

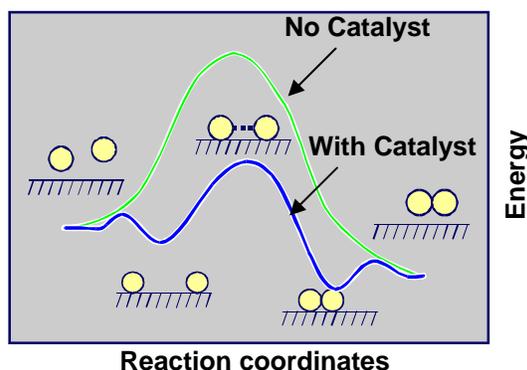
## APPLICATIONS OF NANOTECHNOLOGY: CATALYSIS

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Catalysis is of vital importance in our society and constitutes a cornerstone of life from biological processes to large-scale production of bulk chemicals. The availability of plentiful and inexpensive chemicals relies on industrial catalytic processes. Other technologies also depend on catalysis, including production of pharmaceuticals, means of environmental protection, and **production and distribution of sustainable energy**. Much technological advancement required to render alternative energy carriers to fossil fuels an economically viable option (such as sun light and hydrogen) relies on optimizing a catalytic process. For instance, for water to be split into hydrogen and oxygen with sunlight to feed a fuel cell, researchers need to improve the activity of the catalyst, for instance  $\text{TiO}_2$ .

In simple words, a catalyst is a substance that increases a chemical reaction rate without being consumed or chemically altered. This means that it can accelerate a chemical reaction dramatically or change its product distribution towards a specific compound without being consumed during the reaction. From an energy point of view, this means that a catalysts can reduce the energy barrier needed for a reaction to take place, i.e., that a lower temperature can be employed for the reaction to occur (**Figure 1**). Nature's catalysts are called enzymes and are able to assemble specific end products, always finding pathways by which reactions take place with minimum energy consumption and operating at ambient temperature. Man-made catalysts are not so energy efficient. They are

often made of metal particles fixed on an oxide surface, working on a hot reactant stream (to reduce the 'catalyst poisoning' which occurs when species dispersed in the atmosphere, such as CO, occupy the active sites of the catalysts).



**Figure 1** Effect of a catalyst on a reaction path (note the change in sub-products and reduction of energy barrier).

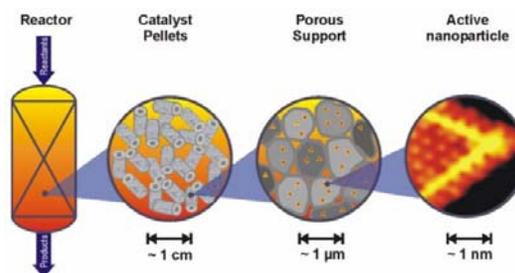
One of the most important properties of a catalyst is its **active surface** where the reaction takes place. The active surface increases when the size of the catalysts is decreased: the smaller the catalysts particles, the greater the ratio of surface-to-volume. The higher is the catalysts active surface, the greater is the reaction efficiency. Research has shown that the spatial organization of the active sites in a catalyst is also important. Both properties (nanoparticle size and molecular structure/distribution) can be controlled using nanotechnology. Achieving a high degree of **selectively** in catalysis is also recognized as a crucial challenge for the

future. While nature attains 100% selectivity in nanometre-scale enzyme catalysts, such selectivity in synthetic systems is still a challenge. The geometrical and electronic structures of nanoscale catalysts particles play a major role in selectivity. Thus, a synthetic method to obtain highly controlled particle-size distribution is desirable. The combination of selectivity and lower temperature needed for a reaction to occur make heterogeneous catalysis a prime energy saving technology.

The manufacturing of structures on the nanometre scale has been a central issue in catalysis research and development for decades. This fact relates to the structure of a heterogeneous catalyst, which requires control of materials ranging from macroscopic dimensions down to the nanoscale. Heterogeneous catalysis therefore has in a sense always had a nanoscience component. Since catalytic action takes place at a surface, and catalytic materials are often very expensive (as they use rare materials such as Pt), the goal for chemists has always been to fabricate catalysts with as high surface-to-volume ratio as possible, so to maximize the surface exposed to the reaction and minimize the amount of catalyst required. A typical heterogeneous catalyst consists of few nanometre wide catalytically active nanoparticles dispersed on a highly porous support material which can have surface areas up to 250 m<sup>2</sup> per gram.

Application of nanotechnology concepts in catalysis is already beginning to show a great industrial impact. The detailed understanding of the chemistry of nanostructures and the ability to control materials on the nanometre scale will ensure a more rational and cost-efficient development of new and improved catalysts for chemical production. An important tool that has revolutionized research in catalysis is the **scanning tunnelling microscope (STM)**, which is an instrument capable of achieving true atomic-scale resolution in real space. The ability of the STM to directly resolve the local atomic-scale

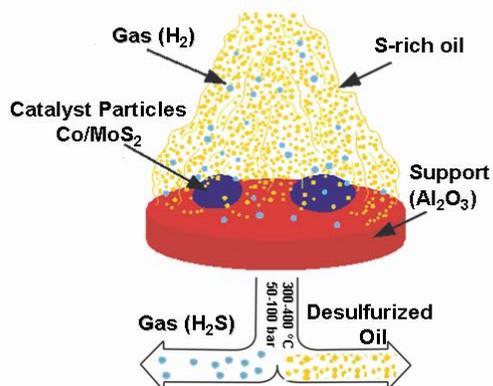
structure has revealed essential insight and, in particular, emphasized the catalytic importance of edges, kinks, atom vacancies or other surface defects, which are only visible on the nanoscale and therefore often overlooked with other techniques<sup>1</sup>. The STM Scanning Tunnelling Microscope (STM) technique was first introduced to the scientific community in the mid 1980s; in 1986 Gerd Binnig and Heinrich Rohrer from the IBM Zurich Research Laboratory in Switzerland were awarded the Nobel Prize in Physics for its discovery. Later, other scanning probe microscopy (SPM) techniques were developed, such as the atomic force microscope (AFM). As it was recently commented in Nature Nanotechnology, “with the emergence of scanning probe microscopy (SPM) and related techniques in the 1980s, the door to the nanoworld was pushed wide open”<sup>2</sup>. In the following sections some examples of STM studies of model catalysts are reported to show how this nanotechnological tool can be instrumental in the understanding and implementation of novel, more efficient catalysts.



**Figure 2** Schematic representation showing how nanoparticles could be included in the catalyst material of a desulphurizing fuel reactor. The image on the far right is a real Scanning Tunnelling Microscope (STM) image of a MoS<sub>2</sub> nanocrystal on Au(111) showing peculiar atomic distribution at the edges of the crystal.

### HYDRODESULFURIZATION MODEL CATALYSTS STUDIED BY STM<sup>1</sup>

In the Aarhus STM Laboratories associated with iNANO, researchers over the years have used a home-built, high-resolution STM to study a number of technologically relevant nanocatalysts, and these detailed STM studies have provided a breakthrough in the atomic-scale understanding of their reactivity<sup>3</sup>. Recent nanotechnology research performed at iNANO has also aided the Danish company Haldor Topsøe A/S in implementing a new generation of hydrodesulphurization catalysts to be used for sulphur clean-up of fossil fuels worldwide. (Figure 3).



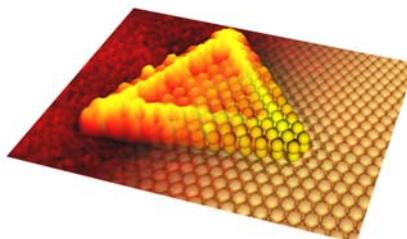
**Figure 3.** Overview of the hydrodesulphurization process

The molybdenum disulphide ( $\text{MoS}_2$ ) based desulphurization catalyst constitutes one of the most important environmental catalysts as it removes sulphur from fossil fuels. Without this removal, the sulphur would cause massive acid rain problems such as forest decline. The recent focus on environmental issues and a stricter legislation on the sulphur content in fuels have generated great interest in understanding and improving the desulphurization catalyst.

<sup>1</sup> Based on “ $\text{MoS}_2$  nanoclusters for desulphurization, size does matter”, by J. Kibsgaard, J.V.Lauritsen, and F.Besenbacher, iNANO Annual Report 2007, page 20.

In the desulphurization process hydrogen reacts with sulphur atoms located on the edges of the triangular  $\text{MoS}_2$  nanoparticle to form hydrogen sulphide, which is removed from the reactor. Soon the resultant vacancy at the nanoparticle edge is filled with sulphur containing oil molecules, which are subsequently removed, leaving the sulphur atom behind; the catalytic cycle is closed.

In 2007 researchers at iNANO revealed that the morphology of  $\text{MoS}_2$  nanoparticles is extremely dependent on their size<sup>3b</sup>. The experiments were conducted by synthesizing a variety of  $\text{MoS}_2$  particles with different sizes and analyzing their morphologies in STM images with atomic resolution.



**Figure 4.** An STM images collected at iNANO of a  $\text{MoS}_2$  nanocrystal (left) and the structure model on the right.

All  $\text{MoS}_2$  nanoparticles, independent of their size, display a very distinct triangular shape. However, a detailed analysis reveals a change in the edge structure when the particle size is reduced to less than 100 atoms in total. As the particle size decreases below this limit, the stoichiometry of the nanoparticles deviates from the bulk  $\text{MoS}_2$  value as the relative sulphur content increases. The observed change in edge structure occurs to lower the sulphur to molybdenum (Mo) ratio in these small particles since they become unstable if they are too rich in sulphur.

The experiments also demonstrated that for particles with more than 100 atoms only particles with a certain “magic” number of molybdenum atoms are stable. This effect is

caused by the tendency of the edge-terminating sulphur dimers to pair up favouring particles with an even number of molybdenum atoms along the edge of the particle. The discovery of the size-dependent shape of MoS<sub>2</sub> nanoparticles may help improve industrial catalysts. The chemical and thus catalytic properties are affected when the edge structure is changed. The results suggest that tailoring the nanoparticles to a specific size can help optimize the desulphurization activity.

#### **Au NANOCCLUSERS ON VARIOUS TiO<sub>2</sub> SURFACES**

The previous example illustrates the concept that 'small is different'. Another one is the surprising reactivity of gold (Au) nanoclusters. Bulk gold is generally known to be a noble metal, therefore non reactive, but with great surprise in the 1980s Haruta<sup>4</sup> found that finely dispersed gold nanoparticles on oxide supports are catalytically very active. In many cases the catalytic activity and selectivity of dispersed Au nanoparticles exceeds those of the commonly used transition metal catalysts such as Pt, Rh, and Pd. Therefore, it is very important to develop stable Au nanocatalysts. The long-term stability of Au nanocatalysts is presently the most serious problem associated with this type of catalysts.

It is now known that the size of Au particles substantially affects the activity, and a high catalytic activity exists only on nanometre-sized Au particles. Furthermore, it is agreed that there is a strong 'support effect' in addition to this 'size effect', which means that the choice of the support material (normally oxides) also influences catalysis on Au nanoparticles or nanoclusters. In this respect, it has been suggested that point defects and step edges on the oxide support are important to the stabilization of the Au particles on the oxide and therefore have an important role in determining the catalytic activity of the Au nanocatalyst. However, the mechanism(s) of catalyzed reactions on dispersed Au

nanocatalysts and the nature of the active Au species still remain(s) unclear.

Researchers at the STM laboratories of iNANO are studying the role of the surface oxide in the catalytic process, in particular the role of missing oxygen atoms on the surface. To do so, they are using STM results in combination with theoretical modelling. Their results suggest that oxygen vacancies are not relevant at all for the stabilization of dispersed Au clusters under real reaction conditions with usually high oxygen pressures. Rather, they propose that oxygen-rich gold support interfaces are important to stabilize the gold nanoclusters. Thus these results show that the oxidation state of the supporting oxide surface is highly relevant and may also indicate that the perimeter of the gold nanoclusters is of special interest for catalytic reactions<sup>5</sup>.

#### **Au/Ni SURFACE ALLOY CATALYST FOR STEAM REFORMING**

In the steam reforming process, natural gas (mainly methane, i.e., CH<sub>4</sub>) and water are converted in H<sub>2</sub> and CO. This process will most likely continue to be the predominant industrial way for producing H<sub>2</sub> until other technologies are optimized. Currently the process employs a Nickel (Ni) catalyst, which is very active, but also catalyses the formation of graphite. Graphite formation impedes the activity of the catalyst and may eventually lead to its breakdown. A fundamental study was performed at iNANO to overcome this limitation<sup>6</sup>. A new catalyst was studied, in the form of a gold/nickel (Au/Ni) alloy. These two metals are immiscible in bulk but form an alloy in the first atomic layer. Catalysis is a surface process therefore the researcher at iNANO studied how this alloy performed in the steam reforming process using scanning tunnelling microscopy (STM), a sophisticated microscope that allows to study material surface in great detail. They found that the Au/Ni surface alloy is less reactive but more robust than pure Ni in decomposing natural gases like CH<sub>4</sub>. These fundamental findings

inspired the synthesis of a high surface area catalyst to be used for practical industrial applications (an  $\text{MgAl}_2\text{O}_4$ -supported Ni catalysts, with 16.5 wt.% Ni that was modified with 0.3 wt% of Au). This catalyst was compared to a conventional Ni catalyst in the steam reforming of n-butane. It was found that whereas the conventional catalyst deactivated rapidly due to the formation of graphite, the activity of this new catalysts remained nearly constant, due to a significant reduction of graphite formation. This work is an example of how fundamental understanding of the atomic process involved in catalysis can be used for the design of new catalysts for the steam reforming process.

#### OUTLOOK AND PERSPECTIVES

In this paper some examples were presented that illustrate how STM studies of catalyst model systems may provide new insights into industrial catalytic systems. The studies emphasize that atomic-scale insights are essential in order to understand certain important aspects of catalysis, such as the identification of active sites, the importance of defects, and substrate effects. STM has proven to be an excellent tool for studying these issues because of its superior atomic-scale resolution. However, it is important to be aware that catalyst model systems may differ significantly from real high surface area catalysts, both with regard to the nature of the surface morphology and to the applied pressure range. Today, different routes are being developed to investigate the so-called material and pressure gaps, and it appears from recent experiments that scanning probe microscopes (SPM) will play a crucial role in exploring these effects. It should be noted also that the STM is limited to the study of conducting surfaces and cannot, therefore, be used to study poorly conducting or insulating materials such as the oxide supports widely used in catalysis. For this purpose the atomic force microscope (AFM) is an ideal instrument, capable of probing conducting and insulating surfaces with a high degree of detail similar to that of the STM. In addition,

a great number of new developments of the STM and related techniques are being pursued, such as STMs operational at high pressures or with high scanning speeds, and have already shown promising results.

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