

Towards the pressure and material gap in heterogeneous catalysis: hydrogenation of acrolein over silver catalyts

M. Bron,[#] M. Bonifer,[#] A. Knop-Gericke,^{\$} D. Teschner,^{\$} J. Kröhnert,^{\$} F.C. Jentoft,^{\$}
R. Schlögl,^{\$} P. Claus[#]

[#] Department of Chemistry, Chemical Technology II, TU Darmstadt, Petersenstr. 20, D-64287 Darmstadt, Germany, ^{\$} Department of Inorganic Chemistry, FHI Berlin, Faradayweg 4-6, D-14195 Berlin, Germany

Introduction

In recent time, increasing effort has been undertaken in order to answer the question, whether it is justified to transfer results from surface science studies, mostly obtained with idealised surfaces under UHV conditions, to "real" catalysis, i.e. high pressures and complex materials (the so-called pressure and material gaps). The DFG (German research foundation) has initialised a priority program (SPP 1091) in order to bring together experts from surface science, materials science, catalysis and theory with the aim of bridging the two gaps in catalysis. Within this priority program, we are currently studying the hydrogenation of acrolein over silver. Acrolein, an α,β -unsaturated aldehyde, can be hydrogenated either to propanal (product of C=C-bond hydrogenation) or to allyl alcohol (product of C=O-bond hydrogenation). Whereas typical hydrogenation catalysts like Pt, Ru or Ni mainly produce the saturated aldehyde, selectivities to allyl alcohol of up to 53 % can be obtained when using monometallic silver (or gold) catalysts [1, 2]. The aim of our studies is to clarify the influence of reaction pressure and material on the selectivity distribution in the acrolein hydrogenation. Catalytic experiments have been carried out with differently structured samples from single crystals to disperse Ag/support catalysts in a broad pressure range (few mbar up to 20 bar). Various methods like *in situ*-XAS and XPS, flow-adsorption calorimetry, infrared spectroscopy, and transient analysis of products (TAP) are performed in order to gain insight into the modes of interaction of acrolein and hydrogen with differently structured silver samples. Effects of particle size and shape are also considered as well as the influence of the support material.

Experimental and Results

Silver samples with different loading (up to 10%) were prepared by incipient wetness method using silica and different ZnO supports. Gas phase hydrogenation of acrolein has been carried out in a flow microreaction system allowing a pressure in the range from 150 mbar up to 20 bar. When using silica supported silver catalysts, clear relations can be drawn concerning the pressure and material dependence of the selectivity to allyl alcohol: increasing partial pressure of either reactant (hydrogen or acrolein) leads to increased selectivity to allyl alcohol, also, smaller particles favour its formation. However, when using ZnO-supported catalysts, the situation becomes more complex. Catalysts of the same loading prepared by the same technique but with different ZnO yielded different selectivities to allyl alcohol at the same conversion. On the other hand, catalysts prepared from different precursors, but with the same support, lead to different activities but similar selectivities to allyl alcohol.

TEM investigations of the Ag/ZnO and Ag/SiO₂ catalysts reveal, that the particle sizes of the silica-supported catalysts are much smaller (2 nm and 15 nm in average for the two most

intensively studied catalysts) whereas the silver particles in the Ag/ZnO catalysts are surprisingly large (50 nm up to several hundreds of nm). This is even more surprising since the activities of the catalysts are in the same order of magnitude, the SiO₂ catalysts however, being a bit more active. All these results indicate, that the product distribution at supported silver catalysts is governed by a complex interplay between particle size (and/or shape), pressure, and, as the obviously most important factor, the support and the interactions between silver and support.

To gain more insight into the reasons for the catalytic behaviour of the Ag/support catalysts, the interaction of hydrogen alone with various silver samples has been studied. TAP (temporal analysis of products) indicates, that hydrogen interacts with nanodisperse Ag/SiO₂ samples, but not with larger unsupported silver particles (several mm in size) like those from electrolyte silver. However, as monitored by transmission infrared spectroscopy, not only the Ag nanoparticles but also the SiO₂ support interacts with hydrogen. SiO₂ and Ag/SiO₂ samples, after reduction and exposure to 100 mbar D₂, show a reversible H-D-exchange, as monitored by the Si-O-H(D) bands. Time resolved IR spectra indicate, that this H-D-exchange is faster at silver-containing samples. From temperature-dependent measurements, activation energies for the H-D-exchange of ca. 28 kJ/mol for Ag/SiO₂ and ca. 38 kJ/mol for SiO₂ have been calculated.

The interaction of acrolein with silver single crystals as well as with supported catalysts has been studied with *in-situ*-XAS and *in-situ* XPS. The samples were measured in mixtures of H₂/acrolein in the mbar pressure range in both techniques. Angular dependent XAS measurements on a Ag(111) single crystal indicated that acrolein is in the *lying-down* orientation. The C1s 1 π^* “C=O” transition is clearly increased compared to the C1s 1 π^* “C=C” for all the measured samples. Consequently, the surface concentration of C=O bonds relative to C=C bonds is higher, which is in line with concomitantly measured mass spectrometric data showing high selectivity towards C=C hydrogenation. *In-situ* XPS revealed that while silver foil is partly oxidic (~5%) the supported silver particles are completely reduced, as Ag is in the zero valence state. XPS data also indicate small amount of oxygen removal from the ZnO supported samples during the contact with hydrogen.

The combination of different results suggests that metal-support interaction plays an important role in the reaction. The major difference in hydrogen activation between supported catalysts and pure silver/support provides us a hint that the so-called “adlineation sites” (the perimeter interface between silver and support) are the key sites in the mechanism.

¹ P. Claus, H. Hofmeister, *J. Phys. Chem. B* **1999**, *103*, 2766.

² P. Claus, A. Brückner, C. Mohr, H. Hofmeister, *J. Am. Chem. Soc.* **2000**, *122*, 11430.