Conference Weimar 2007

Surface Characterization of the Intermetallic Compound PdGa – A Highly Selective Acetylene Hydrogenation Catalyst

K. Kovnir,[1,2] M. Armbrüster,[2] D. Teschner,[2] T.V. Venkov,[2] A. Knop-Gericke,[2] F.C. Jentoft,[2] Yu. Grin,[1] R. Schlögl [2]

[1] Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden
[2] Abteilung Anorganische Chemie, Fritz-Haber-Institut der MPG, Berlin

Selective acetylene hydrogenation to ethylene is an important method for removing traces of acetylene in the ethylene feed for the production of polyethylene. Typical catalysts, like Pd dispersed on metal oxides are widely used for this reaction and show a limited selectivity and long-term stability.[1] This can be attributed to the presence of active-sites ensembles on the catalyst surface.[2] These drawbacks can be overcome by using the intermetallic compound PdGa which only possesses isolated palladium atoms in the crystal structure[3] and shows higher selectivity as well as an increased long-term stability compared to the commercial catalysts.[4]

It was demonstrated by *in situ* XRD and by *in situ* EXAFS experiments that PdGa exhibits high bulk stability during the acetylene hydrogenation reaction.[4] In the present work the surface of the intermetallic compound PdGa was probed by *in situ* XPS as well as CO adsorption using FTIR spectroscopy.

PdGa was prepared by melting the elements under an inert Ar atmosphere followed by further annealing at 800 °C in vacuum. The single phase ingot was powdered in a mortar. For XPS measurements the powdered sample was pressed in a high density pill using the spark plasma sintering (SPS) technique. For FTIR measurements the metallic and nontransparent powder of PdGa was mixed with high surface area silica (Degussa).

Investigations by UHV XPS revealed a significant modification of the Pd electronic state in the intermetallic compound due to covalent bonding: the Pd3$d_{5/2}$ peak is shifted by 1 eV to higher binding energy compared to the metallic palladium (Figure 1). *In situ* measurements showed a high stability of the Pd surface states without appearance of any additional components or significant shifts of the Pd3$d_{5/2}$ peak when applying a reactive atmosphere and temperature (1.0 mbar of H_2 + 0.1 mbar of C_2H_2, t = 120ºC). This is in contrast to metallic palladium for which the formation of an additional Pd component during alkyne hydrogenation was detected.[5] Investigation of carbon and palladium depth profiles for PdGa indicates the absence of a subsurface carbon phase, distinguishing this material decidedly from metallic palladium catalysts.[5]

The adsorption of CO on the PdGa compound at room temperature results in appearance of only one band with a maximum at 2047 cm^{-1}, which corresponds to linear Pd–CO carbonyls. It should be mentioned that the observed band (2047 cm^{-1}) is shifted to lower wavenumbers compared to the respective CO (on-top) species forming upon adsorption on metallic palladium (2100-2080 cm^{-1}),[6] which is an indication for the modification of the Pd electronic states in the investigated intermetallic compound. The absence of bands due to bridged carbonyls in the observed spectra and the fact that the observed band is not coverage dependent, indicated that the active sites in PdGa are really isolated.

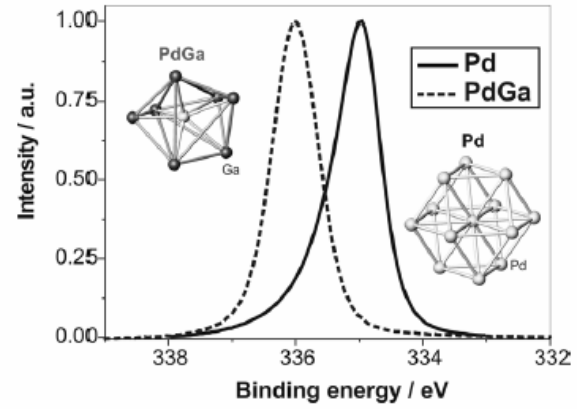

Figure 1: UHV XPS spectra (Pd3$d_{5/2}$) of metallic palladium and the intermetallic compound PdGa. Insets show the coordination of Pd atoms.

References

[1] A. Molnar, A. Sarkany, M. Varga, *J. Mol. Catal. A* **2001,** *173,* 185.
[2] E. G. Derouane, *J. Mol. Catal.* **1984,** *25,* 51.
[3] P. Eßlinger, K. Schubert, *Z. Metallkd.* **1957,** *48,* 126.
[4] J. Osswald, K. Kovnir, M. Armbrüster, R. Giedigkeit, T. Ressler, Yu. Grin, R. Schlögl, *Angew. Chem. Int. Ed.* **2006** submitted; *European patent* pending, **2006**
[5] D. Teschner, et al. *J. Catal.* **2006,** 242, 26–37.
[6] H. Unterhalt, G Rupprechter, H.-J. Freund. *J. Phys. Chem. B* **2002,** *106,* 356-367.