Imaging complex model catalysts in action: From surface science towards industrial practice using high-pressure scanning tunneling microscopy

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Summary and outlook

The work in this thesis showcases how close, at present, we can approach the catalysts and conditions in the chemical industry using high-pressure scanning tunneling microscopy (STM), while maintaining atomic-level detail. Evidently, flat and conductive model catalysts remain a requirement. However, the use of thin oxide films onto which nanoparticles can be deposited does allow one to prepare model catalysts that contain many of the characteristics of their industrial counterparts.

A key aspect in catalysis is to couple structural features to reactivity. Essential to obtaining such structure-activity relationships is to have control over the model catalyst structure. We investigated the example of the preparation of MoO_x nanoparticles on Al_2O_3/NiAl(110). Two methods were used: direct deposition of MoO_x and the deposition of Mo in $5x10^{-7}$ mbar O_2. Despite the fact that both methods yield highly oxidized MoO_x particles, MoO_x prepared via direct deposition of MoO_x produces smaller particles. We interpret this finding in terms of the interaction between the deposited material and the support, which is stronger for MoO_x than for Mo. The observed difference between the two preparation methods suggests that the Mo atoms are oxidized typically only after having attached to a stable Mo or MoO_x nucleus. This interpretation suggests that by increasing the O_2 pressure during the deposition of Mo, one can make a continuous transition from low to high dispersion. Thus, valuable size control may be obtained for the investigation of the size-activity relation of MoO_x/Al_2O_3 catalysts.

A major drawback of using a thin oxide film as support is that the film may not be stable under high-pressure conditions, particularly at elevated temperature. The MoO_x/Al_2O_3/NiAl(110) catalyst proved to be unstable towards H_2S and O_2 even in ultrahigh vacuum, due to the catalytic effect of MoO_x in the dissociation of H_2S and O_2. Hence, an important challenge for the future is to identify which model supports are suitable for high-pressure studies. One promising direction could be the use of oxide films deposited on noble metals such as FeO_x on Pt(111) or Au(111), and MgO on Ag(100), because the metal substrates in these cases are relatively inert. Alternatively, conductive (doped) bulk oxides such as TiO_2 and α-Fe_2O_3 could be employed, possibly in combination with Al_2O_3 or SiO_2 films.

Shifting the focus to realistic operating conditions, we studied the structure of MoS_2 nano-islands on Au(111) during the hydrodesulfurization reaction, in which sulfur is removed from organic molecules. While the Au support is clearly not representative of the industrial alumina support, this study represents the first case in which a nanoparticle catalyst is imaged with single atom resolution under working conditions. Using our corrosion resistant high-pressure STM, we imaged the catalyst in H_2 and during the desulfurization of CH_3SH. The images show that the active edge sites of the catalyst nano-islands adapt their sulfur, hydrogen, and hydrocarbon coverages depending on the gas environment. By comparing the observations to density functional theory calculations, we propose that the dominant edge structure during the desulfurization of CH_3SH contains a mixture of adsorbed sulfur and CH_3SH. Counterintuitively, the edge sulfur content is reduced by the presence of CH_3SH. In contrast, our theoretical analysis shows that a subtle lowering of the C-S bond-breaking barrier would result in sulfur deposition that is able to push the edge sulfur coverage far above its equilibrium value.

Like all surface science studies, our investigation of the hydrodesulfurization reaction only has a phenomenological comparability to industrial catalysis. However, high-pressure, high-temperature studies increase the chance to observe *relevant* phenomena, which also occur under industrial conditions. To further close the gap between our experiments and industrial practice, future experiments could increase the complexity of both the catalyst and the reactant feed. To improve the catalyst, $TiO_2(110)$ may be used as a support and Co or Ni promoters could be added. Especially the latter will have a profound effect on the reaction mechanism, as Co and Ni are known to replace Mo at the active edge sites. To approach a more realistic feed, heavier organosulfur molecules may be used, such as thiophenes. These molecules are significantly more difficult to desulfurize than CH_3SH, and hence are of greater interest.

Improvement of the understanding of catalysis may especially benefit processes that have not yet made it all the way to industrial use. Examples of such processes are oxidation reactions on oxide-supported gold catalysts, which provide a unique set of pathways for green chemistry. To investigate whether Au surface oxides may play a role in the catalysis, we studied their autocatalytic formation and stability on $WO_3/Au(111)$ and $ReO_3/Au(111)$ inverse model catalysts. We find that Au surface oxides are thermodynamically stable over a wide range of catalytically relevant conditions. The formation of the surface oxides requires initial seeds of AuO_x on our model catalysts, but proceeds autocatalytically from there on, with an O_2 dissociation barrier that is mainly entropic. Thus, our data indicate that Au surface oxides at the gas-surface interface of Au oxidation catalysts should be considered as a feasible reaction intermediate.

Two key questions that remain are whether the initial seeds of AuO_x can be generated on oxide-supported Au nanoparticles under typical reaction conditions, and whether the oxide formation rate balances out against the oxide consumption by the reactant that is being oxidized. High-pressure STM observations on various types of oxide nanoparticles on Au(111) during CO oxidation could provide the answer to these questions, although such inverted catalysts may behave differently than the real catalyst. Alternatively, one may image Au nanoparticles on TiO_2 or CeO_2. Although atomic resolution will not be achievable easily on the nanoparticles, changes in the particle height could provide a good indication for the presence of AuO_x. The presence of an oxide will affect the surface free energy of the Au particles and hence their aspect ratio.

To further improve the possibilities of high-pressure STM, we have developed an instrument that combines STM with synchrotron X-ray radiation, enabling chemical sensitivity in the images. By using the tip as a local X-ray absorption detector, one should be able to identify which type of atom is sitting where on the surface with nanometer spatial resolution. When performed in situ, such measurements could provide vital information on the distribution of promoters and reaction intermediates over the catalyst. The local chemical contrast can be obtained by measuring the X-ray induced increase in the tunnel current, which strongly depends on the proximity of X-ray absorbing atoms to the tunnel junction. Because this signal is extremely small compared to the ion currents generated in the gas phase, we used coaxially shielded STM tips. The conductive outer shield of the coaxial tips can be biased to deflect ions away from the tip core. In tunneling contact, the X-ray-induced current is separated from the regular topographic tunneling current using a novel high-speed separation scheme. Using these developments, we were able to detect the local X-ray-induced current on Au(111) in 800 mbar Ar.

After this proof-of-principle for the instrument, the next step is to obtain chemical contrast maps with high spatial resolution. Although the primary focus will initially be technical, a wide range of interesting future studies is possible. For instance, it should be possible to follow adsorbate-induced local changes in the chemical composition of alloys. Another possibility would be to pinpoint the local oxidation state of a substrate during its oxidation or reduction using the local white line absorption intensity.

Although by no means a plug-and-play technique, high-pressure STM has come to the point where the main focus can be on science rather than instrument development. The study of single crystals as well as more complex model catalysts shows that high pressures induce changes in the structure and mechanism of nearly all catalytic systems, which highlights the importance of the transition from vacuum to industrial conditions. Despite the limitations imposed by the requirement of flat and conductive samples, high-pressure STM allows for an unparalleled level of detail in its view on catalysts and should therefore play a key role in *operando* catalysis research. By combining it with X-rays or spectroscopic techniques, an even more complete picture of model catalysts can be drawn.