



Selective gas-phase hydrogenation of C-5 hydrocarbons using palladium and nickel based catalysts

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Aim of the work and scientific background:

Heterogeneous catalysis plays an essential role in the field of chemistry and in chemical manufacturing. The complexity of a catalytic process usually requires that chemistry and engineering intimately mix to deliver the desired effect. The research project Athena (Advanced technology in catalytic chemistry and engineering for novel application) is a joint collaboration of Fritz-Haber-Institute and several British and American institutions presenting a multi-disciplinary approach to investigate heterogeneous catalytic reactions. The aim of *this* project is to investigate Pd and Ni based catalysts in the hydrogenation of C5 molecules containing different functionalities. A focal point of the activities concerns the relationship between selectivity and catalyst properties like structure, shape, carbonaceous deposits and possible support induced effects. Our group attempts to identify the electronic structure of the catalytic system, the role of carbon (deposit and/or incorporated in the bulk) as selectivity inducing co-catalyst [1] and recognizes the role of subsurface hydrogen [2,3] as modifier for chemisorption/electronic structure. For these purpose single crystals, foils and supported catalysts are used and studied by surface sensitive techniques like XPS and NEXAFS. These measurements are performed *in-situ* as this is the only way to gain information about a catalyst in the working state. Our novel *in-situ* XPS (and NEXAFS) set-up based on differentially pumped electrostatic lens-system is well suited for the experiments. This report summarizes the results obtained during the measurements at BESSY.

Results:

Hydrogenation of trans-2-pentene (t-2-p) was observed on polycrystalline Pd foil (RT and 100 °C), but not on Pd(111) single crystal [4]. We observed the reaction in the presence of a significant amount of carbon (more than

60 %) in the information depth of ~ 1 nm. On Pd(111) mainly graphite was present while other components, C-H (chemisorbed species) and C-Pd (interface carbon), were also formed on the foil to a greater extent. The d-band of the foil showed a remarkable up-shift towards E_{FERMI} as compared to Pd(111). The palladium foil lost its activity at elevated temperature (250 °C), most probably due to desorption of hydrogen. Using additional UPS measurements on adsorbed trans-2-pentene we concluded that t-2-p reacts with hydrogen in σ -bonded chemisorption modus, at least in UHV conditions.

In the hydrogenation of 1-pentyne the palladium samples were examined by XPS and an industrial nickel/alumina catalyst by XAS (because of charging no XPS was possible). On the palladium samples the selectivity towards single hydrogenation is high. Lower temperature enhances the total hydrogenation selectivity on the supported samples. Very low total hydrogenation was found on Pd foil, and no pentane was observed on Pd(111). Bulk palladium tends to hinder total hydrogenation. The single crystal was not inactive in single hydrogenation, as in the t-2-pentene case, however its activity was at least three times lower than that of polycrystalline foil. Palladium 3d (5/2) core level of a 5% Pd/carbon-nanotubes shows an adsorbate induced state (BE: ~335.5-335.6 eV) evolving at the high-BE side of the bulk Pd3d after introducing the reaction mixture (*Figure 1*). Its intensity increases with increasing temperature to 85 °C, at which temperature maximum activity is observed. A similar trend was found with the polycrystalline foil sample, as well. Depth-profiling experiment with the planar foil sample using different photon energies clearly indicates that this new state is surface related (*Figure 2*). With the single crystal this signal was weak. The Pd3d surface state correlates well with the catalytic activity. Heating up the foil to 250 °C, the catalytic activity, as well as this Pd 3d feature diminished. By the heating, the carbon content is not sig

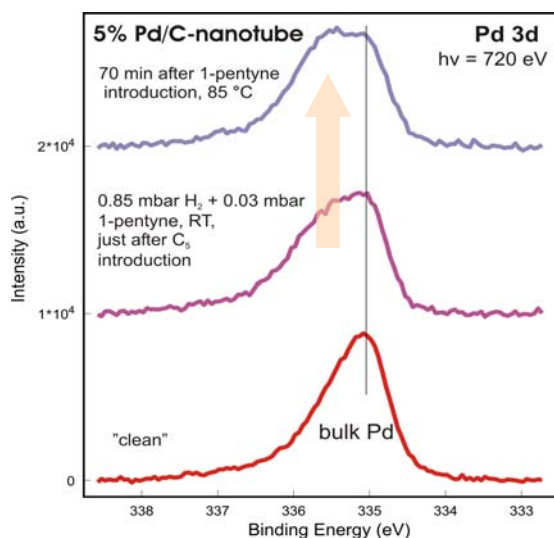


Figure 1: Pd3d of 5% Pd/CNT at different conditions

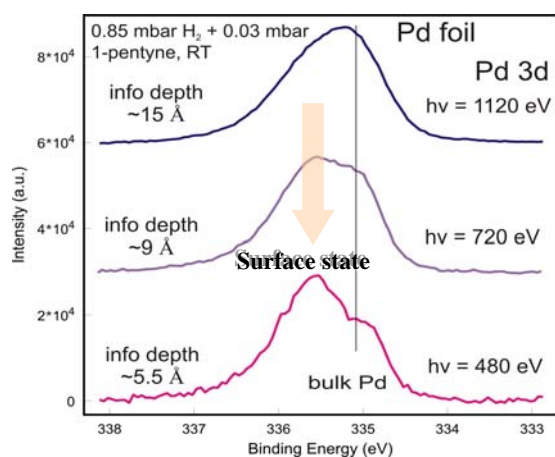


Figure 2: Pd3d of Pd foil at different photon energies

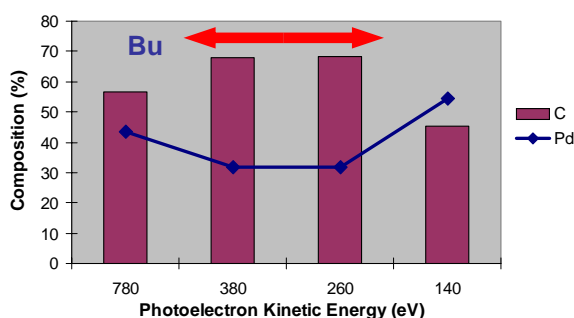


Figure 3: Elemental composition during depth-profiling experiment on Pd foil

References and Notes

- [1] N. Keller, N. Maksimova, V. V. Roddatis, M. Schur, G. Mestl, Y. V. Butenko, V.L. Kuznetsov, R. Schlögl, *Angew. Chem. Int. Ed.* 41 (2002) 1885.
- [2] S. T. Ceyer, *Acc. Chem. Res.* 34 (2001) 737.
- [3] Sh. Shaikhutdinov, M. Heemeier, M. Bäumer, T. Lear, D. Lennon, R. J. Oldman, S. D. Jackson, H.-J. Freund, *J. Catal.*, 200 (2001) 330.
- [4] D. Teschner, A. Pestryakov, E. Kleimenov, M. Hävecker, H. Bluhm, H. Sauer, A. Knop-Gericke, R. Schlögl, *J. Catal.*, (Part II) in press
- [5] D. Teschner, A. Pestryakov, E. Kleimenov, M. Hävecker, H. Bluhm, H. Sauer, A. Knop-Gericke, R. Schlögl, *J. Catal.*, (Part I) in press

nificantly altered, thus the loss of the Pd3d component cannot be correlated with the total carbon content. Desorption of surface hydrogen at higher T is the reason of the loss of activity.

A significant amount of subsurface carbon was found from the depth profiling experiments (Figure 3) as the carbon content showed a maximum curve as a function of photoelectron kinetic energy (i.e. inelastic mean free path). Carbon in subsurface position blocks the way of hydrogen entering the surface from the bulk. This hydrogen has a higher energy compared to surface hydrogen [2] therefore it is less selective. The lower total hydrogenation thus is in good accord with the blocking role of subsurface carbon species.

The palladium β -hydride state was also investigated [5]. The palladium 3d core level is changed compared to clean Pd; the peak is shifted slightly ($\sim +0.15$ eV) to higher binding energy and the asymmetry of the peak is much less. Therefore the palladium surface state (335.5 eV Pd3d component) during the catalytic experiment is not a hydride-induced state. The valence band measured at 150 eV photon energy reveals a broad hydrogen induced band between ~ 4 -9 eV.

The nickel sample was active (mainly single hydrogenation) after low T redox (O_2 followed by H_2) treatment, although the Ni $L_{3,2}$ edge revealed clearly oxidic Ni (NiO). As the information depth of XAS is approx. the same as the mean particle size and as the reaction is not expected to proceed on oxides, the top surface layer of the NiO is most probably metallic. After high T redox treatment (500 °C) the sample was approx. twice as active and Ni was metallic. Moreover, the selectivity towards total hydrogenation increased as well. Hydrogen is known to readily dissolve in the bulk of metallic Ni particles. As a consequence, the NiO core of the particles played a similar role as subsurface carbon in Pd, namely avoiding the participation of high-energy hydrogen in the hydrogenation, thus increasing selectivity.

Acknowledgements

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