11. Prof. dr. R.A. van Santen
Inorganic Chemistry and Catalysis

11.1 General introduction

Main goal is the development of an approach to (heterogeneous) catalysis that will improve the predictability of catalytic science. State of the art theory and spectroscopy are used to study working catalytic systems. In these fundamental studies reference has to be made to model systems to validate theory by experiment. However, whereas on a well-defined system for a single elementary reaction step the predicted reaction rate can be directly compared, the bridge between practical catalysis and model catalysis is far from being closed. Mechanistic knowledge of reactions catalysed by four commonly used catalytic systems (zeolites, transition metals, sulphides and transition metal electrodes) is developed. This knowledge is quantified by computational simulation that is experimentally validated and used in catalytic kinetics modeling.

The catalyst synthesis and characterization programme of the group deals with the inorganic chemistry of catalytic materials and focuses on the mimicking of proposed heterogeneous active sites using the techniques of organometallic chemistry. A synthesis programme to molecularly model proposed heterogeneous catalyst reaction centres is developed. These new catalytic systems are used to develop new catalysis.

11.2 Programme design in brief (related to NRC-C Area 2)

Main objective of the NRC-C related research is: “To achieve precise molecular control in heterogeneous catalyst synthesis and thereby enable selective catalytic reactions up to the level of enantiocontrol.” Robust nanostructured building blocks (POSS metal derivatives) are assembled to larger aggregates and finally catalytic materials. Lego chemistry is developed to eventually make mesoporous catalysts with uniform metal sites. These include catalytic ensembles, inspired on the functionality of heme enzymes with regard to the presence of a hydrophobic cavity and functions for substrate recognition.

11.2 Programme design in brief (related to NRC-C Area 2 and 4) Rutger

Main objective of the NRC-C related research is: “Prediction of optimum catalyst for a particular chosen reaction”. Can one simulate the response of the immuno-system to a “transition state” type molecule to self assemble chemo-catalysts? Of special interest is inspiration by insights in molecular control of biochemical systems. A theoretical as well as an experimental approach is followed.

Three research themes of our research group over the period 2003-2004 can be distinguished. They all share the common feature to understand or control a catalytic system at a molecular level.
(i) **Modelling of catalytic reactivity** concerns mainly theoretical quantum-chemical studies on reaction mechanism and Dynamic Monte Carlo studies to relate theory with kinetics (NRC-C area 4). Physical chemical studies are done to support theoretical model building. Systems studied are cation and proton containing zeolites as well as transition metals. Key results concern the identification of reaction intermediate transitions and the incorporation of molecule-molecule interactions in the catalytic studies. Diffusion is studied using radiochemical PEP techniques and solid state NMR.

(ii) **Bioelectrocatalysis** is a new and significant theme in our group, which focuses on interrogating the catalytic activity of proteins, enzymes or their co-factors adsorbed on electrodes by a combination of electrochemical techniques and other in situ spectroscopic methods (FTIR, Surface Enhanced Resonance Raman Spectroscopy, on-line mass spectrometry, quartz-crystal nanobalance). The research in this area is not only concerned with modelling the catalytic activity of enzymes, but also with designing new catalysts for particular transformations by studying derived systems inspired by biochemical catalysts.

(iii) "**Self assembled micro- and mesoporous systems**" concerns the experimental identification of the key intermediates that control self-assembly of micro- and mesoporous zeolitic systems, using advanced spectroscopic techniques (NRC-C Area 2). The physical chemical knowledge obtained is used in synthesis programmes to develop new mesoporous systems based on zeolitic nanoblocks and to develop lego chemistry for molecular self assembly based on silsesquioxane building blocks. A third synthetic approach exploits understanding of biogenic silica formation to synthesis silica particles with interesting morphologies, e.g. hollow spheres.

### 11.3 Overview of scientific results related to NRC-C

#### 11.3.1 Contribution of NRC-C (personnel)

**Kinetic Monte Carlo simulations**

_C.G.M. Hermse (NRSC-C PhD-student) and T.T. Trinh (NRSC-C PhD-student)_ use kinetic Monte Carlo simulation to study the kinetics of catalytic processes. The group has been one of the first to do kinetic Monte Carlo (kMC) simulations, which is currently widely used for surface reactions. Main interest has been the simulation of temperature-programmed desorption and voltammetry, and in particular the effect of interactions between adsorbates, so-called lateral interactions. (We have written a review on these interactions for Specialist Periodical Report Catalysis Volume 19 of the Royal Society of Chemistry that will appear shortly.) These interactions have been known to be important, because they lead to structured adlayers at low temperatures. Their role in catalysis however is often ignored, even though a simple back-of-the-envelop calculation shows that they can change reaction rates by an order of magnitude or more. Lateral interactions cannot really be described by the normal macroscopic rate equations, and kMC simulations are essential.

We have done several studies to increase the little quantitative data on lateral interactions in the literature. We have done density-functional theory (DFT) calculations of lateral interactions for NO reduction on Rh(111) and Rh(100) and for tartaric acid on Cu(110). The results of these DFT calculations were used in kMC simulations to show that the lateral interactions between NO molecules on the Rh surfaces are responsible for the suppression of the dissociation of NO at even moderate coverages. They also determine the selectivity towards N₂. The interactions between tartaric acid molecules explain the formation of chiral domains on Cu(110).
As an alternative we have combined kMC simulations with optimisation methods from the field of evolutionary computations (e.g., genetic algorithms), to obtain lateral interactions from fitting simulation results to experiments. Work on temperature-programmed desorption of CO from Rh(100) and multi-isotherms of N/Rh(111) have shown that lateral interactions in one system can vary by more than an order of magnitude. The strong interactions lead to structured adlayers even at high temperatures at high coverages, whereas the weak interactions affect the kinetics at low coverages.

Bio-electrocatalysis

The aim of our initial studies in bio-electrocatalysis (NRSC-C PhD-student M.T. de Groot) have focused on obtaining an understanding of the factors that govern selectivity in nitric oxide (NO) reduction. Four stable products can be formed in this reduction: N₂O, N₂, NH₂OH and NH₃. NO reductases, such as the enzyme cytochrome P450nor are able to selectively reduce NO to N₂O, whereas metals like platinum and palladium can also reduce NO to N₂, NH₂OH and NH₃.

We have studied NO reduction using protein film voltammetry (PFV) (Leger, C.; Elliott, S. J.; Hoke, K. R.; Jeuken, L. J. C.; Jones, A. K.; Armstrong, F. A. Biochemistry 2003, 42, 8653-8662.), a technique that enables fast electron transfer between the electrode and the redox active groups of the protein. Therefore electron-donating half reactions are no longer needed in catalysis. The technique used to immobilize proteins was incorporation of the protein in a didodecyldimethylammonium bromide (DDAB) film (Rusling, J. F.; Nassar, A. E. F. J. Am. Chem. Soc. 1993, 115, 11891-11897) However, it appeared that DDAB induces the dissociation of the heme group from the protein (Figure 1) and therefore studying protein-catalyzed NO reduction with PFV appears problematic.

The heme groups incorporated in the DDAB film do still provide an interesting system to study NO reduction, since it can be regarded as intermediary between biological and inorganic NO reduction. Two NO reduction mechanisms were observed in voltammetry (Figure 2). One mechanism results in the formation of N₂O and the other mechanism results in the formation of NH₂OH, as was evidenced by OnLine Electrochemical Mass Spectroscopy (OLEMS) and the Rotating Ring Disc Electrode (RRDE). Especially the 100% selectivity to hydroxylamine that can be obtained under certain circumstances (mainly in the absence of co-adsorbed DDAB) is very interesting, as this is an important molecule for the chemical and semiconductor industry and at present no metal catalyst is able to reach such a high selectivity.

Fig. 1. Cyclic voltammograms of a myoglobin-DDAB film (—) and a hemin-DDAB film (---) on pyrolitic graphite. pH 7; 500 mV/s.

Fig. 2. Cyclic voltammogram of a hemin-DDAB film on pyrolitic graphite in a saturated NO solution. pH 10.2; 50 mV/s; 16 rps.
These results prompt a qualitative comparison between the catalytic activity for NO reduction of enzymes (such as cytochrome P450nor), immobilized heme cofactor (such as the systems studied here), and metal catalysts (such as have been studied extensively by our group previously, De Vooys et al. J.Catal. 202 (2001) 387). A schematic representation is given in the Scheme below:

Schematic overview of the selectivity of NO reduction by P450nor, adsorbed heme, and metal surfaces.

**POSS Chemistry**

Bio-inspired research on catalytic ensembles for epoxidation in aqueous media focused on three topics: 1) Synthesis of rigid, nanostructured silsesquioxane (POSS) compounds with receptors for hydrogen peroxide, 2) optimization of the performance of immobilized catalysts for hydrogen peroxide mediated epoxidation. 3) Development of functional, soluble epoxidation catalysts for nanofiltration applications (See also Self evaluation group Vogt).

Figure 3 (left); homogeneous kinetic investigation of the initiation of a series of homogeneous epoxidation catalysts; (right) $^1$H, $^{29}$Si Goldman Shen 2D NMR of a mesoporous, POSS catalyst indicating close proximity of POSS to the MCM-41 part of the hybrid material.
Embedding of new POSS titanium derivatives in 3D-netted polysiloxane matrices rendered epoxidation catalysts applicable for heterogeneous application with aqueous hydrogen peroxide. Using a Chemspeed AWS1000 workstation, protocols were developed for detailed kinetic investigation of epoxidation catalysts, both for homogeneous and heterogeneous liquid phase application. Quality data were obtained from which firm conclusions could be drawn with respect to catalyst initiation, stability and life span, reaction scope and inhibition by polar co-products or solvents / additives. (NRSC-C PhD-student G. Gerritsen).

As our previous work did not allow control catalyst porosity, we embarked on template assisted assembly of catalysts from newly developed (POSS) building blocks containing polymerizable groups and a robust titanium site relevant for epoxidation catalysis. This approach to organic-inorganic nanocomposite catalysts takes lessons from the synthesis of periodic mesoporous silica MCM-41, where an organic mesophase is replicated in silica. Hybrid, mesoporous catalysts were prepared starting from multifunctional Si(OEt)$_3$ POSS and Si(OEt)$_4$. This technology for catalyst immobilization is scalable: whereas the POSS building blocks provide homogeneous catalysts, larger assemblies could be used for continuous homogeneous catalysis involving catalyst retention by nanofiltrations. New mesoporous catalysts developed last year provided truly heterogeneous catalysts for liquid phase epoxidation with aqueous hydrogen peroxide. (NRSC-C Post-doc, Dr. N. NiBhrian).

11.3.1 Contribution of NRC-C (personnel)
- C. G. M. Hermse (PhD-student, defended his thesis on December 1, 2004) in the project Survival of the Fittest Catalyst.
- T. T. Trinh (PhD-student, started on October 12, 2004) in the project Simulating Zeolite Synthesis.
- M.T. de Groot (PhD-student, started on June 1, 2003) works on the bio-electrocatalysis project
- Dr. N. NiBhrian, Post-doc, POSS mesoporous catalysts.

Selected publications:


11.3.2 Contribution of NRC-C (investment in equipment)

NRSC-C Area 2. NRSC-C has provided an extremely valuable contribution to automated catalyst screening and analysis (Chemspeed AWS1000), reaction monitoring (Fiberoptics IR, Shimazu GC / Autosampler).

11.3.3 Contribution of NRC-C (collaboration / international position)

Our DMC work has been very successful, it has been presented in numerous journals and on conferences, and we think that we are now one of the leading groups in this area. International collaborations are with the group of Prof. V.N. Kuzovkov (University of Latvia) on nonlinear kinetics, with Prof. P. Balbuena (University of South Carolina) on electrochemical processes, and with Prof. R. Imbihl (University of Hannover) on NH3 oxidation on Pt(111). We are using EC methods for two years, and the first publication has been published only recently. A second publication is currently in preparation, and the work for a third is nearly finished.

The bioelectrocatalysis work has only just started but has already attracted substantial attention. Our first paper is currently under consideration for publication in JACS, and the referee reports suggest that our approach is very welcomed by the bioelectrocatalysis community. We expect that our extensive expertise in electrochemistry and associated in situ techniques, in combination with the collaboration with the Protein Engineering group (M.Merkx, E.W.Meijer) at TU/e, will give us a unique position in the field. Also our results on the denaturing influence of the co-surfactant on the immobilized protein are expected to give rise to significance excitement (and perhaps disbelief) in the community. The graduate student involved (M.T. de Groot) is currently spending several months in the group of Professor F.A. Armstrong in Oxford, one of the leading groups in this area. Within NRSC-C, we see possibilities for collaboration with the group of Prof. A.E.Rowan at Nijmegen.

POSS Chemistry. Over the last five years, numerous silsesquioxane metal complexes were synthesized and their structures determined. As a result, models were provided for aluminium sites in zeolites, clays, silica supported polyoxymetalates and metal complexes grafted to silica. Present collaborations related to this proposal involve: consultancy for Degussa and TNO (POSS
material applications), collaboration with Prof. Feher (Univ. Cal. Irvine) through exchange of a TU/e PhD student and subsequent ongoing collaboration in POSS chemistry, collaboration with Prof. Camino (Polytechnic Alessandria) on POSS catalytic flame retardancy. Robust epoxidation catalysts are developed as homogeneous models of the TS-1 catalyst, especially suited for the epoxidation using hydrogen peroxide as the oxidant. The use of membrane technology is investigated for the immobilization of homogeneous catalysts. From a position as associated professor in the Vogt group, Abbenhuis (Inorganic / Organic hybrid catalytic materials) in a sense, bridges the gap between homogeneous and heterogeneous catalysis through several internal collaborations.

There is a strong intertwining of NRC-C-sponsored research and other research activities in our group. The results have led to a large number of publications in journal with high impact factors.

11.4 Programme development

Computational Chemistry

We have focussed in recent years on the role that interactions between adsorbates, so-called lateral interactions, play in the kinetics of surface reactions. This is a subject that receives more and more attention in the field, so we will continue with this work. Our main objective however will be to extend the scope of the kinetic Monte Carlo (kMC) simulations. Except for a few studies kMC simulations always use a grid that represents the possible positions where adsorbates can be found (lattice-gas model). This reflects the idea of well-defined sites of a catalyst’s surface where atoms and molecules adsorb, but it is not appropriate when the coverage becomes high, and the adsorbates push each other away from these sites, or when the surface reconstructs during reactions. We have developed a kMC method that does not use a lattice-gas model. This will allow us to do kMC simulations at high coverages and when the surface reconstructs. Moreover, it will also be possible to do kMC simulations for systems where a lattice-gas model is not valid even as an approximation: e.g., for reactions in the gas phase or in solutions. We have started with the implementation of this method in a computer program, and we will probably do the first simulations within the next coming months. Without a lattice-gas model there is no translational symmetry. Consequently the number of possible processes/reactions with different rate constants increases enormously. In general they can no longer be computed before a kMC simulation, but their calculations becomes part of a kMC job. This makes the computation much more time consuming. For reactions in the gas phase or in solutions, however, there is little variation of the reactions rate constants and diffusion and reorientation of molecules can be handled analytically. For such situations we have shown that a kMC simulation without a lattice-gas model can be still relatively inexpensive. We will therefore start with such a system. In particular, we will start with doing kMC simulations of the synthesis in zeolites in solutions. We hope that in the long run we will be able to use this new kMC approach in biological applications: e.g., to simulate the formation of cells.

Further theoretical work will be continued on three topics:

- Surface reconstruction of transition metal surfaces, which will extend previous studies on lateral interactions by including the mobility of surface atoms. Methods are developed to predict instabilities as a function of coverage.
- Theoretical studies on zeolite synthesis will initially focus on the formation of Si-O-Si bonds in the water phase. In a next step, specific cationic interactions will be included.
- Self-organization and self assembly of protocell systems, which will be initiated with simulation studies of liposome formation in systems with concentration gradients.
Bio-electrocatalysis

The bio-electrocatalysis work is expected to branch into two major directions. First of all, we have as yet to immobilize a protein or an enzyme on an electrode with protein denaturation. In this area, we will collaborate with the group in Oxford who have extensive expertise in attaching enzymes to edge-plane pyrolytic graphite. Our final aim is still to immobilize an NO reductase and to study its mechanism in comparison with the immobilized cofactor and the enzymatic mechanisms suggested in the literature. We will use FTIR to study confirmations of the enzyme, as well as intermediates of the NO reduction reaction. If we are successful in immobilizing the enzyme on gold, utilizing our Surface Enhanced (Resonance) Raman Spectroscopy setup is also a very interesting option. Secondly, the systems studied so far, i.e. hemin adsorbed on pyrolytic graphite in the absence and presence of DDAB, show some very remarkable and novel catalytic properties, in particular the 100% conversion of NO to hydroxylamine. It will be interesting to study the catalytic properties of these systems for nitrite and especially nitrate reduction. Developing a catalyst with a 100% selectivity for either dinitrogen or hydroxylamine is one of the holy grails of catalytic nitrate reduction.

Hybrid Catalysts and POSS Chemistry

In this area, the bio-inspiration character is strongly present as basic concepts from biology are adapted in order to develop highly selective and active catalysts for sustainable processes. Catalysis in water, use of membrane separation, and compartmentation of reactions are some of these principles are in an early stage of exploitation. Simultaneously, new routes to assemble the nano-sized catalytic materials in a simple and efficient way have to be developed. The increase of complexity of the systems studied is expected to lead to the deeper understanding that will finally result in simplified applicable solutions for sustainable processes. Truly sustainable heterogeneous catalysis imposes a challenge for precise molecular control starting at catalyst synthesis. Such control is more demanding than conventional zeolite synthesis or post synthesis modification of zeolites or micro-, or mesoporous supports can offer. As such a strong incentive is provided for further development of POSS Lego chemistry.

(Electro-)Catalysis on a single nanoparticle

We intend to extend our studies in electrocatalysis by making nano-electrodes consisting of a nano-sized support electrode and a single nano-particle. This would allow us to measure the (electro-)catalytic activity of a single nanoparticle, and to study in detail the effect of size and shape on catalytic properties. A collaboration with the Kavli Institute of Nanoscience (Dekker/Lemay) is envisaged.