

Enhancing the Catalytic Activity – Taking the Next Step in the Knowledge-Based Development of Hydrogenation Catalysts

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Supplementary to the usually applied supported catalysts, unsupported intermetallic compounds were introduced to the catalytic community. Maximal reduction of the complexity of the catalytic materials, *i.e.*, the presence of only the catalytically active species, enables a knowledge-based material development. Assigning the observed catalytic properties to a single intermetallic compound allows understanding of the underlying processes responsible for the high selectivity. In the next step, the low specific catalytic activity has to be overcome without losing the excellent selectivity of the materials. Achieving this challenging goal in an industrially applicable way will enhance the use of the materials in large scale.

Introduction

Our knowledge-based approach for a rational catalyst development is based on well characterized and unsupported single-phase intermetallic compounds as catalysts for the industrially important semi-hydrogenation of acetylene [1]. Compared to conventional Al₂O₃-supported catalysts like elemental Pd or substitutional Ag-Pd alloys, the model systems facilitate studying the intrinsic catalytic properties and, thus, a correlation with their bulk and surface characteristics [2–4]. The ground intermetallic compounds PdGa and Pd₂Ga show excellent catalytic properties for the semi-hydrogenation of acetylene. The stability of the compounds under reaction conditions could be shown by various methods. This allows assigning the long-term stability as well as the high selectivity to the spatial isolation of the active sites and the strongly modified electronic structure [4–6]. For these investigations, a low specific surface area and activity was tolerated to avoid additional influences like particle size effects or metal-support interactions.

To enable the industrial use of catalysts based on intermetallic compounds, industrially feasible synthesis routes to nanostructured materials have to be developed. In the following, we summarize our

efforts in this direction, including top-down methods like milling and etching as well as bottom-up synthesis routes [3,4,7,8]. Applying the latter, unsupported and deposited particles can be synthesized which enables to study the influence of the support on the catalytic properties [8]. Finally, an industrially feasible aqueous preparation route was successfully developed [2].

This series of materials allows monitoring the catalytic behavior stepwise from a model catalyst to a complex high performance catalyst with outstanding catalytic properties.

Top-Down Approaches

To overcome the drawback of the low surface area of Pd-Ga intermetallic compounds, milling and chemical etching procedures were applied [7]. Milling experiments showed that the presence of oxygen during the milling is necessary to prevent agglomeration of the particles. After milling in air atmosphere, fine powders with higher surface area were produced. However, XPS and SEM reveal that the surface of such particles is covered with gallium oxide.

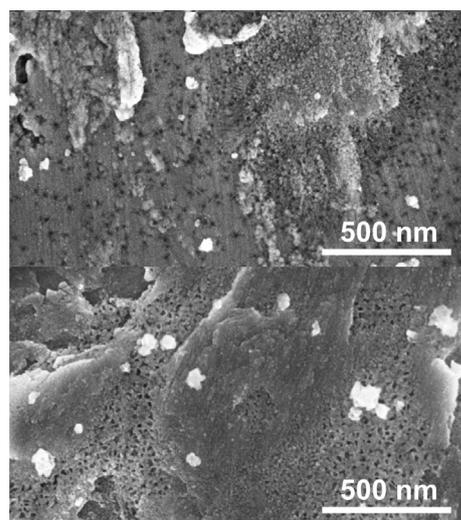


Fig. 1: High resolution SEM pictures (5 keV, SE) of the surface of chemically etched PdGa (top: pH = 9.0; bottom: pH = 9.8).

Thus, after milling, an etching procedure with ammonia solution was applied to increase the active surface area of the catalysts by removing the inactive gallium oxide overlayer. The chemical etching led to considerable, but not complete removal of the oxides as well as to the formation of nanosized caverns (Fig. 1). This process optimizes the catalyst's active surface by a combination of higher surface area, higher surface Pd concentration and, possibly, by forming more active Pd ensembles. A partial destruction of the surface of the intermetallic compound and formation of Pd-rich areas was observed. This effect increases with increasing of the pH of etching ammonia solution.

Unsupported Nanoparticulate Synthesis

Unfortunately, the easy-to-apply etching methods resulted in a strong disturbance of the intermetallic surface and thus in a partial loss of the excellent catalytic properties. To avoid the partial destruction of the site isolation provided by the crystal structures of the compounds, a two-step bottom-up synthesis of nanoparticulate PdGa and Pd₂Ga was developed. Two pre-conditions have to be fulfilled for a successful synthesis protocol: i) the samples must be single-phase, so all byproducts must either be gaseous or soluble and ii) the necessary accessibility of the surface forbids the use of surface stabilizing agents like surfactants. The synthesis of unsupported single-phase intermetallic Ga-compounds is not straightforward since the low redox-potential and the high Lewis acidity of Ga³⁺ results in the formation of very stable complexes. Another challenge is the low melting point of elemental Ga, easily leading to an uncontrolled coagulation, thus hindering a successful preparation.

The desired intermetallic nanoparticles could be obtained by co-reduction of Pd(acac)₂ and GaCl₃. A strong reducing agent like Superhydride[®] (LiHBEt₃ in THF), which was already successfully applied for the synthesis of ordered as well as disordered Cu₆₀Pd₄₀ by our group [9], is necessary to reduce Ga³⁺. After the co-reduction, a subsequent annealing step in dioctylether at elevated temperatures is needed to form the desired crystal structures [8]. For a successful synthesis, the reaction parameters are crucial. Ga³⁺ is not directly reduced but the reduction is mediated by the elemental Pd particles, which are formed initially. In this first step, core-

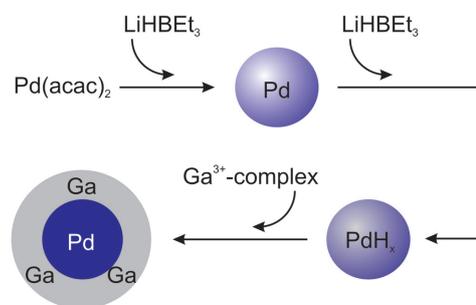
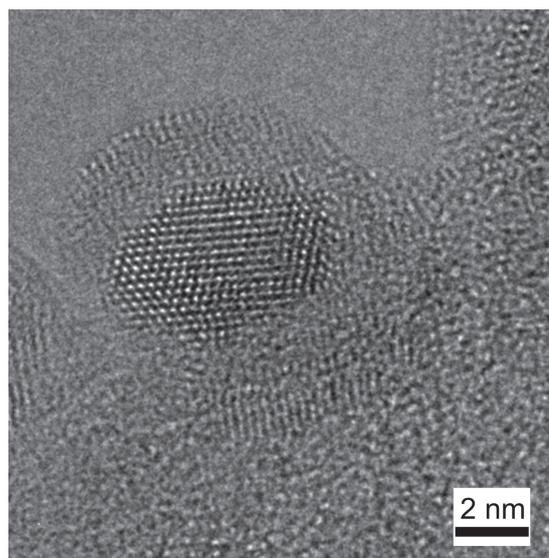


Fig. 2: Top: High resolution aberration-corrected TEM after co-reduction of nanoparticles obtained during PdGa preparation. Bottom: Proposed mechanism for the formation of Ga.

shell bimetallic nanoparticles are formed by Ga being reduced at the Pd surface exclusively (Fig. 2).

Annealing the samples leads to the complete diffusion of Ga into the Pd particles, which results in the desired crystal structures. The samples were characterized by XRD, chemical analyses, TEM, disk centrifuge as well as Kr BET measurements. The latter confirmed the disk centrifuge measurements, resulting in specific surface areas of 2 m²g⁻¹ and 12 m²g⁻¹ for PdGa and Pd₂Ga, respectively, with particle sizes around 3 nm–10 nm. To avoid the strong agglomeration of the particles during the annealing step as revealed by TEM investigations, the particles were also deposited on α -Al₂O₃ after the co-reduction.

Figure 3 summarizes the catalytic properties of the different catalytic materials based on the Ga-Pd intermetallic compounds in comparison to a commercial 5 wt.-% Pd/Al₂O₃ and an unsupported Pd₂₀Ag₈₀ alloy. Nanostructuring the material

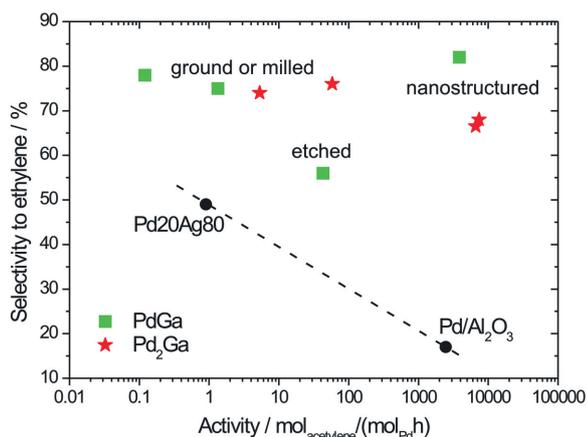


Fig. 3: Selectivity to ethylene in % over rate of acetylene hydrogenation of model systems and technical catalysts (dashed line is a guide to the eye).

increases the activity by a factor of 90 and more than 180 for unsupported Pd_2Ga and PdGa , respectively. Deposition of the particles, thus largely preventing agglomeration, results in an activity increase by a factor of nearly 35,000 for PdGa and 1,300 in the case of Pd_2Ga compared to the ground bulk materials. In summary it could be shown that neither the decrease of the particle size to a nanoparticulate state nor the presence of the support dramatically influences the excellent properties of PdGa and Pd_2Ga .

Industrial Synthesis - HTLc Precursors

Having shown that the extraordinary catalytic properties of the intermetallic compounds can be transferred to highly active materials, the development of an industrial feasible, environmentally benign synthesis route to supported intermetallics is desirable.

The wide-spread wet-impregnation techniques are not suited to obtain supported intermetallic catalysts yet because of the resulting phase mixtures and the presence of unreacted palladium. Co-precipitation of well-defined Mg-Pd-Ga hydrotalcites on the other hand opens a synthetic pathway to intermetallic Pd_2Ga . Careful reductive pretreatments result in the absence of elemental Pd due to the intimate contact of Pd and Ga ions in the material. In contrast to the nanoparticulate synthesis, the hydrotalcite approach does not rely on air-sensitive and expensive reactants, thus presenting an industrially feasible synthesis [4].

Conclusions

Having gained a deep understanding of the catalytic properties of Ga-Pd intermetallic compounds formed the basis for a knowledge-based transfer of the excellent selectivity and long-term stability to nanostructured intermetallic materials with activities in the same region as highly active elemental palladium.

Our approach presents a successful strategy for the development of a novel class of catalysts. Selecting appropriate intermetallic compounds by taking fundamental aspects into account, it was possible to gradually create high performance catalysts. Contrary to trial-and-error experiments, this knowledge-based material development is an innovative alternative, which demonstrates the superiority and relevance of intermetallic compounds as selective hydrogenation catalysts as well as their potential for industrial applications.

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