin of life. As told in section 7.5 an essential question is how to induce liposomic particles enclosed by a membrane to divide. A dividing system would make it possible to optimize for a particular chemical parameter. We would like them to be catalytic systems. Once the system is optimal, one has to convert them into an inorganic solid catalyst; incorporating the membrane in a siliceous matrix has this result.

The highlight of this work was the discovery, initially by Henk Dokter but later in greater detail by de Moor, of the formation of aggregates of 3 and sometimes 10 nm in solutions just before zeolite crystal formation. They are consumed when crystallization starts. It started a significant debate in the scientific community about how zeolite nucleation actually occurs. Is it through the aggregation of preformed silicate clusters, or should we consider subsequent incorporation of single silicate monomers? We discussed

this question extensively with Mark Davis and his Japanese colleagues. Recognizing the significance of this discovery for his own work, at the end of the nineties Mark decided to come to Eindhoven to spend some time with us as a visiting scientist. We were more than happy to have him in our institute.

Parallel to our discovery was the report of the formation of structured nano-sized aggregates with zeolite resembling structures by the Leuven group. We are still carrying out joint

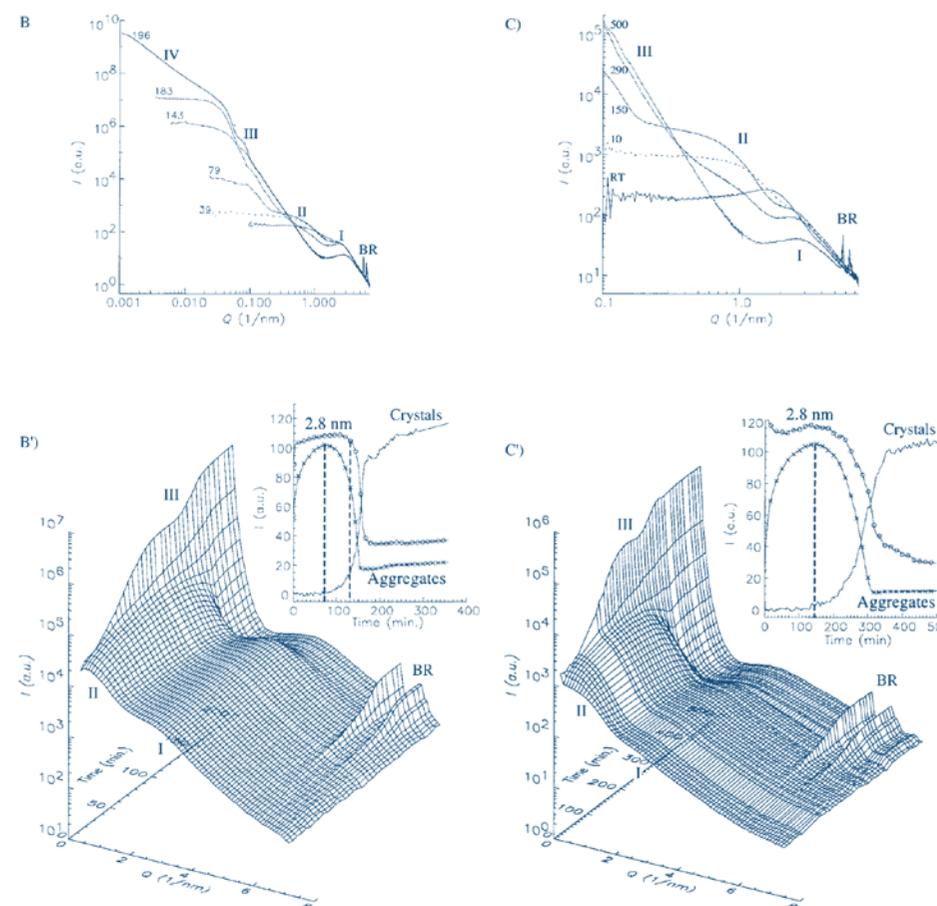
investigations with them on the formation of these intermediates. Thanks to a Chinese-Dutch program with Can Li in Dalian, we are currently modeling this process with Bartek Szyja, using a molecular dynamics simulation of cluster aggregation in a solution influenced by organic cations. With the help of Evert-Jan Meijer from the University of Amsterdam, Tuat Trinh and I initiated quantum chemical and molecular dynamics studies of the influence of different cations on silicate formation in solution.

namely, that before crystallization silicate oligomers form preaggregated structures, was unsuspected. Aggregates of the order of 2.8 nm are initially formed that disappear with the onset of crystallization. Larger aggregates can be formed with altered pH of the solution. This observation generated much dispute in the literature on the actual zeolite synthesis process.

The figures 6.6 give time-dependent scattering curves for Si-TPA-MFI: A and A': Si/OH = 2.42, B and B': Si/OH = 3.02, C and C': Si/OH = 2.78, and TEOS as the

silica source. The reaction times are denoted on the curves. Scattering particle types include: I = primary units, II = aggregates, III = crystals, IV = crystal aggregates, and BR = Bragg reflections. The inset figures on A', B', and C' show the scattering intensity from the different particle populations and the crystallinity. The patterns at short reaction times in A, B, and C do not extend to (very) small angles, since no (very) large structures are present in the sample, and so no excess scattering intensity was detected above the background.

Figure 6.6



## RESEARCH HIGHLIGHT

PETER-PAUL E.A. DE MOOR, THEO P.M. BEELEN, BERND U. KOMANSCHEK, LARRY W. BECK, PAUL WAGNER, MARK E. DAVIS AND RUTGER A. VAN SANTEN (1999). *Imaging the Assembly Process of the Organic-Mediated Synthesis of a Zeolite. Chem. Eur. J., 1999, 5, No. 7, 2083–2088.*

### Imaging the Assembly Process of the Organic-Mediated Synthesis of a Zeolite

**ABSTRACT** The mechanisms by which complicated structures assemble from atoms and/or molecules to macroscale entities are far from understood. Clear insights into the rules concerning complete assembly processes, whether they be organic, inorganic, or hybrid organic-inorganic, are of general use. Here, we report on the assembly of the tetrapropylammonium-containing (TPA) pure-silica zeolite ZSM-5 (MFI), by monitoring in situ the processes that occur over scales spanning more than four orders of magnitude (0.17 nm–6  $\mu$ m). The combination of wide-angle, small-angle, and ultra-small-angle x-ray scattering (WAXS, SAXS, and USAXS, respectively) allows the direct imaging of the assembly pro-

cess of the hybrid material TPA-MFI. It is shown that 2.8 nm entities, comprised of TPA and silicate, function as primary building units that aggregate to form structures up to 10 nm in size, which in turn form viable nuclei that initiate the growth of zeolite crystals. The nucleation mechanism of TPA-MFI thus involves ordering initially on the nanometer scale, followed by order at larger scales derived from the primary building units. The primary building units are specific for the crystal structure formed. The sequential formation of order from small (primary units), to medium (nuclei), to large scales (crystals) is consistent with other assembly processes, such as the construction of biological entities.

### Nanoparticle Precursor Complexes in Zeolite Synthesis

**COMMENT** The fundamentals of the zeolite formation process have been the subject of our research for many years. This experimental x-ray scattering paper studies precrystallization phenomena that occur during the self-assembly process of silicate oligomers

in solution. In the transparent solution of a reaction mixture that ultimately forms zeolitic silicate, initially small siliceous aggregates of sizes between 1 and 100 nm are formed that become consumed when crystallization of the zeolite starts to appear. This finding,

# POSITRON EMISSION PROFILING TECHNIQUE

By *Rutger van Santen*

At the end of the eighties at Shell Research Amsterdam, we started to study in situ changes of the state of catalysts using isotope-labeled reagent molecules under realistic reaction conditions. The essential idea was to measure the surface concentration of adsorbed reaction intermediates in a reacting system. The positron-emitting isotopes we intended to use would enable us to study the reaction at high pressure in a steel wall reactor. The analytical laboratory was highly experienced in the use of radiochemical isotopes. New was the idea to use radiochemically labeled reagent molecules such as hydrocarbons or carbon monoxide. Gert Jonkers and Kurt Vonkeman, freshly hired by Shell as a junior scientist, were instrumental in setting up the experiment.

Our investigations started with  $^{14}\text{C}$ -labeled carbon monoxide and studying exhaust catalysis. Since the decay time of  $^{14}\text{C}$  is ten minutes, the experiments had to be done on line at a cyclotron. Positron-emitting isotopes generate to x-rays with opposite momentum. It is possible to use coincidence x-ray spectroscopy to follow the  $^{14}\text{C}$  signals through the reactor. The initial measurements were done at the veterinary center in Ghent because the medical hospitals that use PEP scanners would not allow the type of technical experiments we do in their environment. I was fortunate enough to be able to continue these studies at Eindhoven with Martin de Voigt, who had been appointed from Groningen as the chair of nuclear physics at the same time as me. Leo van IJzendoorn, who at that time was an assistant

professor in his laboratory, and Arthur de Jong, who had recently graduated under Hans Niemantsverdriet, were essential in helping to get the experiments going.

The experiments could be done at Eindhoven because there is a cyclotron there, which we needed to produce the isotopes. Philips Electronics Company had earlier donated the cyclotron to TU/e. We were able to finance several PhD students in the Physics Department to build the sophisticated detectors needed. We decided to make radiochemically labeled hydrocarbons for studies in zeolites. For this we used Tijs Koerts' (see section 5.4) carbon incorporation method into hydrocarbons to produce  $\text{C}_5$ - and  $\text{C}_6$ / $^{14}\text{C}$ -labeled hydrocarbons inside the cyclotron within very short timescales. Robert Cunningham, a Canadian who came to the project as a postdoctoral fellow, and Joop van Gondelle were key to this successful project from our side;

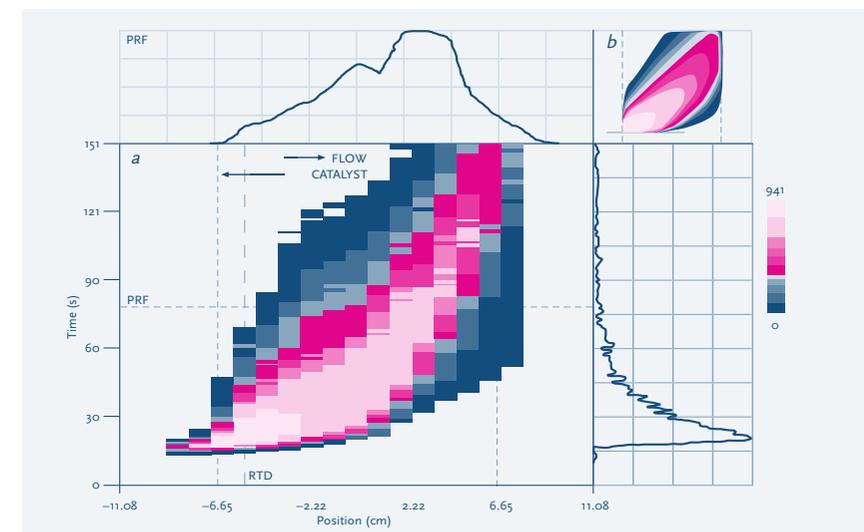
With this method we were able to determine the pore occupation with hydrocarbons during a catalytic reaction. It varies significantly according to the pore size of the zeolites. By using differently labeled hydrocarbons in hydrocarbon mixtures, we were also able to study competitive adsorption effects. For the bifunctional catalysts, we observed that extremely small platinum particles within these materials are only selective for dehydrogenation when covered with carbon. We also studied ammonia oxidation with PhD student Derek Sobzjek (see also section 5.6). For this purpose we developed a method to make radiochemically labeled ammonia.

## Surface Catalysis Studied by In Situ Positron Emission

**ABSTRACT** A complete understanding of heterogeneous catalytic processes requires quantitative in situ information on the concentrations of reactants present on the catalyst surface, but few techniques are available to supply this information. Here we show that positron-emitter labeling and scanning, using the isotopes  $^{14}\text{C}$ ,  $^{13}\text{N}$ , and  $^{15}\text{O}$ , can be used to study the reactions taking place during the catalytic conversion of automotive exhaust. By introducing small pulses of labeled molecules into a reactant stream passing through the catalyst, in situ quantitative information on the concentrations and residence times of reactants in the reactor is obtained.

The labels are detected using a positron camera, an imaging device adapted from nuclear medicine, and the recorded data are presented as “reaction images,” showing quantitatively the distribution of the label in the catalyst bed as a function of position and time. These data can then be used to quantify reaction kinetics by serving as the input to mathematical simulations based on elementary reaction steps.

Figure 6.6



## In Situ Measurements of Intermediate Reactants

**COMMENT** Using isotopes as chemical tracers, it is possible to probe the local concentration of reactants in a catalytic reactor. Initiated by this paper with colleagues at Shell Research Amsterdam, we continued the work with positron-emitting isotopes to follow reaction and diffusion in several systems. The initial work concerned carbon monoxide oxidation and NO reduction. Later we succeeded in labeling small hydrocarbons with  $^{14}\text{C}$  and applied the technique to hydroisomerization and with positron-emitting nitrogen also to ammonia oxidation. The technique turns out to be useful for studying the phase changes of catalytically reactive particles in the course of a reaction, as well as concentration profiles of hydrocarbons in zeolites during reactions.

## 7.1

# FROM ELECTRONS TO SULFIDES

By *Rob van Veen*

Rob van Veen (1948) was senior principal scientist at Shell Research Amsterdam, Netherlands. His main interests were the electrocatalysis of fuel cell reactions and the characterization and development of all types of hydroprocessing catalysts. He was also part-time professor of electrocatalysis and the chemistry of catalyst preparation at TU/e (1988–2006).

After my stint at the Shell Research Center at Grand-Couronne, France, the question of what to do next loomed large once again. Since joining Shell Research in 1974, I had been involved in fuel cell electrocatalysis, coal constitution and reactivity, and, from 1982 onward, catalyst preparation chemistry and R & D on hydroprocessing catalysts. In 1987, just back from France, the basic science department of which I was a member was shaping up to become very fundamental once again, while “my” subject moved to another, rather applied, department. For me, personally, the best solution, I decided, was to move to this new department so that I could continue with the mix of inorganic and physical chemistry in the service of catalysis which I had come to like, but to also seek a part-time position at a university so as to be able to conduct the necessary fundamental studies myself—and what better person to ask how to go about this than Rutger? He had been my boss at Shell, had been teaching at VU University Amsterdam, had held a part-time professorship at Eindhoven, and was just in the process of moving there full time.

My timing turned out to be perfect because the catalysis group, which Rutger would be heading, had just been enriched with an electrocatalysis part, a legacy of Professor Barendrecht, and Rutger immediately saw the op-

portunity to have me direct that part together with Wil Visscher. This was not quite what I was looking for in the first instance, but the opportunity was too good to miss, and to my great surprise (and delight) Rutger arranged this with Shell and TU/e in no time at all so that I could already start in September 1988 at Eindhoven.

In the beginning, of course, the PhD projects I supervised addressed some questions that were still on my mind since my own electrocatalytic times: they concerned, on the one hand, the understanding and improvement of pyrolyzed metalloporphyrin/carbon catalysts for the electrochemical reduction of dioxygen and, on the other hand, PtRu/C catalysts for the electrochemical oxidation of methanol, both in acidic electrolyte. But since the context of these studies, the direct methanol fuel cell, was of no direct interest to Shell anymore, which, after all, was paying me, I felt I had to broaden my scope.

A very nice cooperation developed with Guy Marin and Ben Kuster in a shared project financed by the Dutch Technology Foundation STW. In it we were able to adduce convincing proof that the oxidation of sugars in an aqueous medium over platinum/carbon catalysts should be described in electrochemical rather than general catalytic terms (that is, as resulting from a superposition of the electro-

oxidation of the organic molecule and the electroreduction of dioxygen on a platinum surface, covered with a variable amount of O(H) groups determined by the potential established on the surface through the reaction conditions).

One of Rutger's projects at that time concerned the oxidation of ammonia in the gas phase, and in the context of this STW project (which also involved the reduction of nitrate to hydroxyl amine, the user being DSM in the person of Leon Lefferts, now a professor at the University of Twente) we were able to do some interesting comparative experiments in the liquid phase. And these, in turn, led to a further PhD project on the electrochemical behavior of small N-bearing molecules.

All very interesting, indeed, but it was becoming clear to me that to make real progress here, I should either start cooperating with a technology provider (such as the Dutch energy research center ECN) or delve deeper into the fundamentals. This latter course fitted best with the general direction of catalysis research at Eindhoven, but it would involve working with single-crystal electrodes, not something I was looking forward to, having escaped this in Amsterdam (see above). But fortune again favored the prepared: a super candidate to do this, Marc Koper (now a professor at Leiden University), suddenly appeared to be available, and in one of Rutger's fast moves, his coming to Eindhoven on a fellowship from the Royal Netherlands Academy of Arts and Sciences (KNAW) was assured. This freed me of my electrocatalytic endeavors so that I could concentrate on what was my prime objective anyway: the chemistry of catalyst preparation and understanding hydroprocessing catalysts.

By the way, joining the TU/e greatly facilitated productive contacts with other academics (e.g., Roel Prins, ETH; Johannes Lercher, now at Munich; Johan Martens, Leuven; the sulfide

groups at Lille and Caen), a side effect for which I remain forever grateful.

As to the hydroprocessing catalysts projects I was involved in, I should like to confine myself to two highlights. The first concerns an STW project that also involved Rutger (of course) and San de Beer on the Eindhoven side, and Professors Jacob Moulijn and Tiong Sie (another Shell connection) together with Dick van Langeveld and Adri van der Kraan on the Delft side. The project was grandly titled "Design Rules for Sulfide Catalysts," and my idea was that twenty-five years' or so worth of research on hydrotreating catalysts at TU/e and Delft University of Technology should now be consolidated to produce those design rules—the actual work was performed by three great PhD students: at TU/e Emiel Hensen (reaction mechanisms and support effects) and Marcel Vissenberg (catalyst preparation and activation aspects—this also touched upon zeolites, so dear to Rutger's heart), and Hank Reinhoudt (catalyst characterization and testing, PtPd catalysts) at Delft. Any precise design rules have remained elusive, of course, but nevertheless the project was quite successful in terms of new insights, the number of publications, and indeed industrial relevance: personally I learned a lot that I could usefully apply in my Shell projects. Discussions with Rutger were relatively rare, but always a wonderful and thought-provoking experience. Besides, my collaboration on Mössbauer spectroscopy and extended x-ray absorption fine structure (EXAFS) with Adri, which had already started before 1988, was immensely deepened in the course of this STW work, which proved to be of great value in later projects involving hydrocracking and Fischer-Tropsch catalysts.

The second highlight was a project on model sulfide catalysts originated by Hans Niemantsverdriet, which in combining x-ray photoelectron spectroscopy (XPS) with flat, (but still

practically relevant) wafer catalysts provided further insight into the relations between preparation chemistry, activation procedure, and catalytic activity—also a great experience, and a useful one to boot. Usefulness in this connection means that one learns through thinking about the same problems in different ways (i.e., academic versus industrial), that is to say, by trying to translate practical matters into academically interesting questions, and then attempting to translate any answers to those questions back into the practical context; and although this back translation is never simple, insights gained were nevertheless often quite helpful in industrial catalyst development.

My last project was a good illustration of this: it concerned the synthesis of amorphous silica-aluminas (ASAs), specifically how acidic sites are generated during the synthesis, of what type

they are, and how their number could be influenced. Working a lot with these materials at Shell had given me some feel for the matter, of course, but I thought a PhD project would be ideal to dot the i's and cross the t's, and indeed it was—not that we now have better ASAs, but it has become very clear where to look for them.

It is also funny to reflect on the fact that my successor at Shell, Thomas Weber, whom I became acquainted with at Eindhoven and have collaborated with while he was at ETH Zürich, is now also in a way my successor, as a part-time professor at TU/e. Some things come full circle.

In sum, but for Rutger, my scientific life would have been much more restricted and therefore much less fun. And, indeed, I am happy that our contact continues after my retirement in the form of a project on catalyst R & D valorization.

Table 7.1: Top coauthors in this theme, with the number of papers together with Rutger van Santen and their affiliation. Source: TU/e Library

146 PUBLICATIONS		
39	HENSEN, E.J.M.	TU/e
28	BEER, V.H.J. DE	retired
23	ABBENHUIS, H.C.L.	Hybrid Catalysis, Eindhoven
19	MAGUSIN, P.C.M.M.	TU/e
16	VEEN, J.A.R. VAN	Shell, retired
14	LI, CAN	Dalian Institute of Chemical Physics, China
12	VISSENBERG, M.J.	TU/e
11	DUCHATEAU, R.	Sabic, Geleen
11	JANSEN, A.P.J.	TU/e
11	KOOIJMAN, H.	Delft University of Technology

## SULFIDE CATALYSIS

By Rutger van Santen

Since his thesis with Schuit in 1975, San de Beer had been leading research in desulfurization catalysis and had obtained considerable international recognition. When I arrived at Eindhoven, we also decided to continue working together. This was for me the beginning of a fruitful collaboration and a fascinating period of confrontation with these complex systems. It was also a period of close collaboration with the Jacob Moulijn group at Delft and the high-resolution electron microscopy work of Zandbergen and Patricia Kooyman, as well as the Mössbauer group of Adri van der Kraan at Delft. At Eindhoven Gert Vorbeck and Jan de Haan started the xenon nuclear magnetic resonance (NMR) studies to characterize the micropores of zeolitic systems containing active desulfurization components. Actually, while in Houston with Shell, I had been involved with some of the methods relating to “chimie douce” for sulfide phase preparation, so the field was not completely new to me.

The focus of the work at Eindhoven was on preparing improved catalysts. Because of our expertise in zeolite catalysis, we also decided to investigate sulfide-containing zeolitic systems with PhD student Wim Welters. They are active hydrocracking catalysts. There was little known about their desulfurization activity. It was a beneficial choice because it enabled us to study the reactivity of small sulfide clusters of nickel and cobalt independent from the  $\text{MoS}_2$  or  $\text{WS}_2$  phases that they are conventionally used with. It turns out that small sulfide clusters of cobalt or nickel by themselves are very active for desulfurization. It also motivated the early computational study

of nickel sulfide hydrodesulfurization with Matthew Neurock.

With Emiel Hensen, then a PhD student, we investigated whether differences in reactivities of different sulfides relate to Sabatier-type behavior when plotted as a function of M–S bond energy. Leading groups in Denmark and Paris had made the claim that promoting cobalt or nickel in mixed sulfides with  $\text{MoS}_2$  or  $\text{WS}_2$  would optimize the M–S interaction with reagents on the sulfide surface. Maximum activity then would relate for these systems to the balance of C–S cleaving surface reactions and sulfur removal reactions. Kinetic measurements can decide whether maximum activity relates to the Sabatier optimum of balancing rates or to the optimization of one rate-controlling reaction step, which does not alter with changes to M–S surface bond energy.

Rob van Veen, then also a part-time professor at Eindhoven, initiated many fundamental studies on the chemistry of catalyst preparation. Especially he studied the fate of the molybdate clusters upon impregnation from solution in contact with the alumina support in great detail.

A fundamental question that we addressed computationally, with Arnaud Travert, as well as experimentally is the synergetic effect found for the interaction of  $\text{MoS}_2$  or  $\text{WS}_2$  in contact with small nickel sulfide or cobalt sulfide clusters. The  $\text{H}_2$ – $\text{D}_2$  exchange experiments of Emiel were essential in the comparison of theory that studied the same simple reaction. At the interface of molybdenum sulfide and nickel or cobalt sulfide, unique sites are generated by exchange of the

divalent cations  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$  with four-valent  $\text{Mo}^{4+}$ . The resulting electrostatic destabilization creates sulfur surface vacancies that give these materials unique enhanced reactivity. Many international visitors were interested in

exploring these systems: Micha Sychev visited us many times from Kiev and we had long-term visits from Japan from Hiroyuki Nakamura and Ryutaro Koide, employed by the Japanese Energy Corporation.

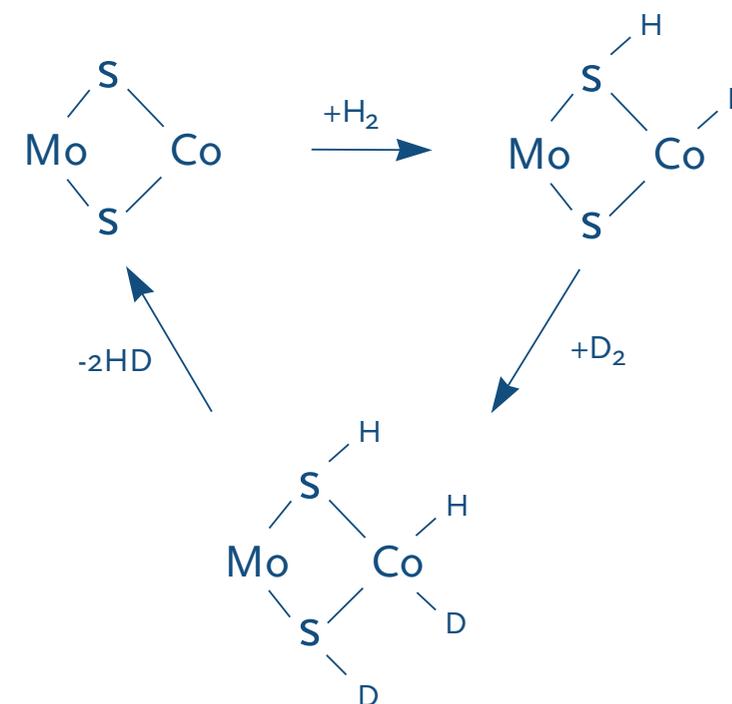


Figure 7.1

## RESEARCH HIGHLIGHT

E.J.M. HENSEN, G.M.H.J. LARDINOIS, V.H.J. DE BEER, J.A.R. VAN VEEN AND R.A. VAN SANTEN (1999). *Hydrogen–Deuterium Equilibration over Transition Metal Sulfide Catalysts: On the Synergetic Effect in CoMo Catalysts*. *Journal of Catalysis*, 187, 95–108.

## Hydrogen–Deuterium Equilibration over Transition Metal Sulfide Catalysts: On the Synergetic Effect in CoMo Catalysts

**ABSTRACT**  $\text{H}_2$ – $\text{D}_2$  equilibration was used to study the synergetic effect between Co and Mo in carbon-supported CoMo sulfide catalysts. The reaction was carried out in a recirculation apparatus with continuous on-line analysis of all gas-phase components ( $\text{H}_2$ – $\text{D}_2$ , HD,  $\text{H}_2\text{S}$ ,  $\text{D}_2\text{S}$ , and HDS) by a mass spectrometer. The low reaction temperature (423 K) allowed for the first time a comparison to be made of the catalytic activity between Co sulfide

particles in low-temperature sulfided (373 K) carbon-supported Co and those in standard sulfided (673 K) carbon-supported CoMo, which have similar  $^{57}\text{Co}$  MES parameters. On the basis of the much higher activity of the bimetallic catalyst than of the monometallic catalysts (Co and Mo sulfide), it is concluded that the observed synergy is related neither to the effect of the high dispersion of the Co sulfide nor seemingly to spillover effects as put

forward by the remote control model. The results indicate that the sulfur atoms that bridge between  $\text{Co}^{2+}$  and  $\text{Mo}^{4+}$  play a crucial role during the catalytic cycle. During the equilibration reaction also extensive exchange takes place between hydrogen (deuterium) atoms adsorbed on the sulfided phase and hydrogen atoms present at the carbon support surface.

This spillover process is accelerated by admixture of  $\text{H}_2\text{S}$ , which most probably leads to an increase of terminal SH groups by dissociative  $\text{H}_2\text{S}$  adsorption.

### Promoter Effects in Hydrodesulfurization

**COMMENT** This paper resolved an important open question on the workings of cobalt-promoted, molybdenum-based desulfurization catalysts using  $\text{H}_2$ - $\text{D}_2$  exchange experiments. Earlier work had suggested that  $\text{MoS}_2$  acts as a support to CoS. It was thought to be essential for stabilizing CoS at high dispersion. This study showed that CoS dispersed on  $\text{MoS}_2$  is intrinsically more

reactive than CoS dispersed on an inert support. There is also a correlation between the initial rate of  $\text{H}_2$ - $\text{D}_2$  exchange and hydrodesulfurization activity. The site model proposed has since been validated in later quantum chemical studies. Figure 7.2 gives a schematic representation of catalytic  $\text{H}_2$ - $\text{D}_2$  equilibration over a “Co-Mo-S-type” site.

These SH groups are thought to form hydrogen bridges with the carbon support functional groups. Both  $\text{H}_2$  and  $\text{H}_2\text{S}$  compete for adsorption on the same coordinatively unsaturated sites. While heterolytic dissociation of  $\text{H}_2$  is considered to lead to a hydride and a bridging SH group between Co and Mo, heterolytic dissociation of  $\text{H}_2\text{S}$  would lead to the formation of two SH groups, one bridging SH group and one terminal SH group active in forming hydrogen bridges with the support surface functional groups.

Table 7.2

ACTIVITY IN $\text{H}_2$ - $\text{D}_2$ EQUILIBRATION REACTION ( $T = 423 \text{ K}$ ; $P_{\text{H}_2} = P_{\text{D}_2} = 6.5 \text{ kPa}$ )	
Catalyst	Initial rate of HD formation (mol/mol · h)
$\text{MoS}_2$ (673 K)	0.003 <sup>a</sup>
Mo/C(673 K)	2.8 <sup>a</sup>
CoMo/C(673 K)	9.1 <sup>a</sup> ; 30.3 <sup>b</sup>
Co/C(373 K)	0.15 <sup>b</sup>
Co/C(373 K, $\text{H}_2$ )	0.19 <sup>b</sup>
Co/C(673 K)	0.02 <sup>b</sup>
CoNaY/C(573 K)	0.11 <sup>b</sup>

<sup>a</sup> Per mol Mo. <sup>b</sup> Per mol Co.

## 7.3

# IRON OXYCATION CLUSTERS

By *Rutger van Santen*

$\text{N}_2\text{O}$  decomposition and the use of  $\text{N}_2\text{O}$  as an oxidant of benzene to produce phenol (the Panov reaction) became an important topic that we have extensively studied experimentally as well as theoretically over the past decade.  $\text{N}_2\text{O}$  is a greenhouse gas. The preferred catalyst for this reaction is a microporous zeolite activated by iron oxy-cation clusters. The relevant scientific question is why isolated  $\text{Fe}^{2+}$  cations located in the micropores of particular zeolites are uniquely selective for phenol formation, as opposed to  $\text{Fe}^{3+}$ -containing dimeric cationic clusters, which are preferred for  $\text{N}_2\text{O}$  decomposition. This was a joint program with Emiel Hensen, which was initiated by Barbara Mojet as well.

The initial work, undertaken in the midnineties, was inspired by Wolfgang Sachtler's work at Northwestern, which indicated that significant reorganization of the iron oxy-cations takes place during the catalytic reaction. Oscillatory time-dependent conversions had been reported that indicate self-organization of the reactive centers under influence of the reaction. With Alexei Yakovlev, who joined us from Novosibirsk, we started computational work on these systems. A Dutch-Russian collaboration made it possible to develop a long-term joint project on this topic with the group in Novosibirsk headed by G.D. Zhdimirov. These early studies did not indicate significant differences in the reactivity of several reactive site models studied.

Ten years later, in collaboration with Isik Onal's Ankara group at Middle Eastern Technical Univer-

sity (METU), Ferdi Fellah made a substantial advance that agreed with experimental work by Emiel Hensen. He found computationally that iron dimeric clusters are essential for  $\text{N}_2\text{O}$  decomposition to oxygen, but that single-center  $\text{Fe}^{2+}$  as well as the dimeric  $\text{Fe}^{3+}$  clusters are active for phenol formation. This explained the experimental observation that larger iron-oxide clusters are necessary for the  $\text{N}_2\text{O}$  decomposition reaction. Subsequent computational work showed that single center  $\text{Fe}^{2+}$  cations suppress nonselective oligomerization reactions of phenol that deactivate the catalyst.

Emiel and his PhD student Q. Zhu discovered experimentally the beneficial effect of coadsorption with aluminum on phenol selectivity. Some of the characterization work was done in collaboration with Chao's group in Taiwan. The collaboration was made possible through a joint program sponsored by the Netherlands Organization for Scientific Research (NWO).

The activity and lifespan of the materials is significantly enhanced by creating zeolitic walls in mesoporous materials to support the right  $\text{Fe}^{2+}$  centers. The wider pores can accommodate the phenolic polymers that ultimately deactivate the catalysts. This enhances their stability significantly. In the experimental work intensive cooperation also developed with the Fang and Can Li groups from Dalian, China. We were able to exploit their unique Raman spectroscopy facilities as part of the long-term Dalian-Eindhoven collaboration.

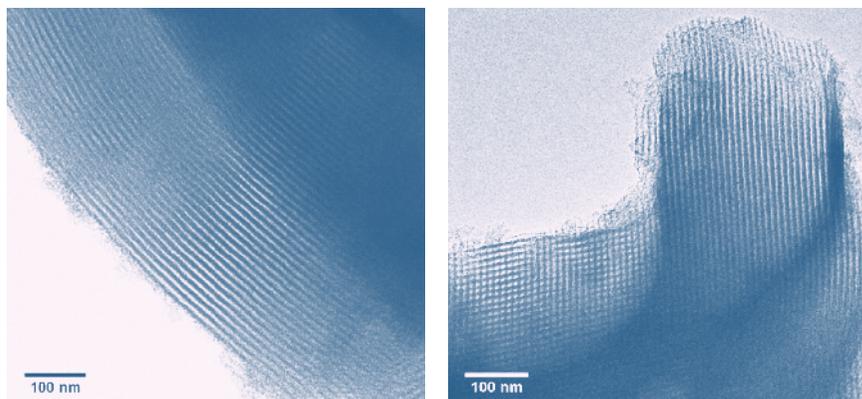


Figure 7.2

## RESEARCH HIGHLIGHT

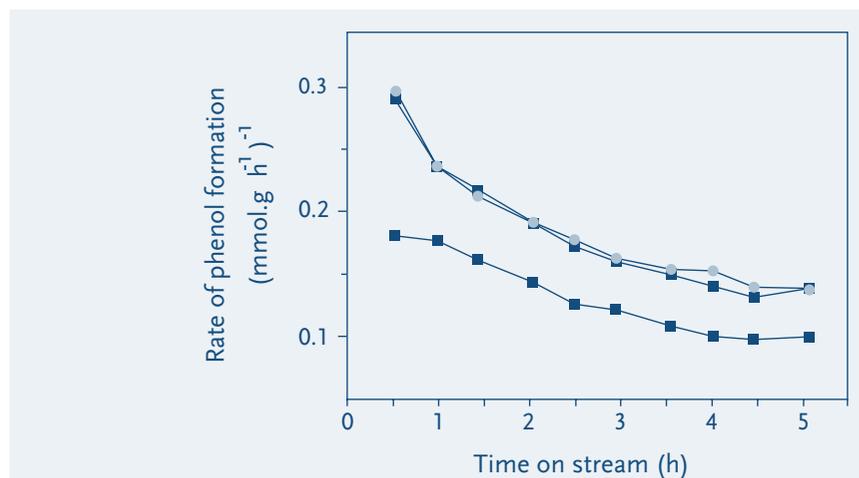
YING LI, Z. FENG, R.A. VAN SANTEN, E.J.M. HENSEN AND CAN LI (2008). *Surface Functionalization of SBA-15 Ordered Mesoporous Silicas: Oxidation of Benzene to Phenol Nitrous Oxide*. *J. Catal.*, 255(2), 190–196.

### Surface Functionalization of SBA-15 Ordered Mesoporous Silicas: Oxidation of Benzene to Phenol Nitrous Oxide

**ABSTRACT** We report the preparation and catalytic properties of highly ordered mesoporous Fe–Ga–SBA-15 materials via direct hydrothermal synthesis. Gallium and iron ions were introduced directly into the synthesis gel typical for the preparation of SBA-15. The resulting materials had hexagonally ordered mesopores of about 6 nm and surface areas >1000 m<sup>2</sup>/g. In Fe–SBA-15, the iron species were mainly tetrahedrally coordinated in the amorphous silica walls. In the presence of Ga (Fe–Ga–SBA-15), Fe species were

located at the silica surface as isolated species, as determined by Raman and diffuse-reflectance UV-Vis spectroscopy measurements. The Fe species in Fe–Ga–SBA-15 displayed similar properties as the FeZSM-5 zeolites toward nitrous oxide decomposition and were active in the oxidation of benzene to phenol by nitrous oxide. Ga–SBA-15 and Fe–SBA-15, on the other hand, showed no catalytic activity. Compared with Fe–Al–SBA-15, Fe–Ga–SBA-15 displayed greater selectivity to the desired phenol product.

Figure 7.3



## Single-Site versus Dual-Site Catalysis

**COMMENT** It has generally been believed that the iron-containing ZSM-5 catalyst is a unique catalyst for selective oxidation of benzene to phenol. This paper demonstrated that mesoporous silicas could also be induced to have similar initial reactivities when promoted by gallium or aluminum. One requires stabilizing isolated Fe<sup>2+</sup> cations. An extension of this work later demonstrated that mesoporous materials with zeolitic pore walls have superior activity. Due to the mesoporous nature of the system, formation of carbonaceous residue will not de-

activate the system as strongly as for the zeolite. Later computational work explained the need for isolated iron sites. Reactive extra lattice oxygen atoms in larger dimeric or larger iron oxycations induce undesired site reactions that initiate formation of deactivating phenolic ethers.

Figure 7.2 shows representative TEM images of calcined Fe–Ga–SBA-15(0.03). Figure 7.3 gives the reaction rate of phenol as a function of reaction time for (K) calcined Fe–Ga–SBA-15(0.01), (k) Fe–Ga–SBA-15(0.03) and (O) Fe–Al–SBA-15 as a function of reaction time.

## SILSESQUIOXANES

By *Rutger van Santen*

Ultimately, the success of the molecular approach to catalysis should lead to molecular control of the reactive catalytic center. This requires molecular control of its synthesis. One approach is to actually prepare the heterogeneous catalyst in a molecularly controlled way, possibly through self-assembly from molecularly defined building blocks. The work on zeolite synthesis provides many suggestions on how to do this.

I was thrilled when in 1995 Eric Abbenhuis, from Gerard van Koten's group at Utrecht, chose to apply for a KNAW Huygens Fellowship to join our group with the specific purpose of initiating such a program. We decided to focus on studying silsesquioxanes as the building blocks of catalytic synthesis. To learn more about these systems, I visited Frank Feher, one of the leaders in this field, who was then at Irvine, California, when I was there for a catalysis conference. He was interested in collaborating and invited Eric for a short stay.

The contact with Frank continued and ten years later he helped Eric gain contracts when he began the start-up company "Hybrid Catalysis." Eric's drive to produce the silsesquioxanes cheaply enough to make them commercially appealing was the origin of the company.

The silsesquioxanes are cubic siliceous clusters in which reactive atoms can be substituted; organic groups terminate them. The topic very quickly attracted the interest of companies such as Solvay, DSM, and Degussa, which generated several patents. They had an interest in applying these materials as epoxidation and polymerization catalysts and also as components in polymer-based materials.

We were able to design silsesquioxanes such as models of acidic zeolite defect sites (with PhD student Tessa Dijkstra), epoxidation (with PhD student Simon Krijnen), and polymerization catalysts (with postdoc John Severin). The latter became a significant part of our activity when our group hired Rob Duchateau, an organometallic chemist. Although I had had very good contact with my colleague Jan van Hooff for many years, this was the first time we had had an interesting joint publication. It concerned immobilizing a titanium-containing silsesquioxane cluster in the micropore of a zeolite. The material is an active epoxidation catalyst.

Through our collaboration with Can Li, who sent Lei Zhang to Eindhoven, we continued to study these silsesquioxanes in hydrophobic matrices to mimic the biochemical processes of enzymatic systems.

## RESEARCH HIGHLIGHT

SIMON KRIJNEN, HENDRIKUS C.L. ABBENHUIS, ROB W.J.M. HANSEN, JAN H.C. VAN HOOFF AND RUTGER A. VAN SANTEN (1998).

*Solid-Phase Immobilization of a New Epoxidation Catalyst. Angew. Chem. Int. Ed.*, 37, 356–358.

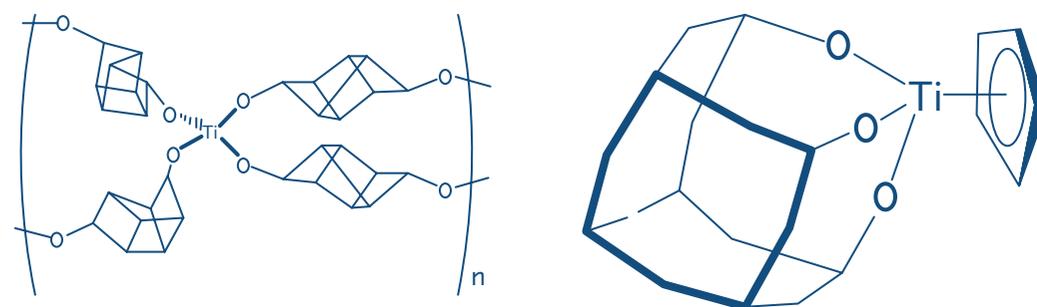
## Solid-Phase Immobilization of a New Epoxidation Catalyst

**ABSTRACT** We investigate the influence of the polarity of the framework on the adsorption of substrates by monitoring the competitive adsorption of 1,2-epoxyoctane and 1-octene. When an aluminum-containing MCM-41 molecular sieve is used, the 1,2-epoxyoctane/1-octene ratio decreased from 1 to 0 in several minutes, while in the case of an aluminum-free MCM-41 this ratio levels off at about 0.2. This demonstrates that the affinity of the hydrophilic aluminum-containing MCM-41 for the more polar epoxide is higher than that of the relatively hydrophobic aluminum-free MCM-41 framework. This observation is supported by thermogravimetric analysis, which indicated that both the water content and the dehydration temperature for the aluminum-free MCM-41 (1%, 49VC) are much lower than that of the aluminum-containing MCM-41

(5%, 60VC). The higher polarity of the aluminum-containing MCM-41 materials is likely to induce leaching. In contrast, the degree of apolarity of an aluminum-free MCM-41 molecular sieve is ideal for both strong adsorption of the catalyst, leading to a heterogeneous system, and diffusion of the organics through the MCM-41 channel. In contrast to physically enclosed systems, this will lead to a self-assembled heterogeneous catalyst that is prone to neither leaching nor deactivation.

Conventional silica gel also adsorbs this complex. During catalyst testing, however, this material undergoes a significant degree of leaching. From this finding we conclude that a silica with channel-type pores such as an aluminum-free MCM-41 molecular sieve is essential for an irreversible adsorption of the silsesquioxane complex.

Figure 7.4

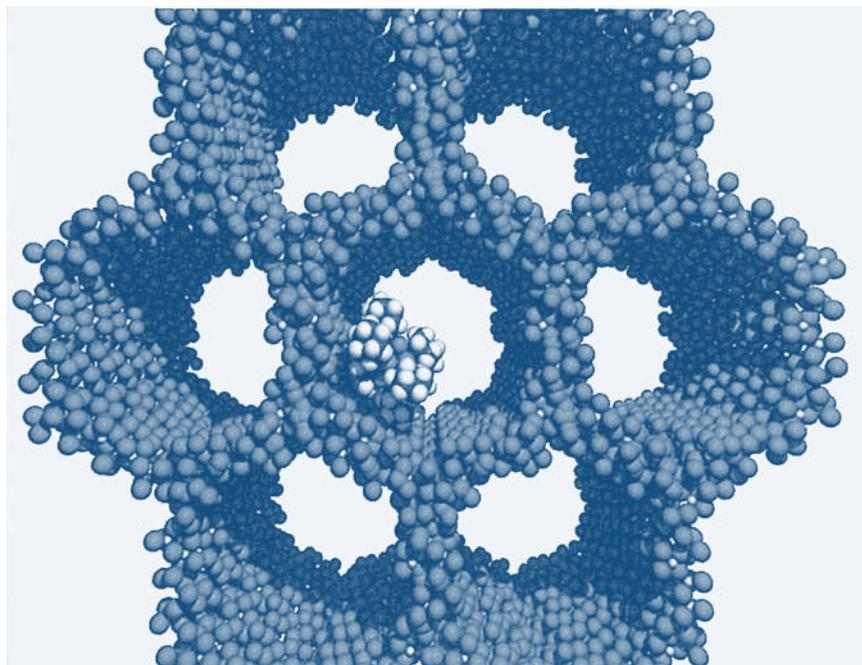


## The Design of a Molecular Heterogeneous Catalyst

**COMMENT** Successful prediction of catalytic performance, based on the understanding of the relation of catalytic reactivity with molecular structure and composition, requires the synthesis of catalytic materials defined on the molecular level. The siliceous cubes from Frank Feher and Thomas Masch-

meyer can be imagined as molecular building units for such molecularly designed catalysts. This paper was the first of a series of papers where we explored this idea. Seven cyclohexyl groups surround the silsesquioxane complex. Large adhesive forces will develop between the organic ligands and silica frameworks leading to a stable, new, and useful heterogeneous catalytic system.

Figure 7.5



## 7.5

# MICROPOROUS/ MESOPOROUS MATERIALS

By *Rutger van Santen*

To actually design new microporous materials is the dream of every heterogeneous catalytic chemist. We need such materials to increase the exposed surface area and to have proper transport properties. Throughout my career I have been successful in creating some new materials.

My first new material that became patented was the discovery at Shell Research Amsterdam along with Gosse Boxhoorn that some cyanides can separate carbon dioxide from methane. It was a spin-off from research on polymerization catalysts. Interestingly, current popular metal organic framework (MOF) materials are in some way connected to the early Prussian salt-related systems we studied.

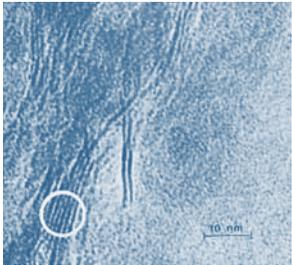
Around 1980 Jan Gaaf and I became interested in the synthesis of acidic clays and the expansion of their surface area by intercalation with inorganic clusters. At Eindhoven we continued the study of layered materials with Mischa Sychev and his group from Kiev. We not only studied acidic-clay-type materials but also extended this by exploring the basic hydrotalcites.

To our delight, the ideas derived from our small-angle-wide-angle x-ray scattering (SAXS-WAXS) studies on

silica gel synthesis led to the design of some very interesting novel hollow sphere silica materials. We were fortunate enough to interest Nico Sommerdijk from Bert Meijer's group in our systems. He contributed his unique knowledge of the role of organics in mineral crystallization. The novel hollow sphere silica materials he designed consisted of a sphere, whose shell is mesoporous. This is the result of silica deposition on self-assembled amphiphilic block copolymers.

In the context of the recently established Institute for Complex Molecular Systems (ICMS), we are currently exploring computationally the self-assembly of lipophilic molecules in vesicles with Bart Markvoort and Peter Hilbers. Our aim is to design systems that can divide and multiply. We are inspired by the work of Pier Luigi Luisi of ETH Zürich and Jack Szostak of Harvard. The colloid chemists Ben de Kruijf and Antoinette Kilian became interested in starting experimental studies on such systems. We hope that this program will lead to a novel way to optimize catalyst synthesis through multiplication or optimization of catalytically active vesicles that, if needed, will be coated with an inorganic material to make them more robust.

X-RAY DIFFRACTION DATA AND CATALYTIC PERFORMANCE AND CROSS-LINKED AND NON-CROSS-LINKED Pd-NI-SSM MATERIAL IN COMPARISON WITH HYDROISOMERIZATION		
Pd-Ni-SSM sample	X.R.D.	$k$ ( $\text{g g}^{-1} \text{h}^{-1}$ )
Before cross-linking	1.26	2.5
After cross-linking	1.73	3.6



## RESEARCH HIGHLIGHT

JAN GAAF, RUTGER VAN SANTEN, ARIE KNOESTER AND BOB VAN WIN-GERDEN (1983). *Synthesis and Catalytic Properties of Pillared Nickel Substituted Mica Montmorillonite Clays*. *J. Chem. Soc., Chem. Commun.*, 55–657

## Synthesis and Catalytic Properties of Pillared Nickel Substituted Mica Montmorillonite Clays

**ABSTRACT** Nickel substituted mica montmorillonite (Ni-SMM) clay can be intercalated successfully with aluminum and silica-alumina oligomers leading to pillared clays; transmission

electron microscopy has revealed agglomeration of the particles, which leads to suppression of hydroisomerization catalysis.

## To Convert Layers into Microcavities

**COMMENT** This synthetic clay material, nickel-substituted montmorillonite, activated by alumina oligomers, was the first new nanoporous material I made.

Figure 7.6 is a transmission electron micrograph of Ni-SMM. It shows the

layered structure of this clay material. It has improved activity for the hydroisomerization of pentane. I introduced alumina oligomers to act as “pillars” between the layers of the acidic clay to make the internal surface area accessible to reactions.

## RESEARCH HIGHLIGHT

QIANYAO SUN, PATRICIA J. KOOYMAN, J. GÜNTER GROSSMANN, PAUL H.H. BOMANS, PETER M. FREDERIK, PIETER C.M.M. MAGUSIN, THEO P.M. BEELEN, RUTGER A. VAN SANTEN AND NICO A.J.M. SOMMERDIJK (2003). *The Formation of Well-Defined Hollow Silica Spheres with Multilamellar Shell Structure*. *Adv. Mat.*, 2003, 15

## The Formation of Well-Defined Hollow Silica Spheres with Multilamellar Shell Structure

**ABSTRACT** Silica hollow spheres can be produced with high uniformity in size, thin multilamellar shell structure, and high thermal stability via an efficient single-step procedure using inexpensive, commercially available reagents. The materials can be produced using a quick route employing a temperature of 80 °C, or room temperature. The first route would be suited to produce thermally stable materials

with a highly defined wall structure for applications such as insulators, separation agents, and sorbents, whereas the second route would allow the inclusion of temperature-sensitive agents, e.g., in drug-delivery applications. The combination of SAXS, cryo-TEM, and solid-state NMR spectroscopy allows the monitoring of the formation these well-defined mesoporous materials as a function of time.

## To Design a Catalyst with Structural Control on Different Length Scales

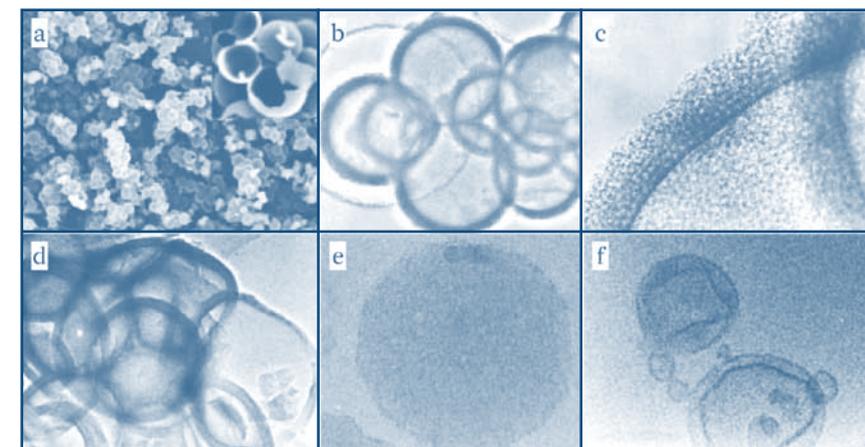
**COMMENT** Hollow siliceous particles with a well-defined mesoporous wall can be made using the templating and colloidal properties of polyether triblock copolymers in mixtures of trimethylbenzene and water. The siliceous shell is deposited on the droplets of apolar trimethylbenzene coated with the polyether surfactant that stabilizes the organic droplet in the water solution. At the same time the polyether triblock copolymer induces the mesoporous structure in the silica wall that appears on silication.

It is possible to generalize this fixation process, in which an organic particle (the droplet) is converted into an inorganic material. One can imagine to apply this to liposome particles that are surrounded by a lipophilic membrane in water solution. This would be interesting for catalyst synthesis of the liposome particles, which would have desirable catalytic activity through incorporated catalytically reactive cen-

ters. In the next paper we describe a division-induced process that would multiply such liposomes. To convert the organic liposome into a heterogeneous solid catalyst, a similar silicate fixation process could be used, as demonstrated to work in this paper.

Figure 7.7 shows electron microscopy pictures: a) SEM, as-prepared (80 °C) silica hollow spheres (bar represents 10  $\mu\text{m}$ ), inset, high magnification (bar represents 1  $\mu\text{m}$ ); b) TEM, as-prepared (80 °C) silica hollow spheres (low magnification, bar represents 380 nm); c) TEM, as-prepared (80 °C) silica hollow spheres (high magnification, bar represents 33 nm); d) TEM, as-prepared silica hollow spheres at room temperature for 1 h (bar represents 430 nm); e) cryo-TEM, silica composite at room temperature, 7 min after the addition of silicate solution (bar represents 100 nm); f) cryo-TEM, silica vesicles at room temperature, 1.2 h after the addition of silicate solution (bar represents 100 nm).

Figure 7.7



ALBERT J. MARKVOORT, NICOLE PFLEGER, RUTGER STAFFHORST,  
PETER A.J. HILBERS, RUTGER A. VAN SANTEN, JJ. ANTOINETTE KILLIAN AND  
BEN DE KRUIJFF (2010). *Self-Reproduction of Fatty Acid Vesicles:  
A Combined Experimental and Simulation Study. Biophysical Journal,*  
*99, 1520–1528.*

### Self-Reproduction of Fatty Acid Vesicles: A Combined Experimental and Simulation Study

**ABSTRACT** Dilution of a fatty acid micellar solution at basic pH toward neutrality results in spontaneous formation of vesicles with a broad size distribution. However, when vesicles of a defined size are present before dilution, the size distribution of the newly formed vesicles is strongly biased toward that of the seed vesicles. This so-called matrix effect is believed to be a key feature of early life. Here we reproduced this effect for oleate micelles and seed vesicles of either oleate or dioleoylphosphatidylcholine. Fluorescence measurements showed that the vesicle contents do not leak out during the replication process. We hypothe-

sized that the matrix effect results from vesicle fission induced by an imbalance of material across both leaflets of the vesicle upon initial insertion of fatty acids into the outer leaflet of the seed vesicle. This was supported by experiments that showed a significant increase in vesicle size when the equilibration of oleate over both leaflets was enhanced by either slowing down the rate of fatty acid addition or increasing the rate of fatty acid transbilayer movement. Coarse-grained molecular dynamics simulations showed excellent agreement with the experimental results and provided further mechanistic details of the replication process.

### Can a Man-Made Particle Divide?

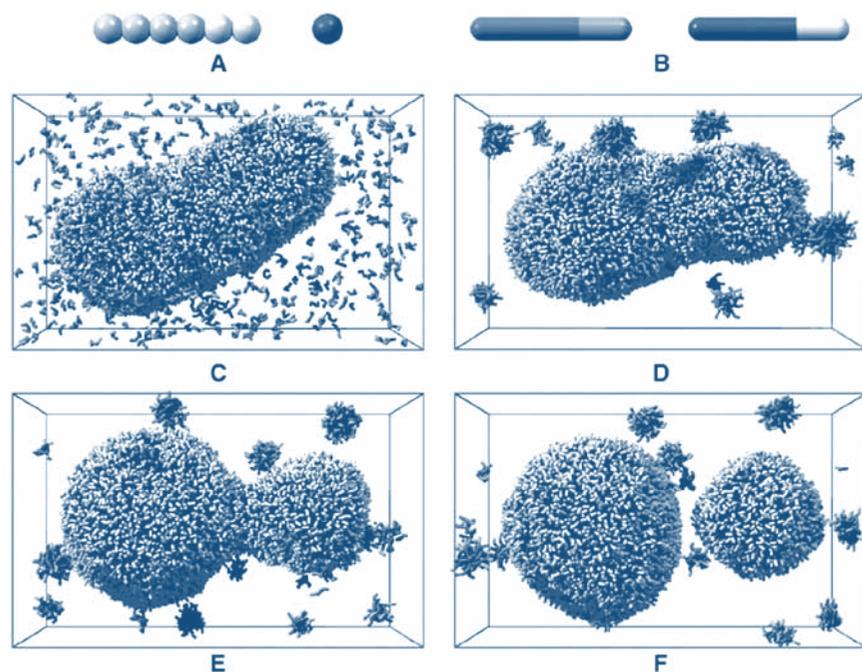
**COMMENT** This paper contains a computational and experimental study to investigate physicochemical parameters that induce liposomes with a membrane from lipophilic molecules to divide. The work is part of a research dream to develop catalytic systems that are part of membranes that self-assemble and multiply.

Our work on zeolite synthesis provided the inspiration for this project. Zeolite research had shown how organic templates, which can be considered to emulate transition states, influence the formation of shaped cavities in zeolite crystallites. The cavities are shaped around the templating molecule like a glove around a hand. Through synthesis, such organic templating molecules

can in principle also be attached to the surfactant lipophilic molecules that form the liposome membrane. On silylation, the silica shell walls that form then would generate a stereochemical recognition function, which can be exploited in catalysis.

The division of the liposome particle is illustrated in figure 7.8: (a) CG fatty acid and water model, (b) representation of the fatty acids used in frames C–F (gray for fatty acids in preformed vesicle, and red for freshly added fatty acids), (c) the initial configuration, (d) the final configuration of the first simulation, (e) an intermediate of the second simulation (iteration 1,100,000), and (f) the final configuration of the second simulation.

Figure 7.8



# 8

## Chapter 8 Longing for New Ideas

# 8

## SCIENCE POLICY AND THE FUTURE OF TECHNOLOGY

By *Bram Vermeer*

See the biography of Bram Vermeer in section 1.5.

### 1. Governing the University: Seeking Strength

In 2001 came a new twist in the career of Rutger van Santen. In terms of research, he stood at the top. Rutger's group had grown fast. Around the year 2000 he had twenty-five to thirty PhD students working for him. "It was intense. The days were filled with discussions with each individual researcher, but it was increasingly difficult to stick to that schedule." The top research school Catalysis had triggered a lot of new research, as was the case with the Spinoza Prize. "I had been able to put all my ideas into practice. I needed fresh insights to initialize something new. But there was no time for it. I got up at five o'clock in the morning. It was very nice, but very busy. It was burning up my creativity."

When his wife died after a period of illness, it was time for a change. Around that time, university president Henk de Wilt asked him to become rector magnificus. "That was the diversion that then suited me. Earlier I had experienced how well the university board had fostered high-quality research, and I wanted to continue this tradition. So I decided to run for the rectorate and I was elected. It worked out well." When he later also remarried, he was "suddenly full of ideas. I was fueled again by things I had never thought about. Suddenly it was there again."

#### *Profiling research*

At that time, there was close contact between the three universities of technology in the Netherlands. "I was in

favor of very close cooperation. I thought all three would benefit if we could all focus on our own strengths, avoiding an overlap with the others." That model had been successful in the Catalysis research school, which coordinated research over most chemistry departments in the Netherlands. The members of the school even took concerted action in the appointment of new professors.

As rector, Rutger thought a similar coordination between the universities of technology could prove beneficial, with strong but different research fields at each university. So he started an internal discussion about the areas of strength at Eindhoven. "As a board, we had made an analysis of strong and weak research areas, along with a number of industry representatives. That was obviously tricky, but a group of foreign advisers came independently to the same conclusion as we did. And actually it is not so difficult to pinpoint the real pearls. They glow, visible to everyone." Eventually, Eindhoven identified ten profile areas: biomedical engineering, functional materials and devices, dynamics of fluids and solids, catalysis and process engineering, polymers, broadband telecommunication, embedded systems, business processes and innovation, ambient intelligence, and comfort technology.

"We had written down a much clearer profile than the other two universities. But the discussions between the three universities were difficult; everyone feared it would turn out to

be a cost-cutting exercise. But I saw it as an opportunity to free money from weak areas so that we could invest it in our strengths.” Eventually, they only managed to coordinate their education. The three universities agreed to have six national master’s programs, in which each university had its own specific teaching. “It was a clear model. Bachelor education would be a local matter, where all three offer a broad program. The specialization in the master’s stage is coordinated between the three universities.”

### *Reforming education*

Thinking in terms of “bachelor” and “master” was new at that time. The new European structure of university education was introduced in the Netherlands during Rutger’s rectorate. The link between higher education and university enrollment was a difficult issue in that new structure: “It was completely unclear how graduates from colleges could enroll in the university’s master’s program. I have visited many colleges in Brabant and Limburg to coordinate education. At the same time, we needed to set up a large administration in order to get the master’s programs recognized. It all took quite a lot of energy.”

Added to that was the difficulty of convincing the lecturers at the university of a new focus. “Teachers who have put much energy into the quality of their teaching are usually not inclined to make profound changes in their program. They won’t be told what to do. Yet that is what you need if you want to implement a change. It is basically an impossible task.” Rutger soon realized that positive examples from elsewhere would help acceptance. He visited several colleagues in Europe to ask about their experience with the new university structure. “We were basing our vision on their stories. We went for a broad bachelor phase, followed by a specialized master’s program. That would also fit perfectly in the collaboration with other

universities. It would even be possible to combine master’s degrees on an international level, which eventually happened.”

The high school teacher training courses came off worst in the new bachelor-master structure. Previously, students of a normal academic course could easily get a teaching degree. That took a few more months. “I had done it myself. It was quite natural that a full academic be qualified for the classroom,” says Rutger. But in the new program, teaching was a two-year specialization after the bachelor phase. “The departments of the university did little for the teaching program; they preferred that students would enter research. Teacher training was therefore not in the best hands.” Rutger coordinated with higher education authorities in the region to set up a separate teacher training college. “That succeeded; we have really improved the level of training.”

### *The emancipation of design*

At that same time, there was quite some discussion about the role of design at the university. Can design be taught at the same academic level as science? And would it be possible to graduate on a physical design, instead of a written thesis? Rutger felt at home in this discussion. Throughout his career he had tried to bridge the gap between the scientific endeavor and its applications. He had never chosen to work entirely on the side of applications, nor did he practice basic science without a link to its use. He now plainly supported the design schools in their attempt at emancipation. “I always felt a connection with applications needs to be made, and designers do just that. Physicists and chemists also say that their research is relevant, but that relevance is often abstracted from social needs. That’s why I thought it was important to have people on campus who establish a more direct connection. I’m not a designer, but there must be people

at the university who are on that side. That’s also important as a model for our students.”

Rutger received support for these ideas from industry. Martin Schuurmans, then head of Philips Research, came up with a special invitation. Philips wanted to set up a biomedical training program in Shenyang, China, together with TU/e as an academic foundation for its investments in China. At the same time, the university president was working to set up a joint Industrial Design training program in Singapore. Both initiatives had an emphasis on design. The new training centers would also prove to be a bridge to Asia; they brought an influx of new students to Eindhoven. Rutger travelled to Singapore to open the new institute. This journey was also important for another reason—this was the first time he traveled with Edith, the woman he would marry soon after.

### *Academic reflections*

Rutger reflected on these ideas and insights in his annual addresses at the opening of the academic year in September. He enjoyed those speeches, and he also put a great deal of work into them. He spoke, for example, about the responsibility of science, the relationship between academic freedom and entrepreneurship, and the need for educational reform. In all those speeches, it is striking how he points to social problems. That theme had stayed with him since his days

working at Shell. After his rectorate he was to take up this theme again in a new way.

His first period as rector was nearing an end. The viscosity of university management increasingly palled on him. “Two thirds of the budget for research is decentralized. It falls directly under a professor; the board has little say in it. So it’s hard to keep everyone focused on the bigger picture. The then president, Amandus Lundqvist, was very good at massaging everyone. Virtually no one noticed that he was winning people over to his position. Since this is not my strength, we complemented each other well.”

It was clear that Rutger was energized again; he was full of ideas. The leave from his research group had been beneficial. At home he had found an inspiring base after marrying Edith. He had never abandoned active science. PhD students and postdocs came to see him on Fridays. During his rectorship he wrote a book on catalysis with the American chemist Matthew Neurock, with whom he had continued to collaborate after Matthew’s stay in the nineties as a postdoc at Eindhoven. He got up at five every morning so he could work on the book before the administrative work began. “That kept me on my feet, but it was a tremendous effort. In retrospect, I do not understand how I was able to do it, because also most evenings I was on duty as rector.” Rutger now longed to return to science in daylight.

## 2. Back into Research: Adventures into the Future

In 2005 Rutger was to be appointed Academy Professor at the Royal Netherlands Academy of Arts and Sciences, a special honor, which also brought some funding for new research with it. The condition was that he would have no administrative responsibility. Rutger decided to accept it; he had missed the active scientific practice. He didn’t run for reelection as rector. “It was a

huge relief that I was freed from the syrupy administrative culture,” he says.

Rutger came back in a chemistry department where his return had not been expected. The scientists, who once were engaged by Rutger, had now become group leaders and had partially continued Rutger’s topics. “That gave me the freedom to do what I wanted. But I also realized that I

would quickly enter into the waters of others. So I therefore decided not to interfere with the research of others. That was a good decision.”

### *Revitalizing Fischer-Tropsch*

Rutger did again research on the mechanisms of the Fischer-Tropsch process and came to new insights on the key role of carbon monoxide. The process had come into the spotlight again by growing concerns regarding climate change and the depletion of fossil fuels. The necessity to convert biomass into a usable liquid form led to an increased interest in catalysts for Fischer-Tropsch. As a consultant to the South African oil company Sasol, Rutger had become part of an effort to use computational catalysis to develop deeper insights into the mechanism of the reaction.

The nonlinear aspects of its kinetics relate catalysis research to complexity science, which were also explored in the Institute of Complex Molecular Systems (ICMS), then initiated by Bert Meijer. “The paradigm in chemistry is shifting from reduction to synthesis. We need to put greater emphasis on interactions and systems,” Rutger says. “This approach will lead to more in-depth insight into self-organization in the catalytic processes, and hence different design options for catalysis improvement.” And, possibly, one day into deeper insight into the genesis of life itself. This builds further upon the increasing understanding of synthesis by self-assembly of the microporous zeolitic materials used as catalysts. Rutger also initiated research inspired by theories of the chemical origin of life. With Bart Markvoort he became interested in simulations of self-dividing vesicles. This would be a way to replicate catalytic systems, provided they are catalytically active. He realized that nature had optimized chemical processes over millions of years and that the study of it could lead to further optimization of processes in industry.

### *The need to look forward*

But Rutger also wanted to broaden his field of study. He wanted to clarify the relationship between the scientific endeavor and social needs, a subject he had mentioned so emphatically in his speeches as rector. With the fiftieth anniversary of the university approaching, he saw a good opportunity to do so. He wanted the academic community to not only look backward; the scientific endeavor should be directed toward the future. He decided to publish a book that would define a social research agenda, facing the challenges ahead and connecting the needs of society with the promises of technology. The often told story of the discovery of ammonia synthesis, amidst the European turmoil preceding World War I, led him to believe that breakthroughs can be forced, provided there was enough societal pressure and that it is clear which breakthroughs are needed.

### *A common framework*

This was the start of a remarkable adventure into the future. Rutger contacted the Dutch science journalist Bram Vermeer. Shortly after, Djan Khoe joined the team. As professor of electro-optical communication at Eindhoven, he brought in a thorough knowledge of networks. The three talked to many scientists and technologists about the kind of research that would be necessary in the years ahead. Do we have the means to influence the course of history? What breakthroughs will be needed to make the world a better place? “My inspiration was John Desmond Bernal,” says Rutger. His volumes *Science in its History* had struck him twenty years before. Bernal had related scientific questions to the technologies of every age, from the Middle Ages until today.”

“Through the interviews, I soon discovered that a number of societal problems have important parallels, despite their nature being very different. The complexity of science, which

is so powerful in getting to grips with catalytic mechanisms, also proves useful in many other areas where many processes have become inter-related. This is true for such disparate subjects as financial crises, failures in microelectronics, and the outbreak of a flu pandemic. These critical phenomena can, on a deeper level, be described within a common framework.” That insight helped to identify turning points and necessary breakthroughs and to compile a research agenda to improve sustainability, stability, and crisis prevention. After an initial Dutch edition, he published the result of his quest in English as *2030: Technology That Will Change the World*, which was translated into Chinese, Korean, Arabic, and Indonesian.[1]

Initially, Rutger had left out most chemical challenges from the book. “I didn’t want to push my own research agenda,” he explains. Only gradually, he integrated catalysis research into this grand vision. This is maybe most clearly in an editorial, which he wrote in 2011 for *Angewandte Chemie*, where he reconciled the immediate need to change our energy systems with progress in pure science.[2] He describes how the implementation of new

chemical technologies is limited by the inertia of complex industrial networks, which he compares with a biotope. The challenge is to make existing systems more flexible by accelerating its innovation rate. And this is where pure science comes to its aid. New computational tools, based on basic research into reaction mechanisms, will enable a faster implementation of new technology. This would make the entire system more agile and adaptive to change.

After a long career, Rutger van Santen is now back at the point where it all started, biology. As in the Frisian meadow, it’s not the individual species that interests him, but the ensemble. The interplay within the industrial system, or the chemical processes that preceded life, or the multiple interactions on the surface of a catalyst. Understanding its complexity is the only way to improve it.

**REFERENCES** / 1. Santen, R.A. van, Khoe, G.D. & Vermeer, B. (2010). *2030: Technology That Will Change the World*. Oxford: Oxford University Press. / 2. Santen, R.A. van (2011). *Editorial: Problem Solvers and Thinkers*. *Angew. Chem. Int. Ed.*, 50, 11808–11809.

## UNRAVELING COMPLEXITY

By *Bert Meijer*

E.W. “Bert” Meijer is a distinguished university professor and professor of organic chemistry at TU/e and scientific director of the Institute for Complex Molecular Systems (ICMS). In his research, he has increasingly focused on supramolecular systems to connect molecular behavior with macroscopic properties. Today his main interest is the engineering of adaptive complex molecular systems, namely, the noncovalent synthesis of complex molecular systems.

It was in 1991 that I first met and, if I’m honest, first heard of Rutger van Santen. Heterogeneous catalysis had largely passed me by. I was an organic chemist, totally caught up with the dream of making new, functional materials, with a high precision at both the macroscopic and the molecular scale. I quickly realized that Rutger was going to be a fascinating colleague—unique in our faculty. He acts sometimes as chemistry’s answer to Johan Cruyff with the inimitable way he approaches things and his occasionally chaotic stream of words. But Rutger is obsessed with science. He constantly wants to share his knowledge with others, and he has a great knack for running organizations too. So I wasn’t surprised when he became the first chemist to receive the Spinoza Award—the “Dutch Nobel Prize.” Over the years, I’ve got to know Rutger as a fantastic colleague, who is always ready to help. Because he looks at problems in a unique way, he always comes up with solutions from a surprising angle. Since we drew up the research plan together for NRSC-C—the Dutch National Research School Combination Catalysis—our professional relationship has developed into a friendship that extends well beyond our professional lives.

I vividly remember the Monday before Christmas 2000: Rutger came into my office to ask my advice on how

he should respond to the request of Henk de Wilt—then chairman of the executive board—to become the new rector magnificus for three to four days a week. Rutger is a true scientist and was asked to continue doing great science once rector, which meant he would be a new kind of rector. The position came with onerous administrative duties, but also included time to continue doing science. It seemed too good to be true, but the only advice I could come up with was, “If you really want to do it, then you absolutely should. You have what it takes, and we’ll be right behind you.” It was an intense period, with personal highs and lows. It also saw the beginning of Rutger van Santen’s authorial career. To mark the TU/e’s fiftieth anniversary, Rutger took the initiative to write the book *Thinking Pills*, which led him to interview a series of celebrated international researchers.[1] The book proved a great success, thanks not least to the great collaboration with Djan Khoe and Bram Vermeer. The publication prompted another slim volume on catalysis and—the highlight to date—an expanded and updated version of the original book, with the title *2030: Technology That Will Change the World*. [2,3] It offers a fascinating glance into the technological future, and it has been greeted enthusiastically all over the world and translated into several other languages. To cap

## 9

Chapter 9  
Unraveling Complexity

it all off, Rutger has now also been named Academy Professor at the Royal Netherlands Academy of Arts and Sciences (KNAW), allowing him to focus again on catalysis research and on the future of science and technology.

As a relative outsider, I'm always a little jealous of catalysis as a field. It seems to me like little more than a technique for speeding up reactions. But catalysis researchers don't have any difficulty pointing out the social and scientific importance of what they do. After all, it's not hard to demonstrate that you can't make chemicals and polymers without catalysts and that every car out there has a catalytic converter. The catalysis community likes to claim, for good measure, that the polymer industry owes its entire output to their research. In other words, catalysis researchers have arranged things very nicely for themselves, and their field is highly organized. If you then add Rutger's scientific insights and original thinking to those already significant advantages, you end up with a highly successful research group. Not so long ago, catalysis seemed to be losing a little of its shine. But the need to make the world more sustainable has placed this research right back at the center of attention.

Catalysis can contribute to a solution in two ways. Firstly, heterogeneous catalysis should deliver techniques for, say, producing useful products from biowaste. To do that, however, a further advance is required. So far, the molecules to be reacted have been relatively small. Much larger molecules now have to be converted, which means an increase in complexity. One way of realizing such processes would be the introduction of several catalytic centers on the same surface so that the nonlinear link between them can generate new possibilities. You can only do that with a thorough knowledge of surface dynamics. Secondly, catalysis needs to take nature as its example. The intriguing complexity

of natural catalytic systems and their unparalleled selectivity and exclusion show that we are only at the beginning of the optimization of chemical reactions. An important factor here is the interplay of many different molecules in a small compartment (a cell, for instance), in which molecular interactions and chemical transformations are directly linked with one another. Such processes also feature numerous positive and negative feedback loops, with nonequilibrium states being the rule rather than the exception. Although lots of objectives could be adopted in this regard, it makes sense to choose energy as the focus. We need to develop new processes that convert electricity (or solar energy) into chemical binding energy.

Once again, it was Rutger's forward-looking thinking that led to that choice in the course of the NRSC-C program, firmly establishing an important goal for fresh catalysis research. With these twin focuses, catalysis research has reaffirmed its important scientific position and its strong industrial and social relevance. The new lines of research also dovetail perfectly with the scientific agenda of the TU/e's new interfaculty body: the Institute for Complex Molecular Systems.

When the TU/e's executive board approached me with the request to set up a new institute, I immediately turned to Rutger to help brainstorm the best approach. Could we do it? Should it be on a large or a small scale? Should we take on the big challenges, or should we play it safe? Rutger and I have both reached the stage in our lives where we have knowledge and skills we can share with researchers at the beginning of their careers. Together, we took up the challenge of fleshing out the institute's broad outlines. It had been clear to me for some time that new steps needed to be taken in the self-assembly of molecules to take us beyond pretty structures and architectures. What it's all about now

is achieving new functions. We wanted to take our example from nature: we were keen to understand how nature, in all its complexity, functions so well. We also wanted to fathom out the mechanisms of complex processes in industry. The formulation of coatings and plastics should no longer be an empirical art or a matter of trial and error: for further progress, it needs to become a science-based technology. That will only be possible if supramolecular chemistry is founded on three pillars: a strong link is needed with mathematics and theoretical physics; it has to be firmly anchored in biology and biomedical science; and research has to advance through the application of new technology, such as microfluidics. To achieve those things, the institute must act in an interdisciplinary way, linking up with the different faculties. It also has to operate at the forefront of science, focusing only indirectly on applications. And we must make sure we build the institute for, with, and around young researchers.

The ICMS has been solidly supported from the outset by Rutger, Mark Pelletier, and Sagitta Peters and has continuously enjoyed the consistent and strong backing of rector

magnificus Hans van Duijn. That same enthusiasm has helped the institute in becoming a breeding ground for all TU/e people who want to help shape the world of the future through new technologies. Hence the foundation of an Advanced Study Centre at the ICMS's new building will be instrumental in discovering future trends; Rutger's books will take lead the way in that process. Finally, I hope that Rutger van Santen will continue for many more years to surprise me and my young colleagues with his fresh insights from unexpected angles in the areas of science, technology, and personal development.

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“When I met Edith,  
I was suddenly full  
of ideas. I was fueled  
again by things I had  
never thought about.”



# 10

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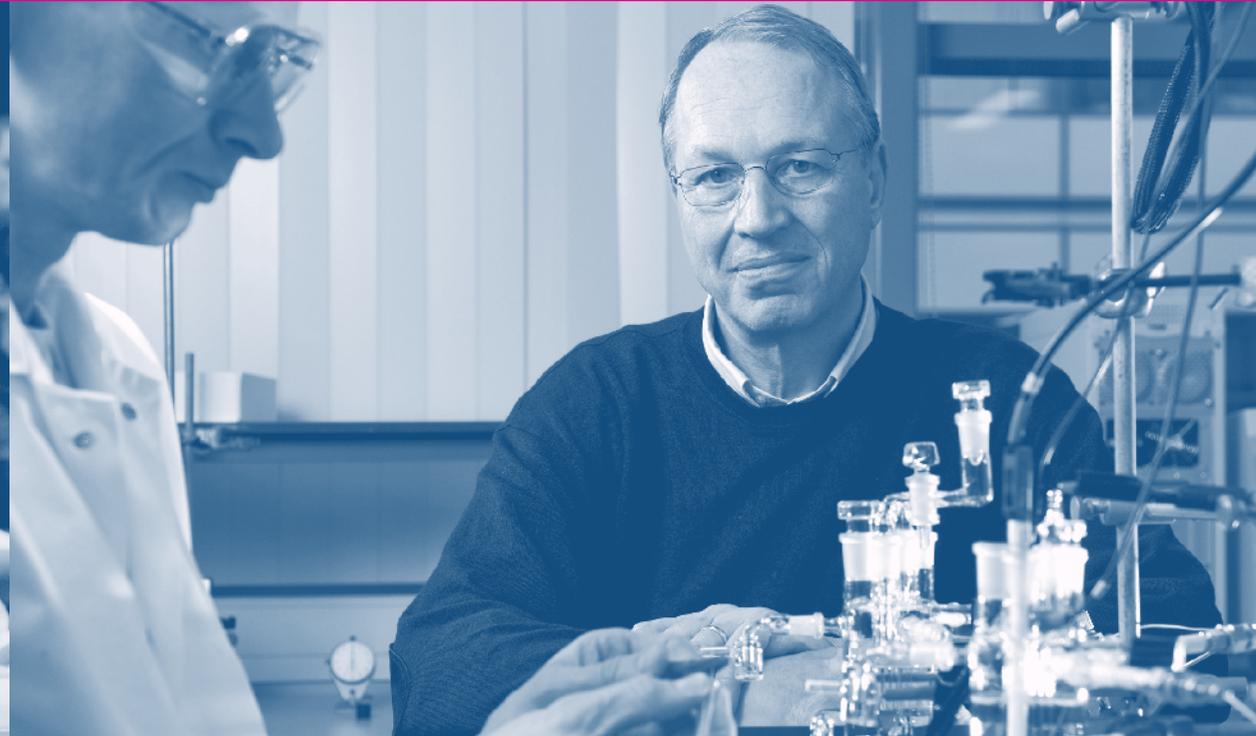
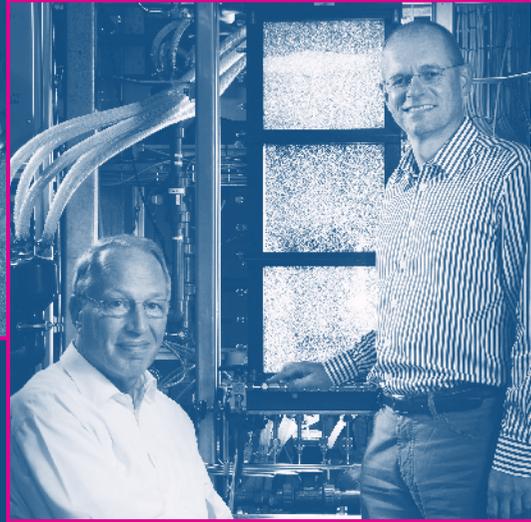
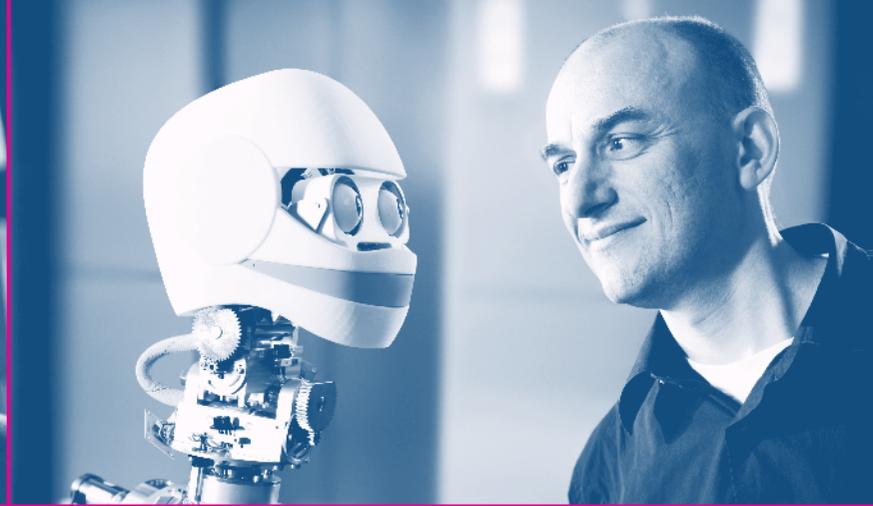
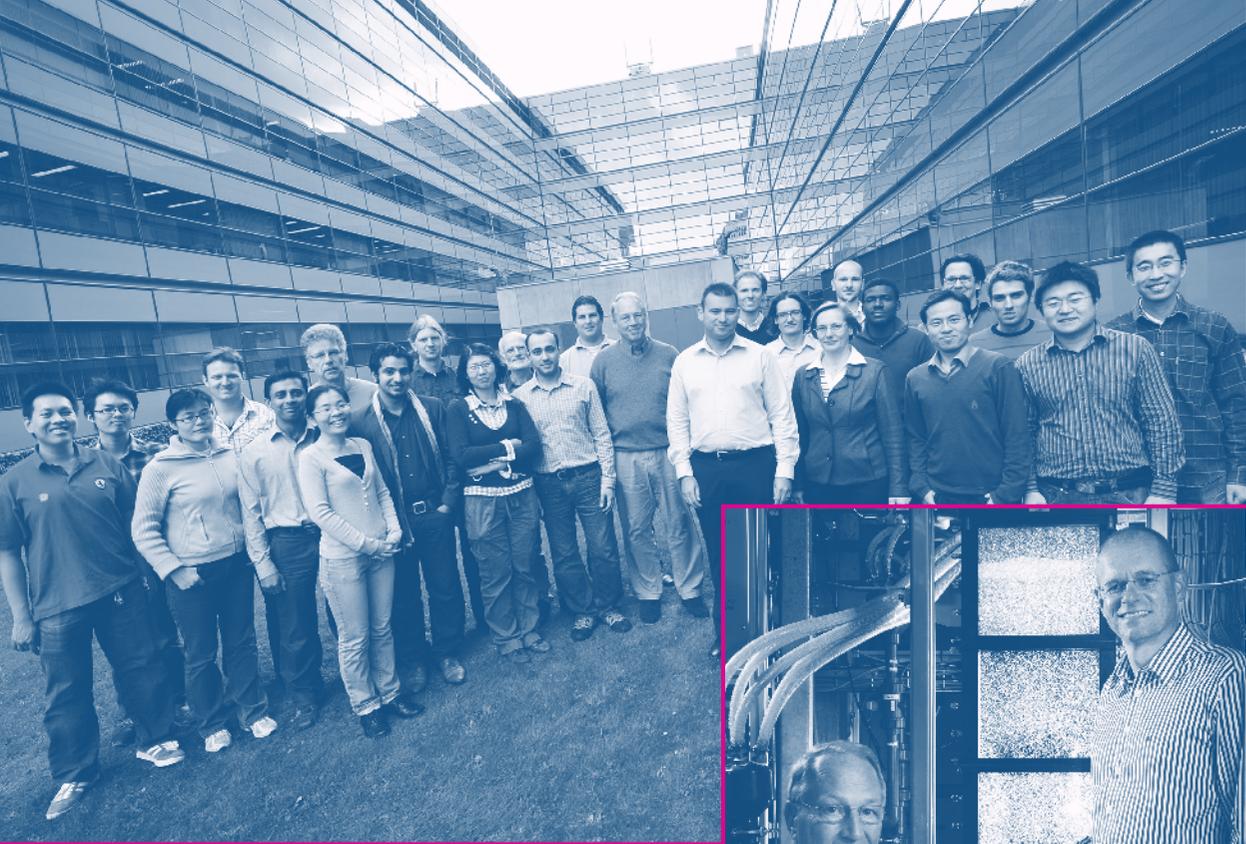
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