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A new approach to well-defined, stable and site-isolated catalysts

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Abstract

A new concept to circumvent some of the problems that are hindering a rational metallic catalyst development is introduced. Investigation of conventional metal catalysts — which consist of supported metals, metal mixtures or alloys — is handicapped by the presence of a variety of active sites, their possible agglomeration, metal–support interactions as well as segregation of the components. In order to avoid most of the drawbacks, we employ well-defined, ordered and *in-situ* stable unsupported intermetallic compounds. Knowledge of the chemical bonding in the compounds and the defined neighbourhood of the active sites allows a rational approach to catalysts with excellent selectivity as well as long-term stability. The concept is demonstrated for the intermetallic compound PdGa, which is applied as catalyst for the selective hydrogenation of acetylene to ethylene.

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1. Introduction

Because the terms “intermetallic compound” and “alloy” are often mixed up in the literature, we will start by defining the two terms. Hereafter, an “intermetallic compound” is a chemical compound of two or more metallic elements and adopts an — at least partly — ordered crystal structure that differs from those of the constituent metals. Intermetallic compounds are single-phase materials and often hold a wide homogeneity range. On the other hand, an “alloy” is a mixture of metals, intermetallic compounds and/or non-metals, and thus it can contain more than one phase.

The use of intermetallic compounds in catalysis (not as catalysts!) is widespread. The most well-known examples are the Raney-type catalysts, where an intermetallic compound — or an alloy — is leached in order to produce

a high-surface-area catalyst [1,2]. During leaching, the intermetallic compound (e.g. NiAl₃ [3]) is decomposed, resulting in the pure metal (very often Ni) as the catalytically active species.

In most of the other reports in which intermetallic compounds are used in catalysis, they are decomposed during the catalytic reaction. A good and well-explored example is the hydrogenation of CO over RE–Ni and RE–Cu (RE = rare earth metal) intermetallic compounds, which are decomposed *in-situ* to elemental nickel or copper particles and the corresponding rare earth oxide [4–8].

Intermetallic compounds can also be formed *in-situ* due to strong metal–support interactions or by the reaction between different supported metallic species. Examples where strong metal–support interactions were detected are the selective hydrogenation of crotonaldehyde over Pt/ZnO [9,10] and the steam reforming of methanol over Pd/ZnO [11,12]. Under reaction conditions the intermetallic compounds PtZn and PdZn are formed, and the high selectivity and activity is attributed to their presence.

In these cases (i.e. the decomposition or formation of intermetallic compounds *in-situ*) it is not easy to determine

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whether the intermetallic compound, the decomposition products and/or other components (e.g. the support) are catalytically active. This lack of knowledge prevents a rational development and improvement of these catalysts.

To circumvent these complications, our rational approach is based on the application of intermetallic compounds as pure as possible, stable and unsupported with ordered crystal structures as catalysts. The latter, in contrast to disordered alloys, leads to a uniform surrounding of the active sites, and thus the number of neighbouring sites as well as the distance between them are known. By selecting intermetallic compounds with a suitable crystal structure, the active sites can be tailored to the needs of the reaction.

A reaction for which isolated active sites are needed [13,14] is the partial hydrogenation of acetylene in a large excess of ethylene — an important step in the purification of the ethylene feed for the production of polyethylene (industrial production $> 50 \times 10^6$ t/a). The reaction has to be highly selective to avoid the hydrogenation of ethylene, while at the same time the concentration of acetylene has to be reduced from $\sim 1\%$ to the low ppm range to prevent the poisoning of the polymerization catalyst. It has been shown recently that π -adsorbed ethylene can further be hydrogenated to ethane, while di- σ -adsorbed ethylene leads to ethylidyne and vinylidene species, which do not desorb from the surface and cause deactivation [15–17]. The isolation of Pd atoms will lead to increased stability of the catalysts due to suppressed carbon deposition. Additionally, absence of neighbouring Pd sites will significantly reduce the surface and sub-surface hydrogen supply, which should improve the selectivity towards semi-hydrogenation [18]. Thus, in order to obtain highly selective catalysts, neighbouring active sites have to be avoided. Applying our concept, we tested the intermetallic compound PdGa with isolated Pd atoms successfully as catalyst for the selective acetylene hydrogenation reaction — as will be shown later on.

It has already been pointed out that the *in-situ* stability of the intermetallic compounds is crucial in order to connect the catalytic properties to the well-defined crystal structure. Since this is experimentally challenging and also time consuming, we employ quantum chemical methods beforehand, namely the electron localization function (ELF) and the electron localization indicator (ELI), to explore the chemical bonding in the compounds [19,20]. If covalent bonding (which corresponds to directed bonds, and thus chemical stability) is revealed, the stability is investigated by different *in-situ* techniques. Recently, we have introduced the intermetallic compounds PdGa and Pd₃Ga₇ as highly selective catalysts for the semi-hydrogenation of acetylene [21]. It was shown that the chosen intermetallic compounds fulfil the suggested concept of active-site isolation and possesses excellent bulk *in-situ* stability proven by *in-situ* extended X-ray absorption fine structure spectroscopy (EXAFS) (for the short-range order) and *in-situ* X-ray powder diffraction (XRD) (for

the long-range order). CO chemisorption as well as *ex-situ* X-ray photoelectron spectroscopy (XPS) was applied in order to characterize the Pd surface states of the synthesized catalysts before the reaction. Additionally, an effective way to enhance the Pd active surface — chemical etching — was introduced [21], which is described in detail in [22].

In our current contribution, we concentrate on the surface characterization of PdGa: according to our concept we apply quantum-chemical calculations (including the electron localizability indicator ELI) for the characterization of the electronic structure of PdGa. *In-situ* XPS and FTIR spectroscopy were performed in order to monitor changes in the surface composition of PdGa during the reaction and to prove the isolation of the Pd active sites, respectively. Furthermore, the obtained results are compared with elemental Pd in order to gain a deeper understanding of the high selectivity and stability of the investigated catalyst.

2. Experimental

2.1. Preparation

PdGa was prepared by melting the appropriate amounts of the metals (Pd: ChemPur 99.95%, Ga: ChemPur 99.99%) under a protective Ar atmosphere in a high-frequency furnace (Hüttinger TIG 5/300) and subsequent annealing of the ingot in an evacuated quartz glass ampoule at 1073 K for 170 h. The phase purity was controlled by XRD. For the catalytic investigations, the material was powdered and transferred to the reactor inside a glove box (Ar atmosphere, O₂ and H₂O below 1 ppm) to avoid significant contamination of the surface.

2.2. Quantum chemical calculations

Electronic structure calculation and bonding analysis in PdGa was carried out using the tight binding–linear muffin tin orbitals–atomic sphere approximation (TB–LMTO–ASA) program package [23]. The following crystal structure model was used [24]: space group $P2_13$ (no. 198), $a = 4.909$ Å; 4 Pd in Wyckoff position $4a$, xxx , $x = 0.14266$, 4 Ga in Wyckoff position $4a$, xxx , $x = -0.1568$. The Barth–Hedin exchange potential [25] was employed for the local density approximation (LDA) calculations. The radial scalar-relativistic Dirac equation was solved to obtain the partial waves. Although the calculation within the ASA should include corrections for the neglect of interstitial regions and partial waves of higher order [26], an addition of empty spheres was not necessary. The following radii of the atomic spheres were applied for the calculations for PdGa: $r(\text{Pd}) = 1.499$ Å, $r(\text{Ga}) = 1.529$ Å. A basis set containing Pd($5s, 5p, 4d$) and Ga($4s, 4p$) orbitals was employed for a self-consistent calculation, with Pd($4f$) and Ga($4d$)

functions being downfolded. The calculations were performed spin-polarized.

The ELF (η) [27] and the ELI (Y) [28] were evaluated with modules implemented within the TB-LMTO-ASA program package [23]. The topology of ELI and ELF was analysed using the program Basin [29] with consecutive integration of the electron density in basins, which are bounded by zero-flux surfaces in the ELI (ELF) gradient field.

This procedure, similar to the one proposed by Bader for the electron density [30], allows assigning an electron count for each basin, revealing the basic information about the chemical bonding.

2.3. Characterization

In-situ high-pressure XPS experiments were performed at beamline U49/2-PGM1 at BESSY (Berlin, Germany). Details of the set-up have been published earlier [31]. Briefly, the photoelectron spectrometer system uses a differentially pumped lens system between the sample cell and the electron analyser, allowing XPS investigations during catalytic conditions in the mbar pressure range. For the measurements, a dense pill of PdGa (8 mm in diameter and 1 mm thick) was produced by spark plasma sintering (SPS) at 873 K and 400 MPa in WC pressing tools. XPS investigations were performed in UHV (10^{-8} mbar) and *in-situ* conditions (1.0 mbar of H_2 (Westfalen Gas, 5.0) + 0.1 mbar of C_2H_2 (solvent free, Linde, 2.6) at 400 K). Gas-phase analysis was carried out using a quadrupole Balzers mass spectrometer connected by a leak valve to the experimental cell. The geometry of the XPS cell is inadequate to realize significant conversion — especially for SPS-pressed pills that feature a very low surface area. Thus, mass spectrometry was used to confirm that the reaction takes place.

Fourier transform infrared spectroscopy (FTIR) measurements were carried out using a Perkin-Elmer S 2000 spectrometer with a resolution of 4 cm^{-1} and an accumulation of 32 scans. PdGa powder was mixed with high-surface-area silica (Degussa) and subsequently pressed into thin wafers. The sample was treated in a heatable section of the IR cell which was connected to a vacuum line with a residual pressure of 10^{-6} mbar. Presented are difference spectra obtained by subtraction of the spectrum of the treated sample in vacuum from the spectrum in the presence of the probe molecule CO. Catalytic investigations were conducted in a plug-flow reactor consisting of a quartz glass tube (inner diameter 7 mm, length 300 mm), which was equipped with a sintered glass frit to support the catalyst bed. Activity, selectivity and long-term stability were measured in a mixture of 0.5% C_2H_2 , 5% H_2 and 50% C_2H_4 in helium (total flow of 30 ml/min) at 473 K. Gases were obtained from Westfalen Gas: 5% of C_2H_2 (2.6) in He (4.6), H_2 (5.0), C_2H_4 (3.5) and He (5.0). The concentrations of the educts and products were monitored by a micro gas chromatograph (Varian CP 4900). A commercial Pd/ Al_2O_3 catalyst (Sigma-Aldrich 205710, 5 wt.% Pd, BET surface: $114\text{ m}^2/\text{g}$, Pd surface $6\text{ m}^2/\text{g}$) was used as reference.

3. Results and discussion

A single-phase material was obtained by melting the metals together. The obtained powder XRD pattern is in accordance with the published data of PdGa [32]. The crystal structure of PdGa (FeSi type) is displayed in Fig. 1a. As has been pointed out above, isolated Pd atoms are required for the selective partial hydrogenation of acetylene and — as can be seen in Fig. 1b — the Pd atoms in PdGa are well separated by the surrounding Ga shell. The Pd–Ga distances within the first shell are in the range

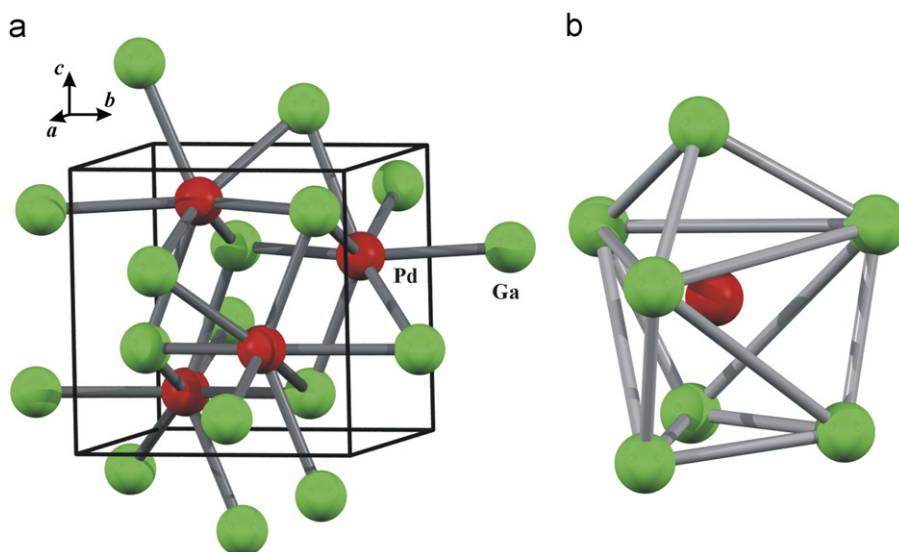


Fig. 1. (a) Crystal structure of PdGa (FeSi type, space group $P2_13$, $a = 4.909\text{ \AA}$). (b) Each Pd atom is surrounded by a shell of seven Ga atoms (Pd–Ga distances range between 2.543 and 2.712 $\text{\AA}$, the shortest Pd–Pd distance is 3.016 $\text{\AA}$).

of 2.543–2.712 Å. The separation results in a shortest Pd–Pd distance of 3.016 Å — an increase of almost 10% compared with the distance in metallic Pd, viz. 2.751 Å [33].

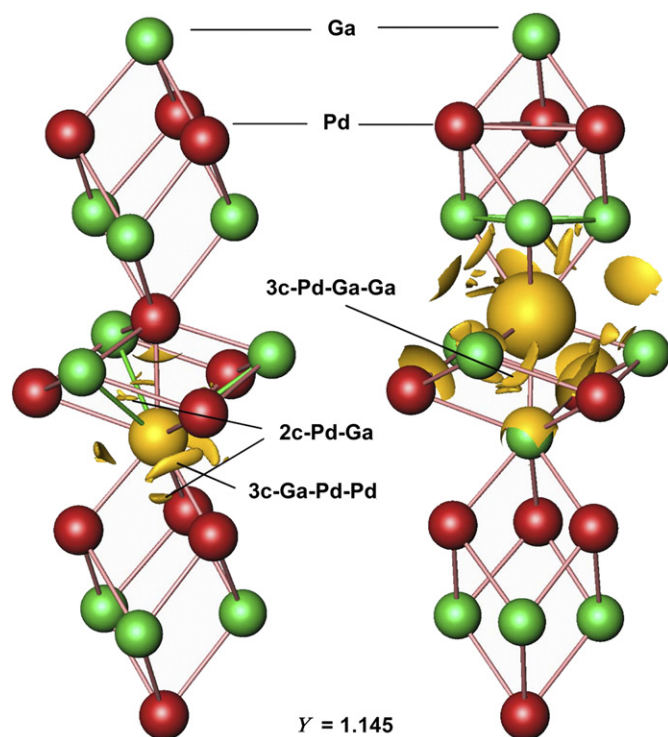


Fig. 2. Electron localizability indicator (isosurface with $Y = 1.145$) and in-teratomic interactions in PdGa: (left) positions of the ELI maxima in the vicinity of the gallium atoms; (right) ELI maxima around the palladium atoms.

A further requirement for an effective catalyst is the presence of covalent bonding to stabilize the desired geometry under reaction conditions, thus preventing deactivation of the catalysts. In Fig. 2, the results of the quantum chemical calculation of the ELI are shown. As illustrated by the isosurface with $ELI = 1.145$ (Fig. 2), the inner shells of Pd and Ga atoms are non-structured, which suggests that the electrons of these shells do not participate relevantly in the bonding in the valence region. In turn, the valence region reveals strong structuring, indicating the more directed (covalent) atomic interactions in PdGa. The local maxima appear mainly in the triangles between one Ga and two Pd atoms or between one Pd and two Ga atoms. The positions of the maxima can be interpreted as follows. Each Ga atom (Fig. 2, left) is participating in a two-centre (2c) interaction with the nearest Pd atom ($d = 2.543$ Å), three three-centre (3c) interactions Pd–Ga–Pd and three 3c interactions Ga–Pd–Ga. Each Pd atom (Fig. 2, right) forms one 2c bond Pd–Ga, three Pd–Ga–Pd and three Ga–Pd–Ga bonds. No homoatomic interactions were found by ELI analysis. As a result, a three-dimensional well-ordered framework is formed, indicating high structural stability in agreement with the high melting point of the compound (1318 K) [34]. A more detailed analysis of the chemical bonding will be the subject of a forthcoming publication.

In Fig. 3, the electron density of states (DOS) of PdGa and Pd metal with contributions of Pd 4d and Pd 5s orbitals are shown. Comparison of the two DOS clearly reveals that in case of elemental Pd the Pd 4d states lie in the vicinity of the Fermi level and are not completely filled, while in case of PdGa they are shifted below the Fermi

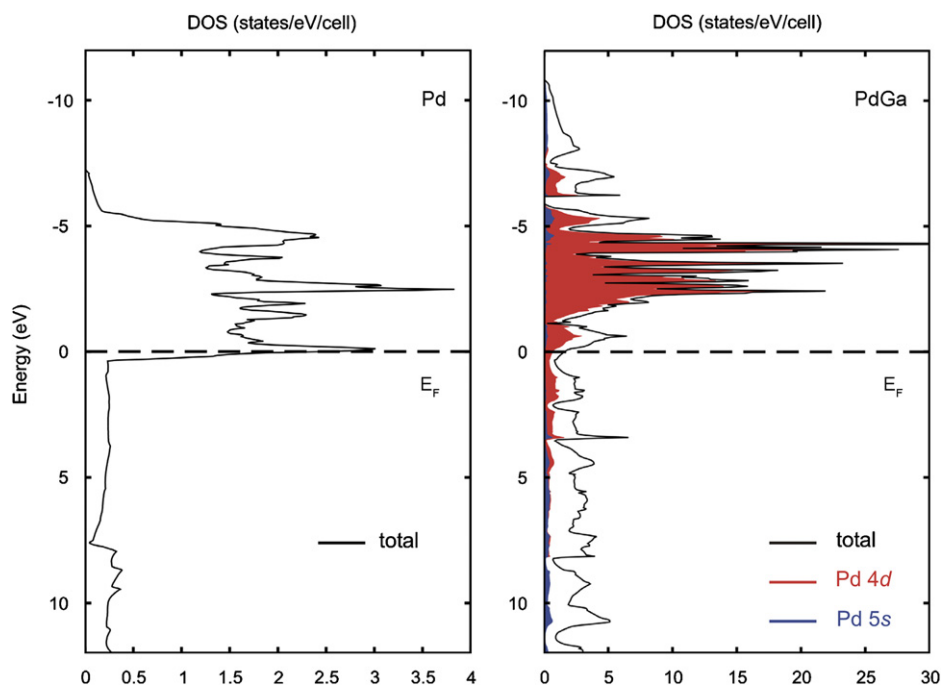


Fig. 3. Electron density of states (DOS) of PdGa with the partial contributions of the 4d and 5s orbitals (right) in comparison to the DOS for elemental Pd (left).

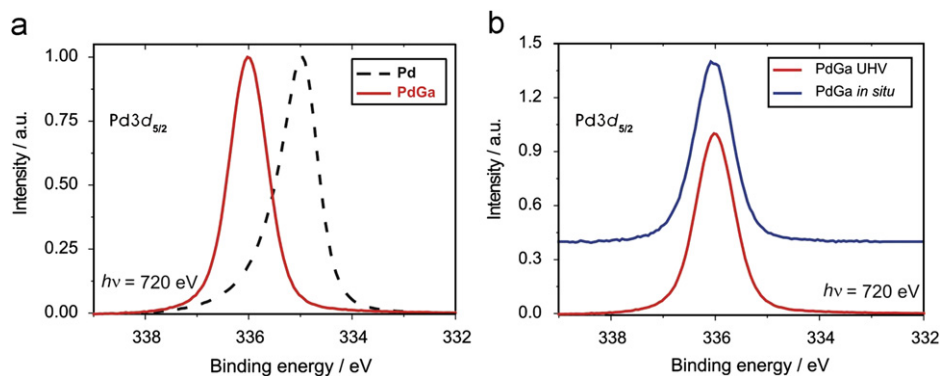


Fig. 4. (a) Comparison of the Pd_{3d_{5/2}} UHV XPS spectra of metallic Pd and PdGa. The shift to higher binding energy for PdGa is clearly visible. (b) Identical Pd_{3d_{5/2}} spectra of PdGa in UHV and *in-situ* conditions evidence no shift or additional components.

level. For PdGa, the states close to the Fermi level are composed of Pd as well as Ga orbitals. The shift of the Pd 4d orbitals should have an influence on the adsorption properties of PdGa, as will be demonstrated by FTIR.

As expected from the ELI, it could be shown by means of *in-situ* XRD and *in-situ* EXAFS that PdGa indeed holds the necessary bulk stability under reaction conditions [21]. Even though powder X-ray diffraction is sensitive to changes in the long-range order and EXAFS can detect variations in the local environment, they are both bulk methods. Since catalysis takes place on the surface of the material, we were also interested in the behaviour of the surface, especially under reaction conditions. Therefore, UHV and *in-situ* high-pressure XPS as well as FTIR spectroscopy were employed to probe the surface.

UHV XPS measurements revealed a significant modification of the Pd electronic states in the intermetallic compound compared with Pd metal: the Pd_{3d_{5/2}} peak is shifted by 1 eV to higher binding energy (Fig. 4). Thus, the difference in the electronic structure of PdGa and metallic Pd is pronounced not only in the states close to the Fermi level (compare DOS, Fig. 3) but also in the low-lying Pd_{3d} levels ($E \approx -336$ eV). This modification of the Pd electronic states in PdGa is likely caused by the presence of covalent bonding. A similar positive shift of Pd_{3d} binding energy was observed for a Pd–Zn surface alloy, where the formation of intermetallic compounds can be expected [35].

How is the electronic structure of Pd in PdGa affected by the reactive gases? To answer this question, high-pressure *in-situ* XPS was used to explore the surface electronic structure of PdGa during the partial hydrogenation of acetylene. The measurements, performed at ~1 mbar pressure, revealed a high stability of the Pd surface states (Fig. 4). Neither does the Pd_{3d_{5/2}} peak show a significant shift nor do additional components appear. This is in contrast to Pd metal for which the *in-situ* formation of an additional Pd component during 1-pentyne hydrogenation was detected recently [36]. The formed component, which shows a higher binding energy (335.6–335.7 eV) than metallic Pd (335.0 eV), corresponds to a carbon-containing palladium surface phase. This phase was proposed to be responsible for the selective pentyne hydrogenation process

instead of Pd metal [36]. In the case of PdGa, the Pd electronic states are already changed due to the presence of intermetallic chemical bonding — leading to a binding energy of ~336.0 eV — so no further modification with carbon and/or hydrogen is necessary or possible to gain the catalytic properties. This also results in a suppression of the subsurface chemistry (incorporation of hydrogen or carbon), which is observed in the case of pure Pd [13,36–38].

The Ga_{2p} and Pd_{3d} XP spectra were measured at different photon energies of the X-ray beam in such a way that the kinetic energy of the produced photoelectrons (KE) was alike, thus allowing one to obtain information for both elements from the same penetration depth. After correction for the sensitivity factors, the Pd/Ga ratio was calculated to be equal to 0.9 for the very surface sensitive mode, KE = 150 eV. This is a strong argument that the bulk and the surface compositions of PdGa are identical.

Since the PdGa SPS pill was in contact with air, some carbon-containing species were adsorbed on the surface, as was revealed by UHV XPS. *In-situ* measurements of the C1s XP spectrum (not shown) indicated the expected increase in surface carbon concentration due to adsorbed hydrocarbon species, but no significant shift or formation of additional carbon components was detected. Depth profiling of the pill — measurements were performed at different photon energies of the X-ray beam in order to obtain information from different penetration depths — was performed for Pd_{3d} and C1s peaks. Peak positions and shapes remain unaltered, while the carbon content decreases monotonically with increasing penetration depth, which confirms the absence of a carbon-containing surface phase.

In the case of metallic Pd, hydrocarbon deposits and hydrocarbon decomposition with subsequent formation of carbonaceous deposits are regarded as the main reasons for deactivation of the catalyst [39–41]. PdGa does not have adjacent Pd atoms which are necessary to form carbon deposits. Thus, the significantly enhanced long-term stability compared with metallic Pd can be attributed to geometric as well as electronic reasons (*vide infra*).

While XPS provides information about the electronic structure of the surface Pd sites, the local environment can be probed by CO adsorption using FTIR spectroscopy. Adsorption of CO on PdGa at room temperature results in the appearance of only one sharp band with a maximum at 2047 cm^{-1} (Fig. 5). This band was reproducible even after oxidation of the catalyst (200 mbar O_2 at 400°C for 30 min and 60 min evacuation before CO adsorption at room temperature), which is in good agreement with the *in-situ* bulk [21] and surface stability of PdGa. The observed band disappears easily after short evacuation of the sample at room temperature. Since CO molecules adsorbed on two or more Pd atoms reveal significantly higher stability compared with the linearly adsorbed CO on Pd [42], we assign this band to CO adsorbed on Pd in the on-top position.

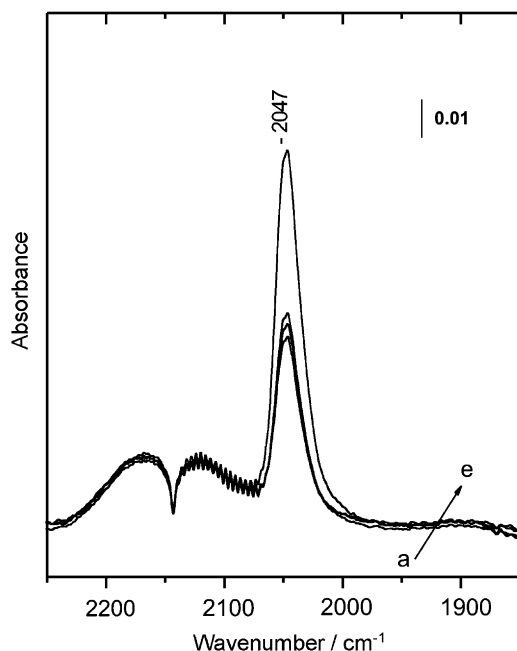


Fig. 5. FTIR spectra of CO adsorbed on PdGa at room temperature. The sequence from a to e corresponds to increasing exposition times: immediately after introducing 50 mbar of CO (a), after 1, 5, 10 and 60 min (e).

The shift of the observed band to lower wavenumbers — compared with CO on-top on metallic Pd ($2080\text{--}2100\text{ cm}^{-1}$) [42] — may be due to the modification of the Pd electronic states by the covalent bonding in PdGa. In addition to the bands arising from on-top species, pronounced bands in the region of $1900\text{--}2000\text{ cm}^{-1}$ are observed for metallic Pd, corresponding to CO molecules bridging neighboring Pd atoms [42–44]. The absence of such species on PdGa is directly connected to the isolation of Pd active sites on the surface. Further insight can be gained by the coverage dependence of the vibration frequency. CO molecules adsorbed on-top on neighbouring Pd atoms on Pd metal influence each other through dipole–dipole interactions, resulting in a coverage-dependence of the frequency [42,45]. No such shift was observed in the case of PdGa (Fig. 5). Together with the absence of bands due to bridging CO, this is a clear indication that the active sites of PdGa are really isolated.

Summarizing the XPS and FTIR results, one can expect long-term stability and high selectivity for the PdGa catalyst in the partial hydrogenation of acetylene since only isolated and stable Pd sites are present on the surface.

Catalytic testing proved that this is the case. Activity, selectivity and long-term stability were determined in an excess of ethylene ($\text{C}_2\text{H}_4/\text{C}_2\text{H}_2$ ratio 100:1), thus simulating industrial conditions. Isothermal experiments were performed by heating the catalysts — 400 mg of PdGa or 0.1 mg $\text{Pd}/\text{Al}_2\text{O}_3$ for comparison — in helium to a temperature of 473 K, followed by switching to the ethylene-rich feed (ratio $\text{C}_2\text{H}_4/\text{H}_2/\text{C}_2\text{H}_2 = 100/10/1$). The obtained conversion of acetylene and the corresponding selectivity to ethylene are shown in Fig. 6. During 20 h on stream PdGa showed a stable conversion of 70%, whereas $\text{Pd}/\text{Al}_2\text{O}_3$ exhibited a strong deactivation (from 100% to 45%). In addition to a high long-term stability, PdGa possessed a high and long-time stable selectivity of over 75% compared with less than 20% selectivity of $\text{Pd}/\text{Al}_2\text{O}_3$.

To compare the activities of the catalysts, the very different Pd concentrations as well as the unlike specific surface areas have to be considered. The surface area of the PdGa used in this study was below the limit of conventional nitrogen BET measurements. However, after milling and chemical etching,

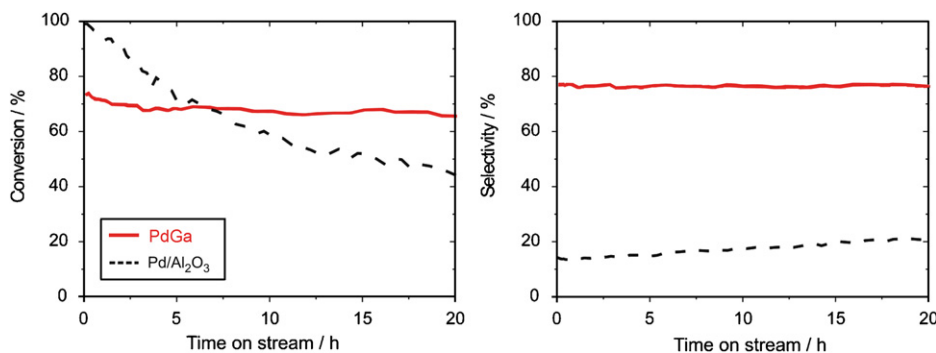


Fig. 6. Catalytic data for the hydrogenation of acetylene to ethylene catalysed by PdGa (400 mg) and $\text{Pd}/\text{Al}_2\text{O}_3$ (0.1 mg) (see text for details). While the supported Pd exhibits low selectivity as well as strong deactivation with time on stream, PdGa possesses high and stable selectivity.

PdGa possesses a higher surface area of $\sim 2 \text{ m}^2/\text{g}$ resulting in a Pd surface of $2 \text{ m}^2/\text{g} \times 0.5 = 1.0 \text{ m}^2/\text{g}$, assuming a stoichiometric composition of the surface [22]. The surface area of Pd/ Al_2O_3 was $114 \text{ m}^2/\text{g}$ with an active Pd surface of $6 \text{ m}^2/\text{g}$ (measured by CO chemisorption) and 0.15 mg of the catalyst reached a conversion of $>95\%$. In order to reach a similar acetylene conversion, only 1.5 mg of milled and etched PdGa was necessary [22]. The total Pd surfaces were $1.5 \text{ mg} \times 1.0 \text{ m}^2/\text{g} = 1.5 \times 10^{-3} \text{ m}^2$ for PdGa and $0.15 \text{ mg} \times 6 \text{ m}^2/\text{g} = 0.9 \times 10^{-3} \text{ m}^2$ for Pd/ Al_2O_3 , which are similar values, clearly demonstrating that the surface activity of PdGa is comparable to that of the supported Pd catalysts. From the point of activity per gram Pd, 1.5 mg of PdGa contains $1.5 \text{ mg} \times 0.6 = 0.9 \text{ mg}$ of Pd, while 0.15 mg of Pd/ Al_2O_3 holds $0.15 \text{ mg} \times 0.05 = 0.0075 \text{ mg}$ of Pd. From this, it follows that the reference catalyst is about 120 times more active. Taking the different Pd active surface areas into account (1.0 and $6.0 \text{ m}^2/\text{g}_{\text{catalyst}}$ for PdGa and Pd/ Al_2O_3 , respectively) results in Pd surface areas of $1.0 \text{ m}^2/\text{g}_{\text{catalyst}}/0.6 = 1.67 \text{ m}^2/\text{g}_{\text{Pd}}$ for PdGa and $6.0 \text{ m}^2/\text{g}_{\text{catalyst}}/0.05 = 120 \text{ m}^2/\text{g}_{\text{Pd}}$ for Pd/ Al_2O_3 . Hence, the reference catalyst possesses a 72 times higher active Pd surface, which explains the higher activity (per gram of Pd) of the reference catalyst.

It would be desirable to compare the catalysts by their TOFs. Unfortunately, this is hindered by the low surface area of untreated PdGa, which is below the detection limit of the standard BET method. In addition, CO chemisorption on PdGa results in no detectable adsorption at room temperature [21].

As has been shown, our rational approach to a well-defined, stable and site-isolated catalyst is indeed working. Furthermore, due to knowledge of the active species, we showed that isolated sites are responsible for the high selectivity and thus for the semi-hydrogenation of acetylene. Further improvement of the catalyst is possible, since the catalytic properties can be undoubtedly assigned to the compound PdGa, e.g. the dependence of selectivity on the Pd–Pd distance in different intermetallic compounds can be investigated.

4. Conclusion

By applying a new and rational approach to well-defined, stable and site-isolated catalysts, it was possible to identify PdGa as a highly selective and long-term stable catalyst for the semihydrogenation of acetylene.

Quantum chemical calculations and XPS measurements revealed a significant difference between the electronic structures of PdGa and Pd metal in combination with covalent bonding detected by the ELI. By means of XPS and FTIR measurements, it has been shown that the surface only holds isolated Pd atoms, thus providing high selectivity and long-term stability — the latter most probably due to the absence of carbon deposits.

Utilizing our concept, it is not only possible to assign the catalytic properties to a specific compound but also a further rational development is conceivable.

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References

- [1] M. Raney, US 1563587, 1925.
- [2] M. Raney, US 1628190, 1927.
- [3] S. Sane, J.M. Bonnier, J.P. Damon, J. Masson, Appl. Catal. 9 (1984) 69.
- [4] R.M. Nix, T. Rayment, R.M. Lambert, J.R. Jennings, G. Owen, J. Catal. 106 (1987) 216.
- [5] C.M. Hay, J.R. Jennings, R.M. Lambert, R.M. Nix, G. Owen, T. Rayment, Appl. Catal. 37 (1988) 291.
- [6] H. Imamura, W.E. Wallace, Am. Chem. Soc. Div. Fuel Chem. 25 (1979) 82.
- [7] J.E. France, W.E. Wallace, Lanthan. Actin. Res. 2 (1988) 165.
- [8] V.T. Coon, W.E. Wallace, R.S. Craig, in: G.J. McCarthy, J.J. Rhyne (Eds.), Rare Earths in Modern Science and Technology, Plenum Press, New York, 1978, p. 93.
- [9] M. Consonni, D. Jokic, D.Y. Murzin, R. Touroude, J. Catal. 188 (1999) 165.
- [10] F. Ammari, J. Lamotte, R. Touroude, J. Catal. 221 (2004) 32.
- [11] Y.-H. Chin, R. Dagle, J. Hu, A.C. Dohnalkova, Y. Wang, Catal. Today 77 (2002) 79.
- [12] A. Karim, T. Conant, A. Datye, J. Catal. 243 (2006) 420.
- [13] A. Borodzinski, G.C. Bond, Catal. Rev. 48 (2006) 91 and references cited herein.
- [14] J. Panpranot, L. Nakkararung, B. Ngamsom, P. Praserttham, Catal. Lett. 103 (2005) 53.
- [15] A.M. Doyle, S.K. Shaikhutdinov, H.-J. Freund, J. Catal. 223 (2004) 444.
- [16] S.K. Shaikhutdinov, M. Heemeier, M. Bäumer, T. Lear, D. Lennon, R.J. Oldman, S.D. Jackson, H.-J. Freund, J. Catal. 200 (2001) 330.
- [17] S.K. Shaikhutdinov, M. Frank, M. Bäumer, S.D. Jackson, R.J. Oldman, J.C. Hemminger, H.-J. Freund, Catal. Lett. 80 (2002) 115.
- [18] G.C. Bond, P.B. Wells, J. Catal. 5 (1966) 65.
- [19] M. Boström, Yu. Prots, Yu. Grin, J. Solid State Chem. 179 (2006) 2472.
- [20] Yu. Grin, F.R. Wagner, M. Armbrüster, M. Kohout, A. Leithe-Jasper, U. Schwarz, U. Wedig, H.G. von Schnering, J. Solid State Chem. 179 (2006) 1707.
- [21] J. Osswald, K. Kovnir, M. Armbrüster, R.E. Jentoft, R. Giedigkeit, T. Ressler, Y. Grin, R. Schlögl, Angew. Chem. Int. Ed. (2007), submitted.
- [22] K. Kovnir, J. Osswald, M. Armbrüster, R. Giedigkeit, T. Ressler, Y. Grin, R. Schlögl, Stud. Surf. Sci. Catal. 162 (2006) 481.
- [23] O. Jepsen, A. Burkhardt, O.K. Andersen, The Program TB-LMTO-ASA. Version 4.7, Max-Planck-Institut für Festkörperforschung, Stuttgart, 1999.
- [24] R. Giedigkeit, Ph.D. Thesis, Technische Universität Dresden, 2007.
- [25] U. Barth, L. Hedin, J. Phys. C 5 (1972) 1629.
- [26] O.K. Andersen, Phys. Rev. B 12 (1975) 3060.
- [27] A. Savin, H.J. Flad, J. Flad, H. Preuss, H.G. von Schnering, Angew. Chem. 104 (1992) 185; A. Savin, H.J. Flad, J. Flad, H. Preuss, H.G. von Schnering, Angew. Chem. Int. Ed. Engl. 31 (1992) 185.
- [28] M. Kohout, Int. J. Quantum Chem. 97 (2004) 651.
- [29] M. Kohout, Basin, Version 2.3, Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, 2001.
- [30] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, 1999.
- [31] H. Bluhm, M. Hävecker, A. Knop-Gericke, E. Kleimenov, R. Schlögl, D. Teschner, V.I. Bukhtiyarov, D.F. Ogletree, M. Salmeron, J. Phys. Chem. B 108 (2004) 14340.

- [32] M.K. Bhargava, A.A. Gadalla, K. Schubert, *J. Less-Common Met.* 42 (1975) 69.
- [33] H.E. Swanson, E. Tatge, *Nat. Bur. Stand.* 359 (1953) 21.
- [34] T.B. Massalski, in: T.B. Massalski (Ed.), *Binary Alloy Phase Diagrams*, vol. 2, ASM International, Materials Park, OH, 1990, p. 1836.
- [35] J.A. Rodriguez, *J. Phys. Chem.* 98 (1994) 5758.
- [36] D. Teschner, E. Vass, M. Hävecker, S. Zafeiratos, P. Schnörch, H. Sauer, A. Knop-Gericke, R. Schlögl, M. Chamam, A. Wootsch, A.S. Canning, J.J. Gamman, S.D. Jackson, J. McGregor, L.F. Gladden, *J. Catal.* 242 (2006) 26.
- [37] W. Palczewska, Z. Paal, P.G. Denon, *Hydrogen Effects in Catalysis*, Marcel Decker, New York, 1988, p. 372.
- [38] A.M. Doyle, S.K. Shaikhutdinov, S.D. Jackson, H.J. Freund, *Angew. Chem. Int. Ed.* 42 (2003) 5240.
- [39] P. Albers, J. Pietsch, S.F. Parker, *J. Mol. Catal. A* 173 (2001) 275.
- [40] H. Arnold, F. Döbert, J. Gaube, in: G. Ertl, H. Knoerzinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, VCH, Weinheim, 1997, p. 2165.
- [41] A. Molnár, A. Sarkany, M. Varga, *J. Mol. Catal. A* 173 (2001) 185.
- [42] H. Unterhalt, G. Rupprechter, H.-J. Freund, *J. Phys. Chem. B* 106 (2002) 356.
- [43] D. Tessier, A. Rakai, F. Bozon-Verduraz, *J. Chem. Soc. Faraday Trans.* 88 (1992) 741.
- [44] E.W. Shin, C.H. Choi, K.S. Chang, Y.H. Na, S.H. Moon, *Catal. Today* 44 (1998) 137.
- [45] S. Bertarione, D. Scarano, A. Zecchina, V. Johanek, J. Hoffmann, S. Schauer mann, M.M. Frank, J. Libuda, G. Rupprechter, H.-J. Freund, *J. Phys. Chem. B* 108 (2004) 3603.