Pd-Ga Intermetallic Compounds – A New Approach to Heterogeneous Hydrogenation Catalysts

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Introduction

More than 90% of the chemicals in the world are produced utilizing catalysts [1]. Heterogeneous catalysis is of huge importance to fulfill raising demands, reduce the production costs and to minimize the environmental impact. Novel, highly selective catalysts are required. A development based on sophisticated concepts, rather than on trial-and-error procedures, is expected to be cost and time efficient.

Supported bimetallic catalysts are widely used in industrial processes, but are complex to prepare and characterize. Challenges are achieving a uniform particle composition and controlling strong metal-support interactions which influence the nature of the active sites. Furthermore, the active metals in these catalysts may be present as elements, disordered alloys, intermetallic compounds, and other compounds – such as oxides – or a mixture of all aforementioned.

As a result, it is close to impossible in these cases – at least very hard – to extract correlations between, e.g., the crystal structure of the active phase and the observed selectivity in bimetallic catalysts, which may be of conceptual importance.

To circumvent these complications, our rational approach is based on using single phase, stable and unsupported intermetallic compounds with ordered crystal structures as catalysts. The latter leads to a uniform surrounding of the active sites, thus, the number of neighboring sites as well as the distance between them are known. By selecting intermetallic compounds with suitable crystal and electronic structures, the active sites can be tailored to the needs of the reaction to be catalyzed [2].

Test Reaction

A reaction, for which literature states that isolated active sites are needed [3], is the partial hydrogenation of acetylene to ethylene in a large excess of ethylene:

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

This heterogeneously catalyzed process is an important step in the purification of the ethylene feed for the production of polyethylene with an annual industrial output of more than 50×10^6 t.

High selectivity is crucial since otherwise valuable ethylene is lost by total hydrogenation. At the same time the concentration of acetylene has to be reduced from ~ 1% to the low ppm level to prevent poisoning of the subsequently employed polymerization catalyst.

Typical Pd-based catalysts used in industry show only a limited selectivity and long-term stability. Both restrictions can be assigned to large active-site

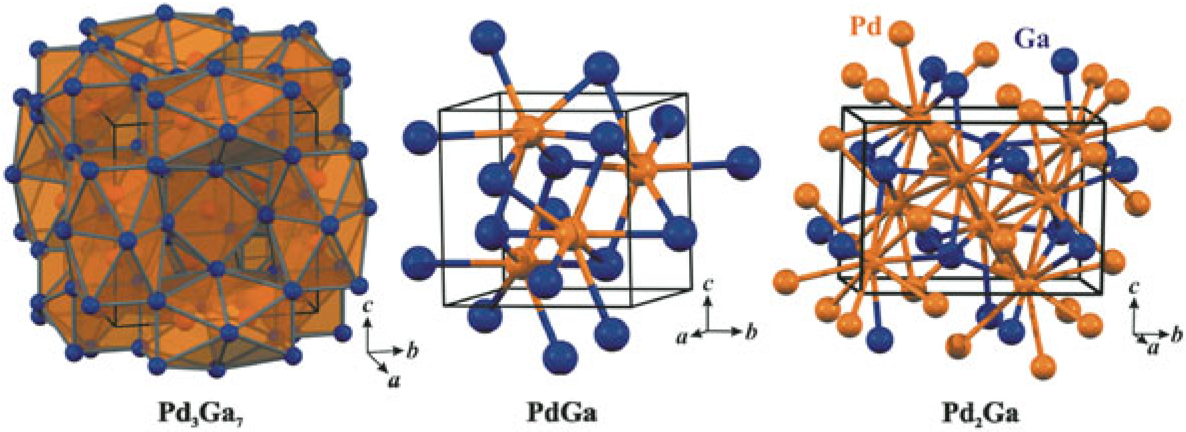

Fig. 1: Crystal structures of Pd$_3$Ga$_7$, PdGa and Pd$_2$Ga. In all structures, the Pd atoms possess fewer Pd neighbors than in elemental Pd, achieving active-site isolation on different levels.

ensembles, enabling different adsorption configurations, leading not only to ethane, but to carbonaceous deposits, which deactivate the catalyst. Moreover, the *in situ* formation of the very active β-PdH$_x$ is a selectivity diminishing factor [4].

Catalysts

For the reasons above, isolation of the Pd atoms should improve the selectivity towards semi-hydrogenation and the stability of the catalysts due to suppressed carbon deposition.

Currently, this active-site isolation is approached by diluting Pd with catalytically inactive Ag in disordered alloys [5]. While the selectivity is improved, the long term stability is threatened by segregation, leading to either large Pd ensembles or an inactive Ag surface.

Applying our concept, the well-characterized intermetallic compounds Pd_3Ga_7, PdGa, and Pd_2Ga (Fig. 1) were tested as unsupported catalysts for the selective hydrogenation of acetylene in the presence of large amounts of ethylene. All three compounds posses a reduced number of Pd neighbors – compared to Pd metal – in the crystal structure [6-8]. Moreover, they are characterized by covalent bonding between the atoms according to quantum chemical calculations [2]. While the isolation should lead to high selectivity, the covalent bonding should prevent hydride formation and segregation, thus further increasing the selectivity and stability of the catalyst.

In situ investigations

The local environment of active sites on the surface of palladium catalysts can be probed by carbon monoxide adsorption using Fourier transform infrared spectroscopy (FTIR).

Adsorption of CO on PdGa at room temperature results in the appearance of only one sharp band at 2047 cm^{-1} (Fig. 2). The signal disappears after short evacuation, and can be assigned to CO adsorbed on Pd in on-top position, since CO molecules adsorbed on two or more Pd atoms reveal significantly higher stability compared to linearly adsorbed CO on Pd [9]. The shift to lower wavenumbers compared to CO on-top on metallic palladium (2080-2100 cm^{-1}), expresses the altered adsorption properties due to the modification of the Pd electronic structure by the covalent bonding in PdGa. CO molecules adsorbed on adjacent surface atoms influence each other through dipole-dipole interactions resulting in a coverage-dependent frequency shift. No such shift was observed for CO on PdGa. Together with the absence of additional signals, this is a clear indication that the adsorption sites in PdGa are really isolated.

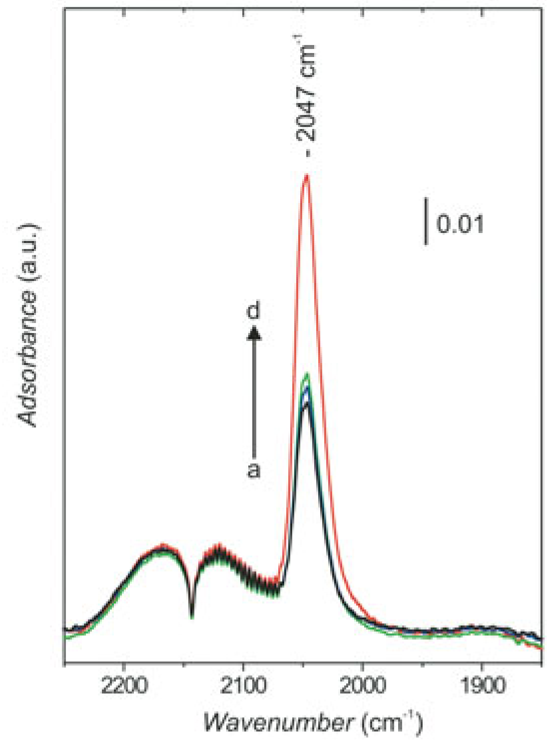

Fig. 2: FTIR spectra of CO adsorbed on PdGa at room temperature with increasing exposition times (a: immediately after introducing 50 mbar of CO; d: after 60 min).

To verify the claimed structural stability – thus the active-site isolation – of the intermetallic compounds under reaction conditions, *in situ* high-pressure X-ray photoelectron spectroscopy (XPS) was performed at BESSY (line U49/2-PGM1). Furthermore, XPS under ultra high vacuum (UHV) conditions allowed to measure the variations in the electronic structure of the intermetallic compounds compared to elemental palladium.

XPS measurements in UHV revealed a significant shift of the Pd3$d_{5/2}$ XPS signal to higher binding energy for the intermetallic compounds compared to metallic Pd (Fig. 3). Also evident from the measurements is a strong modification of the valence band. Quantum chemical calculations suggest that the Pd *d* band is filled to a higher

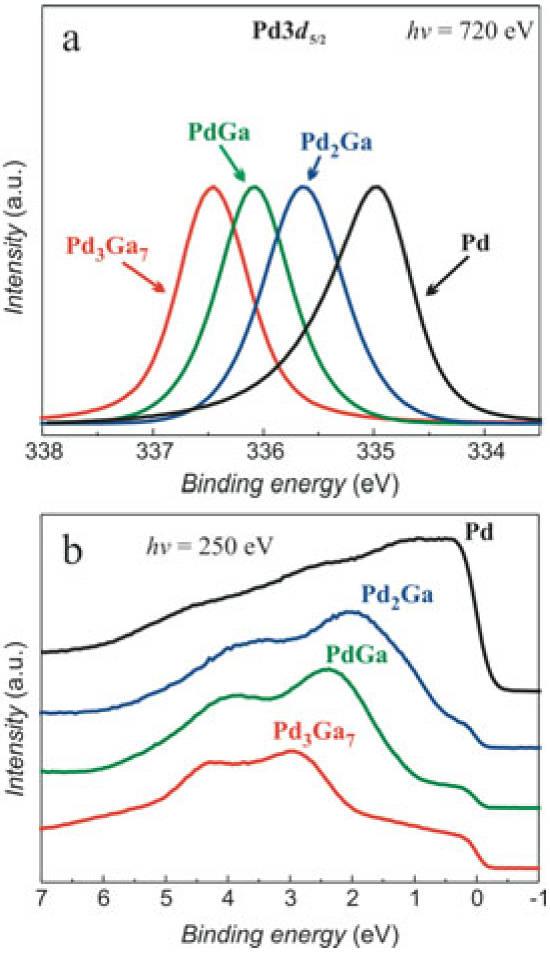

Fig. 3: Pd3d$_{5/2}$ *(a) and valence band (b) XP spectra of Pd*$_3$*Ga*$_7$*, PdGa, Pd*$_2$*Ga, revealing the alterations in the electronic structure in comparison to elemental Pd.*

degree by the chemical bonding between Ga and Pd. Indeed, an increasing shift with decreasing Pd content is observed in XPS.

In situ XPS measurements did not show the appearance of any additional components or significant shifts of the Pd3$d_{5/2}$ signals when applying reactive atmosphere and temperature (1.0 mbar of H_2 + 0.1 mbar of C_2H_2 at 120 ºC, Fig. 4). Carbon and palladium depth profiles confirmed the absence of subsurface carbon-containing phases, distinguishing the intermetallic compounds further from metallic palladium catalysts.

In situ prompt gamma activation analysis (PGAA) is a recently developed technique detecting and quantifying dissolved hydrogen atoms in catalysts *in situ* [10]. For PdGa the atomic H/Pd ratio reaches 0.010 in hydrogen atmosphere at room temperature and 0.012 in the H_2/C_2H_2 feed at 323 K. The two values are equal within the experimental error and indicate that no hydrogen is dissolved in the intermetallic compound since only *ad*sorbed hydrogen contributes to the observed signal. In contrast to PdGa, elemental palladium readily *ab*sorbs hydrogen, forming β-PdH$_{0.7}$ according to the PGAA measurements.

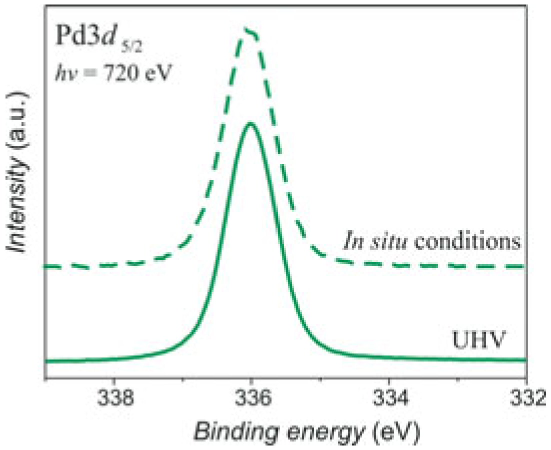

*Fig. 4: Comparison of the Pd3*d$_{5/2}$ *XP spectra of PdGa under* in situ *and UHV conditions shows the stability under reaction conditions.*

The stability of the intermetallic compounds was further investigated by *in situ* EXAFS to probe the structural short-range order and by *in situ* XRD to detect changes in the long-range order of the crystal structures [11]. Combination of the *in situ* investigations clearly reveals:

- the presence of only isolated active sites
- the stability under *in situ* conditions
- the absence of hydride formation

Catalytic Properties

While the covalent Pd-Ga interactions prevent the formation of active but unselective sub-surface hydrides, the stable isolation of the active sites should lead to increased selectivity and stability under reaction conditions.

For the catalytic tests (Fig. 5), the acetylene concentration was chosen close to industrial conditions, i.e. a molar ratio of 1:100 for acetylene to ethylene. While the 5 wt.%-Pd/Al_2O_3 reference catalyst deactivates strongly due to carbonaceous deposits, the intermetallic compounds reveal a remarkable long-term stability during 20 h on stream [12]. This can be attributed to the isolation of the active sites, which suppresses unfavorable side reactions and agglomeration.

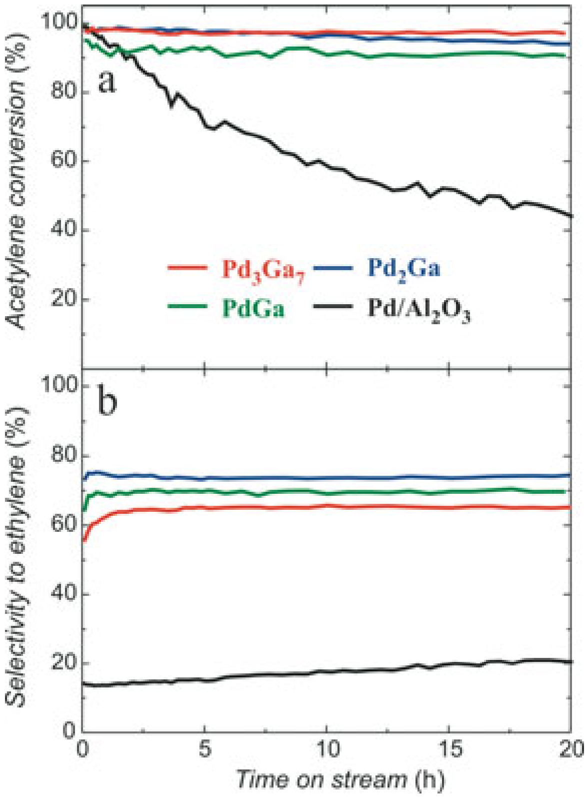

Fig. 5: Acetylene conversion (a) and selectivity to ethylene (b) at 473 K for Pd_3Ga_7 (50 mg), PdGa (20 mg), Pd_2Ga (10 mg) and 5 wt.%-Pd/Al_2O_3 (0.1 mg). Feed composition: 0.5% C_2H_2, 5% H_2 and 50% C_2H_4 in helium, with a total flow of 30 ml/min.

A comparison of the selectivities achieved by the different catalysts clearly demonstrates the consequences of the active site isolation and the absence of hydride formation. In contrast to Pd/Al_2O_3, the Pd-Ga intermetallic compounds show considerably higher selectivity in the hydrogenation of acetylene to ethylene. The high selectivity observed for all intermetallic compounds indicates that not only the geometric site isolation is important to achieve superior catalytic properties. In addition, the modification of the electronic structure prevents hydride formation and segregation.

Conclusions

Applying a new and rational approach to well-defined, stable and site-isolated catalysts, it was possible to identify Pd-Ga intermetallic compounds as highly selective and long-term stable catalysts for the semi-hydrogenation of acetylene in the presence of ethylene.

Quantum chemical calculations revealed the presence of covalent bonding, leading to high stability of the site isolation. *In situ* investigations by different methods proved the presence of only isolated active sites, high stability, and the absence of hydride formation.

Since the observed catalytic properties in each case can be assigned to a specific intermetallic compound, further rational development is conceivable. The results demonstrate that structurally well-defined intermetallic compounds possess high potential in heterogeneous catalysis and are promising candidates for industrial applications [13-14].

References

[1] *J.M. Thomas and W.J. Thomas,* in Principles and Practice of Heterogeneous Catalysis, 3rd edition, VCH, Weinheim (2005).

[2] *K. Kovnir, M. Armbrüster, D. Teschner, T. V. Venkov, F. C. Jentoft, A. Knop-Gericke, Yu. Grin, and R. Schlögl*, Sci. Technol. Adv. Mater. **8** (2007) 420.

[3] *A. Borodzinski and G. C. Bond,* Catal. Rev. **48** (2006) 91.

[4] *G. C. Bond and P. B. Wells*, J. Catal. **5** (1966) 65.

[5] *M. M. Johnson, D.W. Walke,r and G.P. Nowack*, US Patent 4404124 (1983).

[6] *M. K. Bhargava, A.A. Gadalla, and K. Schubert*, J. Less-Common Met. **42** (1975) 76.

[7] *K. Khalaff and K. Schubert*, J. Less-Common Met. **37** (1974) 129.

[8] *K. Kovnir, M. Schmidt, C. Waurisch, M. Armbrüster, Y. Prots, and Y. Grin*, Z. Kristallogr. NCS **223** (2008) 7.

[9] *H. Unterhalt, G. Rupprechter, and H.-J. Freund*, J. Phys. Chem. B **106** (2002) 356.

[10] *Z. Révay, T. Belgya, L. Szentmiklósi, Z. Kis, A. Wootsch, D. Teschner, M. Swoboda, R. Schlögl, J. Borsodi, and R. Zepernick*, Anal. Chem. **80** (2008) 6066.

[11] *J. Osswald, R. Giedigkeit, R. E. Jentoft, M. Armbrüster, F. Girgsdies, K. Kovnir, T. Ressler, Yu. Grin, and R. Schlögl*, J. Catal. **258** (2008) 210.

[12] *J. Osswald, K. Kovnir, M. Armbrüster, R. Giedigkeit, R.E. Jentoft, U. Wild, Yu. Grin, and R. Schlögl,* J. Catal. **258** (2008) 219.

[13] *J. Osswald, R. Giedigkeit, M. Armbrüster, K. Kovnir, R. E. Jentoft, T. Ressler, Yu. Grin, and R. Schlögl,* International Patent WO2007104569 (2007).

[14] *M. Armbrüster, M. Schmidt, K. Kovnir, M. Friedrich, K. Weinhold, Yu. Grin, and R. Schlögl,* International Patent PCT/EP2008/062424 (2008).

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