



Pinning the catalytic centre: A new concept for catalysts development

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Heterogeneous catalysis is 'perennially relevant, endlessly fascinating and deeply enigmatic' stated a text book on catalysis [1]. This statement might be biased, but there can be no doubt about its huge importance. After all, more than 90% of the chemicals in the world are produced utilizing catalysts. To fulfill raising demands, lower the production costs and to minimize the environmental impact, novel highly selective catalysts are required. Thereby, catalyst development based on experimental functional evidence rather than on trial and error becomes a viable alternative.

Supported bimetallic catalysts are widely used in industrial processes. These catalysts are complex objects for the preparation and characterisation and it is difficult to achieve a uniform particle composition and exclude strong metal-support interactions. A prediction for the nature of the active sites in such catalysts is strongly limited because the supported particles of the two metals may coexist as elements or form clusters of different compositions.

more than 50 million tons produced worldwide per annum. During its synthesis the ethylene monomer feed needs to be cleaned from acetylene admixtures by selective hydrogenation. For this catalytic process selectivity is crucial since otherwise valuable ethylene is lost. Typical Pd-based catalysts show a limited selectivity and long-term stability, which is attributed to the formation of β -Pd-hydride and the presence of active-site ensembles [3]. In our study we tested three well-characterized intermetallic compounds – Pd₃Ga₇, PdGa, and Pd₂Ga (Fig. 1) – with different crystal structures, and thus with differently isolated Pd active sites.

In-situ high-pressure X-ray photoelectron spectroscopy (XPS) characterisation was performed at beamline U49-2_PGM-1. The IMCs are characterised by a significant shift of the Pd3d_{5/2} X-ray photoelectron peak to higher binding energy compared to metallic Pd, and by a modified valence band (Fig. 2). Quantum chemical calculations suggest that their Pd *d*-band is further filled and shifted to higher binding energy by the chemical bonding

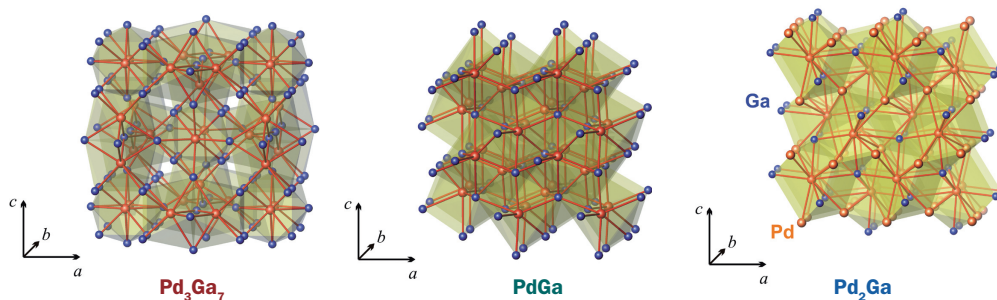
between Ga and Pd (Fig. 3). Indeed, an increasing shift with lower Pd:Ga ratio is observed in XPS. In turn, the alteration of the valence band region leads to a different screening of the core hole, which is indicated by the changes of the Pd3d spectra.

In situ XPS measurements, performed at ~1 mbar pressure, showed a high stability of the Pd surface states (Fig. 4) without the appearance of any additional

component or significant shift of the Pd3d_{5/2} peak, when applying the reactive atmosphere and temperature (1.0 mbar of H₂ + 0.1 mbar of C₂H₂ at 400K). The metastable Pd-hydride phase, which is formed in conventional Pd-catalysts, is clearly not present in our system. Investigation of C and Pd depth profiles confirmed the absence of a sub-surface carbon-containing phase, distinguishing these materials from metallic palladium catalysts [4].

Filling of the Pd *d*-band and the covalent Pd-Ga interaction prevents the formation of sub-surface hydrides, as confirmed by the bulk-sensitive Prompt Gamma Activation Analysis

Fig. 1:
The crystal structures of Pd₃Ga₇, PdGa and Pd₂Ga.
Pd: orange; Ga: blue.



References:

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Materials that can surmount these drawbacks and be utilized for the development and testing of concepts are 'well-ordered unsupported intermetallic compounds (IMCs)'. Here, the atomic environment of the catalytically active metal is pinned in the crystal structure due to the partly covalent bonding. This leads to a homogeneous distribution of the active sites and to a significantly reduced segregation and to negligible sub-surface chemistry [2].

We chose the palladium-(Pd)-based catalyst involved in the production of polyethylene as candidate to validate the proposed concept. Polyethylene is a widely used polymer with

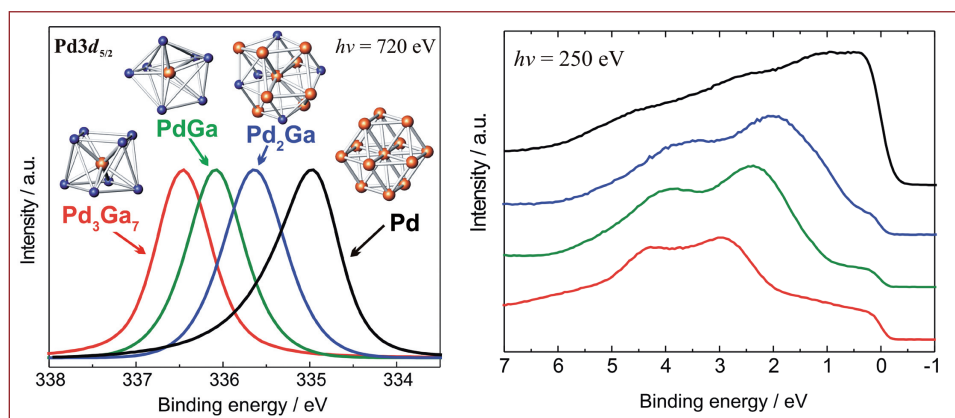


Fig. 2: Pd $3d_{5/2}$ XP spectrum peaks (left) and valence band regions (right) of Pd $_3$ Ga $_7$, PdGa, Pd $_2$ Ga and elemental Pd. Spectra were recorded in UHV. The nearest neighbours of the Pd atoms in the structures are shown.

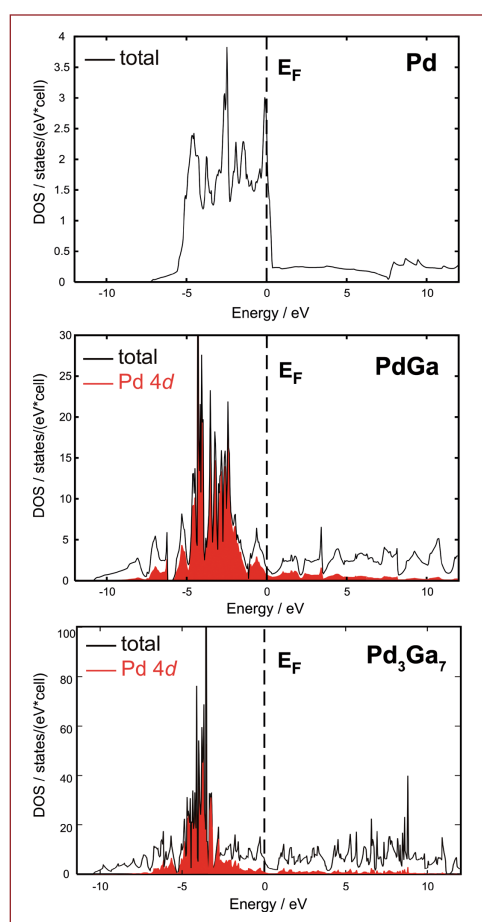


Fig. 3: Electron density of states (DOS) of elemental Pd (top), PdGa (middle) and Pd $_3$ Ga $_7$ (bottom).

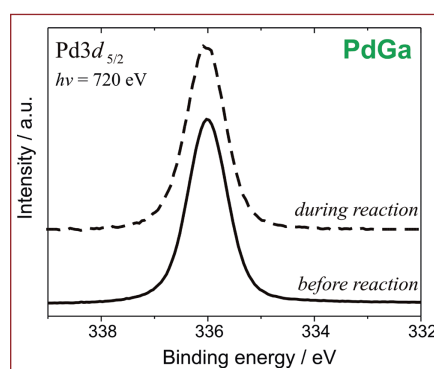


Fig. 4: UHV and *in situ* Pd $3d_{5/2}$ XP spectra of PdGa does not reveal any modification of the surface.

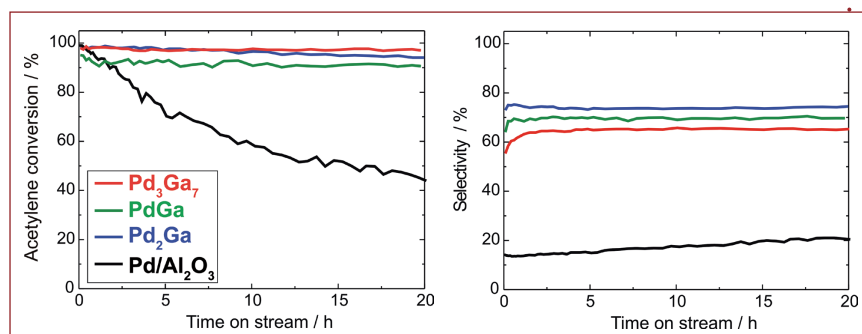


Fig. 5: Acetylene conversion (left) and selectivity (right) at 473 K for Pd $_3$ Ga $_7$ (50 mg), PdGa (20 mg), Pd $_2$ Ga (10 mg) and a commercial 5%-Pd/Al $_2$ O $_3$ (0.1 mg). Feed composition: 0.5% C $_2$ H $_2$, 5% H $_2$ and 50% C $_2$ H $_4$ in helium, total flow of 30 ml/min.

under reaction conditions. The absence of hydrogen incorporated in the catalyst is expected to diminish the hydrogen supply for the unselective, total hydrogenation, and thus to increase the selectivity [4,5]. Certainly, the Pd-Ga IMCs show considerably higher selectivity in the hydrogenation of acetylene to ethylene compared to the reference catalyst Pd/Al $_2$ O $_3$ (Fig. 5). Moreover, the IMCs exhibit a remarkable catalytic long-term stability, because of the isolation of the active Pd sites bonding, thus preventing polycondensation side-reactions. The high selectivity observed for all compounds indicates that not only the

surface geometric site isolation, but also the suppression of hydride formation through a covalent bonding interaction absent in conventional Pd alloys are important for achieving superior catalytic properties. Our results demonstrate that structurally well-defined intermetallic compounds exhibit a high potential in heterogeneous catalysis and are promising candidates for industrial applications.

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