Dr Louis B.J. Vertegaal
DIRECTOR ACTS
& NWO CHEMICAL &
PHYSICAL SCIENCES
DIVISION
Dear reader,

I am proud to present the final publication of the ASPECT programme of ACTS (Advanced Chemical Technologies for Sustainability). You will find an overview of ten years of ASPECT: the objectives we had and the results we accomplished. You will also find a look ahead to the future.

The ASPECT programme focuses on the catalysis of chemical processes in bulk chemistry to increase the sustainability and effectiveness of these processes. With improved catalysts, processes proceed cleaner and more efficiently, for example by producing less waste or using less energy. With new catalysts, new pathways can be designed to existing or novel products. Also, sustainable or renewable raw materials may be used. To provide the conditions for the processes within bulk chemistry to proceed in a more sustainable manner, a joint effort between universities and industry is required, as innovation in industry is realised on the basis of new knowledge. Universities, knowledge institutions and companies are brought together in ASPECT, resulting in a guaranteed rapid uptake of usable results and concepts by the participating companies.

At the start of the programme, we dreamt about improvement of catalytic processes and a decrease of waste production. About sustainable and renewable feedstocks, which are convertible to valuable chemicals. We also looked for new, innovative tools that could give us a better understanding of the fundamentals of catalysts and catalytic processes. Ten years, 32 projects and 12.5 M€ later, ASPECT contributed considerably to reaching these goals and many of our ambitions came to reality. We can be proud of these results.

The programme was special in another way; the biggest chemical companies in The Netherlands were working together in one consortium. This gave us a unique position. Academic research groups had the opportunity to discuss their results with industrial partners, and industry had the opportunity to explore and experience scientific capabilities in university research groups. As you can read in the interviews with Garry Meima (Dow Benelux) and Wim Hesselink (Shell), ASPECT has surely aided in an intensive collaboration between academia and industry. This collaboration has led to first-class research, of which you can read a beautiful example in the interview with Krijn de Jong, Hirsia Torres Galvis (both Utrecht University), Matthijs Ruitenbeek (Dow Benelux) and Andrew Ward (Sabic).

As pointed out in the interview with Bert Weckhuysen (Utrecht University), there are still ample challenges left in catalysis, but I am sure that you will be impressed by the scientific creativity, the expertise of chemical companies and the collective results they achieved. I believe that our results will inspire you to make chemistry yet more sustainable. Be inspired!

Dr Louis B.J. Vertegaal
## Contents

Foreword by Louis B.J. Vertegaal, Director of ACTS  
Garry Meima “Fundamental, exploratory and aimed at future needs”  
Bert Weckhuysen “ Consortia are all about finding the right balance and size”  
Wim Hesselink “Truly successful with a bonus”  
Krijn de Jong, Matthijs Ruitenbeek, Hiris Torres Galvis, Andrew Ward "When everything comes together"  
Facts and Figures

**Project overview**

- **Freek Kapteijn:** Bifunctional catalytic processing for the production of alkenes?  
  *A structured and combinatorial approach*  
  26

- **Bert Weckhuysen:** From liquid biofeed to bulk chemicals: a rational approach based on  
  *liquid-phase in-situ spectroscopy*  
  28

- **Krijn de Jong:** Process intensification in alkylation processes using zeolite catalysts with molecular traffic control  
  30

- **Leon Lefferts:** Alkane oxygenation using oxide ion conducting membrane  
  32

- **Bert Weckhuysen:** Spatially and time-resolved in-situ spectroscopy on catalyst extrudates:  
  *Understanding the physico-chemical principles of catalyst impregnation and drying*  
  34

- **Harry Bitter:** μ-oxo binuclear catalysts for the production of methanol from methane and oxygen  
  36

- **Bert Weckhuysen:** Spectroscopic control of heterogeneously catalyzed processes  
  38

- **Martin van Sint Annaland:** Simultaneous production of ethylene and synthesis gas combining the oxidative  
  coupling and reforming of methane in a reverse flow membrane reactor with a dual function catalyst  
  40

- **Dieter Vogt:** Amines from C4 and C1 feed stocks and ammonia  
  42

- **Jaap Schouten:** Improving liquid phase reaction in bulk chemical processes by application of micro reaction technology  
  44

- **Kulathuier Seshan:** Oxi-cracking as a route to olefins – Efficient conversion of alkanes to olefins over  
  nanometer range clusters of non-redox alkaline earth oxide catalysts  
  46

- **Krijn de Jong:** Direct production of lower olefins from synthesis gas using iron based catalysts  
  48

- **Bert Weckhuysen:** Towards catalyst diagnostics and on-line reactor control via in-situ UV-Vis/Raman spectroscopy:  
  *Proto-type development and implementation in industrial dehydrogenation, alkylation and hydrotreating pilot-scale reactors*  
  50

- **Johan Sanders:** Amino aids to chemical products for the chemical and plastics industries  
  52

- **Bert Weckhuysen:** Activation of hydrocarbons catalyzed by supported noble-metal nanoparticles  
  54
• Bert Weckhuysen: Crude glycerol and sucrose, renewable feedstock for the sustainable production of novel bulk chemicals  
56
• Erik Heeres: Conversion of C6-sugars to green polymer precursors  
58
• Ludo Juurlink: Defect densities all at once  
60
• Lies Bouwman: Sustainable atom-efficient routes to large-scale industrial chemicals  
62
• Jacco van Haveren: Bulk Chemicals from glycerol; the development of selective oxidation and hydrogenolysis pathways  
64
• Leon Lefferts: Oxidative dehydrogenation with CO2 as a soft oxidant  
66
• Gadi Rothenberg: Oxidative dehydrogenation of propane using doped ceria redox catalysts  
68
• Bert Weckhuysen: Real-time three-dimensional imaging of a single catalyst extrudate in action: Probing hydrogenation reactions over Ni-, Pt- and Pd-based catalysts under true reaction conditions  
70
• Bert Weckhuysen: Sustainable catalytic production of novel polyglycols from renewable resources  
72
• Bert Weckhuysen: Spatiotemporal spectroscopic studies on the deactivation of catalytic solids by poisoning  
74
• Dieter Vogt: Primary amines from C4-feed stocks - hydroaminomethylation with ammonium carbamate  
76
• Leon Lefferts: Reaction integration on particle scale: demonstration for combined oxidative coupling and steam reforming of methane  
78
• Krijn de Jong: Ethanol from synthesis gas using highly dispersed cobalt catalysts  
80
• Jarl van der Vlugt: Tailor-made metal species for the activation of ammonia: toward hydroaminaton of alkenes with NH3  
82
• Ekkes Brück: Simultaneous operando Mössbauer and infrared spectroscopy of heterogeneous catalysts: probing the active sites in iron based oxidation catalysts  
84
• Maurice Franssen: Catalytic production of acrylamide and methacrylamide from renewable resources  
86
• Ludo Juurlink: The large reveals the small  
88
Consensus
“When I look back at the ASPECT programme, several conclusions come to mind. It amazes me to what extent my conclusions coincide with the feedback other consortium partners gave. Although, I should not be surprised. It is exactly in line with the consensus experienced at the Programme Committee meetings. This consensus and absence of interfering corporate interests made the project selection and guidance very successful.

This consensus comes from the fact that the themes on catalysis and feedstocks were very well chosen: fundamental, exploratory and aimed at future needs; qualifying perfectly for pre-competitive research. Breakthrough developments in these areas are required to meet the demands in feedstocks and associated environmental footprint for decades to come. Furthermore, the selected themes require several steps before commercialization and they call for support from academia. In the course of the programme there was some discussion on how to attract more projects on the use of biomass, which remained somewhat underexposed initially. In the end, excellent proposals could be rewarded on this subject too. Project proposals by applicants were generally of high quality and to the point.

Consortium partners had no hidden agendas, which is reason for satisfaction. There were special bilateral collaborations to facilitate setting the research in the right direction and to offer assistance. Collaborations were not hidden from others, nor were they regarded as competition.”

Good organisational structure
“The Programme Committee structure was well-organised with biannual evaluation meetings. Again, consensus ruled while discussing the progress in the various projects and any necessary measures. In some cases, these measures gave the researcher the necessary grip on the matter or pointed out other research possibilities. Feedback was generally accepted positively. It contributed to better end results. Good conferences and networking facilities further supported the programme. After the start of the first
projects, the need for closer guidance from industry became apparent. The gap between industry and academia was an issue in some cases, although this partly depended on the individual PhD-students and postdocs. It was a positive idea to set up Industrial Contact Groups during the programme. These often contributed to more intense technical discussions. Undoubtedly, I advise future industrial user committees to start simultaneously with the projects."

**Excellent science**

"NWO can be very proud of the scientific results of ASPECT. Articles in the highest rated journals (e.g. Science, see pages 18 till 21) and worldwide press exposure are good examples. Unfortunately, the yield in Intellectual Property (IP) is rather limited – although not very surprising for a long term exploratory programme. Still, IP deserves further attention in future programmes. In practice, the IP-regulation proved to be complex and probably has also limited the IP-yield. For a follow-up programme, called Technology Areas for Sustainable Chemistry (TASC), this aspect is now under review for improvements. Another issue that may have hampered patent filing is publication planning. Deadlines for sending in draft publications and presentations were seldomly met. Therefore industrial partners were informed of this too late. When a draft finally came in, time was often too short for a good review and for discussions on potential IP possibilities. Although sometimes understandable, given publication deadlines, this ‘last minute work’ is a pity for all parties involved. More attention should be given to this aspect in future programmes.

"*Academia can still learn a lot about the meaning, value and function of IP for industry.*"

Academia can still learn a lot about the meaning, value and function of IP for industry. The example of some American entrepreneurial universities is appealing, but the concept often is poorly understood. A patent in our field generally does not refer to just some new product, but involves a whole process, that still has to be developed commercially at high cost and high risk.

The development phase is often underestimated, and the original invention mostly represents only about ten per cent of the effort towards commercial exploitation of a patent. Of course this does not downgrade the value of an invention, but things need to be put into perspective."

**High reputation**

"ASPECT has been a success, but the concept cannot be continued as it is, since times have changed. During a recession it is more difficult to secure funding for long term fundamental research projects. There is less patience for results. Therefore, the time has come for smaller teams with a strong focus, and partners with non-conflicting interests. At the same time, companies put more emphasis on exclusive IP and wish to excel in their own areas of expertise, which they can turn to good account. Even the largest companies know they cannot solve the highly complex challenges by themselves. However, I am very positive that these challenges will be met, as long as the extraordinary scientific level of the academia in the projects is maintained.

I reserve my last remark for the very high level of many of the PhD-students and postdocs that participated in the programme. An international top manager, who visited a scientific meeting, stated these were some of the best presentations he had ever seen from PhD-students. Dutch universities succeed in attracting and educating international talent. Dutch catalysis research has a globally renown reputation that should be maintained and supported."
Glycerol is considered as an important platform molecule in existing and future biorefineries as it can be produced from sugars as well as fatty esters. Glycerol can be etherified towards di- and tri-glycerol, which have numerous applications e.g. in cosmetic and pharmaceutical industries. In a collaborative project between the universities of Utrecht, Delft and Twente - led by prof. Bert Weckhuysen (Utrecht University) - ASPECT researchers focused on the development of suitable solid catalysts for the selective etherification of glycerol, in combination with the development of in-situ spectroscopy for characterization of heterogeneous catalysts in liquid phase reactions. They discovered a new highly active colloidal CaO catalyst material for glycerol oligomerization. The research resulted in a patent application and several publications in, amongst others, *Chemistry - A European Journal.*
Consortia are all about finding the right balance and size

“The public-private partnership (PPP) format of ASPECT offered academic and industrial partners the opportunity to meet on a regular basis. This created plenty of opportunities for discussion and interaction in a pleasant and open way”, says Weckhuysen. “In particular, this input has been beneficial to the PhD-students and young post-docs employed in the various research projects. They got a balanced mix of input from academia and from industry in a closed community with a broad scope.”

“Definitely, a consortium has added value over bilateral relations between industry and academia, although it does not replace them”, says Bert Weckhuysen, Professor of Inorganic Chemistry and Catalysis at Utrecht University and academic member of the ASPECT Programme Committee. “As scientific challenges mostly are very complex and require multi-disciplinary approaches, consortia may bring together the expertise that is required to solve them.”

“A SPECT offered both PhD-students and industry a broader scope and more comparison.”

The format provided companies with the opportunity to observe and recruit talent, which occurred regularly. Weckhuysen: “Of course, this also works the other way around. PhD-students come in contact with industrial partners, get to know them, receive input for their work in a closed setting. Apart from the network possibilities and the boost of presentation skills, this contact occasionally concluded in a job offer.”

Weckhuysen puts this into perspective; bilateral contacts might also lead to job offerings. “But ASPECT offered both PhD-students and industry a broader scope and more comparison.”

Pendulum

“On the condition that partners are allowed by their organisations to speak relatively freely, community building between people has many advantages. A diversity of input and background has a lot of added value in the process of science and technology development. PhD-students who were very enthusiastic about ASPECT, benefit from a setting in which they can compare the different levels of involvement, technological directions and corporate cultures of various companies.

In general, I believe that consortia have an advantage over purely bilateral collaboration, in which the discussion may be limited to the insight of only one industrial and one academic partner. However, at this moment the pendulum swings towards smaller consortia involved in more application-oriented
research and more direct involvement.”

In the follow-up programme, Technology Areas for Sustainable Chemistry (TASC), this broader scope is somewhat narrowed down. “Industry requested smaller consortia. But I think it is important to preserve the added value of a bigger consortium, and make sure that lively and fruitful discussions can still thrive.”

Weckhuysen agrees that too many parties in a consortium contribute little extra. “Too large a number of partners might prevent, rather than stimulate, open scientific discussions. It is all about finding the right balance and size. The future will learn what is the right scale to go, but it could be that the pendulum has gone so far in one direction, that some benefits of research consortia will disappear. The difference between bilateral relations and the TASC set-up could then become close to cosmetic.”

A lot of exciting new research

Beside these worries for the future, with pleasure Weckhuysen looks back on a research programme that has been very successful. “I am very happy that the ASPECT programme turned many ambitions from the Roadmap Catalysis* into reality. It is an immense achievement by the Dutch catalysis community, which has been beneficial to many research groups and industry partners alike. For the scientific harvest and the careers of young scientists it has been extremely valuable.”

Of course there are still ample challenges left in catalysis after more than ten years. “It is time to renew the Roadmap Catalysis. What has been established? What ‘Terra Incognita’ is left? What new challenges are ahead of us? And how can we fill the knowledge gap to tackle these challenges?”

An example of such a knowledge gap is to understand and control the functioning of catalyst materials on length scales from nanometers to millimeters. Weckhuysen: “This becomes even more important now that developments lead to a single catalyst particle and a single molecule analysis and understanding. How can these fundamental insights be translated into the design and synthesis of novel or improved catalyst materials? A lot of exciting new research still lies ahead of us.”

Lignocellulosic biomass is a very promising feedstock for the production of biobased chemicals. The C6-sugars in lignocellulosic biomass like for example straw or paper pulp waste are interesting precursors for a broad range of chemicals. An example of such chemicals is 5-hydroxymethylfurfural (HMF). ASPECT researchers in the group of prof. Erik Heeres (University of Groningen) studied the conversion of HMF to caprolactam, the monomer for the widely used synthetic polymer nylon-6. They identified a pathway that allows the conversion of HMF into caprolactam in only four steps, whereas the current caprolactam process needs six steps from benzene and ammonia. The research resulted in a patent application and a publication in *Angewandte Chemie*. 
“Taking the definition of success that was drawn up at the start of the programme, ASPECT can be considered truly successful,” says Wim Hesselink, formerly manager Chemistry & Process Development at Shell Research in Amsterdam: “But the programme had some bonus deliverables as well. I am referring to its function as a networking, training and HRM platform. Once you know people, it becomes so much easier to contact them and to discuss ideas and opportunities together.”

“Right from the start, Shell has been very positive about ACTS. We contributed substantially through our participation in three out of four programmes. ASPECT was one of these”, says Hesselink. He recently retired, but has a track record as long-time chairman of the ASPECT Programme Committee. “Within Shell, we recognized the benefits of a public-private partnership (PPP) and the relevance of collaboration for the industry in general, and for us as part of this industry. The government contribution, favourable university tariffs, and sponsoring by multiple industrial partners, creates high efficiency for the research dollar.”

"The government contribution, favourable university tariffs, and sponsoring by multiple industrial partners, creates high efficiency for the research dollar.”

Evolution
Collaboration between universities, government and industry was unique when ASPECT started ten years ago. And the PPP concept evolved since then, Hesselink remarks. “It started out with open calls, connected to generic research goals like ‘alternative feedstocks for the chemical industry’. The Dutch universities and large technology institutes could send in proposals within that framework. The Programme Committee then selected projects on the basis of technical excellence - as determined by reports from international referees - and relevance for industry. This procedure slightly limited the steering and control from industry, because you had to wait and see which proposals were submitted.”

Hesselink stresses that each industrial partner was interested in some of the proposed topics, but other topics met less enthusiasm. “For instance because they were too distant from their core activities or from market application.”

In the follow-up programme Technology Areas for Sustainable Chemistry (TASC), universities and industry
can launch project ideas in a joint effort of a small consortium set-up. “This kind of evolution is logical, given the fact that industry became more focused on specific results on a shorter term.” Hesselink: “The present adjustments should be regarded as a product of the changing circumstances.”

Success parameters

“When ASPECT started, we drew up a definition of success”, says Hesselink. Success would include five directly applicable methods and technologies for the industry, ten promising concepts for further development, a hundred publications in refereed journals and five patents.

“It is hard to define instantly applicable methods. I would say this goal was nearly attained with three to five of such methods and technologies”, Hesselink states. As an example he mentions the methodology to follow real-time and in detail how a catalyst behaves in an industrial reactor. “ASPECT focused on inventions. The number of ten inventions was certainly attained, although it is still hard to tell how important these inventions, on for instance alternative feedstocks like methane and biomass, will turn out.” These leads have to be further developed in TASC.

Hesselink has not always been confident that the ambition of a hundred publications in international science journals would be attained. “Project leaders have always been positive about achieving this ambition, and I am glad that they were right. Of course, we are also very proud that we reached three patent applications, although originally we aimed at five. This is still a very respectable result. So all in all, we are very satisfied that most success parameters were met”, Hesselink concludes.

Other deliverables

The programme offered some bonus deliverables as well. Hesselink explains: “With about ten university research groups, the field in the Netherlands is limited. These groups got to know each other better, and are now aware of each other’s strengths and opportunities, thanks to ACTS. Industry is also better informed about their scientific capabilities. And whereas for instance the Utrecht University groups already had contacts with many universities and industry, the Wageningen groups have now gained better entry into this community. The two-day conferences that were organised not only worked to follow project progress, but also functioned as network boosters. Once you know people, it becomes so much easier to explore ideas and opportunities.”

“Once you know people, it becomes so much easier to explore ideas and opportunities.”

ASPECT worked wonders as a platform for training of PhD-students and post-docs, who had to present their work to a critical audience: “Young scientists could benefit from industrial contacts, who were willing to advise them. The programme has been favourable for HRM as well, both for the candidates and from an industrial perspective. Shell hired a number of the young scientists from ASPECT. The connections within the Dutch field have been tightened all over and this can only work out beneficially for the future.”
The proteins that are left in the byproducts from bioethanol and biodiesel production can be valuable building blocks for chemicals. Especially the non-essential amino acids in these proteins, which have no significant value for food or feed, are interesting starting materials for a variety of nitrogen containing products. ASPECT researchers in the group of prof. Johan Sanders (Wageningen University) investigated new sustainable routes to convert glutamic acid, the most abundant amino acid in many plant proteins, into industrial chemicals. They illustrated that it is possible to make biobased chemicals, such as acrylonitrile and N-alkyl pyrrolidones, from glutamic acid using catalysis as a tool. The research resulted in several publications in, amongst others, *Green Chemistry* and *ChemSusChem*. 
One of the projects in the ASPECT-programme led to the development of a catalyst which can convert synthesis gas, an alternative for crude oil, into building blocks for lower olefins production. This invention was the basis for a patent application, as well as a highly valued article in Science. The project generated publicity all over the world. What was the key to this success? Krijn de Jong: “All ingredients were there: a good idea, bright researchers, close collaboration, serendipity and an effective organisation.”

“The idea was to develop a new catalyst for the production of lower olefins”, says Hirsa Torres Galvis, who worked at the project as a PhD-student. “We wanted to use an iron catalyst. The properties of such a catalyst are largely known, but we looked for a better performance.”

It was not as simple as it sounds. “We had to design a strategy to study various factors of the catalyst performance: the influence of the support material, the preparation of the catalyst, the size of the iron nanoparticles and the role of the chemical promoters sodium and sulphur.” This led to a lot of information. The main conclusion in the Science article was that the support material plays a decisive role, although particle size and promoters are important as well.

“The interaction with industry partners turned out to be valuable for the end results of the project. Like us, they also put in a lot of effort. It was the teamwork that created success. To show results, to discuss and to get an expert opinion has been really meaningful”. Torres Galvis concludes: “Also, the network that was created can give my future career a boost”.

Patent
Torres Galvis is very pleased with the project results. Besides an acclaimed article, the patent application is an important project deliverable. Andrew Ward, Business Science Specialist at Sabic UK: “Sabic is a big producer of olefins, so yes, we are interested in this patent application. We even encouraged the ASPECT-organisation to file patents. At the start of the project, we expected some Intellectual Property (IP), although we did not have a particular outcome or number of patents in mind. Participating in a large programme like ASPECT is like fishing with a trawler: you do not know what you will catch.” Matthijs Ruitenbeek, Senior Scientist at Dow Benelux agrees: “ASPECT was not primarily meant to generate IP, but to generate long term knowledge. IP should be regarded as a bonus”.

"ASPECT was not primarily meant to generate IP, but to generate long term knowledge."
At this point, it is still difficult to assess how important the patent is to Sabic. Ward explains: “It is part of a larger complex of innovation, a brick in the wall. Therefore it is difficult to value, more so because it not only allows us to do something, but also because it stops others without a license. How can you put a price tag on that last aspect?”

**Consortia**

Ward was a member of the ASPECT Programme Committee. “It allowed me to read and discuss all the papers within the programme. It also gave the opportunity to steer. But to be honest, this would be easier in a bipartite cooperation. ASPECT had a wide range of subjects. This means that for us, the average significance of projects was low; roughly half of the projects was of no interest to us.”Sabic is engaged in a lot of bipartite research, focused on direct corporate interests. Ward: “In the future we will concentrate on specific bipartite projects, in which the IP-ownership is exclusively for us. In ASPECT, some participants are direct competitors, having an equal right to licensing. Even when a patent turns out to be useful, there is hardly competitive edge; and in this case sharing makes it half as good as it could have been.”

Ruitenbeek has a balanced view on programmes within consortia: “When you participate, you have the possibility to contribute to its success. That is the very concept of participation. Collaboration is about giving and taking, contributing and receiving. The amount of effort you invest also defines your steering opportunities. Commitment sometimes offers the opportunity to co-publish, so all parties benefit.

*"The amount of effort you invest also defines your steering opportunities."*

Contributing is not possible without intrinsic interest. Before you are willing to participate, a project should comply with some preconditions. In my opinion, projects come in different categories. The worst case is having no match with your own business interests. Some projects in the programme were not initiated by industry, nor interesting for the industry partners in ASPECT. It can be hard to contribute to such an academic project. Do not get me wrong; the science can be brilliant, and we have seen examples of that in ASPECT.

A second type of project is covering potentially interesting chemistry or tools; this might correspond to an attitude of ‘just wait and see’. But when the expectations are not defined and no clear input is given, this is not optimal either. The third category includes industrially relevant projects. These are the ones we are looking for, as long as they are not too close to the core business. Then the consortium approach is too open. When it comes too close, we generally abstain. There have to be connections with the other partners, but preferably no overlap. We are very selective, but when all conditions are right, we are committed and can really go for it.”

Dow whole-heartedly participated in some projects within ASPECT. “We went for the Supported Iron Nanoparticles project. It was close to our core business but we went for it since the project covered a lot of the fundamental aspects of chemistry. There was real collaboration, two of our researchers working at Utrecht, exchange of materials and (background) knowledge and tests under industrially relevant conditions at Dow.”

**Follow up**

Ward expects that the ASPECT-concept will be adjusted to somewhat smaller consortia, where participants are aiming at specific results. “But all in all, we were happy with ASPECT and especially with this project. It generated good science: not in the first place for patenting, but also to enlarge our knowledge of fundamental, underlying processes. Besides, it has been important for the training of young scientists and engineers. We employ a lot of people in the Netherlands and such a programme contributes to meeting potential employees.”
Ruitenbeek has the same expectations as Ward. "We were involved in proposals for Technology Areas for Sustainable Chemistry (TASC), the follow-up programme of ACTS. Experiences from ASPECT were applied in TASC. Corporate commitment counts, only applied projects are admitted and consortia become smaller. This enlarges the chance of true collaboration and generates more successes.

Serendipity
De Jong concludes: "This project was a scientific highlight, not only with implications for industry, but also for sustainable development." He calls it an excellent example of what happens when everything works out well. "To start with, you have to have a good idea. And then there is serendipity, ‘the luck of the prepared mind’ as I like to call it. But in the end, it is all about people: PhD-students with potential, sound supervision by senior scientists, excellent people from industry, all in close collaboration. Good people and good teamwork create successes. In this project the input from TU Delft for Mössbauer spectroscopy, to get fundamental understanding of the catalyst’s behaviour, was also very valuable."

Though it did not look great from the start, De Jong recalls: "In the beginning a lot of hurdles had to be taken, it demanded patience and cooperation to overcome. For instance, the catalyst could not be reproduced. The first years were demanding, but eventually it all came together.” It is attractive to create the circumstances that result in good science. De Jong: “We should be aware that organisational aspects can demotivate people. Organisation cannot create good science, but it can prevent bureaucratic burden; the ASPECT office did a good job in this respect. The challenge is to keep the organisation as simple as possible in order to keep the exchange of ideas between partners flowing. Working physically close together helps to attain that goal."
Lower olefins (ethylene, propylene and butylenes) are key building blocks for the production of a wide range of products such as plastics, pharmaceuticals and cosmetics. Conventionally, lower olefins are derived from naphtha cracking and other petrochemical processes. However, since fossil fuels are running out, alternatives have to be found to allow the production of lower olefins from other carbon sources such as biomass. ASPECT researcher Hirsa Torres in the group of prof. Krijn de Jong (Utrecht University) succeeded in the development of an iron nanoparticle catalyst, which allows the conversion of synthesis gas (a mixture of CO and H2 that can be produced from any carbon source) into lower olefins. The research resulted in a patent application and a publication in *Science*. 
Facts & Figures

Number of projects

<table>
<thead>
<tr>
<th>Round</th>
<th>Year</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>First round</td>
<td>2004</td>
<td>11</td>
</tr>
<tr>
<td>Second round</td>
<td>2006</td>
<td>10</td>
</tr>
<tr>
<td>Third round</td>
<td>2009</td>
<td>11</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>32</td>
</tr>
</tbody>
</table>

Output (October 2012)

<table>
<thead>
<tr>
<th>Type</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scientific papers</td>
<td>110</td>
</tr>
<tr>
<td>Posters (The Netherlands)</td>
<td>55</td>
</tr>
<tr>
<td>Posters (abroad)</td>
<td>30</td>
</tr>
<tr>
<td>Presentations (The Netherlands)</td>
<td>45</td>
</tr>
<tr>
<td>Presentations (abroad)</td>
<td>63</td>
</tr>
<tr>
<td>Total</td>
<td>303</td>
</tr>
</tbody>
</table>

Researchers and staff

<table>
<thead>
<tr>
<th>Role</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhDs</td>
<td>25</td>
</tr>
<tr>
<td>Postdocs</td>
<td>37</td>
</tr>
<tr>
<td>Technicians</td>
<td>11</td>
</tr>
<tr>
<td>Total</td>
<td>73</td>
</tr>
</tbody>
</table>

Total budget

M€ 12.5

Advanced Sustainable Processes by Engaging Catalytic Technologies (ASPECT)

The aim of the ASPECT program is the improvement of sustainability in the bulk chemical industry. The main vehicle is the development of new, or significantly improved catalytic processes, leading to a step change in performance. Key for the development is the joint use of universities, knowledge institutes and industry through cross-disciplinary research resulting in both catalytic and chemical engineers. Medium term the activities focus on significantly improved selectivity, and development of new routes to existing products. Long term the aim is to enable a transition to the use of renewable feedstock for bulk chemicals by developing bio-catalytic processes, or hybrids with chemo-catalytic processes. An integral part of the program is the development of innovative enabling tools, such as in-situ monitoring of processes and new reactor concepts.
Industrial partners

Albemarle Catalysts
BASF
Dow Benelux
DSM
ExxonMobil
Johnson Matthey
SABIC
Shell

Patent applications

1. *Process for the conversion of glycerol and catalytically active material suitable therefore*,
   A.M. Ruppert and B.M. Weckhuysen
2. *Production of lower olefins from synthesis gas*,
   H.M. Torres Galvis, J.H. Bitter and K.P. de Jong
3. *Preparation of caprolactone, caprolactam, 2,5-tetrahydrofuran dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from 5-hydroxymethyl-2-furfuraldehyde*, J.G. de Vries, Teddy, P.H. Phua, I.V. Melian Cabrera and H.J. Heeres

Chairs programme committee

Dr T. (Teun) Graafland 2002 - 2004
Dr W. (Wim) Hesselink 2004 - 2012
Dr G.R. (Garry) Meima 2012 - 2012

Project meetings

<table>
<thead>
<tr>
<th>Event</th>
<th>Dates</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASPECT closed meetings</td>
<td>2005 - 2010</td>
<td>9</td>
</tr>
<tr>
<td>TransACTS</td>
<td>2011 - 2012</td>
<td>2</td>
</tr>
<tr>
<td>Final ACTS</td>
<td>2012</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>12</td>
</tr>
</tbody>
</table>
ASPECT Projects
Bifunctional catalytic processing for the production of alkenes? A structured and combinatorial approach

Development of
• solid oxygen sponges for a new cyclic process to produce propylene, a feedstock for the manufacturing of polymers, and;
• an advanced pulse reactor to study transient processes as related to these sponges.
Results
The project focused on the development of solid oxygen reservoirs and an advanced pulse reactor, called TAP (Temporal Analysis of Products). Solid oxygen reservoirs are used to develop a new, more efficient process to produce feedstock for polymerization processes, by dehydrogenation of alkanes to alkenes and hydrogen. This process needs heat input and has a limited conversion due to thermodynamic constraints. These limitations can be overcome by removing the hydrogen through oxidation to water, providing the energy for the reaction and alleviating the conversion limits. For safety reasons the use of pure oxygen is out of the question, and solid oxygen reservoirs are used instead. These materials should have a high oxygen capacity, be used in many oxidation-reduction cycles and only react with hydrogen and not with the hydrocarbons. Several solid oxygen reservoirs have successfully been developed based on doped ceria, that satisfy these requirements. This was enabled by applying combinatorial techniques generating several generations of materials.

An interesting spin-off-project application of the oxygen storage materials as support for hydrogen production catalysts from methane was explored. These results, published in Green Chemistry, were featured in Chemistry World and in New Scientist. The advanced TAP reactor is used to study rate processes of gas-solid reactions with a high time resolution and to study reaction mechanisms of these processes. The developed instrument is a tremendous improvement over existing types, especially with respect to sensitivity, quantification and time resolution. This current type is extremely suited to study the transient interaction between the gaseous reactants and the solid oxygen reservoirs and determining rate constants of these processes. Both the materials development and the kinetic study are part of a follow-up project in optimizing the best solid oxygen reservoirs and the development of a conceptual design of such a new cyclic dehydrogenation process.

Project leader
- Prof. F. (Freek) Kapteijn (TUD)

Co-applicants
- Prof. G. (Gadi) Rothenberg (UvA)

Researchers
- Jorrit Posthuma de Boer (TUD, Postdoc)
- Bart van der Linden (TUD, Technician)
- Jurriaan Beckers (UvA, PhD)
- Paul Collignon (UvA, Technician)

Duration
- 2005-2010

Budget
- k€ 603

Highlights
- Development of high capacity solid oxygen reservoirs through combinatorial optimization.
- Highly selective hydrogen oxidation performance of ceria or lead based solid oxygen sponges.
- A high performance TAP reactor system for transient studies, outperforming existing systems.
- Results featured in in Chemistry World and in New Scientist, see:
  - http://www.rsc.org/chemistryworld/News/2009/April/28040902.asp, and
From liquid biofeed to bulk chemicals:
a rational approach based on liquid-phase in-situ spectroscopy

Glycerol will be one of the main building blocks in future biorefinery operations and novel routes for the catalytic conversion and valorization of glycerol need to be developed. Carefully prepared solid bases are excellent catalysts for making glycerol oligomers, which can be used in the cosmetics, surfactant and pharmaceutical industry.
Results

The conversion of biomass derived feed streams into bulk chemicals has attracted a lot of attention in recent years. Due to the growing production of biodiesel, the supply of its by-product glycerol is also increasing. Conversion of this excess of glycerol is important from an economic and environmental point of view. Among its possible uses, glycerol can be etherified towards di- and tri-glycerol, which have numerous applications e.g. in cosmetic and pharmaceutical industries. Currently in industry this etherification of glycerol is catalyzed by homogeneous (soluble) basic catalysts. It would be more beneficial to use a heterogeneous catalyst, which could be recycled and which application limits the amount of aqueous waste as produced in the current process. This project focused on the development of suitable solid catalysts for the selective etherification of glycerol to di- and tri-glycerol, in combination with the development of in-situ spectroscopy for characterization of heterogeneous catalysts in liquid phase reactions. For a series of alkaline earth metal oxide-based catalysts it was found that glycerol conversion increased with increasing catalyst basicity in the order: MgO < CaO < SrO < BaO. For environmental reasons (due to its much lower toxicity than BaO), CaO was chosen for a more detailed study. As a result, a plausible new reaction mechanism of glycerol etherification was deduced that takes into account not only basicity but also other physicochemical properties of a catalyst. The in-situ spectroscopy work revealed the complexity of the interference of the bulk liquid phase and adsorbates on the catalysts. Both reaction monitoring, as well as study of catalyst-reactant or product interactions were analyzed by ATR spectroscopy. Extension of the spectroscopic work to the conversion of other biomass derived molecules showed the suitability of in-situ liquid phase spectroscopy for the mechanistic investigation of liquid phase catalysts. For example, for lactic acid hydrogenation a clear effect was found of the catalyst support material on activity of ruthenium.

Project leader
- Prof. B.M. (Bert) Weckhuysen (UU)

Co-applicants
- Prof. L. (Leon) Lefferts (UT)
- Prof. G. (Guido) Mul (TUD/UT)

Researchers
- Genevieve Joorst (UU, PhD)
- Agnieszka Ruppert (UU, Postdoc)
- Hans Gelten (UT, PhD)
- Barbara Mojet (UT, Postdoc)
- M. Baca (TUD, Postdoc)
- Jerome Taboada (TUD, Postdoc)

Duration
- 2004-2011

Budget
- k€ 665

Highlights
- A new highly active colloidal CaO catalyst material has been found for glycerol oligomerization.
- The combination of catalyst characterization studies with computational efforts provided much insight into the requirements for this highly active solid base catalyst for glycerol oligomerization.
- Two new spectroscopic cells have been designed and constructed, namely a Raman-ATR-IR cell and a flow-through solid-liquid EXAFS cell.
Process intensification in alkylation processes using zeolite catalysts with molecular traffic control

Fundamental studies to design and use zeolites for alkylation of benzene with propene.
Results
Catalysts are needed to manufacture our daily life products such as medicines, plastics and fuels. Zeolites are an important class of catalysts. Molecular transport in zeolites is key for active, selective and stable catalysts. We have described and facilitated this transport by detailed simulations in combination with experimental research. Also the products obtained contain less of the undesirable by-products thereby reducing energy consumption for purification. Computer simulations were used to explain the formation of these mesopores.

Project leader
• Prof. K.P. (Krijn) de Jong (UU)

Co-applicants
• Dr J.H. (Harry) Bitter (UU)
• Prof. J.P.J.M. (Jan) van der Eerden (UU)
• Prof. T.J.H. (Thijs) Vlugt (TUD)

Researchers
• Adri van Laak (UU, PhD)
• Shuai Ban (UU, PhD)

Duration
• 2005-2011

Budget
• k€ 508

Highlights
• Fundamental insight in transport in and de-alumination of Mordenite.
• Hierarchical zeolites with improved molecular transport properties
• Zeolite Mordenite with excellent properties for alkylation of benzene with propene.
Alkane oxygenation using oxide ion conducting membranes

Selective oxidation of alkanes has been notoriously challenging because the desired products, i.e. olefins and oxygenates, are much more easily activated than alkanes, resulting in low yields due to consecutive reactions. In this project, a novel approach is explored in which oxygen is supplied to the alkane using a mixed-conducting oxygen-permeable ceramic membrane.
Selective oxidation of alkanes is a notorious challenge because alkanes are much more difficult to activate than the desired products as olefins and oxygenates. Therefore, the desired products easily convert to COx, destroying the efficiency of the reaction. The products are essential for efficient and cost-effective production routes of polymers with minimal energy consumption. This project has explored a novel approach, in which oxygen is supplied to the alkane via a mixed-conducting oxygen-permeable ceramic membrane. The result is that alkane is now interacting directly with oxygen anions at the surface of the membrane, rather than with gaseous oxygen molecules.

It was demonstrated that selective oxidation can indeed be achieved in the targeted mode of operation. For viable operation, however, the required temperature is too high, while the design of the catalytic membrane reactor needs serious considerations. As it is now, the ratio between the volume of the reactor and the surface area of the membrane is too low. The work, however, has provided new ideas and strategies to achieve the ultimate objectives of the project. Other accomplishments include successful demonstrations that pulse experiments enable evaluation of the intrinsic catalytic activity and selectivity of lattice oxygen ions, and, using a $^{18}$O-$^{16}$O isotope exchange technique, the rate of oxygen surface exchange of the mixed-conducting oxides.

### Project leader
- Prof. L. (Leon) Lefferts (UT)

### Co-applicants
- Dr H.J.M. (Henny) Bouwmeester (UT)

### Researchers
- Salvatore Crapanzano (UT, PhD)

### Duration
- 2005-2012

### Budget
- k€ 283

### Highlights
- Selective oxidation of alkanes by the controlled supply of lattice oxygen via a mixed-conducting oxygen-permeable membrane.
- Pulse experiments can be used as a tool to reveal the intrinsic catalytic activity and selectivity of lattice oxygen ions.
- Development of a novel pulse $^{18}$O-$^{16}$O isotope exchange technique for rapid evaluation of the surface exchange rate of mixed-conducting oxides.
Spatially and time-resolved in-situ spectroscopy on catalyst extrudates: Understanding the physico-chemical principles of catalyst impregnation and drying

A promising innovative approach to understand how to prepare new catalyst materials is to perform spatially and time resolved spectroscopy. In this work, the possibilities of different space and time resolved spectroscopic techniques during the preparation of Ni and Pd on alumina pellet and extrudate hydrogenation catalysts have been explored.
Results
A large number of industrial catalysts are supported metal (oxide) catalysts that require a high dispersion of the active component and have the shape of bodies such as pellets, spheres or extrudates with sizes from tens of micrometers to millimeters. The classical preparation method of industrial catalysts includes pore volume impregnation and drying followed by a thermal treatment. As a result of the preparation methodology, different macro-distributions of the active species along the catalyst bodies can be obtained which are known as uniform (the active species spread homogeneously within the body), egg-shell (the active component concentrated in the edges of the body), egg-white (the active component is enriched in a concentric ring in the body) and egg-yolk (the active species concentrated in the core of the body). Each of these macro-distributions has its own industrial applications. Consequently, a perfect control of the preparation method is of utmost importance to obtain more efficient catalysts in chemical processes that will assist the improvement of chemical and technological development with the ultimate goal of sustainable development. A promising innovative approach to understand how to prepare new catalyst materials is to perform spatially and time resolved spectroscopy. In this work, the possibilities of different space and time resolved spectroscopic techniques during the preparation of Ni and Pd on alumina pellet and extrudate hydrogenation catalysts have been explored. Moreover, different experimental conditions were tuned in order to investigate their role in the development of the different macro-distributions of the active component. Important findings obtained only thanks to these techniques are that by tuning the solution pH and the concentration of additional Cl- (aq) ions, the macro-distribution of Pd within an alumina pellet can be tuned from egg-shell to egg-yolk. The addition of chelating agents on aqueous Ni(NO₃)₂ solutions favors the formation of Ni egg-shell profiles within an alumina pellet, which are very difficult to obtain. Additionally, the application of other techniques, which are very popular in other research areas, such as MRI or TEDDI, has been investigated and their potential in the field of catalyst preparation has been demonstrated.

Project leader
- Prof. B.M. (Bert) Weckhuysen (UU)

Co-applicants
- Prof. K.P. (Krijn) de Jong (UU)

Researchers
- Leticia Espinosa Alonso (UU, PhD)

Duration
- 2005-2010

Budget
- k€ 274

Highlights
- Invasive (UV-Vis and IR micro-spectroscopy) and non-invasive (MRI and TEDDI) imaging methods have been developed and used to investigate the preparation processes of Ni and Pd on alumina pellet and extrudate hydrogenation catalysts.
- Tuning of the solution pH and the concentration of additional Cl- (aq) ions may alter the macro-distribution of Pd within an alumina pellet from egg-shell to egg-yolk.
- The addition of chelating agents on aqueous Ni(NO₃)₂ solutions favors the formation of Ni egg-shell profiles within an alumina pellet, which are very difficult to obtain.
$\mu$-oxo binuclear catalysts for the production of methanol from methane and oxygen

Opposite influence of cluster size for Co-oxo and Cu-oxo clusters supported on ZSM5 with respect to their selectivity towards methanol from methane and oxygen – larger Co clusters are more selective while smaller (possibly binuclear) Cu clusters are more selective.
**Results**

Selective production of methanol from methane and oxygen is one of the grand challenges in heterogeneous catalysis. In this research we aimed at understanding which factors determine the selectivity towards methanol of metal exchanged zeolites. To gain this insight different Cu-ZSM-5 and Co-ZSM-5 were prepared, characterized and tested for methanol production. It turned out that for Cu-ZSM-5 a quantitative relation exists between the amount of methanol and the concentration of highly dispersed, probably binuclear, Cu clusters inside the zeolite channels. Larger Cu-oxidic cluster, present on the external surface of the zeolite were more selective for the production of formaldehyde.

For Co-ZSM-5 zeolites this was reversed i.e. Co-oxidic species were more selective towards methanol while highly dispersed Co-species were more selective towards formaldehyde. The concentration of the Co-oxidic species on the zeolites could be increased by making zeolites with more space for these species, i.e. by creating mesopores (large cavities) in the zeolitic material. The selectivity towards methanol was increased for these samples.
Spectroscopic control of heterogeneously catalyzed processes

By using a novel combined operando Raman and UV-Vis spectroscopy set-up it was made possible to monitor and control the coke amounts and catalytically active phase for industrially relevant large-scale processes, such as the dehydrogenation of propane and the selective oxidation of butane.
Results
The research goal was to control of heterogeneously catalyzed chemical processes by spectroscopic techniques, from laboratory scale to pilot plants level. Two catalytic systems were studied; i.e., the dehydrogenation of propane and the selective oxidation of n-butane to maleic anhydride. Both reactions were optimized and controlled, by following the coke formation on a CrO$_x$/Al$_2$O$_3$ catalyst in the first case and in the second case, monitoring the transformation of VPO phases. In both cases a combination of Raman and UV-Vis spectroscopy could be used to semi quantify species formed during reaction and correlating this to the catalytic activity. The life of the catalysts and efficacy of the reactions could be improved, by on-line reactor control using these spectroscopic techniques. To up-scale this system and implement this principle to a pilot plant reactor, studies for the design and construction of a new probe were carried out. The initial idea was to insert a probe similar to a thermo well. Raman probes were tested, which are different from UV-Vis probes as a lens is attached to the end of the probe. Furthermore, a set of mirrors was tested to switch between the two spectroscopic techniques. Two different prototypes of probe were designed, which could successfully collect the Raman spectra. Nevertheless due to thermal expansion problems, other methods are required.

Project leader
- Prof. B.M. (Bert) Weckhuysen (UU)

Researchers
- Bastiaan Vogelaar (UU, Postdoc)
- Simona Bennici (UU, Postdoc)
- Maria Arias (UU, Postdoc)

Duration
- 2005-2011

Budget
- k€ 175

Highlights
- Combined UV-Vis/Raman operando spectroscopy allows monitoring on-line in a reactor system the coke amount in an active CrO$_x$/Al$_2$O$_3$ catalyst material. A computer program has been made which allow to automatically regenerate the reactor system once a certain level of coke formation has been reached.

- The same operando set-up has been used to monitor the changes in the vanadium phosphate oxide phase and correlate deactivation of the system with the appearance of a specific catalyst phase.
Simultaneous production of ethylene and synthesis gas combining the oxidative coupling and reforming of methane in a reverse flow membrane reactor with a dual function catalyst

Production of ethylene directly from natural gas: How to integrate exothermic and endothermic reactions on the catalyst particle and reactor scale?
Results
With the inevitable increase of industrial development and growth of global welfare, the demand for industrial chemicals, such as ethylene, will increase while the resources available per capita are decreasing. Anticipating that fossil fuels will remain an important source of primary energy and bulk chemicals, it is essential to search for alternative production methods based on different feedstocks and with significantly enhanced efficiencies.

For ethylene production, a direct method of converting natural gas into higher hydrocarbons is the heterogeneously catalyzed oxidative coupling of methane (OCM), however, only with hydrocarbon yields limited to 30 to 35 per cent despite enormous efforts to optimize the catalysts. By combining OCM with a secondary process, namely steam reforming of methane (SRM), the methane conversion can be increased significantly, while improving temperature control and simultaneously producing valuable synthesis gas.

In this research project, the feasibility of the integration of the exothermic OCM and endothermic SRM reactions into a single catalyst particle or in a single reactor was studied in detail, considering both the catalyst development and reactor development in parallel, and both by experimental and modeling studies.

Project leader
- Prof. M. (Martin) van Sint Annaland (UT)

Co-applicants
- Dr J.G. (Jan) van Ommen (UT)

Researchers
- Patrick Graf (UT, PhD)
- Tymen Tiemersma (UT, PhD)

Duration
- 2004-2011

Budget
- k€ 576
Amines from C4 and C1 feed stocks and ammonia

Catalytic auto tandem reactions for the atom-efficient and selective production of primary amines were investigated by making use of amines and ammonia as cheap and versatile reagents. In the course of these studies also very efficient catalyst recycling by use of ionic liquid two-phase systems was developed.
Results
Amines, especially primary amines are important building blocks in chemical industry for example for the production of polyamides, surfactants, and anti-corrosion agents. Today’s production of amines is often accompanied by large amounts of waste.

The hydroaminomethylation is a waste-free and atom-efficient catalytic reaction, using readily available starting materials (alkenes, synthesis gas (CO/H₂), and ammonia).

In this project new catalysts were developed for this reaction that show very high activity and selectivity to linear amines. It was shown that rhodium as the sole catalyst metal in combination with certain, newly developed ligands, can be highly efficient for all relevant steps in this process (hydroformylation and hydrogenation). It was shown that a protic co-solvent plays an important role for this efficiency.

The catalyst could be easily separated and reused applying the reaction in ionic liquids (ILs). This is very important for process intensification, lowering energy consumption and operating costs. As an important step towards the selective production of primary amines, the concept of using carbon dioxide as a dynamic protective group was introduced.

The further development of this technology will allow the waste-free production of primary amines selectively and without further purification steps needed.

Project leader
- Prof. D. (Dieter) Vogt (TU/e)

Co-applicants
- Dr C. (Christian) Müller (TU/e)

Researchers
- Bart Hamers (TU/e, PhD student)
- Ton Staring (TU/e, Technician)

Duration
- 2005-2009

Budget
- k€ 381

Highlights
- Highly selective Rh-catalyzed auto tandem reaction from alkenes to amines.
- Efficient catalyst recycling in ionic liquids.
- The role of protic co-solvents for the hydrogenation activity of the catalyst was elucidated.
Improving liquid phase reaction in bulk chemical processes by application of micro reaction technology

The research focused on the design of a prototype of a novel, safer reactor cum production way to produce the industrially highly relevant compound ε-caprolactam, based on internal circulation of immiscible liquids in a static micro mixer / micro reactor system, thereby using different temperature zones for mixing and reaction.
Results

The objective of the research was the demonstration of the feasibility of micro technology for a bulk chemical process, i.e. the production of ε-caprolactam, a precursor in the production of nylon-6, via the very fast and strongly exothermic reaction of cyclohexanone oxime with oleum. Main results of the study are given below:

• Because of the very corrosive nature of the reactants the choice of base material for reactors and mixers is important. Best choice proved to be a diamond-like coating on stainless steel;
• Flow patterns and flow regimes were studied using three types of micro mixer. Mixing behaviour was studied in glass micro chips with microscopic fluorescence imaging, using various liquids with viscosities comparable to those of the reactants. These results combined with CFD calculations were used to optimize the most promising type of mixer;
• To improve the radial mass transfer in the viscous liquid in the micro reactor, internal circulation in a two-phase dispersed flow of oleum and inert solvent with dissolved oxime was applied. The needed high interfacial area (up to 20500 m² m⁻³) could so be obtained;
• A conversion of 100 per cent was found at a residence time of four seconds. With the optimized mixer up to 99 per cent selectivity was found at reaction temperatures between 80 and 120 °C and at high oleum-oxime feed ratio;
• Experiments with total recycle and continuous separation of reaction mixture and inert liquid gave selectivity up to 99.5 per cent at an oleum-oxime feed ratio of 2.6. To mimic the industrial process, however, a feed ratio of 1.4 is needed. Selectivity above 99 per cent at 100 per cent conversion could be obtained by performing the mixing at 65 °C and the reaction at 100 – 130 °C. It was possible to increase the oxime concentration in the reactor seven times compared to industrial conditions;
• Finally, a prototype multi channel reactor with integrated heat exchanger was designed and built, in which all micro reaction channels have identical temperature and flow conditions.

Project leader
• Prof. J.C. (Jaap) Schouten (TU/e)

Co-applicants
• Dr M.H.J.M. (Mart) de Croon (TU/e)

Researchers
• Niek Zuidhof (TU/e, PhD)

Duration
• 2004-2009

Budget
• k€ 423

Highlights
Oxi-cracking as a route to olefins – Efficient conversion of alkanes to olefins over nanometer range clusters of non-redox alkaline earth oxide catalysts

Design of efficient mild oxidation heterogeneous catalysts for a new route to controlled production of different olefins which are building blocks for most of the fuels and chemicals available today. This process and catalyst allows to maximize propene which is a premium olefin currently.
Steam cracking, the major, current existing route for light olefin production, is the most energy consuming process in the chemical industry. The need for an energy efficient processes, urged substantial research work for the development of new catalytic technologies. Steam cracking maximizes ethylene formation and propylene is produced only as a secondary product. The faster increase in demand of propylene than that of ethylene makes steam cracking a less attractive route for the production of propylene. The project investigated catalytic pathways for n-hexane cracking, as a model compound of naphtha, in the presence of oxygen. Compared to steam cracking, this work aimed towards achieving:

- lower cracking temperatures making the overall process less energy consuming and;
- higher selectivities to both propylene and butylenes.

The catalyst developed in this project, Li/MgO, has no formal red-ox character and together with its inherent strong Bronsted basicity, minimizes re-adsorption and sequential combustion of formed olefins. The catalyst is promising for the oxidative conversion of low alkanes (ethane, propane and butane) with ~60 mol per cent selectivity to light olefins (C2 = C3 =). In the oxidative cracking of n-hexane, which is representative model for naphtha used in steam cracking, selectivities to C2-C4 olefins (60 mol per cent) just as in the case of lower alkanes are observed. Promotion of Li/MgO with Mo results in significant improvements in both activity and stability of the catalyst because presence of Mo helps to reduce the amount of Li2CO3 on the catalyst.

Finally, oxygen in the feed allows for an auto-thermal operation during oxidative cracking where part of the heat of reaction is provided in situ from combustion of part of the feed, thus reducing the external fuel combustion. It is established from a technical and economic feasibility study that the profitability of the process is dependent on the design of more selective catalysts.

Project leader
- Prof. K. (Kulathuiyer) Seshan (UT)

Co-applicants
- Prof. L. (Leon) Lefferts (UT)

Researchers
- Cassia Boyadjian (UT, PhD)

Duration
- 2005-2011

Budget
- k€ 228

Highlights
- Design and development of efficient catalysts for the oxidative cracking of naptha range hydrocarbons to lower olefins.
- Possibility to control olefin selectivity and achieve higher yields to currently premium olefins such as propylene, butenes rather than ethylene.
- Demonstration of a novel method for activation/cracking of C-C, C-H bonds in hydrocarbons under milder conditions using cold dielectric discharge plasma.
Direct production of lower olefins from synthesis gas using iron based catalysts

The research dealt with the development of a catalyst for a process that transforms alternative feedstocks (coal, natural gas or biomass) to produce major chemical commodities (ethylene, propylene and butylenes) which are traditionally derived from oil.
Results

Lower olefins (ethylene, propylene and butylenes) are key building blocks of the chemical industry which are used for manufacturing a wide range of products from plastics, solvents and fuel additives to pharmaceuticals and cosmetics. Conventionally, lower olefins are derived from naphtha cracking and other petrochemical processes. In view of the need of production processes with reduced carbon footprint, oil availability and the fluctuations on its price and many other strategic reasons, there is a growing interest in processes that allow the production of lower olefins from alternative carbon sources such as coal, natural gas or biomass. The main goal of this project was to develop a catalyst that would allow the conversion of synthesis gas, a mixture of CO and H₂ that can be produced from any carbon source, into lower olefins in a process without intermediate steps. Catalysts that fulfill this goal have been synthesized in the past but they have not been used industrially due to their low chemical and mechanical stability under the severe reaction conditions required for this process (high temperatures and CO-rich feed gas). The strategy to develop an improved catalyst was to provide a good mechanical stability by using a support material to disperse iron-containing nanoparticles which are ultimately transformed into the active phase for the reaction. During the research it was found that several factors influence the catalytic performance and that they have to be taken into account while developing a selective, active and stable catalyst: the preparation method and the precursors used thereof, the nature of the support material, the size of the iron-containing nanoparticles and the modification of the catalyst properties by addition of promoters. Additionally, it was found that not only the catalyst properties have to be optimized but also that conditions used during Fischer-Tropsch reaction play a major role on determining the industrial life and the performance of the catalyst.

Project leader
• Prof. K.P. (Krijn) de Jong (UU)

Researchers
• Hirsa Torres Galvis (UU, PhD)
• Ad Mens (UU, Technician)

Duration
• 2007 - 2012

Budget
• k€ 354

Highlights
• Patent application on a catalyst for the selective production of lower olefins from synthesis gas; license agreement in place.
• Results published in top scientific journals (Angew. Chem, Science, etc.).
• Follow-up project (TASC proposal submitted).
Towards catalyst diagnostics and on-line reactor control via in-situ UV-Vis/Raman spectroscopy: Proto-type development and implementation in industrial dehydrogenation, alkylation and hydrotreating pilot-scale reactors

Designing, constructing and testing of an operando spectroscopic device inserted in a pilot reactor in order to study in detail large-scale catalytic processes, such as the dehydrogenation of propane.
Results
Large-scale industrial reactors are employed in a wide variety of companies to produce bulk chemicals. Optimal reaction conditions are achieved by analyzing the product stream from the reactor and changing the conditions accordingly. A more sophisticated method would be to directly study the inside of the reactor by in-situ spectroscopic techniques. The goal of this research was to develop a novel combined Raman and UV-Vis probe to study the deactivation of a commercial \( \text{CrO}_x/\text{Al}_2\text{O}_3 \) catalyst material used for propane dehydrogenation in a pilot plant reactor set-up. Coke deposition is a major problem when using this kind of system and it would be advantageous to study this process. For this a pilot plant set-up was designed, which has a set of UV-Vis probes inserted along the reactors length. The initial experiments with conventional high temperature probes failed, as coke was deposited on the tips of the probes, which made it impossible to study the catalyst materials. The high temperatures of the reaction, especially during the combustion of the carbon deposits, would damage the probe. Furthermore, these probes proved to be unsuitable for Raman spectroscopy, as too much signal was lost. To counter these problems, a novel probe was designed, which had a flow of nitrogen running through the probe, cooling it and keeping the tip free from any coke deposits. This system proved to be effective, as we were able to successfully study the formation of carbon deposits on the catalyst inside the pilot plant. We found that coke deposition is non-homogeneously spread across the reactor: at the top coke is deposited at a higher rate, and larger amounts of coke are detected.

Project leader
- Prof. B.M. (Bert) Weckhuysen (UU)

Researchers
- Maria Arias (UU, Postdoc)
- Jesper Sättler (UU, PhD)

Duration
- 2007-2012

Budget
- k€ 313

Highlights
- The deactivation of a commercial \( \text{CrO}_x/\text{Al}_2\text{O}_3 \) propane dehydrogenation catalyst material has been investigated by operando UV-Vis spectroscopy in a pilot plant reactor set-up.
- Zoning of coke deposits across the reactor bed has been observed, which goes hand in hand with temperature gradients and propene yields.
Amino acids to chemical products for the chemical and plastics industries

There is growing awareness for the need to produce chemicals, materials and fuels from renewable, non-fossil resources. While others have focused on more established carbohydrate based routes, here we use non-conventional protein rest streams in a holistic approach to the production of chemicals.
Results
The chemical industry is in transition from a petrochemical based towards a more biobased industry. Large scale production of biobased chemicals is becoming reality, as is shown by Solvay’s plant for the production of epichlorohydrin from glycerol that is in operation since 2007. Apart from this example, the current worldwide research effort in the search for biobased chemicals is enormous. Most of this research focuses on the use of carbohydrates, but the proteins that are left in the byproducts from bioethanol and biodiesel production could also be valuable building blocks for chemicals. Especially the non-essential amino acids in these proteins, which have no significant value for food or feed, can be interesting starting materials for a variety of nitrogen-containing products. The most abundant (and non-essential) amino acid in many plant proteins is glutamic acid. This project focused on finding new, catalytic and sustainable routes from glutamic acid to industrial chemicals. The goal was to create the possibility to replace oil by glutamic acid as the feedstock for these chemicals. The application of glutamic acid as a feedstock would be especially valuable for chemicals that contain nitrogen, because the introduction of nitrogen into molecules is very energy-intensive, while glutamic acid already contains nitrogen. Therefore the chosen targets were N-methylpyrrolidone (NMP), N-vinylpyrrolidone (NVP), 1,4-diaminobutane and acrylonitrile. In order to be able to achieve synthesis the areas of catalytic decarboxylation, oxidative decarboxylation, decarbonylation-elimination, methylation and water transfer were developed. Allied to this it was found that the decarbonylation-elimination reaction could also be applied to fatty acids to form 1-alkenes with high conversion and very high selectivity. During the research a techno-economic feasibility and life cycle assessment were carried out. It was found that certain routes showed attractive results compared to conventional routes. However, in some cases bottlenecks were identified. This has spurred us on to carry out more research in these defined areas and currently this looks very promising.
Results

The selective oxidation of hydrocarbons is of vital importance for the production of valuable chemicals from crude oil and natural gas resources. Unfortunately, this class of chemical reactions offers tremendous difficulties. This arises from the fact that in any reaction of hydrocarbons and oxygen, the formation of the total combustion products carbon dioxide and water is the most favorable. This project aimed to contribute to the development and fundamental understanding of novel, more efficient, selective alkane oxidation routes, using molecular oxygen. The research involved can be organized in three interconnected parts.

• In a first part the potential of gold-based catalysts for the selective production of hydrogen for fuel cell application by partial oxidation has been explored. Promotion of the gold-based catalysts with alkaline earth and lanthanum oxides resulted in a significant improvement of the catalyst performance. A detailed in-situ characterization of the gold catalysts ‘at work’ revealed that the described promotion effect results from the stabilization of metallic gold atoms in the oxygen atmosphere.

• In a second part, the applicability of gold catalysts for the selective oxidation of cyclohexane and methane has been investigated. The oxidation of cyclohexane is practised on commercial scale in the production of nylon, and suffers from very low efficiency. Selective oxidation of methane to methanol would offer a possibility for exploiting vast
natural gas reserves that are nowadays unused. A considerable number of research papers have already reported on the promising properties of gold catalysts for the selective oxidation of cyclohexane. In contrast with literature results, the gold catalysts did not establish any improvement as compared to the commercial cyclohexane autoxidation process. This strong deviation from the literature results was explained by the inadequate experimental procedures as were employed in the particular research articles. Also in the case of partial methane oxidation, no indication of selective C-H bond activation by the gold catalysts was found.

The last part of the research aimed to find a solution for the low efficiency of commercial cyclohexane oxidation. A novel catalytic process has been developed, according to which the yield of valuable cyclic molecules from cyclohexane oxidation can potentially be doubled. Cyclohexyl hydroperoxide, formed by the autoxidation of cyclohexane with molecular oxygen, was used to selectively epoxidize cyclohexene and cyclododecene over mesoporous titanium-silicates. Under optimized conditions, a selectivity of 170 per cent based on peroxide conversion was obtained, which yields a large improvement when compared to the ~ 90 per cent selectivity obtained in the commercially applied deperoxidation process. The catalysts showed a stable performance over four subsequent reaction cycles.

Finally, a mechanistic study into the epoxidation reaction is described. Different reactions, namely epoxidation, deperoxidation and allylic oxidation were identified and found to compete. In all three reactions the role of radical species was confirmed. Possible side reactions in cyclohexene epoxidation, like hydrolysis and isomerisation of the epoxide, were found to be negligible. The participation of molecular oxygen was investigated, and found to play a major role in the observed solvent oxidation and the direct allylic oxidation. Eventually the formation of titanium-hydroperoxo groups as the active intermediate species was confirmed.

Project leader
- Prof. B.M. (Bert) Weckhuysen (UU)

Researchers
- Bart Hereijgers (UU, PhD)

Duration
- 2007-2012

Budget
- k€ 321

Highlights
- Promotion of gold-based catalysts with lanthanum oxide leads to a significant improvement in the selective production of hydrogen for fuel cell application by the partial oxidation of methanol.
- Literature results on the selective oxidation of cyclohexane with oxygen making use of gold-based catalysts could not be reproduced. This discrepancy could be explained by the inadequate experimental procedures as were employed in the particular research articles. Furthermore, supported gold catalysts are also not able to activate methane in the presence of molecular oxygen.
- A novel catalytic process has been developed, according to which the yield of valuable cyclic molecules from cyclohexane oxidation can potentially be doubled. Cyclohexyl hydroperoxide, formed by the autoxidation of cyclohexane with molecular oxygen, was used to selectively epoxidize cyclohexene and cyclododecene over mesoporous titanium-silicates.
Crude glycerol and sucrose, renewable feedstock for the sustainable production of novel bulk chemicals

Two complementary catalytic routes have been developed to convert various renewable building blocks, including crude glycerol, a biodiesel waste product, into valuable bulk chemicals that can be used in surfactant, polymer and cosmetics applications.
Results
The production of bulk chemicals from renewable resources can greatly contribute to the transition to a more sustainable society. In this project, the aim was to develop new catalytic technology for the production of renewable-based chemicals. Crude glycerol, available as byproduct of the biodiesel industry, was initially identified as a highly attractive, yet challenging renewable building block for the production of such renewable bulk chemicals. Two routes, each requiring the development of different catalysts, were selected for the conversion of glycerol and other renewable substrates. The solid acid-catalyzed etherification of glycerol proved possible using selected zeolite solid acids, H-Beta in particular, in high selectivity, but limited yields using pure glycerol. Other alcohols, for example 1,2-propanediol, also showed excellent selectivity now combined with much better activity. A detailed micro-spectroscopic study on large H-Beta zeolite crystals provided key insights into the spatial interaction with the two reagents in the etherification reaction and rationalized the observed differences in activity. Crude glycerol could not be converted via the solid acid-catalyzed etherification route, but the alternative Pd-catalyzed telomerization reaction proved very well capable of this. A catalyst screening study identified a particular Pd/phosphine combination as a highly active and selective catalyst for glycerol telomerization. Further studies showed that not only glycerol, but various polyols and sugars could be used as renewable substrates. Detailed mechanistic studies provided insight into the intricacies of the reaction, highlighting the importance of alternative reaction pathways available to the phosphine ligand and giving access to a facile preparation route for the key intermediate in the catalytic cycle, greatly facilitating mechanistic studies. Two routes were developed for the heterogenization of the homogeneous Pd/phosphine catalyst, with immobilization of the catalyst on a basic support resulting in a shift in selectivity of the process allowing different products to be obtained.

Project leader
- Prof. B.M. (Bert) Weckhuysen (UU)

Co-applicants
- Prof. R.J.M. (Bert) Klein Gebbink (UU)

Researchers
- Peter Hausoul (UU, PhD)
- Ilenia Nieddu (UU, Postdoc)
- Kees Kruithof (UU, Postdoc)
- Andrei Parvulescu (UU, Postdoc)

Duration
- 2007-2012

Budget
- € 459

Highlights
- The first report of the telomerization of actual, crude glycerol an unrefined byproduct of the biodiesel industry.
- Elucidation, based on synthetic organometallic chemistry as well as a detailed micro-spectroscopic characterization approach, of the mechanistic intricacies and deactivation modes in two catalytic routes, namely telomerization and etherification.
Conversion of C6-sugars to green polymer precursors

From biomass to green nylon; synthesis of caprolactam, an important bulk chemical for nylon production, from biobased hydroxymethylfurfural using catalytic hydrogenation/ringopening approaches.

> Results

Lignocellulosic biomass is a very promising feedstock for the production of biobased chemicals. The C6-sugars (e.g. D-glucose, D-fructose and D-mannose) in lignocellulosic biomass like wood chips and agricultural residues (e.g. straw, corn stover) as well as paper pulp waste are interesting precursors for a broad range of chemicals with high application potential. Apart from fermentation to bioethanol and reforming to CO/H2 the direct conversion of these sugars to useful platform chemicals is highly attractive. Examples of such chemicals are levulinic acid and 5-hydroxymethylfurfural (HMF). HMF can be prepared in high yield from D-fructose, although research is underway to convert D-glucose or even cellulose directly into HMF. It can be converted into a range of derivatives with potential applications as a biofuel (furanics) and as building blocks for the polymer and solvent industry.

We have performed research activities on the conversion of HMF to caprolactam, the monomer for nylon-6, a widely used synthetic polymer with a production of about 4 million tons annually. The reaction scheme for the conversion of HMF into caprolactam, via 1,6-hexanediol (1,6-HD), is shown in eq 1.
A major breakthrough, that was needed in this research is the conversion of HMF to 1,6-hexanediol. For the feasibility of a bulk chemical process, it is absolutely essential that all conversions proceed with a selectivity in excess of 90 per cent, preferable even higher. High conversion is desirable, but not a prerequisite and indeed many bulk processes, in particular oxidations, are run at very low conversions in order to maintain a high selectivity.

A two step route was developed from HMF to 1,6-HD (eq 2). It turned out that it is essential to perform the reaction with THF-dimethanol (THFDM) instead of HMF to achieve good chemo-selectivity. THFDM was prepared in high yields from HMF using a standard heterogeneous hydrogenation reaction (eq 2). The hydrogenation of THFDM using a bimetallic Rh-Re/SiO₂ catalyst in the presence of a solid acid catalyst (Nafion SAC-13) gave full conversion after 20 h with a very promising selectivity to 1,6-HD of 86 per cent. Other solid acids showed similar activities but led to slightly lower selectivities.

The subsequent dehydrogenation of 1,6-HD to caprolactone (eq 1) was performed using homogeneous ruthenium catalysts and gave the lactone in >99 per cent yield at mild conditions. The conversion of the caprolactone into caprolactam via reaction with ammonia is well established and has already been used on production scale.

In conclusion, we have identified a pathway that allows the conversion of HMF, which can be obtained from renewable resources like D-fructose, into caprolactone with very good overall selectivity. Using the one-pot conversion of THFDM to 1,6-HD, we can now convert HMF to caprolactam in only four steps, whereas the current caprolactam process needs six steps from benzene and ammonia.

---

**Project leader**
- Prof. H.J. (Erik) Heeres (RUG)

**Co-applicants**
- Dr I.V. (Ignacio) Melián Cabrera (RUG)
- Prof. J.G. (Hans) de Vries (RUG)

**Researchers**
- Sebastien Noel (RUG, Postdoc)
- Pim-Huat Phua (RUG, Postdoc)
- Teddy (RUG, PhD)

**Duration**
- 2007-2012

**Budget**
- k€ 454

**Highlights**
- Patent application: NWO-ACTS, Teddy Buntara, Pim Huat Phua, Ignacio Melián-Cabrera, Johannes G. de Vries, Hero J. Heeres; Preparation of caprolactone, caprolactam, 2,5-tetrahydrofuram-dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from 5-hydroxymethyl-2-furfuraldehyde; WO 2011149339(A1), 12-01-2011.
- Teddy Buntara, Sebastien Noel, Pim Huat Phua, Ignacio Melián-Cabrera, Johannes G. de Vries, Hero J. Heeres; From 5-hydroxymethylfurfural to polymer precursors: catalyst screening studies on the conversion of 1,2,6-hexanetriol to 1,6-hexanediol; Top. Cat. 2012, 55, 612.
Defect densities all at once

We have designed and characterized a new research tool that enables us to study chemical reactions at the 'hot spots' of catalytic surfaces.
**Results**

In Defect densities all at once, we have successfully pursued to develop a new technology to study the influence of defects on catalytic reactions. We can now quickly scan for the structure of surface atoms that facilitates the dissociation of small molecules impinging onto a clean metal from the gas phase. In contrary to most research being performed in this field we did not use flat single crystals as a model for a catalytic surface, but a large cylindrically shaped single crystal ring. We have shown that this change of crystal form allows us to vary defect type and defect density smoothly and have observed effects in hydrogen dissociation and recombination from such defective surfaces.

**Project leader**
- Dr. L.B.F. (Ludo) Juurlink (UL)

**Researchers**
- Otto Berg (UL, Postdoc)
- Irene Groot (UL, PhD)
- Ying Liu (UL, Postdoc)
- Klaas-Jan Schouten (UL, Technician)
- Junjun Shan (UL, Postdoc)

**Duration**
- 2007-2011

**Budget**
- € 227

**Highlights**

- First publication on using MCP LEED analysis to determining surface local structure on cylindrical single crystals; R.V. Mom, C. Hahn, L. Jacobse, and L.B.F. Juurlink, LEED Analysis of a nickel cylindrical single crystal (submitted).

Sustainable atom-efficient routes to large-scale industrial chemicals

Attempts have been undertaken to develop a catalyst for a new atom-efficient reaction to N-alkylamides, which in the future may be applied to replace industrial processes based on classical chemistry.
Results
We have studied the development of catalysts for a novel catalytic route for the synthesis of primary alkylamides. This is a class of compounds that may form important intermediates for alkylamines, but this route may also be of high importance for the development of a sustainable production of the nylon precursor caprolactam. The present process to this nylon precursor involves stoichiometric reactions by which large amounts of byproducts are formed. Worldwide approximately six million tonnes of caprolactam is produced per year.
The novel route uses simple feedstock carbon monoxide, hydrogen gas, an alkene and an amide. The catalyst activates these reactants in a single reactor and binds them together to form the desired product, preferentially without any side-products being formed. We have indeed developed a catalyst that can selectively perform this desired reaction. The desired alkylamides were formed in good yield and selectivity, and we have given proof-of-principle of the conversion of such an alkylamide to the corresponding alkylamine.
If the catalyst can be developed in such a way that it can perform the reaction with higher efficiency and with a longer life-time, the nylon precursor caprolactam in the future may be produced in a two-step process without the concurrent formation of by-products. In the long term it is our goal to apply this new chemistry using biomass as feedstock for the production of ‘green’ nylon.

Project leader
• Prof. E. (Lies) Bouwman (UL)

Co-applicants
• Prof. E. (Eite) Drent (UL)

Researchers
• Susmit Basu (UL, Postdoc)

Duration
• 2007-2009

Budget
• k€ 203

Highlights
• The reaction appeared to be too complicated to be completely solved in this two-year research. With a new PhD student (Catchbio) it has taken another three years to reach complete insight in the complicated and challenging cascade reaction. Now a patent will be filed and then we can start publishing the results.
Bulk Chemicals from glycerol; the development of selective oxidation and hydrogenolysis pathways

Innovative methods have been developed for the heterogeneously catalysed conversion of glycerol, a byproduct of the biodiesel industry, into (racemic) lactic acid, an important platform chemical. The processes developed result in higher space-time-yields than fermentative processes. Pt and Au based catalysts show highest selectivity. Racemic lactic acid is an attractive building block for acrylic acid synthesis, the synthesis of lactic acid based solvent and resins and potentially even high molecular weight polymers.
Results

The production of biodiesel via the triglyceride transesterification process results in the formation of approximately 10 per cent of glycerol as a byproduct. In order to make the overall biodiesel production more economically viable, it is necessary to develop new added value outlets for glycerol. In this project scientific insight and improved catalytic technology has been generated for important glycerol transformations such as hydrogenolysis and oxidation. Hydrogenolysis of glycerol is known to give access to 1,2-propanediol and potentially 1,3-propanediol; both important building blocks for polymers. Selective oxidation of glycerol may result in dihydroxyacetone (fine chemical) or glyceric acid; a potential comonomer in polymers and intermediate in acrylic acid production. The team at TU Delft has explored catalytic hydrogenolysis technology. A review paper on glycerol and polyol hydrogenolysis (dehydroxylation) has been published. Using a D-optimal design, screening of a series of catalysts showed Pt/CaCO3 to be highly selective catalyst for conversion of glycerol into 1,2-propanediol. Interestingly, by addition of boric acid to the system at high pH, the selectivity is changed to lactic acid formation, even under strongly reducing conditions.

The team working at Wageningen and Groningen has explored catalytic oxidation technology. Monometallic and bimetallic catalyst systems were developed with increased selectivity towards methylglycerate oxidation in methanolic solution. Catalytic technology was developed to convert glycerol with high selectivity into lactic acid(esters). Both teams herewith have generated important scientific knowledge for the heterogeneously catalysed conversion of glycerol into lactic acid, an important platform chemical.

Project leader
- Dr J. (Jacco) van Haveren (WUR)

Co-applicants
- K. (Kristina) Djanashvili (TUD)
- Dr U. (Ulf) Hanefeld (TUD)
- Prof. H.J. (Erik) Heeres (RUG)
- Prof. F. (Freek) Kapteijn (TUD)
- Dr I.V. (Ignacio) Melian Cabrera (RUG)
- Dr A.J.J. (Adrie) Straathof (TUD)

Researchers
- Jeroen ten Dam (TUD, PhD)
- Rajeesh Pazhavelikkakath Purushothaman (RUG, PhD)

Duration
- 2007-2012

Budget
- k€ 563

Highlights
- High selectivity of heterogeneously catalysed glycerol conversion towards lactic acid under more moderate conditions than previously reported.
- Improved mechanistic insight in glycerol hydrogenolysis and oxidation pathways.
- Direct synthesis of lactate esters from glycerol at moderate conditions.
Oxidative dehydrogenation with $\text{CO}_2$ as a soft oxidant

The use of $\text{CO}_2$ as soft oxidant is a possible alternative to increase catalyst lifetime and selectivity of oxidation reactions. Dedicated catalyst design is required to optimally benefit from the effect of added $\text{CO}_2$ in the reaction of ethylbenzene to styrene – a building block for plastics and polymers.
Results

Styrene is a building block commonly used to produce polymers such as polystyrene. Styrene is industrially made via the dehydrogenation of ethylbenzene (EB). In this process steam is used as an oxidant to prevent catalyst deactivation via coke deposition. However, the use of steam is extremely energy consuming, and several research groups are searching for a better alternative. It has been suggested that CO₂ is a promising soft oxidant that should be able to replace steam in the EB dehydrogenation. The main goal of the project is the understanding of structure-activity relationship for oxide catalysts in oxidative dehydrogenation of ethylbenzene (EB) using CO₂ as a soft oxidant.

Different types of oxide materials, ZrO₂, TiO₂, and CeO₂, were applied in the reaction with and without CO₂. It was found that all oxides show severe coking during the reaction which resulted in deactivation of the catalysts. The addition of CO₂ showed the largest effect on ZrO₂, mainly resulting in slower deactivation and higher selectivity to the desired product styrene. Further, the effect of different ceria shapes (cubes, wires, particles) on the reaction was studied. In recent years ceria nano particles with a specific geometry attracted considerable attention due to their unique oxygen storage capacity, i.e. the ability of the material to reversibly store and release oxygen depending on the reaction environment. We found a pronounced effect of CO₂ addition for ceria cubes, positively affecting the EB conversion. Moreover, the calcination temperature of the ceria cubes also influenced the EB conversion.

The exact role of CO₂ in the EB dehydrogenation reaction turned out to be very complex, because CO₂ can react directly with the catalyst as well as with the produced hydrogen from the dehydrogenation reaction via a consecutive reaction. This project has shown that use of CO₂ as a replacement for steam in the ethylbenzene dehydrogenation requires dedicated catalyst design.
Oxidative dehydrogenation of propane using doped ceria redox catalysts

How do you oxidise selectively hydrogen out of a mixture of cooking gas without burning all your starting material to CO$_2$? The trick is in the lead. Far from its “heavy metal” image, lead chromate is the best solid oxygen reservoir for this reaction.
Results
The motivation for this project was a follow-up on the discovery of the doped ceria catalysts in a previous ASPECT project. Our objective was to see whether we could optimize these and design an efficient oxidative dehydrogenation process from propane to propene using such solid oxygen carriers. The main challenge was finding a solid oxygen carrier that is both active (has enough available oxygen), selective (burns only hydrogen, rather than propane and propene) and gives an overall exothermic reaction that can balance the endothermic dehydrogenation step. On paper, this is easy. In practice, we screened over 120 materials before we found that lead chromate, PbCrO₄, is a suitable solid oxygen carrier (SOC). In the current project, we focused on the thermochemical redox behaviour of PbCrO₄. We found that under oxidative dehydrogenation conditions it transforms into Pb₂(CrO₄)O, a stable and efficient solid oxygen reservoir for selective hydrogen combustion. Following these findings, the teams in Amsterdam and Delft drew up a comprehensive kinetic scheme for the dehydrogenation reaction. Based on the understanding of the dehydrogenation and oxidative dehydrogenation cycles, we then compiled a conceptual process design for building a 300,000 tpa plant for manufacturing propene from propane.

Project leader
• Prof. G. (Gadi) Rothenberg (UvA)

Co-applicants
• Prof. F. (Freek) Kapteijn (TUD)
• Dr M. (Michiel) Makkee (TUD)

Researchers
• Santiago Gomez Quero (UvA, Postdoc)
• Raza-e-mustafa Shah (TUD, PhD)

Duration
• 2010-2012

Budget
• k€ 229

Highlights
• Understanding the redox behaviour of PbCrO₄. In our previous ASPECT project, leading to this one, we found that PbCrO₄ was the most promising selective hydrogen combustion material for propane oxidative dehydrogenation. We now demonstrate for the first time that PbCrO₄ transforms into Pb₂(CrO₄)O under the reaction conditions, and show the potential of Pb₂(CrO₄)O as a solid oxygen reservoir for the oxidative dehydrogenation of alkanes; especially at T ≥ 773 K, where H₂ oxidation by Pb₂(CrO₄)O is exothermic.

• Conceptual process design of propane oxidative dehydrogenation. A complete conceptual design was developed by Raza-e-mustafa Shah at the TU Delft based on the PbCrO₄ results and further kinetic studies at the UvA. This design can now be used for further process development.

• A comprehensive kinetic study was done, gaining insight into the mechanism of Propane Dehydrogenation over Pt-Sn/Al₂O₃.

• Several lectures and posters.
Real-time three-dimensional imaging of a single catalyst extrudate in action: Probing hydrogenation reactions over Ni-, Pt- and Pd-based catalysts under true reaction conditions

Two spatiotemporal characterization methods, namely X-ray diffraction computer tomography and diagonal offset Raman Spectroscopy, have been developed and explored to shed new insight in the synthesis and catalysis of metal oxide-based Al₂O₃ catalyst bodies at the single particle level.
Catalytic solids are the workhorses of the chemical industries with most bulk chemicals coming into contact with at least one heterogeneous catalyst during their manufacturing process. They are often multi-component, high-surface-area materials, possessing different potential active sites in their structure. Practical heterogeneous catalysts are usually employed in millimeter (mm)-sized pre-shaped forms (e.g. cylindrical pellets) more generally known as catalyst bodies. If one wants to really understand the catalytic chemistry within these catalyst bodies, non-invasive spatiotemporal in situ methods have to be developed, so to provide detailed 3-D information on the active phases as well as potential reaction and deactivation pathways.

This project has focused on the development of two methods for studying catalysts in action: X-ray diffraction computer tomography (XRD-CT) and Diagonal offset Raman Spectroscopy (DORS). The former has been developed as a method to study catalyst preparation and reaction yielding to date 2-D diffraction information during calcination of a Ni/γ-Al₂O₃ and during the methanation of CO. The XRD-CT data revealed that although heat treatment of the catalyst body results in the formation of metallic fcc Ni, the properties of the Ni particles varies in 2-D space. The origin of this variation can be traced back to the solid-state changes of the Ni precursors in the heat induced evolution process. Perhaps the drawback of the technique is that it is predominantly sensitive to the presence of crystalline material. However, it is technically straightforward enough to be combined with conventional μ-absorption-CT in order to correlate the presence of diffracting material with the elemental contrast information.

This combination was used to follow in another ‘experimental first’ the behavior of a Ni/γ-Al₂O₃ catalyst body during CO methanation under operando conditions, revealing the active phase to be the fcc Ni metal phase that remains stable throughout the duration of the catalytic studies. The DORS technique meanwhile has been used to study the catalyst preparation process and in particular for the real time study of the evolving chemistry of Mo species within catalyst bodies during their impregnation onto a porous γ-Al₂O₃ support. The DORS method is able to differentiate between surface, sub-surface and bulk information from the catalyst body and to thereby differentiate between the chemistry evolving on a spatial basis and is particularly powerful at determining the cause/origin of active phase inhomogeneity.
Sustainable catalytic production of novel polyglycols from renewable resources

Polyglycols are polymers that are used in numerous applications. These polyglycols can be produced sustainably from renewable resources such as biomass, but the production process itself still requires improvement. This project has developed new catalyst technology to produce polyglycols in an efficient and sustainable way.
Results

We encounter polymers in almost every aspect of our daily life, from the fibers in the cloth we wear to all the different kinds of plastics around us. Many of these polymer end products contain polyglycols, which are produced in very large amounts by the chemical industry. Currently, most polyglycols are ultimately derived from crude oil and are synthesized via routes that come with environmental and safety issues. Alternative polyglycol production routes, based on renewable sources such as non-edible biomass, are therefore highly desired. Recently, such renewably polyglycols have come on the market, but improvements are still needed to make their production process green and sustainable. These renewable polyglycols are made from glycols such as 1,3-propanediol using the strong acid sulfuric acid as a catalyst. Replacing this corrosive, soluble acid sulfuric acid with a solid acid catalyst would reduce the waste produced, enable reusability of the catalyst and simplify product purification. The development of such a solid acid catalyst comes with considerable challenges with regards to activity and stability. Stability is of primary concern the solid catalyst is subjected to demanding conditions, being run at elevated temperatures in a highly polar liquid phase. Loss of the active acid sites is the major concern here. Several different classes of solid acid catalysts were tested for polyglycols synthesis from various glycols. Stability proved insufficient for most of the tested catalyst, but good results were obtained with an acidic resin. In addition to loss of active acid sites, which expectedly occurred for some of the catalysts, coating of the catalyst surface with the product resulting in a loss of activity, also occurred. Unexpectedly, some catalyst known for their stability highly polar media, completely disintegrated and were lost by dissolution to the liquid phase. The acidic resins, however, showed promise as a substitute for sulfuric acid, as good catalytic activity and limited loss of acid sites was observed.

Project leader
- Prof. B.M. (Bert) Weckhuysen (UU)

Co-applicants
- Dr P.C.A. (Pieter) Bruijnincx (UU)

Researchers
- Andrei-Nicolae Pârvulescu (UU, Postdoc)
- Qingqing Wang (UU, Postdoc)

Duration
- 2010-2012

Budget
- k€ 247

Highlights
- Acidic resins show good promise as recyclable, heterogeneous polymerization catalysts for the production of polyglycols as alternatives to sulfuric acid.
Spatiotemporal spectroscopic studies on the deactivation of catalytic solids by poisoning

A novel toolbox of spatiotemporal characterization methods has been developed and explored to shed new insight in the deactivation phenomena of two industrially important catalyst materials at the single particle level.
Catalyst deactivation phenomena are important in bulk chemicals industries where understanding and improving catalyst lifetime is crucial in ensuring an economically attractive process. Obtaining insight into such processes is the first stage in developing more resistant catalysts although this requires a thorough characterization of the catalyst in its real form. The project aim was to develop spatiotemporal characterization techniques for studying both single micrometre-sized fluid catalytic cracking (FCC) and millimetre-sized methanol synthesis (Cu/Zn/Al₂O₃) catalyst bodies as an example.

One of the first challenges was the visualisation of the active sites in a catalyst. An approach to do this was through ‘selective staining’ to visualize with fluorescence microscopy the Brønsted acidity in the zeolite particles in the FCC catalysts, to map the distribution of the zeolite at the single particle level. In this case the selective staining agents comprised either thiophene or 4-fluorostyrene oligomerised using a combination of temperature and Brønsted acidity. Confirmation of the structural organisation with acidity was obtained from a subsequent combined integrated laser and electron microscope (iLEM) approach thereby allow for the correlating of fluorescence intensity to structural organization. Recently, results have been obtained using combined XRF, XANES and XRD-CT imaging of the distribution and effects of Ni/V poisons on the structure of FCC particles. It is anticipated that the approaches serve as a powerful toolbox in the effort to develop enhanced laboratory deactivation procedures that more closely simulate commercial practice.

The study and characterisation of sulphur poisoning of the much larger 5 mm CuZn/Al₂O₃ pellets has been performed using X-ray diffraction computer tomography (XRD-CT). The study revealed a preferential put down of sulphur at the periphery of the pellet with ZnO acting as a scrubber for the H–2SH–2S in the system through the formation of ZnS/CuS species. It appeared that changes suggest deactivation via crystalline phase transformation instead of site blocking. The second tranche of the project focused on developing novel analytical methods for interrogating poisoned samples. The methods combine pencil beam XAFS and XRD imaging for mapping of pre-sliced poisoned samples to obtain chemical bond contrast over the sample. Recently, the activation and deactivation of the pellets for methanol synthesis has been enabled through the development of operando high pressure XRD-CT.
Primary amines from C4-feed stocks - hydroaminomethylation with ammonium carbamate

Catalytic auto tandem reactions for the atom-efficient and selective production of primary amines were investigated making use of ammonia and ammonium carbamate as cheap and versatile reagents. In the course of these studies also very efficient and selective one pot cascade reactions from alkenes to highly linear acetals and alcohols were found.
Results
The goal of the project was the development and implementation of the hydroaminomethylation (HAM) reaction for the functionalization of C4 feedstocks to primary amines. In this context, the functionalization of butadiene using ammonia, carbon monoxide (C1 feedstock) and hydrogen towards the linear primary amine 1,6-hexamethylenediamine is of very high interest. For the development of suitable hydroaminomethylation reactions for the production of primary amines from C4 feedstocks using ammonia, a complex web of reactions and coupled equilibria have to be faced.

While studying the mechanism and particularly the role of the necessary alcohol solvent, other reactions were discovered, forming either acetals or alcohols in very good chemo- and regioselectivities. The feasibility of the hydroaminomethylation reaction of 1-alkenes with ammonia was investigated. It was more complicated than with amines and a co-catalyst had to be used. Satisfying amine selectivities of up to 87 per cent could be obtained. However, the selectivity towards the primary amines was moderate with up to 38 per cent. Full conversion was achieved using ammoniumcarbamate. However, the selectivity to primary amines remained low.

We could now show that hydroformylation of alkenes under aqueous conditions leads to the formation of alcohols in high selectivity. The aldehydes are formed as real intermediates in this case. Furthermore, the alcohols are formed in high linearity applying Xantphos as the ligand (Figure 1).

Figure 1. Hydroformylation-hydrogenation tandem reaction to highly linear alcohols
In alcohol solvents and with [Rh(cod)2]BF4 as catalyst precursor the corresponding acetals are formed in selectivities up to 99 per cent and with very high linearity (l/b up to 52).

Figure 2. Rh-catalyzed acetal formation
It was shown that the high acetal selectivity is due to a cooperative effect of the Rh catalyst and HBF4 formed in situ from the precursor. Details of these tandem reactions and the scope of reactions will be discussed.
The direct route for the production of ethylene from natural gas via OCM in a single step is still high on the industrial wish-list, but has shown major scientific and technological challenges. The temperature control remains difficult and hence always ends with complex reactor design. However, when the exothermic OCM is combined with endothermic SRM, ethylene and synthesis gas can be produced simultaneously in an overall autothermal process. Thus, a higher methane conversion (avoiding a large methane recycle) and efficient use of the by-products of the OCM can be combined with optimal heat integration. With these ultimate objectives, this project is divided in two parts. The first part focused on the fabrication of the dual function catalyst particle while second part focused on developing novel autothermal reactor concepts and experimental proof-of-principle of combined OCM/SRM process in a packed bed membrane reactor (PBMR) using dual function catalyst.

Two reactor concepts viz. a PBMR with dual function catalyst and a catalytic hollow fibre membrane reactor have been developed and studied numerically. The PBMR simulations have shown the feasibility of autothermal operation using a dual function catalyst ($\Delta r_{OCM}=0.25\text{mm}; \Delta r_{SRM}=20\text{microns}$), making effective use of intraparticle mass transfer limitations. The simulations have also led to a first possible design of a catalytic membrane reactor with impregnation of OCM catalyst on a hollow fibre membrane, which would make the reactor configuration much simpler as...
compared to conventional PBMR with a dual function catalyst. The main advantage of the catalytic hollow fibre concept over the PBMR is a better temperature control with increased product yield using only 6 per cent catalyst volume as compared to the PBMR. In addition, the removal of heat can be realized via external inter-staged cooling for this concept. The experimental proof-of-principle towards these concepts is underway.

The materials required for testing the proposed concept were developed in two stages. The first stage comprised the preparation of powdered catalyst for oxidative coupling and steam reforming of methane to evaluate the kinetic performance of the selected catalytic material. The second step comprised the preparation of catalytic coatings on hollow fibre membrane in order to translate catalytic performance of the evaluated catalyst to obtain the catalytic hollow fibre membrane reactor. OCM catalyst with better activity and selectivity for C₂ and C₃ compared to COₓ have been prepared and were tested in combination with suitable SRM catalyst for the autothermal operation. Moreover, stable coatings of catalytic material on a hollow fibre have been prepared by using dip coating of catalyst suspension with a possibility to vary the coating thickness. Improvement of coating stability at the high reaction temperature has been achieved by doping the coating suspension with additives. The unique approach in this regard is using the additive that also plays a role of catalytically active material for OCM. Both powdered catalyst and the initial coated fibres are being tested to evaluate the experimental proof-of-principle.

> **Project leader**
- Prof. L. (Leon) Lefferts (UT)

> **Co-applicants**
- Prof. M. (Martin) van Sint Annaland (TU/e)

> **Researchers**
- Amit Chaudhari (TU/e, Postdoc)
- Digvijay Thakur (UT, Postdoc)

> **Duration**
- 2010-2012

> **Budget**
- k€ 367

> **Highlights**
- Oxidative coupling of methane.
- Dual function catalyst.
- Ethylene production.
- Membrane reactor.
Ethanol from synthesis gas using highly dispersed cobalt catalysts

High-risk, high-reward research on cobalt catalysts for synthesis of ethanol from synthesis gas. Effort has shown that in our hands cobalt was not sufficiently selective for ethanol formation.
Results
For the chemical industry it is of paramount importance to broaden the feedstock base for the production of base chemicals, in particular (lower) olefins. We have studied the production thereof via gasification of coal or biomass to synthesis gas - a mixture of hydrogen and carbon monoxide - followed by conversion of the synthesis gas to alcohols, in particular ethanol. The research concerned in particular the fundamental research on a new class of cobalt-based catalysts based on carbon nanofibers as support material. The particle size of Co was varied systematically from 1-30 nm and its effects on activity, selectivity and stability in FTO assessed. If successful these nanostructured Co catalysts would open up a new route for the manufacture of the most important building blocks of the chemical industry, i.e. ethene, as the envisaged dehydration of ethanol will be facile. We have found that the smaller the Co nanoparticles the higher the ethanol selectivity. However, the absolute values of ethanol selectivities turned out to be too low for industrial applications.

Project leader
- Prof. K.P. (Krijn) de Jong (UU)

Co-applicants
- Dr J.H. (Harry) Bitter (UU)

Researchers
- Siswati Lestari (UU, Postdoc)
- Rien van Zwienen (UU, Technician)

Duration
- 2010-2012

Budget
- k€ 258

Highlights
- No ethanol selective catalyst on the basis of cobalt has been found.
Tailor-made metal species for the activation of ammonia: toward hydroamination of alkenes with $\text{NH}_3$.

Ammonia: from household-chemical to industrial building block.
Results
The development of mononuclear metal complexes that achieve catalytic intramolecular hydroamination of olefins, with a particular focus on utilizing ammonia. This is envisioned to be accessible through selective N-H activation of amines by late transition metal complexes, followed by metal-assisted addition across an olefin. To that end, uncommon amido complexes of group IX and X metals, proposed intermediates in the desired catalytic system, have been targeted for investigation. We have also investigated the use of reactive ligand systems to promote this conversion. Thus far, N-H activation of ammonia and other challenging amines has not been achieved; efforts toward this goal are ongoing. Additional research into the use of different ligand scaffolds and other metals, including increased use of Group X and XI metals, will continue. Also, the selective, cooperative activation of N-H bonds by the PdI and CuII systems involving PN bifunctional ligands opens up new opportunities for stoichiometric and potentially catalytic studies involving intra- and intermolecular amination reactions.

Project leader
• Dr J.I. (Jarl) van der Vlugt (UvA)

Co-applicants
• Prof. J.N.H. (Joost) Reek (UvA)

Researchers
• Richard Bauer (UvA, Postdoc)
• Erik Duin Berteling (UvA, Technician)
• Yann Gloaguen (UvA, Postdoc)

Duration
• 2010-2012

Budget
• k€ 235

Highlights
• "ERC Starting Grant 2012-2017", J.I. van der Vlugt.
Simultaneous operando Mössbauer and infrared spectroscopy of heterogeneous catalysts: probing the active sites in iron based oxidation catalysts

A state-of-the-art combined Mössbauer/infrared spectroscopic/GC-MS facility for the study of heterogeneous catalysts under real industrial conditions – was developed at Delft University of Technology (Faculty of Applied Sciences) and has been made available to the Netherlands catalysis community.
Results
The development of a state-of-the-art combined Mössbauer/infrared spectroscopic/GC-MS facility for the in-situ/operando study of heterogeneous catalysts was successfully completed at Delft University of Technology (Faculty of Applied Sciences). With this new equipment, the nature of the active sites of iron-based oxidation catalysts is investigated in detail with a view of developing improved catalysts for selective oxidation, viz. the selective oxidation of methane to methanol with nitrous oxide. Another important objective of this project was to make this facility known and available to the Netherlands catalysis community.

The collaboration with Prof. Krijn de Jong from Utrecht University, in the project "Direct production of lower olefins from synthesis gas using iron based catalysts", yielded successful Mössbauer spectroscopy results revealing that the samples with the smallest iron particles showed a higher degree of carbidization compared with catalysts with larger particle sizes. The higher activity of the smaller particles was assigned to a higher content of the active carbodic phase. The project aim is to optimize the iron particle size in order to design promoted catalysts with high C2-C4 olefins selectivity and low methane production while maintaining a high catalytic activity and chemical stability.

A systematic Mössbauer/IR study of the methane oxidation by nitrous oxide was performed using [Fe,Al]MFI zeolite catalysts having different iron (0.14-0.6 wt. per cent) and aluminium (0.63-1.1 wt. per cent) concentrations. It was observed that Fe-bound methoxy groups are formed at 523 K and are completely transformed to formate-like groups at 573 K. Very interestingly, the catalyst with the lowest aluminium loading was the most active in the catalytic oxidation of methane to methanol, similar behaviour being previously reported for the same samples in the benzene to phenol reaction. The presence of aluminium is thought to bring about deactivation of active sites by coke formation attributed to the presence of acidity in the zeolite matrix.
Catalytic production of acrylamide and methacrylamide from renewable resources

This project aims at the environmentally benign conversion of aspartic acid (important constituent of the easy-to-produce protein cyanophycin) into acrylamide, a million-ton scale building block for plastics.
Results

The project is about a new efficient and catalytic route for the production of acrylamide from renewable feedstocks, namely aspartic acid. Acrylamide is a building block of polyacrylamide that is used as a thickener in e.g. wastewater treatment and paper industry. Presently it is made from acrylonitrile, which itself is synthesized from the crude oil-derived feedstock propene as well as ammonia, the production of which is highly energy-consuming. The world market for acrylamide is in excess of 250,000 tpa. In this project we make this compound from aspartic acid, as produced and concentrated by microorganisms in the form of cyanophycin, a protein with a polyaspartic acid backbone and side chains made of arginine. In previous research we have already shown that we can hydrolyse cyanophycin to yield aspartic acid using acids. Subsequently, aspartic acid is selectively enzymatically decarboxylated to beta-alanine. We now investigated in detail the two reactions that transform beta-alanine into acrylamide:
- polymerisation of beta-alanine;
- base-catalysed cleavage of poly(beta-alanine) to form acrylamide.

We have shown that beta-alanine can be converted into its methyl or ethyl ester under very mild conditions by treatment with the respective alcohol and an acidic ion exchange resin. Subsequently, the ester can be polymerised using alkoxides of group (IV) metals like Hf(Ot-Bu)4 or with an enzyme like Candida antarctica lipase. We showed for the first time that Cross-Linked Enzyme Aggregates (CLEAs) are excellent catalysts for polymerisation of the beta-alanine esters. The polymer contains up to 58 units of beta-alanine. Treatment with bases like DBU subsequently converted the polymer into acrylamide. Apart from beta-alanine, other beta-amino acid esters can also be polymerised with our methods. The starting compounds could be made in a very easy way by Michael addition of amines to acrylates. This reaction could be tuned to solely give Michael additions without aminolysis of the ester function. Besides the starting compounds for polymerisation, we have also been able to prepare a series of interesting N-substituted beta amino esters with the methodology we developed.
The large reveals the small

We have built a machine that mimics industrial catalytic reactions such that it shows which sites on catalytic particles are catalytically the most active sites.
Results
The main purpose of this research project was to construct a versatile experimental method that would quickly identify the most active sites for activated adsorption, provide unambiguous insight into the optimal step-to-terrace ratio for overall kinetics in reactions hampered by large activation barriers, set targets for synthesis of the most active metal catalyst particles, and test fundamental assumptions in theoretical, DFT-based studies regarding overall reactivity. To do so, we had to build a unique double (supersonic) molecular beam apparatus allowing for two reactants to impinge onto flat or cylindrical single crystal surfaces, mimicking industrially relevant catalytic processes. The apparatus has been constructed. Initial testing for single beam experiments from either molecular beam has been done using a first flat single crystal. Results from these initial studies are currently being summarized in three manuscripts. One major result is that we have compared A5 and B5 type sites in their ability to break chemical bonds. For hydrogen dissociation we observe the opposite trend compared to the theoretical suggestion for molecules e.g. N₂ and CO where the B5 site is suggested to be more active. We find A5 to be more reactive. Also, this site shows a previously unobserved isotope effect that we likely results for the indirect mechanism via a molecular precursor that leads to dissociation. The project is continued on other funding by PhD and MSc students to investigate surface structure dependencies in overall reactivity on Ru and Pt surfaces using double beam experiments.

Project leader
- Dr L.B.F. (Ludo) Juurlink (UL)

Researchers
- Thijs Hoogenboom (UL, Technician)
- Junjun Shan (UL, Postdoc)
- Arban Uka (UL, Postdoc)

Duration
- 2010-2012

Budget
- k€ 311

Highlights
- Successful design and construction of a complex and unique double molecular beam apparatus allowing detailed investigations of active sites on catalytic surfaces.
- Oral presentation at ECOSS 29 regarding design and construction of this double molecular beam apparatus for measurements on single crystal catalytic surfaces.
- Three manuscripts in preparation.
Colophon

Editors
Marieke van Santen
Sabine Zinsmeister
Maarten de Zwart

Interviews
Bureau Lorient Communicatie

Design
WAT ontwerpers, Utrecht

Photography
Shutterstock
Photo Louis Vertegaal: Jarno Verhoef
Photo Matthijs Ruitenbeek: Ivar Pel
Courtesy of project leaders

Print
Zalsman Kampen