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How to control the selectivity of palladium-based catalysts in hydrogenation reactions: The role of subsurface chemistry

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This paper reviews recent experimental and theoretical results on palladium-based catalysts in selective hydrogenation of alkynes obtained by a number of collaborating working groups in a joint multi-method and multi-material approach. The critical modification of catalytically active Pd surfaces by incorporation of foreign species X in the sub-surface of Pd metal was observed by *in situ* spectroscopy for X = H, C under hydrogenation conditions. Under certain conditions (low H₂ partial pressure) alkyne fragmentation leads to formation of a Pd-C surface phase in the reactant gas feed. The insertion of C as a modifier species in the sub-surface considerably increases the selectivity of alkyne semi-hydrogenation over Pd-based catalysts by decoupling of bulk hydrogen from the outmost active surface layer. DFT calculations confirm that Pd-C hinders the diffusion of hydridic hydrogen. Its formation is dependent on the chemical potential of

carbon (reactant partial pressure) and is suppressed when the hydrogen/alkyne pressure ratio is high leading to rather unselective hydrogenation over *in situ* formed bulk Pd-H. The beneficial effect of the modifier species X on the selectivity, however, is also present in intermetallic compounds with X = Ga. As a great advantage, such Pd_xGa_y catalysts show extended stability under *in situ* conditions. Metallurgical, clean samples were used to determine the intrinsic catalytic properties of PdGa and Pd₃Ga₇. For high performance catalysts, supported nanostructured intermetallic compounds are more preferable and partial reduction of Ga₂O₃ upon heating of Pd/Ga₂O₃ in hydrogen was shown to lead to formation of Pd-Ga intermetallic compounds at moderate temperatures. In this way, Pd₅Ga₂ and Pd₂Ga are accessible in form of supported nanoparticles, in thin film models and realistic powder samples, respectively.

Introduction

Pd is a widely used element in the field of heterogeneous catalysis, which is active in many reactions, among them the industrially important semi-hydrogenation of alkynes. This reaction, which serves as a model reaction for the present study, is applied in course of industrial polymerization of ethylene to polyethylene (ca. 50 Megatons/year) to purify the feedstock from acetylene, which would otherwise poison the downstream

polymerization catalyst. The acetylene content has to be lowered from usually around 1% to the low ppm range. Hence, the requirements for the hydrogenation catalyst are to effectively convert acetylene in an excess of ethylene to protect the polymerization catalyst and to do this at highest possible selectivity avoiding total hydrogenation of acetylene to maximize the final polyethylene yield. Thus, selectivity is of utmost importance in the field of Pd-based semi-hydrogenation catalysts and the problem how to understand variations in selectivity of Pd-based catalysts is academically appealing as well as of very high

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industrial interest. It has triggered much fundamental work in the past and present, recently reviewed by Borodziński and Bond [1,2].

The group at the Fritz-Haber-Institute started to study the question – which factors influence the selectivity of Pd-based catalysts and how it can be controlled – in 2002, first in the framework of the ATHENA project¹ and presently in a loose consortium of European research groups, who contribute their complementary views on this problem. This paper is intended to review the results obtained within this very fruitful collaboration and provides insights into Pd-based catalytic materials from spectroscopic characterization, quantum chemical calculations, reactivity studies and synthesis.

The question why Pd, which is a very active catalyst in the hydrogenation of alkenes to alkanes, can under certain conditions selectively hydrogenate triple bonds and stop at the stage of the double bond, is, of course, not new and numerous views can be found in the literature. One early explanation is the difference in heat of adsorption, which favors desorption of the partially hydrogenated intermediate [3]. It was, however, shown experimentally that ethylene can adsorb on distinct sites on the surface of Pd catalysts in the presence of acetylene [4]. Furthermore, the role of sub-surface or even bulk-hydrogen (formation of the β -palladiumhydride phase) seems to be of importance. It was shown experimentally [5] and theoretically [6,7] that hydrogen dissolved in metals can diffuse to the surface and hydrogenate adsorbates. Compared to surface-adsorbed hydrogen, subsurface-hydrogen species were found to disfavor selective partial hydrogenation by enhancing undesired total hydrogenation [8]. Weakly absorbed bulk-hydrogen was recently reported to be responsible for olefin hydrogenation over Pd nanoparticles and it was suggested that carbonaceous deposits favor the regeneration of the involved hydrogen species [9].

In addition, Pd alloys are seen as an example of the so-called active site isolation concept, which is mainly based on geometric considerations. Isolation of surface Pd atoms by spatial separation is suggested to reduce the surface concentration of the di- σ -adsorbed ethylene, which takes place on neighboring sites forming ethylidyne and vinylidene species strongly bound to the surface [10-12]. These species may oligomerize, act as precursors for carbonaceous deposits hence cause deactivation and decrease the ethylene yield. Oligomerization has been found to be an important issue for the stability and selectivity of monometallic Pd catalysts but also to other hydrogenation metals like Cu or even Au [13]. According to DFT simulations, high carbon formation energy and low alkyne binding energy was obtained to scale with low oligomerization barrier in propyne-propyne coupling [13]. Oligomerization on Pd was essentially not observed without H₂ and was found to decrease with increasing H₂/C₂H₂, [14] and hence an optimal H₂ pressure range exists that facilitate this side reaction. CO feeding was shown to effectively moderate total hydrogenation of alkynes, nevertheless oligomerization selectivity strongly increased upon increasing CO:H₂ feed ratios [15]. DFT calculations by Garcia-Mota et al.

[13] indicated that in the presence of subsurface carbon, the barrier for C-C coupling increased significantly compared to clean Pd, whereas CO feeding reduced the barrier. In addition to the role of Pd surfaces, the support is often reported to contribute in ethylene oligomerization. Carbonaceous deposits separate the active surface sites and reduce their size by surface blocking, which strongly affects the catalytic properties [1,16]. Furthermore, the supply of hydrogen to the surface and sub-surface will be decreased by the absence of neighboring sites, thus changing selectivity [15, 17] as well as catalyst stability. These considerations can also explain the benefit of employing Pd-Ag alloys rather than pure Pd catalysts in industrial semi-hydrogenation, which exhibit superior selectivity [3] and stability. The presence of Ag lowers the surface concentration of Pd and, thus, effectively reduces the average size of the active ensembles [18]. Another interpretation of the beneficial effect of Ag has been reported by Studt et al. [19], who calculated the potential energy diagram of the hydrogenation of acetylene over pure Pd and a PdAg catalyst. They found that the addition of Ag lowers the energy barrier of desorption of the intermediately formed ethylene with respect to the energy barrier of further hydrogenation to ethane and thus makes the catalyst more selective. The same group also pointed out that similar effects are also present in case of other modifying atoms in the subsurface of Pd like carbon [13]. Other groups have recently reported similar results [15, 20] and role of promoters has been recently reviewed by López and Vargas-Fuentes [21].

Our recent results on pure Pd samples, which will be reviewed in this paper, strongly support the idea that the fresh Pd catalyst is modified under reaction conditions as a function of the reactant partial pressures in the feed not only by surface deposits, but also by sub-surface species. Such modifications make the newly formed Pd-X surface phase (X = C, H) the actual catalyst for hydrogenation and are responsible for a dramatic change in selectivity – an increase in case of X = C and a decrease for X = H. This insight inspired our later works focused on more directed and controlled preparation of Pd-X (X = Ga) catalysts and characterization of their structural stability and catalytic properties.

This paper is organized as follows: Firstly, results obtained on pure Pd model catalysts in various alkyne feeds and the decisive role of the Pd-C surface phase will be discussed. These results will then be complemented by theoretical calculations, and subsequently, the replacement of carbon by metal atoms and the effect on the material's and catalytic properties will be described. Unsupported bulk model catalysts of Pd-Ga intermetallic phases and their activity and selectivity in gas and liquid phase hydrogenation reactions are treated afterwards. Then, single crystals surface studies of PdGa will be presented followed by a discussion of, nano-particulate thin film models of Pd-X catalysts (X = Ga, Zn, Si) and powder Pd-Ga/Ga₂O₃ systems with a focus on the role of the oxide support. Finally, the presented results will be put in a generic perspective before a conclusion and outlook will be given at the end of the paper. We note that according to the IUPAC recommendations 2005 [22] and due to consistency with the previous literature the intermetallic compound is named in this review PdGa instead of GaPd.

Research project "Advanced Technology in Catalytic Chemistry and Engineering for Novel Applications" (ATHENA) was a 5-year-long international project aiming to gain a fundamental understanding of the relationship between catalyst properties under reaction condition and selectivity in various heterogeneously catalyzed reactions in the field of hydrogenation, dehydrogenation and oxidation.

The surface of monometallic Pd catalysts under hydrogenation

Utilizing synchrotron radiation and differential pumping, nowadays it is possible to investigate the surface electronic structure of materials by XPS under catalytic turnover. First [23] we studied the hydrogenation of 1-pentyne over supported and unsupported Pd materials and observed that partial hydrogenation was the dominant reaction path at the reduced pressure condition of few mbar applied during XPS experiments. Moreover, the reaction was accompanied by the build-up of a surface Pd-C phase, via fragmentation of reactant molecules and carbon dissolving in the top few Pd layers. This was identified by the ~ 335.5 eV Pd 3d component; its contribution to the overall Pd 3d envelop strongly exceeding the limit of surface core level shift component of hydrocarbonaceous adsorbates. Additionally, the low binding energy C 1s component (283.4 eV), being close to those of carbides, substantiated the assignment of carbon occupying subsurface positions. By performing non-destructive depth profiling via photon energy variation, we concluded that the Pd-C phase was 2-3 atomic layer thick. Thus the Pd-C surface phase defines the top few Pd layers with subsurface carbon participation. Later [24, 25], we have generalized these observations (Fig. 1), as other alkynes were also shown to react in partial hydrogenation on a carbon modified Pd surface, whereas alkenes never induced such surface modification. Note, when acetylene was hydrogenated (Fig. 1F) the new Pd 3d component was much more enhanced and hence the Pd-C layer was thicker than mentioned above. When studying the temporal evolution of Pd-C, we observed a two step process: a fast initial C uptake likely related to the occupation of the first subsurface sites, and a second slow process of further growth of Pd-C. We show that by applying a high hydrogen/alkyne pressure ratio the alkyne total hydrogenation starts to be the prevailing reaction path. This can be correlated to the vanishing Pd-C component at higher H_2/C_5 ratios [24]. Therefore we concluded that alkynes are selectively hydrogenated on Pd-C, whereas unselective alkyne hydrogenation as well as alkene hydrogenation proceeds on Pd surfaces without subsurface C modification. Changes in the selectivity pattern with variation of the hydrogen-to-hydrocarbon ration have also been observed for hydrogenation of polyunsaturated substrates over Pd-based catalysts [26].

The quantification of surface hydrogen concentration under hydrogenation conditions is extremely challenging (if possible at all), and hence there is no clear description in the literature about the way hydrogen changes hydrogenation selectivity quite abruptly. By measuring the bulk hydrogen content of Pd under different hydrogenation conditions utilizing *in situ* Prompt Gamma Activation Analysis (PGAA) [27] we tried to correlate the bulk hydrogen content with the activity and reaction selectivity, on the assumption that bulk is equilibrated with the surface under steady state hydrogenation conditions. Figure 2 shows one experiment, in which we compare the conversion of 1-pentyne hydrogenation (selectivity is higher than 95% toward pentene formation) and the corresponding bulk hydrogen content at the same experimental conditions, however at different stages of a long-term (several days long) measurement. It is strikingly obvious that there is no correlation between activity in the regime of selective hydrogenation and the amount of hydrogen dissolved in palladium. Furthermore, selective partial hydrogenation is compatible with both, high (β -palladiumhydride) and low bulk hydrogen concentration. This indicates that there should be a mechanism (involving Pd-C) that decouples the rate of steady state hydrogenation from the bulk hydrogen content.

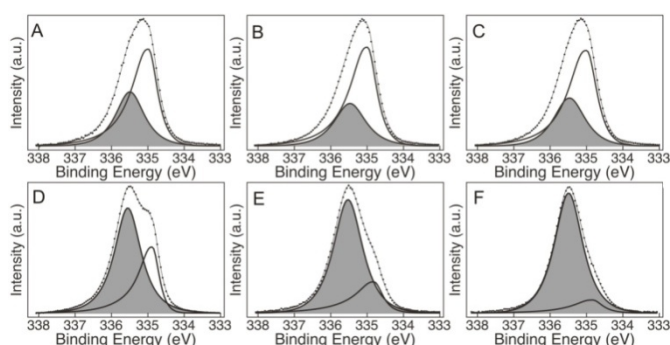


Figure 1: Comparison of *in situ* Pd 3d_{5/2} spectra of Pd foil under alkene and alkyne hydrogenation at 1 mbar (H_2/C_xH_y : 9/1) and 343-353 K. A: 1-pentene; B: propene; C: ethylene; D: 1-pentyne; E: propyne; F: acetylene.

Additional hydrogenation experiments at total alkyne hydrogenation as well as with alkenes indicate that the bulk exists exclusively in hydride form, underlining the missing decoupling mechanism in these cases. Recent *in situ* PGAA experiments [28] with H/D exchange show that hydrogen can diffuse through the Pd-C layers but this process, as estimated by theory, is significantly slowed down due to the increased diffusion barrier (see also next section).

In summary, *in situ* observations clearly showed the formation of a Pd-C sub-surface phase associated with selective hydrogenation of alkynes. The superior selectivity of this *in situ* formed catalytic phase seems to be due to a decoupling of the bulk hydride phase from the outmost active surface layer, hindering the supply of hydrogen from the subsurface and below.

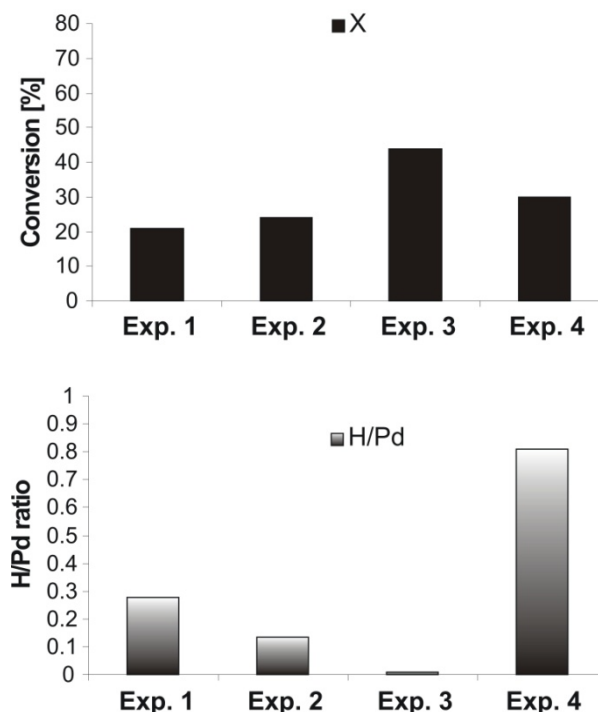


Figure 2: 1-pentyne conversion and corresponding H/Pd values during *in situ* PGAA experiments utilizing an unsupported Pd black catalyst. All these experiments were carried out using $4 \text{ cm}^3\text{min}^{-1}$ hydrogen and $1.6 \text{ cm}^3\text{min}^{-1}$ 1-pentyne flow. 1-Pentyne was dosed via N_2 flow through a saturator. Experiments have not been performed directly after each other and the prehistory of the sample was always different.

Insights from theory into the Pd-C-H system

Experimental observations of modifications of the Pd surface in the near-surface region, including the formation of a carbonized surface phase (Pd-C phase) or the presence of a metal hydride phase, due to external pressure conditions and total fragmentation of a significant amount of reactant molecules, have been described in the previous section. To understand the formation of both phases, the stability of carbon and hydrogen on the surface and in the subsurface of Pd was further studied from DFT calculations and first principle thermodynamics.

Carbon binds strongly on the surface of Pd(111), with an adsorption energy of -6.9 eV in three-fold hollow sites, but adsorption in the subsurface octahedral site is even more stable by -0.6 eV. The optimal coverage of carbon in this subsurface is 1/3 ML and above this value repulsion between the carbon atoms occurs. Adsorption of C in the second interlayer is only slightly less stable and, for a coverage higher than 1/3 ML, carbon atoms will prefer to be distributed between first and second inter-layers. Similarly, above a coverage of 2/3 ML, the third interlayer will be populated in the most stable carbon distribution. In this process, a surface carbide is formed with a local formula of Pd₇₅C₂₅, in reasonable agreement with the experimentally determined concentration [23]. Such a Pd carbide does not exist as a macroscopic bulk phase and is specific to the surface.

The energy of these structures with different amount of subsurface C cannot be compared directly, and their relative stability is a function of the carbon chemical potential. The surface free energy of the most stable termination, as a function of carbon chemical potential μ_C , is shown on Figure 3. If μ_C is very low, the bare surface is the most stable termination. However above a critical value ($\mu_C \approx -8.8$ eV) the termination with a 1/3 ML coverage of subsurface carbon becomes most stable. For even higher μ_C values, two layers, and then 3 layers, etc ... will be occupied. The thickness of the Pd-C is hence directly related with the chemical potential of carbon.

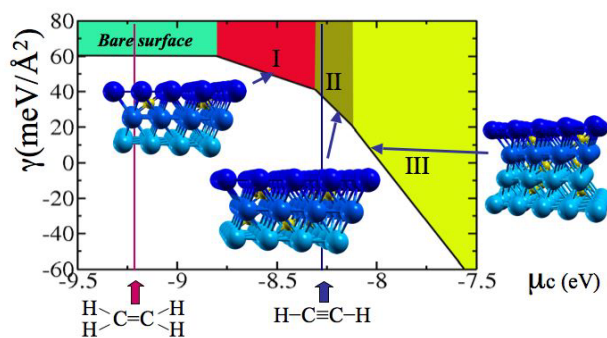
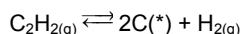


Figure 3: Surface free energy γ (meV/Å²) of the most stable Pd/C termination as a function of the carbon chemical potential μ_C in eV (the reference for μ_C is the non spin-polarized C atom). The vertical blue and red bars indicate the μ_C value of acetylene and ethylene respectively in the model conditions of hydrogenation of Figure 1.

The effective value of μ_C under hydrogenation conditions depends on the choice of the unsaturated molecule. For example if the reactant is acetylene the carbon formation reaction is



And hence the effective μ_C can be obtained from the chemical potential of the gas phase molecules, derived from the statistical thermodynamics of the ideal gas:

$$\mu_C = \frac{1}{2} (\mu_{\text{C}_2\text{H}_2} - \mu_{\text{H}_2})$$

In the conditions of the model reaction shown in Figure 1, μ_C is -8.25 eV and is in the region of the diagram where a two layer Pd-C phase is the most stable termination. Increasing the C₂H₂ pressure increases μ_C and hence favors the formation of the Pd-C phase, while an increased H₂ partial pressure or temperature acts in the opposite direction. The calculated thickness of the Pd-C phase is lower than the experimental value. Indeed the extended (111) surface is more difficult to deform and less efficiently accommodates the surface carbide than nanoparticles or a polycrystalline foil. Core level shifts of Pd in the surface carbide have been calculated and they are in good agreement with the measured values [29].

If the hydrocarbon molecule is ethylene, carbon is more stable which is reflected by a lower μ_C value (~ -9.2 eV in the conditions of Figure 3), now in a region of the diagram where the bare Pd surface is the most stable termination. The difference in carbon chemical potential hence explains why the Pd-C surface phase is formed under acetylene hydrogenation but not under ethylene hydrogenation conditions. The approach has been extended to twelve transition metal surfaces in the Groups 8 to 11 of the periodic table and to other reactants as a carbon source. The aim was to understand the trends that govern the formation of surface carbide in the conditions of catalytic reactions. Pd, Ni and Fe surfaces are very prone to this modification [30].

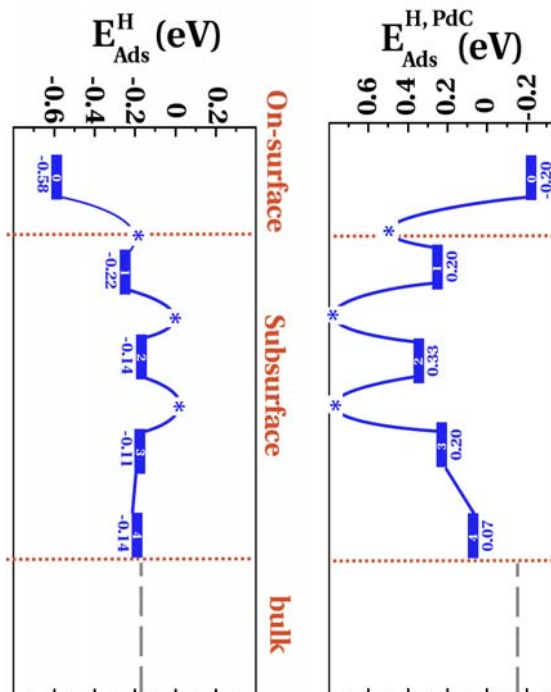


Figure 4: (Right panel) Energy profile for the adsorption and migration of H towards the bulk for pure Pd(111). (Left panel) Energy profile for the adsorption and migration of H towards the bulk in the presence of a 3-layer Pd-C phase. Horizontal dotted lines are used to differentiate the three different binding zones of Pd, while the vertical dashed lines indicate the hydrogen binding energy on bulk Pd.

We also addressed hydrogen accumulation in the near surface region from the study of the hydrogen adsorption on the surface and in the first interlayer for a wide coverage range (Fig. 4). For surface adsorption, threefold hollow sites are the most stable ones, as previously reported [31,32], *fcc* and *hcp* sites being energetically equivalent. For subsurface absorption, several sites are associated to a similar energy, the *hcp-1* tetrahedral sites, with a Pd atom located in the layer below, being the most stable site. The surface adsorption ($E_{\text{ads}} = -0.6$ eV with respect to $\frac{1}{2}$ H₂ in the gas phase) is strongly favored versus subsurface ($E_{\text{ads}} = -0.2$ eV) and bulk absorption in the case of the pure Pd(111) surface and therefore the surface will be populated until a coverage of 1 before subsurface absorption can happen.

The presence of the Pd-C phase strongly weakens hydrogen adsorption. It remains exothermic on the surface, but the adsorption energy is decreased to -0.2 eV, while the penetration of H in the subsurface within the Pd-C phase becomes endothermic by +0.2 eV for the best H position. Hence the presence of hydrogen atoms in the subsurface for the Pd-C phase is thermodynamically disfavored. Over clean Pd, the overall penetration barrier from surface to bulk is 0.6 eV, whereas the extraction barrier is 0.1 eV. On the Pd-C phase, the barrier is only moderately higher for the penetration, 0.9 eV, but considerably increased for the extraction, 0.8 eV. Due to the weaker H absorption, the increased extraction barrier for H and the exclusion zone in the subsurface the surface coverage will be low that strongly facilitates partial hydrogenation.

The thin Pd-C phase also has an important influence on the adsorption of the unsaturated hydrocarbon. In a recent paper, the group of Nørskov addressed the role of surface modifications on the hydrogenation of acetylene [19]. They showed that the heat of adsorption of ethylene and acetylene were the main factors controlling selectivity. In this way, a weakening of ethylene adsorption will lead to a selectivity increase, while a weakening of acetylene bonding will eventually lead to a decrease in the rate of acetylene hydrogenation. Interestingly enough, they found that the presence of subsurface C in Pd weakens the adsorption of the double bond molecule. The olefin will be faster desorbed, hence preventing its further hydrogenation which is a key aspect for the selectivity. Lopez and co-workers calculated the hydrogenation reaction barriers and showed that the surface carbide impacts on the hydrogenation selectivity also by preferential formation of ethene versus ethylidene [15]. In this work it was also reported that the stability of the Pd-C layer depends on the concentration of H₂ and CO. Thus, it is not the best handle to control selectivity.

In summary, DFT calculations confirm the formation of a Pd-C surface phase under selective hydrogenation conditions and indicate that the low exothermic chemisorption energy of H, the endothermic adsorption in subsurface position as well as the increased energy barrier for H penetration through the subsurface are critical ingredients to achieve low surface H coverages resulting in a preferential partial hydrogenation.

Pd-Ga intermetallic compounds as hydrogenation catalysts

The role of subsurface carbon on selectivity has been highlighted in the two first sections of this review, and the question arises, whether it is possible to find a replacement for

the carbon acting in the same way on the catalytic properties of Pd, but which can be reproducibly prepared in a more controlled manner and which exhibit a wider range of stability. The replacement should possess strong covalent bonds to the palladium atoms – excluding conventional alloys – to form a stable compound, which can be easier investigated. Furthermore, it should be effective in decoupling the hydrogenation rate from the bulk hydrogen content (if forming a hydride at all) to enable high selectivity in the semi-hydrogenation of alkynes. The latter should preferably not be dependent on a complex fragmentation mechanism happening *in situ*, but represent the intrinsic structural and electronic properties of the Pd-X material. Besides these two requirements, the compound must be able to activate hydrogen and adsorb the hydrocarbon, *i.e.* there must be free electronic states in the vicinity of the Fermi level.

A class of compounds, which can combine these requirements, are intermetallic compounds [33]. These differ from alloys by being single phase materials. In addition, they possess an at least partially ordered crystal structure, which differs from the crystal structure(s) of the constituent elements [34]. The different crystal structure results in a strongly altered electronic structure, which is influenced by the often covalent interactions between the atoms [35,36]. Since the electronic structure is responsible for the adsorption properties, the catalytic properties of intermetallic compounds can be very different of those of the elements forming the compound [37]. In contrast to alloys, the composition cannot be chosen arbitrarily and the observed catalytic properties cannot be explained by a linear combination of the properties of the constituent elements.

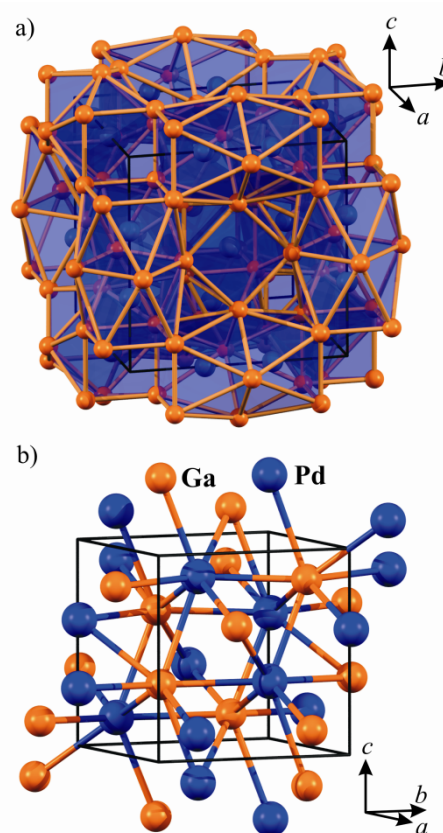


Figure 5: The crystal structures of the intermetallic compounds Pd₃Ga₇ (a) and PdGa (b). While in Pd₃Ga₇ the Pd atoms are grouped in pairs, only single Pd atoms are present in PdGa. In both structures the Pd units are completely isolated from each other by Ga.

One possible replacement for the subsurface carbon is gallium, which forms intermetallic compounds with palladium in different ratios. Examples for Pd-Ga intermetallic compounds are Pd₃Ga₇ and PdGa. Both compounds realize crystal structures in which the Pd atoms possess only one or none Pd atom, respectively, in the first coordination sphere, thus following the active-site isolation concept. Pd₃Ga₇ crystallises in the Ir₃Ge₇ type of structure (*Im $\bar{3}m$* , *a* = 8.7716 Å [38]), while PdGa is a representative of the FeSi type of structure (*P2₁3*, *a* = 4.890 Å, [39]) (Fig. 5).

Using a metallurgical synthesis starting from the elements as sources for Ga and Pd, bulk model catalyst of Pd-Ga intermetallic compounds can be obtained. The unconventional state of the catalysts, i.e. the absence of any support, enables in depth characterization of the compounds before and during the reaction, which allows to detect even small changes to the material under *in situ* conditions. Using unsupported material also facilitates a knowledge-based development of the catalyst because the observed catalytic properties can directly and solely be assigned to the given crystal and electronic structure of the compound – if the compound is stable under *in situ* conditions. The crucial stability tests of Pd₃Ga₇ and PdGa were performed in different atmospheres (H₂, O₂ and acetylene hydrogenation mixture) and investigated by several *in situ* techniques.

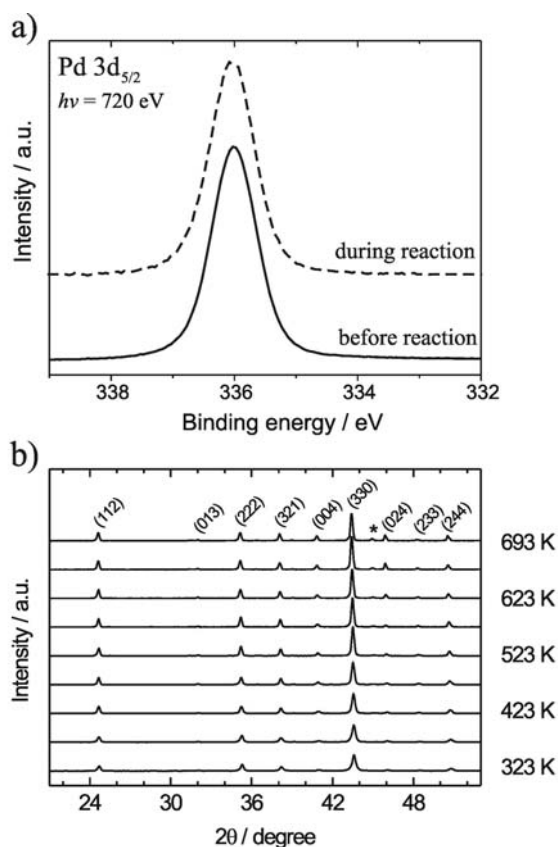


Figure 6: a) Comparison of UHV and high pressure *in situ* XPS measurements (Pd 3d_{5/2}) of PdGa. No significant changes between the two measurements are observed. b) X-ray diffraction of Pd₃Ga₇ in 50% H₂ in helium, proving the absence of hydride formation. At high temperatures, small amounts of PdGa are formed.

Neither bulk (XRD, EXAFS, PGAA, DTA/TG) nor surface sensitive methods (XPS, FTIR) could detect any changes of the material under reactive atmospheres, even above the high

reaction temperature of 200 °C, which was chosen for the catalytic tests (Fig. 6) [40, 41]. High-pressure *in situ* XPS measurements excluded segregation under reaction conditions. Only a narrow single Pd 3d_{5/2} symmetric signal is detected for PdGa with a binding energy of 336.0 eV which is close to the binding energy observed for the subsurface Pd-C (335.5 eV). For Pd₃Ga₇ the shift is more pronounced and the Pd 3d_{5/2} signal is observed at 336.5 eV [42]. No further shift of the Pd 3d core level or any additional signals were detected under *in situ* conditions for both compounds.

Some intermetallic compounds are known to form hydrides upon which they change their electronic and their crystal structure [43]. The formation of hydrides must be excluded to allow the abovementioned correlation between crystal and electronic structure on the one hand and the observed catalytic properties on the other hand. Temperature dependent XRD and PGAA investigations in hydrogen as well as in reactive atmosphere excluded the formation of hydrides very clearly under conditions for which hydride formation of pure Pd is detected [41]. Also, hydride incorporation in the near surface region would have resulted in additional or shifted signals in the *in situ* XPS measurements, which was not the case. To conclude, our *in situ* characterization confirmed the high stability of the bulk as well as the surface and the presence of only site-isolated Pd atoms on the surface. In addition, a strong modification of the electronic structure was observed, which did not change under reaction conditions.

An obvious advantage of PdGa over the *in situ* formed Pd-C phase is the stability of the selective phase in a wide range of experimental conditions (e.g. at high hydrogen/alkyne pressure ratios) as well as the possibility to prepare and characterize the Pd-Ga intermetallic compounds in an intended way prior to the catalytic reaction due to their *in situ* stability. In this case, the subsurface properties are completely rendered by the bulk structure of the catalyst allowing a much higher level of control of the synthetic chemist on the changes usually induced by the subsurface chemistry and, thus, of the related catalytic properties.

The catalytic properties of Pd₃Ga₇ and PdGa were tested in the semi-hydrogenation of acetylene in a large excess of ethylene (0.5% C₂H₂, 5% H₂, 50% C₂H₄ in He) at 200 °C and atmospheric pressure [44]. To exclude influences of the support the compounds were investigated in an unsupported state solely diluted with inactive and inert BN to improve the flow characteristics. As expected, the catalytic properties are excellent (Fig. 7a). Besides a very high selectivity, the compounds also possess a high stability with time on stream. Both observations can be attributed to the small active sites as well as the modified electronic structure. These effects do not only prevent the total hydrogenation to ethane but also avoid side-reactions, which can take place on large surface ensembles and result in coke formation and deactivation of the catalyst [16]. The two-fold beneficial effect of the modified structural and electronic properties can clearly be seen by comparison of the catalytic properties of the intermetallic compounds and elemental palladium in Figure 7. Increasing the activity by top-down methods, e.g. milling or etching, results in structural defects, decreasing the selectivity of the compounds [45,46]. To avoid the structural changes and to prove the applicability of the concept also to materials with high specific surface areas, we developed a synthesis route to unsupported nanoparticulate intermetallic Ga-Pd compounds [47]. Figure 7 comprises catalytic data of such a

highly active nanostructured catalyst, showing the possibility to transfer the excellent catalytic properties also to these highly active materials.

The situation becomes different when the hydrogenation reaction is carried out in the liquid phase in a batch reactor. As model reaction phenylacetylene was hydrogenated to styrene (and ethylbenzene due to total hydrogenation) at 4 bar and 40 °C using octane as inert solvent. When unsupported powdered Pd₂Ga, PdGa and elemental Pd are compared (Fig. 8) no significant differences in the selectivity to styrene (88.5-90.5% at 100% conversion) are visible. Lindlar's catalyst provides a higher selectivity of 95.5% at 100% conversion. The high selectivity of this widely-utilized Pd-Pb/CaCO₃ catalyst [48] is deduced not to be related to alloying or intermetallic compound formation [49]. Partial poisoning of Pd with Pb is ascribed to hinder hydride formation and weakens the olefin adsorption [50] similar as described above for C and Ag promoters. Furthermore, quinoline tend to isolate Pd sites thus minimizing oligomerization. The intermetallic compounds can undergo an oxidative passivation at the outermost surface into oxidized Ga and metallic Pd. The reducing conditions in the liquid phase are not strong enough to re-form the intermetallic compound at the surface, while the selective sites in Lindlar's catalyst are formed *in situ* [51]. Through the high oxophilicity of Ga at the surface a reductive pretreatment and reaction procedure in absence of any traces of oxygen and water is necessary to get a stable intermetallic surface under these conditions.

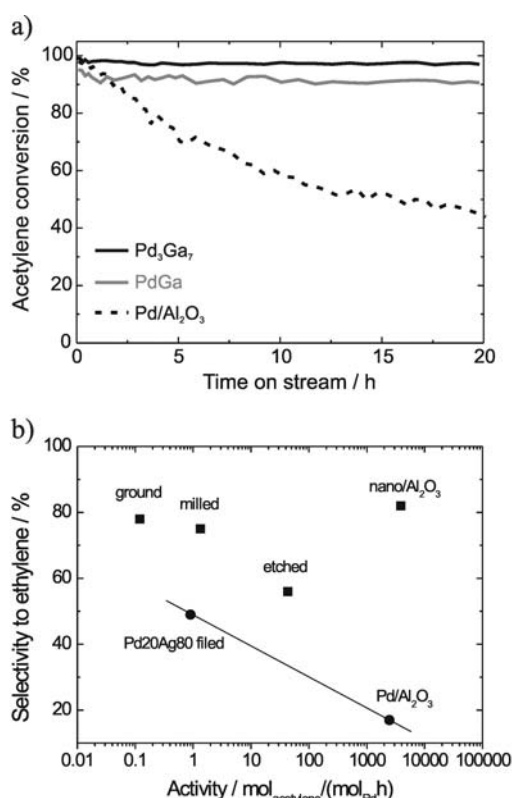


Figure 7: a) Stability with time on stream of the intermetallic compounds Pd₃Ga₇ and PdGa in comparison with a commercial Pd/Al₂O₃. b) Selectivity vs. activity of PdGa (■) after different treatments. The black line indicates the transition of Pd/Al₂O₃ to an unsupported Pd-Ag alloy. Remarkable is the high activity and selectivity of nanoparticulate PdGa supported on Al₂O₃ after synthesis compared with Pd/Al₂O₃.

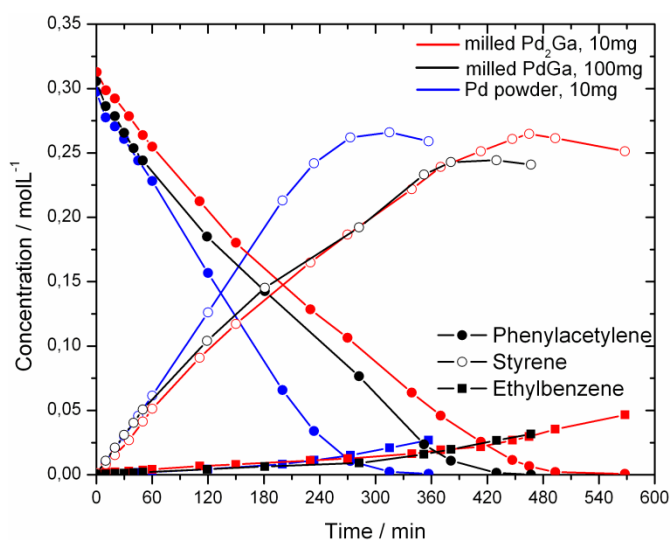


Figure 8: Concentration profile of phenylacetylene and its products during liquid phase hydrogenation in octane at 4 bar and 40°C. Observed selectivities are very similar for Pd₂Ga, PdGa and elemental Pd while the specific activity increases with decreasing Ga content. These catalytic properties are likely not to be characteristic for a perfect intermetallic surface, but represent a decomposed surface with a Pd/Ga-oxide layer.

In summary, Pd-Ga intermetallic compounds were introduced as materials with catalytic characteristics analogous to the selective Pd-C surface phase. In a simple picture, they can be seen as stable bulk analogues of Pd-C providing active site isolation and preventing the formation of bulk-hydrides under hydrogenation conditions due to their modified electronic structures. The nanostructured synthesis combines the excellent selectivity and stability with the desired high activity.

Single Crystal Surfaces of PdGa

Surface science studies of single crystal surfaces can help to relate the structure and composition of surfaces with the reaction rates and selectivities of catalytic reactions [52]. In particular the combination of both single-crystal model catalysts and real catalytic systems using UHV methods and high-pressure kinetic techniques provides valuable insights [53, 54]. As described in detail in the other sections of this review, a large variety of “high-pressure” techniques has already been applied to investigate intermetallic Pd-Ga compounds. These techniques give a good insight into the overall catalytic properties [40,44], but cannot yield a detailed comprehension of the local surface atomic arrangement, the surface electronic structure and the adsorption sites, which is crucial to understand the atomistic catalytic reaction mechanisms. To approach these questions for the intermetallic compound PdGa, structural characterization studies of the (111) and $\overline{1}\overline{1}\overline{1}$ surfaces were performed by means of different UHV techniques. Low energy electron diffraction (LEED)-I(V), scanning tunneling microscopy (STM), XPS, X-ray photoelectron diffraction (XPD), ultra violet photoelectron spectroscopy (UPS,) and thermal desorption spectroscopy (TDS) have been applied together with *ab-initio* thermodynamics calculations [55, 56]. UPS results have been reported for PdGa(110) [57].

XPD patterns of PdGa(111) and PdGa($\overline{1}\overline{1}\overline{1}$) surfaces clearly reveal the absence of surface segregation upon sputter and

annealing cycles. Segregation of individual species to the surface has been observed on other multi-metal hydrogenation catalysts to affect the selectivity pattern and complicate the analysis of the active and selective state of the catalyst [58]. Despite the absence of segregation, more experimental effort was necessary to unambiguously determine the surface termination of the crystal under investigation. The surface of PdGa was observed to be chiral as this material is of the $P2_13$ space group. As a consequence of the crystal structure, the XPD patterns of the (111) and the $(\bar{1}\bar{1}\bar{1})$ surfaces show non-superimposable mirror images of each other [55]. Four unreconstructed (1x1) terminations are possible for each of the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces [55]. The enantiomorphic form of PdGa single crystals and the terminations after annealing at 870 K were unambiguously determined by means of LEED-I(V) and also visualized by high-resolution STM. In Figure 9, an atomically resolved STM image of two terraces at the PdGa(111) surface with an overlaid bulk truncated structure model is shown. Due to a shift of the trimeric atoms in the structure from one terrace to the next one, a match between the STM image and the structure model is only possible for form B, but not for form A. All of the atomically flat terraces of various widths are separated by one unique step height. The latter is equal to 284 pm as indicated in the height histogram in Fig. 9, which corresponds very well to one third of the XRD lattice parameter along the [111] direction [30, 50]. Additionally, the in-plane periodicity of the site isolation of the trimers on the PdGa:B(111) surface being 0.692 nm, whereas on the PdGa:B($\bar{1}\bar{1}\bar{1}$) surface single atoms are separated by the same distance, is clearly discernible.

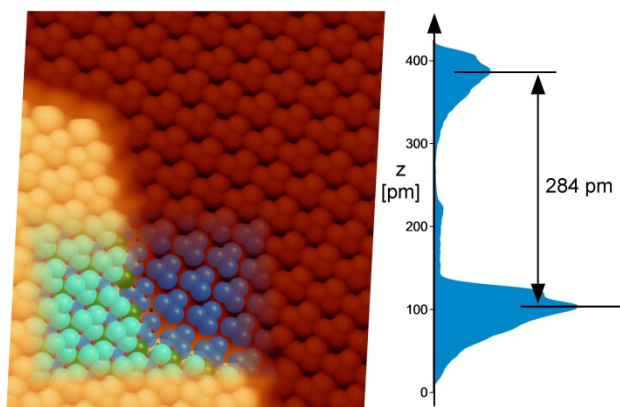


Figure 9: Atomically resolved STM images of two PdGa(111) terraces with overlaid structure model of form B, scan size: $6.9 \times 7.8 \text{ nm}^2$. The height histogram of this STM image to the right reveals the bulk periodicity of equivalent atomic layers of 284 pm along the [111] direction.

In principle CO TDS should also be able to discriminate between the different surface terminations of PdGa due to their different near surface composition. Furthermore, the adsorption properties of the intermetallic surface are directly related to the catalytic properties and can be studied using CO as a probe molecule. CO adsorption was carried out on the PdGa:B($\bar{1}\bar{1}\bar{1}$) surface and additionally on Pd(111) for comparison (Fig. 10).

Intensity calibration and integration of the γ and β states yields one CO molecule per PdGa:B($\bar{1}\bar{1}\bar{1}$) unit cell (0.4153 nm^2), which is 2.4 CO molecules per nm^2 as compared to 11.5 CO molecules per nm^2 for a full coverage of Pd(111). The first order desorption behavior of the γ state in an adsorption series (not

shown here) and the results of LEED-I(V) and STM lead to the assumption of CO adsorption on the isolated Pd_1 ensemble. The very low CO desorption temperature compared to Pd(111) reveals a strong electronic perturbation due to partial covalent intermetallic Pd-Ga bonding [55].

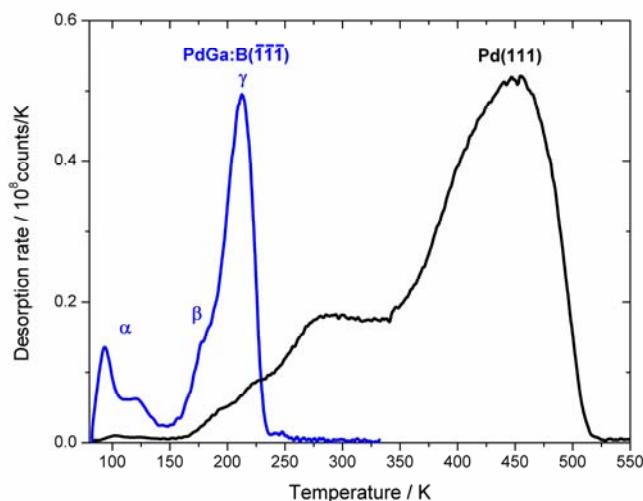


Figure 10: Thermal desorption spectra after adsorption of CO at 85 K on PdGa:B($\bar{1}\bar{1}\bar{1}$) annealed at 870 K (heating rate 1.5 K/s). Additionally CO adsorption was carried out on Pd(111) for comparison (heating rate 1.4 K/s, adsorption temperature 85 K). The spectra for Pd(111) and PdGa:B($\bar{1}\bar{1}\bar{1}$) annealed at 870 K depicts the saturation coverage at 27 and 50 L, respectively.

In summary, it was shown that well-defined terraced surface terminations on the PdGa single crystals can be comprehensively characterized by the applied UHV methods. Such ordered surfaces are ideal candidates to study the catalytic activity of well-defined site-isolated configurations depending on the surface orientation and termination. Additionally, the chirality of the surfaces opens possibilities for enantio-selective reactions on PdGa. In agreement with the concepts of site isolation and stability through covalent bonding, no surface segregation was found on the present crystal and the termination of isolated Pd_1 atoms shows strongly altered adsorption properties compared to monometallic Pd surfaces.

Thin film models of Pd-X (X = Ga, Zn, Si)

In a previous section, Pd-Ga intermetallic compounds were introduced as a novel class of selective hydrogenation catalysts and many fundamental insights were obtained on bulk samples prepared by metallurgical methods and single crystal studies. Unfortunately, these model catalysts suffer from a low specific surface area due to their high temperature preparation. To explore alternative preparation methods, we focus in this section on the solid state reactivity of Pd nanoparticles in contact with different X-oxides to study the formation of Pd-X intermetallic compounds (X = Si, Zn, Ga) under reducing conditions by high-resolution electron microscopy (HRTEM).

The need for adequate electron transparent specimens suited for HRTEM has led to the development of a special type of thin film model catalysts consisting of regular metal particles grown on NaCl(001) cleavage faces and supported by a thin film of the respective oxide. The epitaxially grown nanoparticles provide a well-defined initial state of the Pd/oxide system, and the following

structural and morphological changes can be documented as a function of the respective treatments. Epitaxially grown metal films are very well suited for lattice imaging by HRTEM, especially in the profile-imaging mode which is restricted to particular low-index orientations of the particles and of their surfaces [59]. With help of HRTEM and selected area electron diffraction (SAED), structural details of small metal, oxide or intermetallic compound particles can be revealed at an atomic scale, providing direct evidence for the metal-support interactions important for the synthesis of Pd-X intermetallic compounds. A representative image of the initial, untreated state of such an oxide-supported Pd thin film model catalyst is shown in the upper panel of Figure 11, denoting an overview TEM image of a Pd/ZnO/SiO₂ catalyst (a), along with its SAED pattern, exclusively showing Pd metal reflections due to a [001] zone axis (b). ZnO is amorphous and does not contribute to the SAED pattern.

As a general phenomenon, reductive activation of a series of oxide-supported Pd catalysts in H₂ will induce the formation of Pd-X intermetallic compounds as a function of the reducibility of the respective X-oxide [60], which has also been observed for several Pd-X systems by HRTEM using the above mentioned thin film method (X = Zn [61], Ga [62], In [63], Sn, Ge, Si [64], Al [65]). The formation of the respective Pd-X intermetallic compounds was identified as a subsequent process to formation of Pd-H phases such as β -palladiumhydride, and a strong dependence on the respective support material and activation conditions was observed. Before discussing the reactivity of the Pd-Ga₂O₃ system towards formation of intermetallic compounds, we may pin down the two extreme cases of non-reducible and reducible oxide supports. ZnO serves an example for the latter case, while hard to reduce oxides are represented by SiO₂.

Reduction of the Pd-SiO₂ thin film system at low reduction temperatures (~ 523 K) and subsequent transfer into the vacuum of the microscope leads to complete amorphization of the Pd particles, which is ascribed to the (intermediate) formation of a Pd-H phase probably during cooling of the reduced sample in either clean H₂ or a hydrogenation reaction mixture (e.g. CO₂:H₂ = 1:3) [64]. Figure 8c and d show the corresponding TEM image and the amorphous SAED pattern, respectively. At much higher temperatures (673 K) we observed formation of Pd-Si phases, such as Pd₂Si [64], which do not form hydrides and preserve their crystal structure. We may conclude that the formation of Pd-X intermetallic compounds can effectively suppress the ability of a Pd-based catalytic material to form bulk-hydrides in a range of temperature and H₂ partial pressure, where Pd-H formation is observed for monometallic Pd.

In contrast, highly ordered particles of the intermetallic compound PdZn are formed upon H₂ reduction of Pd particles embedded in a ZnO film already at 473 K. The PdZn particles were observed to be thermally and structurally highly stable upon further heating in H₂ between 473 and 873 K. The lower panel of Figure 11 shows the overview TEM image (e), its SAED pattern (f) and a high-resolution TEM image of a single PdZn particle in [011] zone axis orientation (g) after reduction at 523 K. Even above 873 K only partial decomposition of the intermetallic compound PdZn was observed, accompanied by strong interaction with the SiO₂ support and resulting in the formation of Pd-rich silicides. This broad stability range is clearly due to the higher stability of the 1:1 PdZn intermetallic compound compared to β -palladiumhydride. The higher reactivity of the Pd-ZnO system compared to Pd-SiO₂ can be attributed to the stronger interaction

of Pd with the ZnO support due to its higher reducibility. These results indicate that Pd-X intermetallic compounds are accessible in form of nanoparticles at relatively low temperatures using oxides as the source for X, if the reduction of this oxide is favourable at such conditions. In case of the Pd-Zn system, the importance of this concept for the catalytic properties of Pd/ZnO catalysts has been highlighted for methanol steam reforming and methanol synthesis [66,67].

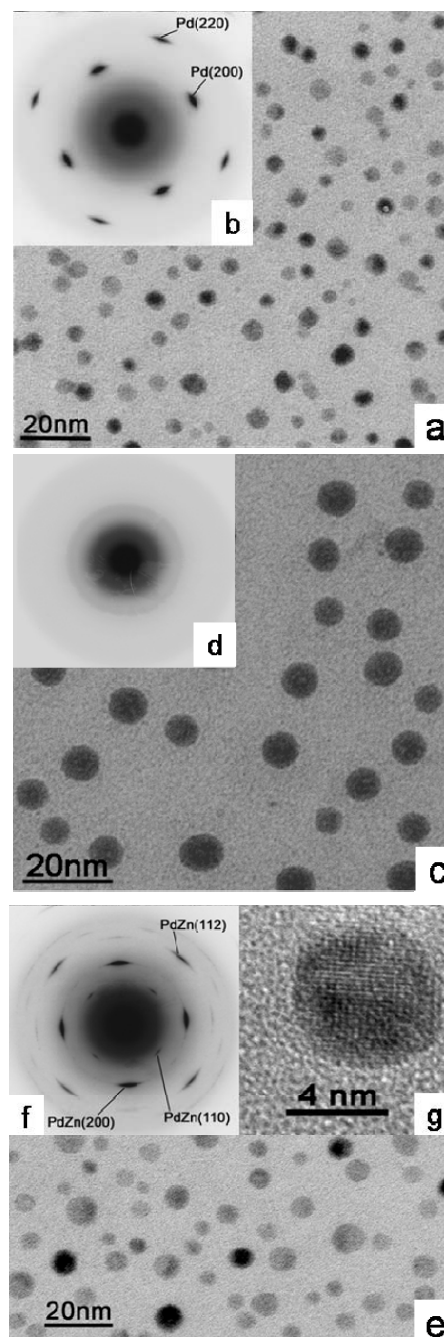


Figure 11: Overview TEM images of the initial, untreated Pd/ZnO/SiO₂ catalyst (a), a Pd/SiO₂ catalyst reduced in H₂ at 523 K (c) and a Pd/ZnO/SiO₂ catalyst reduced at 523 K in H₂ (e). The corresponding SAED patterns are shown as insets (b, d and f). A high-resolution TEM image of a single PdZn particle in [011] zone axis is shown in (g) [61,64]

Finally, the Pd-Ga intermetallic catalyst system was investigated by means of the corresponding Pd-Ga₂O₃ thin film model system. In agreement with literature reports [66], the embedded Pd particles in Ga₂O₃ could indeed be transformed by H₂ reduction at 523 K into a Pd-Ga intermetallic compound. This newly formed phase could be identified by SAED as Pd₅Ga₂ (Fig. 12) confirming the general accessibility of nanoparticulate Pd-Ga intermetallic compound catalysts by reduction at moderate temperatures using Pd and Ga₂O₃ as reactants. Hydride formation, as observed on Pd-Si samples, was again not detected. It has to be noted, however, that in contrast to the PdZn/ZnO system, the resulting Pd₅Ga₂/Ga₂O₃ thin film model catalysts are rather prone to sintering starting at a temperature of 673 K and that significant amounts of unreacted Pd were observed by SAED after reduction (Fig. 12b), which are, however, likely be present only in the cores of the particles while a shell of the intermetallic compound was formed at the metal-oxide interface.

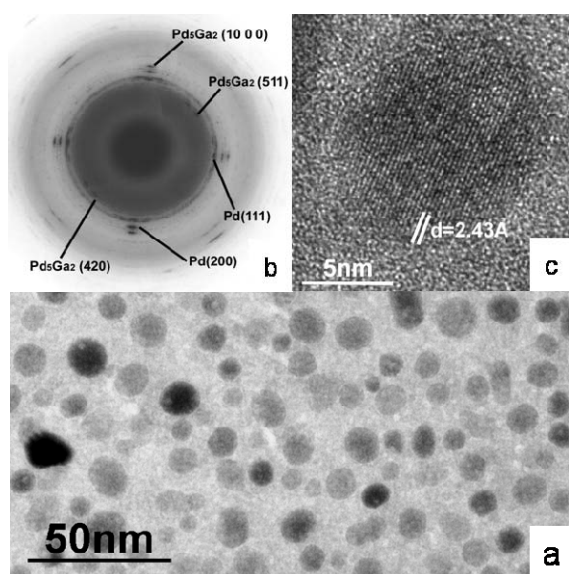


Figure 12: Overview TEM image of the Pd/Ga₂O₃ thin film catalyst after reduction at 673 K in H₂ (a). The corresponding SAED pattern and a HRTEM image of a single Pd₅Ga₂ particle are shown in (b) and (c), respectively [65]

In summary, it was shown by means of model systems that the reducibility of Ga₂O₃ is sufficient to produce well-ordered Pd-Ga intermetallic compounds from nano-structured Pd/Ga₂O₃ samples. This reactivity may lead to a feasible preparation route for high performance hydrogenation catalysts based on Pd-Ga intermetallics.

Intermetallic Pd-Ga powder catalysts

As discussed in previous sections, Pd-Ga intermetallic compound catalysts exhibit great potential in selective hydrogenation reactions. Employment of these systems in technical applications requires high performance catalysts in form of small particles on an inert, high surface area support. Hence, in the last section we focus on Pd nanoparticles supported on technological oxide powder materials, their preparation and chemisorption properties.

Several top down approaches for the preparation of PdGa intermetallic compound catalysts by milling and etching of the compounds have been developed to enlarge the surface area of

the unsupported systems described above [45,46]. Since the increase in surface area always goes hand in hand with a partial destruction of the crystal structure in these cases, the catalytic properties suffer. To ensure an intact surface structure, and thus the excellent catalytic properties, a bottom up approach for the synthesis of Pd-Ga intermetallic compounds in a nanoparticulate state has been developed recently [47]. Physically supporting the particles on γ -Al₂O₃ after the synthesis results in highly selective and very stable catalysts, which show even higher activities than conventional supported Pd-catalysts (Fig. 7).

As an alternative and due to the less difficult synthesis a more feasible approach, we studied co-reduction of PdO-Ga₂O₃ mixtures, prepared by impregnation of commercial Ga₂O₃ with Pd acetate solution followed by calcination at 773 K. It has been elaborated above and reported in literature [66], that hydrogen reduction of Pd/Ga₂O₃ may lead to the formation of Pd-Ga intermetallic compounds. In the following, FTIR spectroscopy of CO adsorption is utilized to investigate and contrast the adsorption sites available on Pd and Pd_xGa_y particles prepared by reduction at temperatures of 298 and 673 K, respectively. Furthermore, in order to examine a possible influence of the support, we compared Pd nanoparticles supported on a non-reducible oxide (Al₂O₃) with those on a reducible oxide support (Ga₂O₃), employing vibrational spectroscopy of CO adsorption after reduction at different temperatures. The mean Pd particle size, as determined by CO and H₂ chemisorption and by HRTEM, was about 4.5 nm for Pd/Al₂O₃ and around 4 nm for Pd/Ga₂O₃ (for details see [68] and [69]).

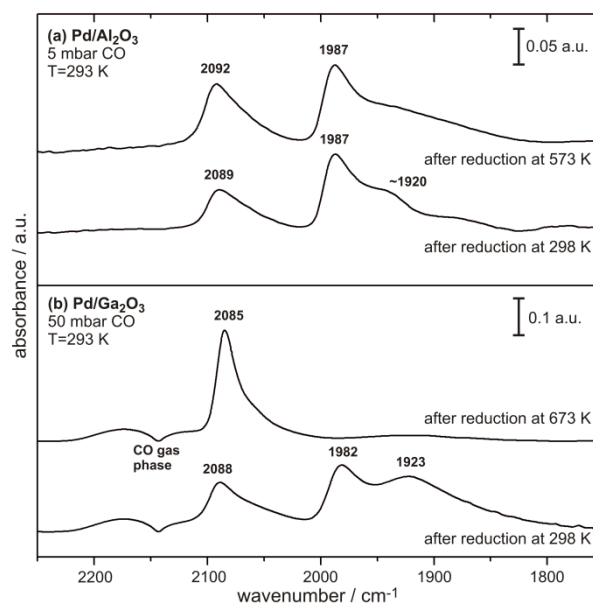


Figure 13: Infrared spectra of CO adsorbed on (a) Pd/Al₂O₃ and (b) Pd/Ga₂O₃ catalysts, following H₂ reduction at room- and elevated temperature.

Spectra of CO adsorption on the 2 wt% Pd/Al₂O₃ catalyst after reduction at room temperature and at elevated temperature (573 K) are shown in Figure 13. The spectra of adsorbed CO were basically identical in terms of intensity and frequency, irrespective of the reduction temperature (Fig. 10a). In 5 mbar CO three vibrational resonances were observed, at ~ 1920 cm⁻¹, ~ 1987 cm⁻¹ and ~ 2090 cm⁻¹. These peaks are characteristic of hollow or bridge bonded CO on (111) facets of pure Pd, of bridge bonded

CO on edges/steps or (100) facets, and of on-top bonded CO, respectively [70,71].

Corresponding IR spectra of CO adsorption on Pd/Ga₂O₃ are displayed in Figure 13b, again after different reduction temperatures. Bands typical of CO adsorbed on metallic Pd were detected after room temperature reduction, similar to the Pd/Al₂O₃ catalyst. However, increasing reduction temperatures decreased the intensity of bridge- and multiply bonded CO, which nearly completely disappeared after reduction at 673 K in hydrogen. This clearly indicated an isolation of Pd atoms by the formation of a Pd-Ga alloy or intermetallic compound. The band of CO adsorbed linearly on (isolated) Pd atoms of Pd_xGa_y/Ga₂O₃ appeared at 2085 cm⁻¹.

The phase and composition of the intermetallic compound formed upon reduction of the Pd/Ga₂O₃ powder catalyst was determined by X-ray diffraction performed *in situ* during heating in a flow of 25% H₂ in He (Fig. 14). Reflections assigned to the crystalline β-Ga₂O₃ support remained unchanged, regardless of temperature. At temperatures from 398 to 523 K the (111) reflection of Pd metal at 2θ = 40.2° was additionally observed. Below 398 K the β-palladiumhydride phase was present, thus no Pd metal reflection was observed (diffractogram not shown). At 673 K reflections at 2θ = 44.6, 41.2, 40.1 and 39.7° were detected that can be assigned to the Pd₂Ga phase [72], which does not form a hydride phase [73].

By combining the information obtained by *in situ* XRD on the bulk structure with the surface-sensitive information from FTIR spectroscopy, we were able to follow the formation of the intermetallic compound in detail. Activation of hydrogen occurs on Pd and hydrogen spillover to Ga₂O₃ leads to (partial) support reduction and intermetallic compound formation. Such a promotional reduction effect of the noble metal through hydrogen spillover from metallic palladium has also been suggested by Collins et al. [74] for Ga–Pd/SiO₂ catalysts. A more detailed study [69] on the temperature range of intermetallic formation indicated surface modifications occurring at temperatures significantly lower than those needed for the formation of crystalline Pd₂Ga.

It is interesting to note that, upon CO chemisorption, a single, though slightly structured band indicating the presence of a single type of adsorption site was also observed for the unsupported metallurgical PdGa model sample (see above) [41]. In this case it was detected at 2047 cm⁻¹ and did not show any partial pressure dependence. Taking the results of the CO chemisorption experiments obtained on this PdGa model sample and on the nano-Pd₂Ga/Ga₂O₃ powder sample into account, it can be concluded that the adsorption properties are similar for PdGa as well as for Pd₂Ga with respect to the absence of multiply bonded CO and, thus, strongly modified compared to pure Pd. The frequency of on-top CO on Pd₂Ga was only slightly shifted to lower wavenumber compared to (pure) Pd nanoparticles, despite intermetallic compound formation. In contrast, other bimetallic alloys (such as PdZn or PdAg) induce red shifts of up to 20–40 cm⁻¹, originating from the increased backdonation from Pd d-bands to CO and a concomitant weakening of the internal C–O bond [75, 76]. For the “Pd-rich” Pd₂Ga system, the effect of intermetallic formation is mainly manifest by decreasing the CO binding energy on bridging and hollow sites, but only a minor effect on the on-top C–O stretching frequency was observed. The destabilisation of bridging and hollow sites is presumably due to the increased Pd–Pd interatomic distances [72] and the amount of

Ga in Pd₂Ga is apparently sufficient to induce the desired “site isolation”. For the (unsupported) PdGa system, apart from site isolation, the electronic interaction is more pronounced, leading to an on-top CO frequency as low as 2047 cm⁻¹. The exact influence of particle size [77], Pd:Ga ratio and of the oxide support on vibrational frequencies of adsorbed CO should, however, be examined in more detail.

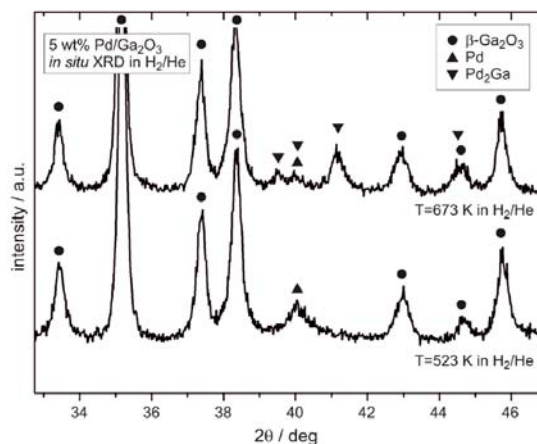


Figure 14: X-ray diffractograms recorded *in situ* at the indicated temperatures during reduction in 25 vol% H₂ in He. Reflections at 2θ = 40.2° correspond to Pd metal (▲), reflections at 2θ = 44.6, 41.2, 40.1 and 39.7° are assigned to the intermetallic compound Pd₂Ga (▼). All other reflexes can be assigned to the β-Ga₂O₃ support (●).

Another promising approach for the preparation of supported Pd₂Ga catalysts comprises co-precipitation of aqueous solutions Pd²⁺ and Ga³⁺ to form a well-defined precursor material with both ionic species in a joint cationic lattice. Layered double hydroxides (LDH) of the general composition Pd_xMg_{0.7-x}Ga_{0.3}(OH)₂(CO₃)_{0.15} · m H₂O (0 ≤ x ≤ 0.025) can be used as they allow a close interaction of Pd and Ga species [78]. The LDH precursors were synthesized under pH controlled conditions and by thermal decomposition and reduction in hydrogen at 823 K intermetallic Pd₂Ga nanoparticles (7 nm) supported on porous MgO/MgGa₂O₄ oxide matrix were obtained. The intermetallic phase formation was evidenced by HRTEM and XPS, while XRD could not provide detailed insights due to the small particle size and low loading. Reaction of Pd with Ga lead to an increased binding energy of the Pd 3d_{5/2} signal to 336.1 eV (Fig 15). The high binding energy is likely a convolutional effect of the modified electronic structure of Pd₂Ga and a final state particle size effect. Catalytic tests in the semi-hydrogenation of acetylene at conditions similar to those of Figure 7 revealed that the nano-Pd₂Ga catalyst reached the high selectivity known from the unsupported bulk model sample indicating structural integrity of the intermetallic compound in the LDH-derived material. As a result of nanosizing, the catalytic activity after a slow activation period at the beginning of the reaction was more than 5000 higher than that of the unsupported model catalyst. Thus, the catalytic properties related to the crystal and electronic structure of the intermetallic compound were successfully transferred from well-defined macroscopic model system to a nanostructured high performance system.

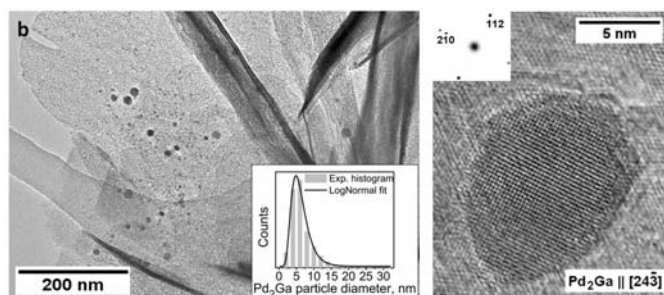
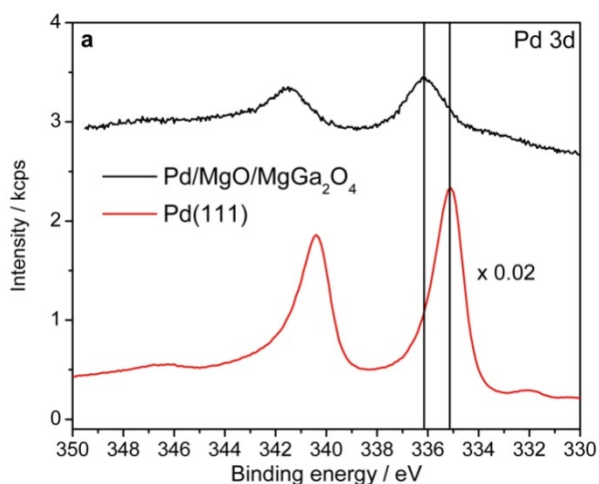


Figure 15: XPS spectra of a $\text{Pd}_2\text{Ga}/\text{MgO}/\text{MgGa}_2\text{O}_4$ catalyst obtained from a PdMgGa -LDH precursor and a monometallic Pd single crystal [78]. The shift in the Pd 3d binding energy of the catalyst compared to Pd metal indicates formation of an intermetallic compound (a). TEM investigation revealed the presence of Pd_2Ga with a particle size of approximately 7 nm (b).

Also co-impregnation of Pd^{2+} and Ga^{3+} species on carbon nanotubes (CNTs) can be used to synthesize nanocrystalline Pd_2Ga intermetallic catalysts, which are active and selective in acetylene hydrogenation [79]. Oxidized vacancies and localized double bonds on CNTs inhibit sintering and loss of the Pd_2Ga nanoparticles during reactions. These nanocrystalline intermetallics possess abundant low coordination sites (edge, steps and kinks, Fig. 16) on their surface, thereby render a high activity. The surface and structure of obtained Pd_2Ga nanoparticles were found to be thermally stable under reaction conditions. The approach of nanosizing intermetallics onto CNTs while obtaining good control of crystallite size may be applicable for synthesizing and supporting other nanocrystalline intermetallics.

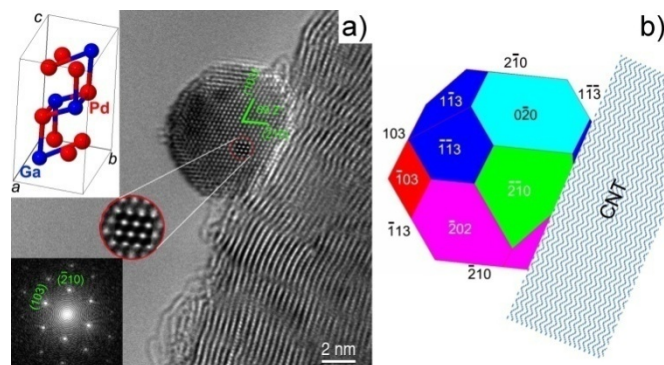


Figure 16. Microstructure characterizations of the $\text{Pd}_2\text{Ga}/\text{CNT}$. a), HRTEM image, with the insets of (top) crystallographic model of Pd_2Ga and (bottom) the Fast Fourier Transform of the local HRTEM image. The circled area represents the image simulation, conditioned at defocus of 6 nm and thickness of 6.1 nm viewed along the $\langle 361 \rangle$ direction of Pd_2Ga . b), The Wulff constructions of the corresponding Pd_2Ga nanoparticle in a).

In summary, Ga_2O_3 -containing powders are interesting Ga-sources for preparation of supported Pd_2Ga nanoparticles, which can be obtained by hydrogen reduction of $\text{Pd}/\text{Ga}_2\text{O}_3$ samples following an H-spillover mechanism. This reaction displays a promising route for feasible preparation of high performance Pd-Ga intermetallic compound catalysts.

Discussion

This work has shown that substantial aggregation of knowledge can be achieved through a collaborative effort addressing in a coordinated way various aspects of the catalytic function of an element. Many aspects were studied before in the substantial literature. Additional insight by targeted experiments and the application of high-level theory allowed joining together many pieces of the puzzle of selectivity control of Pd under high pressure operation conditions.

The following statements assume that mild reaction conditions are applied that allow for the existence of Pd hydrides. Pd is a potent hydrogenation catalyst when its ability to adsorb hydrogen on its surface is augmented by access of the sub-surface regime to hydrogen. This access can be kinetically hindered by using macrocrystals of Pd without grain boundaries. It may also be inhibited by blocking the access of hydrogen at defects through accidental carbon deposits or through intended modifiers such as Pb or sulfur-containing modifiers. In all these cases, Pd's ability to hydrogenate carbon-carbon double bonds is severely diminished. If, however, Pd can be converted to a combination of a sub-surface hydride with surface-adsorbed atomic hydrogen, then the element is a highly active catalyst that can operate in a sustained way as the chemical potential of active hydrogen counteracts the tendency of Pd to dehydrogenate organic molecules to carbonaceous overlayers that were frequently studied in surface science and high pressure situations.

The chemical potential of carbon over Pd is enhanced when alkyne substrates are to be hydrogenated. This class of highly activated molecules can dissolve as carbon in the surface-near volume of Pd without necessarily forming a bulk carbide compound. This carbon "alloy" gives rise to a modified surface electronic structure reducing the bond strength of adsorbed hydrogen and thus lowering its surface concentration. Even more

important is the site blocking action of the dissolved carbon for exchange processes of hydrogen with the Pd bulk: the formation of hydride is inhibited as long as the chemical potential of hydrogen does not exceed a critical value above which the hydrogen is able to gasify the dissolved carbon into volatile compounds and thus de-block the Pd catalyst bulk. In the carbon-modified state Pd is a weaker hydrogenation catalyst exhibiting excellent selectivity to semihydrogenation with a strong suppression of over-hydrogenation.

As no stoichiometric Pd-carbide phases exist, the selective hydrogenation form occurs in situ with some influence of the nature of the Pd on the kinetics of the carbon dissolution process. Very large grains, small clusters and strained particles on strongly interacting supports are less susceptible to carbon dissolution whereas medium-sized Pd nanoparticles above 1-2 nm supported on weakly straining supports such as carbon or carbonates are highly reactive. The kinetics of formation of the selective phase by substrate dehydrogenation and decomposition will further depend on the competition between carbon dissolution into the subsurface on one hand and formation of carbonaceous deposits covering the surface as well as re-hydrogenation of surface carbon species to gas phase species. The exact pre-history of the catalyst or the presence of solvents will also affect the dynamical transformation of pure non-selective Pd.

A narrow window of selective operation exists thus for the dynamical selective form of the Pd catalysts that is given by material properties such as microstructure of the catalyst and the thermodynamic conditions of the reaction. Both the chemical potentials of hydrogen and of hydrocarbon substrates (and solvents) define the boundaries of the window making it difficult to control in real catalytic applications. It gets smaller when the reaction conditions are very mild or harsh with respect to the existence of hydrides. It gets wider when the carbon potential is high for dissolution and low for surface polymerization.

This sensitivity of selective hydrogenation on a critical choice of reaction conditions prompted the development of a designed barrier against hydride formation under a wider range of reaction conditions. Alloying changes the electronic structure by shifting the d-band to lower energies and by reducing the density of states at the Fermi level. This is required to less efficiently activate and bind hydrogen. Many alloys however will not stay intact and thus segregate and/or phase separate in reaction conditions [80]. Typical examples of such systems are the technical semihydrogenation catalyst for acetylene Pd-Ag and compounds in the Pd-Zn or Pd-Si systems. It is noted that the very limited stability of the carbon-modified selective state of Pd follows exactly this scheme of sub-surface driven destabilization of the Pd-C system in accordance with the theoretical results described above.

In this situation a strongly covalent interaction between Pd and a second element as present in intermetallic compounds is a suitable solution as then no kinetic lowering of the segregation barrier can work. Such strongly stabilized compounds are Pd₃Ga₇, PdGa and Pd₂Ga. Our work shows that not only well-structured macroscopic bulk alloy samples but also nanoparticles supported on oxides or carbon retain their chemical stability against hydride formation under reduction conditions. Under the conditions of our semihydrogenation test the novel intermetallic compound-derived catalysts exhibit excellent performance data. This experimental observation is in broad agreement with theoretical predictions

using scaling laws for selecting selective semihydrogenation catalysts. For intermetallic compounds like PdGa, care has to be taken, however, to take the theoretical predictions of electronic structure modifiers too literally, if the calculations are based on simplified statistical fcc alloys. Issues of crystal structure, bonding situation and chemical complexity of the terminating surface deviating much from the model bulk structure can greatly modify the reactivity and stability of such "artificial" Pd systems.

When going from our model conditions to the technically much milder conditions and when using the Pd-Ga intermetallic compounds in liquid phase hydrogenation the performance results are less attractive. This unusual behavior of reduced performance at milder reaction conditions needs some reasoning. The prize to pay for the deliberate modification of the electronic structure of Pd through forming a well-ordered intermetallic compound is an enormous increase in the structural complexity of the surface termination. Not only different orientations of terminating facets but also chemically different compositions of a class of terminations with the same orientation can and will occur when forming the surface of a covalent compound. In addition, the high oxophilicity of the Ga component leads to a large variety of possible Ga oxide-contaminated surfaces of Pd-Ga systems formed by a reversal of the reactive alloying used for its synthesis. Amongst them there are also varieties where a full Pd monolayer terminates the intermetallic compound. Catalytically such terminations are obviously not much different from pure Pd.

Conclusion and Outlook

In the present study, we identify the unintended or intentional control of the hydrogenation activity and selectivity of polycrystalline Pd by modifier atoms in the sub-surface volume of Pd. These results show how sub-surface compound formation can be developed into a design tool for catalyst development. In addition to the nature of the modifier atom, also nanostructuring through particle size and metal-support interaction can kinetically control the reactivity of Pd with species in the subsurface. Thus, more detailed studies of structure and dynamics of the catalyst-reactant interaction are desirable to gain insight into the mutual interactions of catalyst and substrate and to develop synthetic strategies to influence the chemical complexity in the desired way. It will be in particular interesting to use the concept of intermetallic compound formation that here has been introduced for the example of PdGa as a guideline to explore other binary and ternary systems and to develop effective and selective hydrogenation catalysts. The benefit of such efforts will be that we better understand the modes of selectivity control and can adequately adapt our reaction conditions and catalyst selection procedures.

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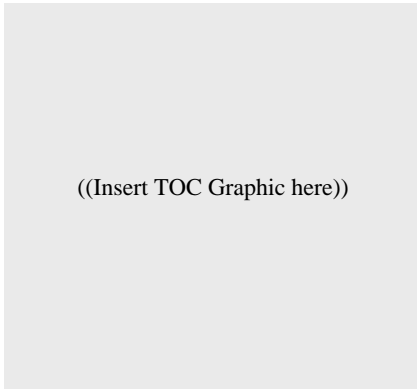
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Page No. – Page No.

((Title))