



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

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Selective acetylene hydrogenation is an important method for removing traces of acetylene in the ethylene feed for the production of polyethylene. Typical catalysts show a limited selectivity and long-term stability. This can be attributed to the presence of active-site ensembles. This drawback can be overcome by using the intermetallic compound PdGa which possesses palladium atoms in the crystal structure well isolated by a gallium shell. PdGa shows higher selectivity and increased long-term stability compared to commercial catalysts.^[1] *In situ* XRD and *in situ* EXAFS experiments demonstrated that PdGa exhibits high bulk stability during acetylene hydrogenation.

The XPS investigation before the reaction 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 (Figure). *In situ* XPS measurements showed a high stability of the Pd surface states 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 H₂ 0.1 mbar C₂H₂ at 120 °C). This is in contrast to Pd metal for which the formation of an additional Pd component during alkyne hydrogenation was reported recently.^[2] The adsorption of CO on PdGa at room temperature results in the appearance of only one band with a maximum at 2047 cm⁻¹, which should correspond to linearly bound CO (Pd-CO). 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), which may be 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 spectra

and the fact that the observed band is not coverage dependent indicates that the active sites in PdGa are really isolated.

Characterization of PdGa revealed high surface stability during the hydrogenation of acetylene and confirms the isolation of the active Pd sites on the surface. In combination with the modified electronic Pd states – perhaps due to the covalent bonding – it leads to superior catalytic properties high selectivity and long-term stability.

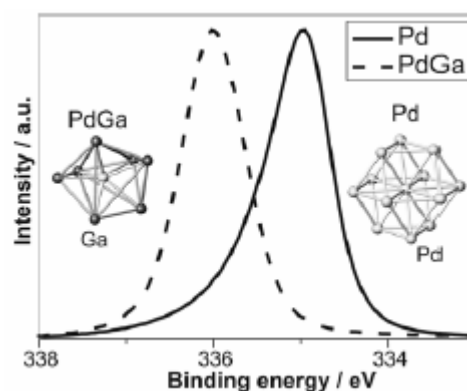


Figure 1: UHV spectra of Pd and PdGa

References

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