

Pd–Ga Intermetallic Compounds as Highly Selective Semihydrogenation Catalysts

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Abstract: The intermetallic compounds Pd₃Ga₇, PdGa, and Pd₂Ga are found to be highly selective semihydrogenation catalysts for acetylene outperforming established systems. The stability of the crystal and electronic structure under reaction conditions allows the direct relation of structural and catalytic properties and a knowledge-based development of new intermetallic catalyst systems. In the crystal structure of PdGa palladium is exclusively surrounded by gallium atoms. The alteration of the Pd coordination in PdGa leads to a strong modification of the electronic structure around the Fermi level in comparison to elemental Pd. Electronic modification and isolation of active sites causes the excellent catalytic semihydrogenation properties.

The selective hydrogenation of C≡C to C=C bonds is a challenge for the synthetic chemist. It is an important step not only in the industrial synthesis of vitamins (e.g., the linalool chemistry) and pharmaceuticals but also in the production of polymers from α-unsaturated molecules. The synthesis of polyethylene requires the removal of traces of acetylene from the ethylene feed, which otherwise deactivate the polymerization catalyst. The semihydrogenation of acetylene to ethylene at 300–500 K is a very elegant way to turn the poison into a valuable reactant.¹ For the most efficient use of resources the loss of ethylene by hydrogenation to ethane must be minimized, requiring highly selective catalysts,^{2,3} posing a similar challenge as in the case of the synthesis of fine chemicals.

Supported palladium catalysts readily hydrogenate alkenes and alkynes through formation of very active hydride phases.^{4–7} In addition to the total hydrogenation, deactivation of the catalyst by polycondensation of unsaturated monomers creates problems. Both side reactions require larger active sites than the semihydrogenation,^{2,8–10} knowledge from which the site-isolation concept leading to higher selectivity and stability was derived.¹¹ Industrially, the site isolation is realized by alloying Pd with Ag^{2,12} or modification with Pb and chinolin (Lindlar's catalyst).¹³ The beneficial effect of the decreased homoatomic Pd coordination by "dilution" with Ag on the selectivity can be seen from Figure 1.

The steady-state high activity of dispersed Pd is damped by about 3 orders of magnitude through addition of Ag, and the selectivity is almost tripled reaching acceptable values and sufficient stability for technical application.² To computationally identify beneficial elemental combinations, Nørskov et al. introduced quantum chemically derived scaling functions for the semihydrogenation of acetylene based on disordered alloy models.¹⁴

A reasonable combination of stability and activity is, however, still a challenge for the technical operation of ethylene purification

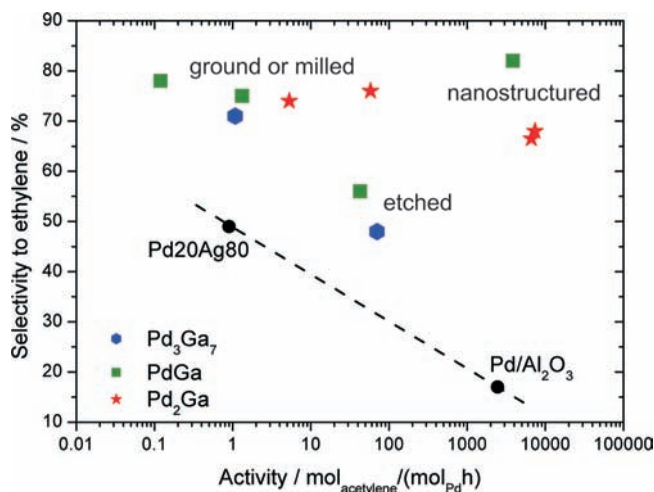


Figure 1. Selectivity to ethylene in % over rate of acetylene hydrogenation of model systems and technical catalysts (dashed line is a guide to the eye). All data after 20 h time on stream at 200 °C in 0.5% C₂H₂, 5% H₂, and 50% C₂H₄ in He with a total flow of 30 mL/min.

units.^{15,16} All Pd-containing alloys are of the solid solution type with little electron localization (covalent bonding) between Pd and the other metal.^{17,18} Consequently, these conventional alloys reveal segregation of Pd to larger active sites with time on stream, resulting in limited selectivity and stability.^{2,12}

Following the site isolation concept, we realized a new class of catalysts by exploiting the covalent interactions in intermetallic compounds to stabilize isolated active Pd sites on the catalyst surface. The intermetallic compounds Pd₃Ga₇,¹⁹ PdGa,²⁰ and Pd₂Ga²¹ exhibit well-ordered crystal structures with mainly heteroatomic Pd coordination and pronounced covalent atomic interactions²² (Figure S8). The latter creates a strong modification of the electronic structure with a reduction of the density of states at the Fermi edge (Figure 2).

In the Pd–Ga intermetallic compounds the unique electronic structure was verified by quantum chemical calculations and by XPS measurements.^{22–24} It is obvious that a strong covalent interaction between Ga and Pd completely alters the electronic structure (Figure 2). A low DOS of Pd 4*d*–Ga 4*p* bands replaces the high DOS at the Fermi edge in elemental Pd. At lower energies the localized bonding between Ga and Pd splits the compact *d* band of pure Pd. The difference in electronegativity between Ga (1.8) and Pd (2.2) implies that the Pd atoms in PdGa are negatively charged which is confirmed by the calculations exploiting QTAIM.²⁵ In addition, the covalent Pd–Ga interactions form a high barrier for subsurface chemistry, segregation, and hydride formation.^{26,27} This can be proven by a combination of *in situ* bulk and surface sensitive methods on pore-free (preventing secondary coke

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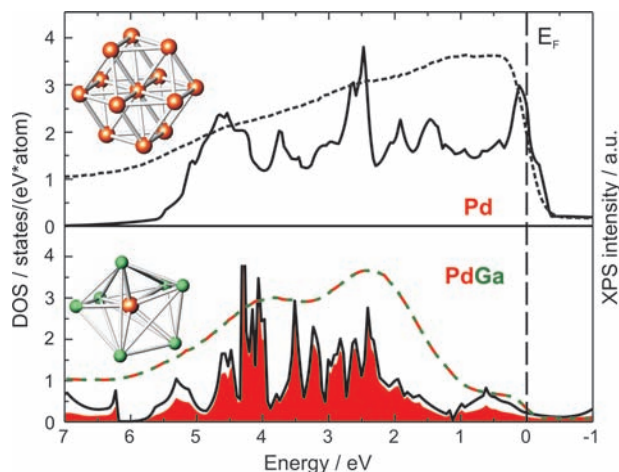


Figure 2. Calculated electronic density of states (DOS) and measured XPS valence band spectra (dashed lines) for elemental Pd (top) and PdGa (bottom).²³ Pd 4d states of PdGa are shown in red. Note the pronounced changes near the Fermi edge. The insets show the neighborhood of Pd.

formation), single-phase, and polycrystalline materials. The *in situ* structural studies (DTA/TG, XRD, EXAFS, and PGAA, see Supporting Information) revealed the excellent stability of the short- and long-range order in Pd₃Ga₇, PdGa, and Pd₂Ga in the corresponding atmospheres.²⁸ There was no indication of hydride formation, phase transitions, or decomposition for any of the compounds up to 600 K. *In situ* XPS reveals the strongly altered electronic structure of the intermetallic compounds, a positive shift of the Pd 3d_{5/2} signal, with respect to metallic Pd (335.0 eV).²⁴ The strong Pd–Ga interactions offset the chemical shift scale, with the “positive shift” indicating a more atom-like ground state than that in Pd metal, caused by the strongly altered electronic structure.

The polarization between Pd and Ga surface sites enhances the propensity of acetylene to form a donor complex on the surface without being activated by backdonation of electrons through Pd *d* states. CO chemisorption coupled with FT-IR verified this trend. In contrast to metallic Pd very readily adsorbing CO and also in contrast to Pd–Ag alloy catalysts still adsorbing CO,^{2,29} a partial pressure of 50 mbar of CO was required at 300 K to monitor the IR stretching frequency of a single sharp band occurring in PdGa at 2047 cm⁻¹ which is characteristic of an on-top adsorption geometry on a modified Pd site.²² This value compares well with data of H-modified Pd(111) (2063–2090 cm⁻¹),⁶ Pd in Pd–Ag systems (2128 cm⁻¹),² and Pd–Ag/Al₂O₃ model systems (2086 cm⁻¹)³⁰ and is consistent with a charge transfer to Pd.

Crushing the brittle intermetallic compounds results in highly selective and stable catalysts but with low activities compared to Pd/Al₂O₃ due to the low specific surface area (Figure 1). Increasing the surface with harsher top-down treatments like milling or even etching with ammonia solution enhances the activity, but especially the etching results in Pd-enriched surfaces by partly decomposing the intermetallic compounds, which leads to lower selectivity.^{31,32} Still, the families of intermetallic catalysts are characterized by intrinsically higher selectivity toward ethylene in comparison to Pd and Pd–Ag systems. The selectivity to C₄ or C₆ hydrocarbons of the intermetallic compounds is 5–10%, and no green oil formation or deactivation during 20 h was observed. The high selectivity toward ethylene is assigned to the geometric site isolation and to the modification of the electronic structure which restricts the availability of active hydrogen.

Establishing higher activity by bottom-up approaches circumvents the partial decomposition and leads to very active, highly selective,

and stable catalysts. This has been achieved by preparing the intermetallic compounds as unsupported nanoparticles and dispersing them subsequently on Al₂O₃ as support.³³ As shown in Figure 1 this leads to catalytic systems, which retain the excellent selectivity while the activity can be increased by several orders of magnitude. Using well-defined Mg–Pd–Ga hydrotalcites as precursors opens a second synthetic pathway to intermetallic Pd₂Ga without elemental Pd being present due to the intimate close contact of Pd and Ga ions in the material (Figure S3). In contrast to the nanoparticulate synthesis the hydrotalcite approach does not rely on air-sensitive and expensive reactants and leads directly to a supported material, thus presenting an industrially feasible synthesis.³⁴ Conventional wet-impregnation techniques are not suited to obtain supported intermetallic catalysts because of the resulting phase mixtures and the presence of unreacted palladium.

Using single-phase unsupported intermetallic compounds as model systems allowed a functional verification and characterization of the electronic structure as well as the short- and long-range order of the material under *in situ* conditions. Increasing the surface area without losing the integrity of the intermetallic compounds resulted in highly active, selective, and stable catalysts, outperforming industrial systems.

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Supporting Information Available: Experimental and quantum chemical procedures, additional figures and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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