



Selective hydrogenation of acrolein using silver catalysts: studied by high-pressure XPS and XAS

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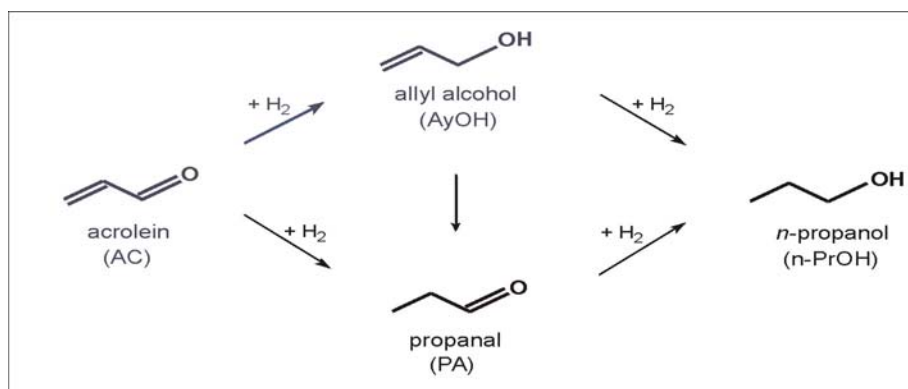
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Introduction

Selective hydrogenation of organic molecules containing numbers of unsaturated functional groups is an important step in the industrial preparation of fine chemicals. The hydrogenation of acrolein, an α,β -unsaturated aldehyde, can proceed either to the saturated aldehyde, propanal, or to the α,β -unsaturated alcohol, allyl alcohol (*Scheme 1*). From both products, the consecutive hydrogenation to *n*-propanol is possible as well as side reactions like decarbonylation. When using silver as catalyst, the selectivity to propanol or by-products is low (in most cases below 5 %), therefore mainly allyl alcohol and propanal are formed [1]. This joint multicenter project attempts to establish relationship between intramolecular selectivity (hydrogenation of C=C vs. C=O bond) and catalyst properties (surface structure, shape, support, precursor salt) and clarify the effect of reaction pressure.

Experimental

High-pressure XAS measurements were carried out on silver single-crystal (Ag(111)), polycrystalline Ag foil and supported catalyst (9Ag/SiO₂). The angle of incident beam to sample surface was varied on the single crystal (90°: normal incidence, 30°: grazing incidence). Carbon K-edge data were collected in the total electron yield mode (TEY). Gas phase and collector plate (surface related plus gas phase) signal were recorded. The reactor cell was operated in batch mode with a gas mixture of 0.01 mbar acrolein, 0.01 mbar argon and 7.48 mbar H₂. The reaction was monitored by online mass spectrometer (MS).



Scheme 1: Selective and total hydrogenation of acrolein

The high-pressure XP spectra were taken with another set-up. Its differentially pumped electrostatic lens system is the key feature, allowing us to investigate the sample in the mbar pressure region. We used here polycrystalline Ag foil and supported catalysts (Ag/ZnO) with different Ag loading and precursor salt. The samples were measured in UHV (RT), in hydrogen and oxygen (RT, 250 °C) and in the reaction mixture of 0.1 mbar acrolein and 0.9 mbar hydrogen (flow mode) at 250 °C.

Results

In the flow experiment no conversion could be detected, most probably because of the very low contact time and pore diffusion problems in the mbar pressure range. However, in the batch experiments we observed the formation of propionaldehyde (hydrogenation of C=C double bond) and almost no allyl alcohol (if any). The conversion was ~1-2%/hour, and was not too sensitive to the silver samples. Considering the broad range of samples (from single crystal to supported sample) and the inactivity of non-supported samples at industrial conditions, the hydrogenation was found to be a beam enhanced process on the illuminated surface. However, the low allyl alcohol (and high propionaldehyde) selectivity fits very well to the pressure dependence of the intermolecular selectivity measured separately in the industrial relevant (1-20 bar) pressure range.

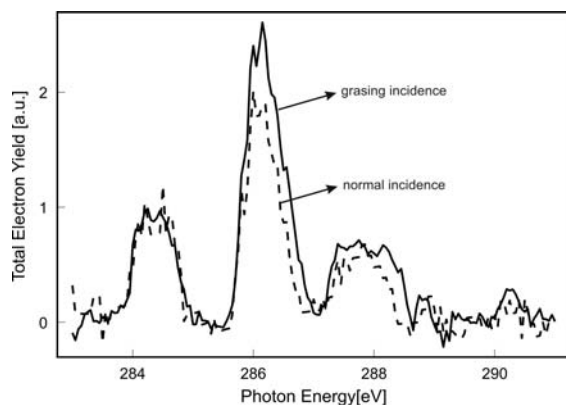


Figure 1: Angular dependent XAS of Ag(111) in the C K-edge (after background subtraction; gas + surface signal). The single crystal is in the gaseous ambient of 0.01 mbar acrolein, 0.01 mbar argon and 7.48 mbar H₂.

Angular dependent XAS measurements on the C K-edge shows that the π -like “C=O” orbital of acrolein lie parallel to the surface and σ^* (C-H) orbitals orientate rather perpendicular. Consequently, the molecule is in the *lying-down* orientation under hydrogenation conditions. A closer analysis of the surface related spectra (not just for Ag(111)) reveals that the $1\pi^*$ transition corresponding to the “C=O

part” of the molecule is clearly increased compared to the “C=C part”, relative to gas phase spectrum of acrolein. As a result, “C=O” is accumulated on the surface, or which is more in line with the catalytic data, C=C double bonds are almost not present on the surface. Therefore, it is very likely that the C=C double bond of acrolein is already hydrogenated and this hydrogenated species is what we detect on the surface.

In the high-pressure XPS set-up, we investigated a series of ZnO supported silver catalysts prepared from two different precursors (lactate or nitrate based Ag salt) with 5 or 10 % nominal Ag loading. Most of the samples were already tested catalytically at 20 bar before our measurements. In the information depth of XPS the apparent silver loading of 5 and 10% Ag/lactate/ZnO samples was nearly the same and was slightly dependent (8-10% Ag) on the gaseous ambient. The apparent silver content (metal dispersion) decreased in the reaction mixture (250 °C). The silver dispersion was low for the “calcined but not reduced” samples, which increases after reduction treatment. The “lactate” samples initially (stored in air) showed Ag₂O (6-8 % of the total Ag content) besides metallic silver. The oxide component was entirely reduced under reaction condition; therefore the reaction proceeds on metallic silver. The “nitrite” samples, exhibiting lower intrinsic activity, showed small residual oxidic part (~2%; ~ the detection limit). Additionally, we measured temperature dependently silver foil (Ag 3d core level) in oxygen (0.5 mbar) ambient, and surprisingly found Ag₂O (9.3%) at 350 °C, at which condition according to the silver/oxygen phase-diagram Ag₂O should be not stable. The oxygen content (mainly ZnO) of the supported samples decreases in the reaction mixture, due to desorption of adsorbed species (water, O-H, oxygenated C). The O/Zn ratio of the samples catalytically tested previously ex-situ were unexpectedly high (4-5), while the “calcined but not reduced” sample and the support itself showed ratios (1.5-2) much closer to the stoichiometric 1. The reason for this extraordinary O/Zn ratio might be in the high carbon content (up to 70%) of the used samples, carbon sitting mainly on Zn ions.

Acknowledgement

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References

- [1] Claus, P., *Topics in Catalysis* **5**, 51(1998)