



In Situ Surface Studies of Site-Isolated Hydrogenation Catalysts – The Intermetallic Compound PdGa

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. Schlögl²

¹ Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

² Department of Inorganic Chemistry, Fritz Haber Institute of the MPG, Berlin, Germany

* Corresponding author: e-mail kovnir@cpfs.mpg.de,

Introduction

Selective acetylene hydrogenation 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] This drawback can be overcome by using the intermetallic compound PdGa which possesses palladium atoms in the crystal structure well isolated from each other by a gallium shell (Figure 1).^[3,4] PdGa shows higher selectivity and increased long-term stability compared to the commercial catalysts, including PdAg alloys.^[4] *In situ* XRD and *in situ* EXAFS experiments demonstrated 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.

Experimental

PdGa was prepared by melting the elements under argon atmosphere followed by further annealing at 800°C in evacuated quartz glass ampoules. The single-phase ingot was subsequently powdered in a mortar. For XPS measurements a high density sample was prepared from the powder by use of the spark plasma sintering (SPS) technique. For FTIR measurements the metallic and non-transparent powder of PdGa was mixed with high surface area silica

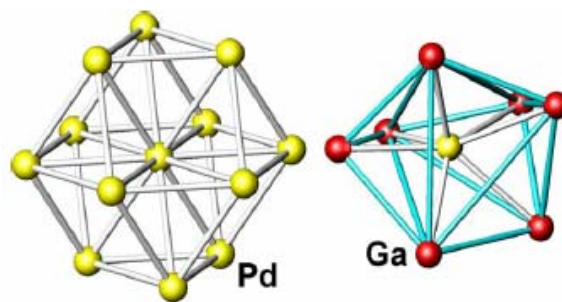


Figure 1: Coordination of Pd atoms in metallic Pd (left) and in PdGa (right).

Results and discussion

The XPS investigation before hydrogenation revealed a significant modification of the Pd electronic state in the intermetallic compound compared to Pd metal: the Pd3d_{5/2} peak is shifted by 1 eV to higher binding energy. *In situ* XPS measurements, performed at ~1 mbar pressure, showed a high stability of the Pd surface states (Figure 2) without appearance of any additional components or significant shifts of the Pd3d_{5/2} peak when applying the reactive atmosphere and temperature (1.0 mbar of H₂ + 0.1 mbar of C₂H₂ at 120 °C). This is in contrast to Pd metal 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-containing phase, distinguishing this material decidedly from metallic palladium catalysts.^[5]

The adsorption of CO on the PdGa compound at room temperature results in the appearance of only one band with a maximum at 2047 cm⁻¹, which corresponds to linear Pd⁰-CO carbonyls (Figure 2). After re-oxidation the

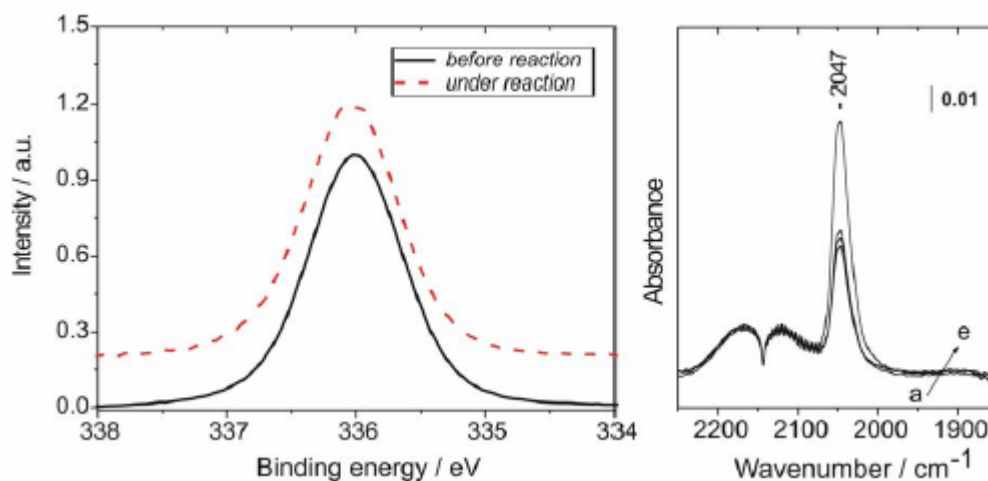


Figure 2: Left: XPS spectra of PdGa before (solid) and during (dashed) the acetylene hydrogenation reaction. Right: FTIR spectra of CO adsorption on PdGa surface at room temperature. Sequence from *a* to *e* corresponds to increasing exposition time: immediately after introducing CO (*a*), after 1, 5, 10 and 60 minutes (*e*).

catalyst at 400 °C the same band was observed which is in good agreement with the *in situ* bulk stability of PdGa.^[4] 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 by covalent bonding 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.

Conclusions

Characterization of PdGa by FTIR and *in situ* XPS revealed high surface stability during the reaction of acetylene hydrogenation and confirms the isolation of the active Pd site on the surface. In combination with modified electronic Pd states due to covalent bonding in the intermetallic compound it leads to superior catalytic properties like high selectivity and long-term stability during the partial hydrogenation of acetylene.

References

- [1] A. Molnar, A. Sarkany, M. Varga, Hydrogenation of carbon-carbon multiple bonds: chemo-, regio- and stereoselectivity, *J. Mol. Catal. A* **2001**, *173*, 185.
- [2] E. G. Derouane, 2nd European symposium on catalysis by metals - multimetallic catalysts in synthesis and transformation of hydrocarbons - concluding remarks, critical issues and perspectives, *J. Mol. Catal.* **1984**, *25*, 51.
- [3] P. Eßlinger, K. Schubert, Zur systematik der strukturfamilie des NiAs .1. Verbreitung der strukturen der NiAs-familie, *Z. Metallkd.* **1957**, *48*, 126.
- [4] J. Osswald, K. Kovnir, M. Armbrüster, R. Giedigkeit, T. Ressler, Yu. Grin, R. Schlögl, *Angew. Chem. Int. Ed.*, Pd-Ga intermetallic compounds as selective catalysts for the hydrogenation of acetylene, **2006** *submitted*.
- [5] D. Teschner, E. Vass, M. Hävecker, S. Zafeirotos, P. Schnörch, H. Sauer, A. Knop-Gericke, R. Schlögl, M. Chamam, A. Wootsch, A.S. Canning, J.J. Gamman, S.D. Jackson, J. McGregor, L.F. Gladden., Alkyne hydrogenation over Pd catalysts: a new paradigm *J. Catal.* **2006**, *242*, 26.
- [6] H. Unterhalt, G Ruppachter, H.-J. Freund. Vibrational sum frequency spectroscopy on Pd(111) and supported Pd nanoparticles: CO adsorption from ultrahigh vacuum to atmospheric pressure, *J. Phys. Chem. B* **2002**, *106*, 356.