



Etching of the Intermetallic Compounds PdGa and Pd₃Ga₇: An Effective Way to Increase Catalytic Activity?

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Abstract

A series of ZnO/Al₂O₃ mixed oxide samples with varying Zn/Al ratio is prepared by coprecipitation, ageing, drying, and calcination. Samples are investigated in the state after drying and calcination. The applied methods include X-ray diffraction, solid-state ²⁷Al magic-angle spinning nuclear magnetic resonance spectroscopy, transmission electron microscopy and thermogravimetric experiments coupled with evolved gas analysis. Phases present in the dried precursor samples include hydrozincite, zaccagnaite, and an unknown phase. After calcination zinc oxide and spinel can be found. All results indicate the substitution of Al ions for Zn ions in zinc oxide of zinc-rich samples.

Keywords: zinc oxide; aluminum ; coprecipitation; heterogeneous catalysis

1. Introduction

The chemical industry permanently demands improved catalysts to decrease production costs and save natural resources. A lot of phenomenological data concerning reactions pathways, intermediates, side-reactions and the formation of by-products have been accumulated during the last century. Generalization of these data allows formulation of the requirements for improved catalysts. But the rational synthesis of novel catalysts is still not well developed, lacking detailed understanding of the processes and knowledgebased new concepts.

Recently, we have introduced structurally well ordered intermetallic compounds as catalysts led by the concept of active-site isolation [1-5]. The employed

intermetallic compounds possess metallic conductivity, a well-defined crystal structure as well as partly covalent bonding between the atoms. Consequently, these intermetallic compounds have a very important advantage compared to conventional alloys: the atomic environment of the catalytically active metal is fixed by the realized crystal structure while in alloys the random distribution of the atoms leads to a number of possible adsorbate configurations on the catalytically active metal. This advantage results not only in a very homogeneous distribution of the active sites in intermetallic compounds but also the phenomenon of segregation is significantly reduced or not present at all due to the covalent bonding between the transition metal and the main groups elements stabilizing the active centers (see e.g. [1, 6]). Furthermore, the covalent bonding

modifies the electronic states of the active metal, which have a high impact on the catalytic properties [1].

To verify the suggested concept the partial hydrogenation of acetylene to ethylene was chosen ($C_2H_2 + H_2 \rightarrow C_2H_4$, $\Delta H = -172$ kJ/mol) as test reaction. Because acetylene poisons the ethylene polymerization catalysts, the acetylene content in the ethylene feed has to be reduced from ~1% to the low ppm range [7,8]. Moreover, economic efficiency requires a high selectivity of the catalyst – especially in the presence of ethylene excess – to prevent the hydrogenation of ethylene to ethane. Typical hydrogenation catalysts contain metallic palladium dispersed on metal oxides [7,8]. The main drawbacks, like deactivation and low selectivity of these catalysts, are widely discussed in literature [9-12].

According to the suggested concept, the structurally well ordered intermetallic compounds PdGa [13] and Pd₃Ga₇ [14] were chosen to prove the active-site isolation concept. In PdGa the palladium atoms are isolated by the surrounding gallium atoms forming a single-capped distorted trigonal prism (Figure 1). The shortest Pd-Pd distance is 3.01 Å. In contrast, the gallium atoms in Pd₃Ga₇ are arranged in paired square antiprisms, resulting in a Pd-Pd separation within the pair of antiprisms of 2.73 Å. The shortest Pd-Pd distance between the Pd atoms of two different pairs is 4.27 Å (Figure 1). It was shown, that these intermetallic compounds possess high structural stability in different atmospheres as well as high selectivity and long-term stability in the selective acetylene hydrogenation [1-4].

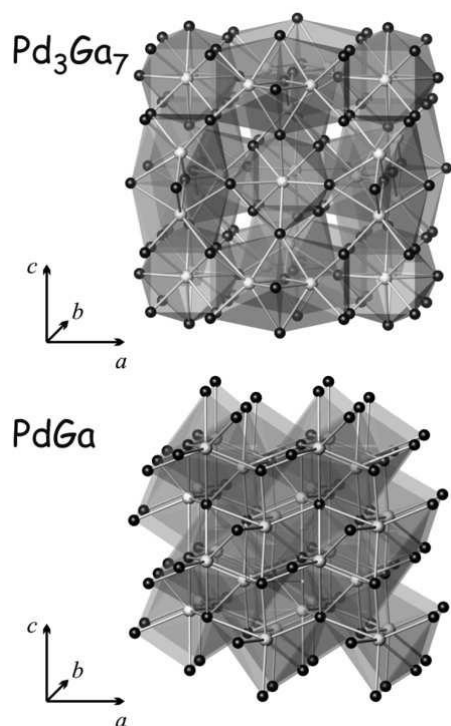


Fig. 1: Crystal structures of Pd₃Ga₇ (top) and PdGa (bottom). Pd: white spheres; Ga: black spheres. Each palladium atom in PdGa is coordinated by seven gallium atoms, while in Pd₃Ga₇ eight gallium atoms are surrounding the Pd atoms as indicated by polyhedra.

However, the use of unsupported intermetallic compounds as hydrogenation catalysts results in a low activity per gram of catalyst, but as advantage, the obtained results can be attributed to a single active compound with well defined crystal structure. Surface characterization of PdGa and Pd₃Ga₇ by X-ray photoelectron spectroscopy (XPS) as well as ion scattering spectroscopy [4] revealed the presence of gallium oxides on the surface of the particles. To increase the catalytic activity a chemical etching procedure with ammonia solution was successfully introduced, aiming at the selective removal of the inactive gallium oxides [5].

Here we report a detailed investigation of the impact of chemical etching on the catalytic properties, the chemical composition of the surface and the particle morphology, which is an important step towards the efficient use of intermetallic compounds as catalysts. Furthermore, the applicability of the chemical etching to intermetallic compounds as catalysts is discussed.

2. Experimental

2.1. Sample preparation

The intermetallic compound PdGa was prepared using elemental Pd (ChemPur, 99.95%) and Ga (ChemPur, 99.99%) as starting materials. The elements were weighted in 1:1 molar ratios in air and subsequently transferred to a glove box filled with argon (O_2 and $H_2O < 1$ ppm). The mixture was placed in a glassy carbon crucible and slowly heated up in a high-frequency induction furnace (Hüttinger TIG 5/300, 30 A, 200 V, 30-300 kHz). After the exothermic reaction of the elements the melt was annealed for ten minutes before the oven was switched off, thus allowing the samples to cool down to ambient temperature. In order to reach thermodynamic equilibrium, the ingots of PdGa were enclosed in evacuated quartz glass ampoules and annealed at 1073 K for one week. Pd₃Ga₇ was prepared similarly by using a 3:7 molar ratio of the components. The obtained ingots expanded during cooling and disintegrated into a fine, grey powder. The powder was pelleted prior to annealing at 673 K for four weeks. After annealing samples were quenched in water, crushed and investigated by X-ray powder diffraction revealing single phase sample.

2.2 Milling

To increase the surface area, one gram of a coarsely crushed sample was milled in a closed 4 ml tungsten carbide (WC) mortar using two WC balls. The milling was performed in a swing mill (Retsch MM 200, 25 Hz) for 2x30 min for PdGa and 2x10 min for Pd₃Ga₇. In each case, different samples were milled in air as well as under argon. For the latter the WC mortar was loaded in a glove box and sealed with air tight tape.

2.3 Etching procedure

Commercial ammonia solution (Merck, 25 % p.a.) was diluted with distilled water to the required pH values. Measurements of pH were performed with a Knick pH-Meter 761 Calimatic equipped with a Mettler-Toledo Inlab 422 electrode. The instrument was calibrated with buffer solutions (Merck centiPUR, pH = 7.0 and 9.0). 50 mg of air-milled PdGa or Pd₃Ga₇ were added to 75 ml of the diluted ammonia solution and stirred for 10 minutes at ambient temperature. The suspension was filtered and the residue was washed with an additional 75 ml of the solution while the filtrate was chemically analyzed. The etched samples were dried by evacuation to 10 mbar for at least 60 minutes in a desiccator. Throughout this manuscript, a set of abbreviations is used: Pd₃Ga₇_milled, Pd₃Ga₇_10.5, etc. The first letters name the intermetallic compound, Pd₃Ga₇ or PdGa, while the last digits indicate the pH value of the etching solution used for preparation of the sample; “milled” corresponds to samples used as obtained from the ball-milling procedure in air without further etching. Also the terms “soft” and “strong” etching are used throughout this paper: soft etching corresponds to samples etched at the *lowest* pH = 9.0 applied for both PdGa and Pd₃Ga₇, while strong etching corresponds to samples etched at the *highest* pH values used, 9.8 and 10.5 for PdGa and Pd₃Ga₇, respectively.

2.4 X-ray powder diffraction

X-ray powder diffraction (XRD) experiments were performed in transmission mode. Samples were finely ground and spread on a 6 μm thick Mylar foil coated with vaseline. For the measurements a Gunier camera (Huber G670, image plate, CuK_{α1} radiation with λ = 1.540562 Å) was utilized.

2.5 Chemical analysis

Chemical analysis of the filtrate after etching was performed by inductively coupled plasma - optical emission spectrometry (ICP-OES) with a Varian Vista RL spectrometer. All values are the averages of at least three replicates.

2.6 Surface area measurements

Adsorption-desorption measurements of N₂ using a Quantachrome Quantasorb Jr. have been performed to determine the surface area of the intermetallic compounds by the multipoint Brunauer-Emmett-Teller (BET) method. The samples (~2 g) were pretreated (20 ml/min He, 393 K, 12 hours) and measurements were performed by determining

the total amount of nitrogen adsorbed using three different nitrogen concentrations.

Milled (in air) samples of PdGa and Pd₃Ga₇ possessed a surface area below the nitrogen BET detection limit and were re-measured using krypton as adsorbate (BELSORP-max). The milled samples (400 mg) were pretreated in vacuum at 373 K for one hour and measurements were performed by determination of the total amount of Kr adsorbed using seven different krypton concentrations.

2.7 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed with an UHV system equipped with a Leybold LHS 12 MCD energy analyzer and further XPS surface analysis tools. The samples for the measurements were prepared from milled and etched PdGa and Pd₃Ga₇ powder. XPS data were obtained using Al K_α radiation (1486.6 eV) and a pass energy of 48 eV resulting in a spectrometer resolution of 1.1 eV. The elemental composition of the nearsurface region was estimated – after satellite subtraction and Shirley background correction – by integration of the peak areas and applying the corresponding sensitivity factors [15]. The gallium content was calculated from the Ga2p_{3/2}, palladium from the sum of Pd3d_{3/2} and Pd3d_{5/2} and carbon from the C1s peak area. The oxygen concentration was derived from the O1s peak area corrected for the Pd3p_{3/2} contribution. The Pd3p_{3/2} peak area was calculated from Pd3d one using a factor of 2.9 for the (Pd3d)/(Pd3p_{3/2}) ratio [4, 15].

2.8 In situ X-ray photoelectron spectroscopy (in situ XPS)

In situ high-pressure X-ray photoelectron spectroscopy (XPS) experiments were performed at beamline U49/2-PGM1 at BESSY (Berlin, Germany). Details of the setup have been published earlier [16]. Briefly, the photoelectron spectrometer system uses a differentially pumped lens system between the sample cell and the electron analyzer, allowing XPS investigations during catalytic conditions in the mbar pressure range. For the measurements dense pills of Pd₃Ga₇_9.8 and Pd₃Ga₇_10.5 (8 mm in diameter, 1 mm thick) were produced by pressing the powders at room temperature in stainless steel pressing tools. XPS investigations were performed in UHV (10–8 mbar) and under *in situ* conditions: 1.0 mbar of H₂ (Westfalen Gas, 99.999%) and 0.1 mbar of C₂H₂ (solvent free, Linde, 99.6%) at 375–400 K. Prior to UHV investigations the samples were sputtered with Ar⁺ ions to clean the surface from possible contaminations. An *in situ* experiment included introduction of the gases at room temperature, equilibration for 15 minutes, heating the sample to the corresponding temperature with 10 K/min rate and equilibration for another 15 minutes, afterwards the XP spectra

were recorded. Pd3d, Ga3p, Ga3d and C1s XP spectra were recorded with varying the wavelength of the incoming radiation resulting in photoelectrons with similar kinetic energy. Thus, the same information depth was probed for the different core levels. Three different kinetic energies were chosen – 780 eV, 380 eV and 150 eV. These correspond to information depths (3-times the inelastic mean free path) of ~4.5 nm, 3 nm and 2 nm, respectively, for clean Pd₃Ga₇ [17]. Element concentrations were determined from Pd3d, Ga3p and C1s peak areas. Gas-phase analysis was carried out using a quadrupole Balzers mass spectrometer connected by a leak valve to the experimental cell. Ion currents corresponding to acetylene ($m/e = 26$), ethylene ($m/e = 27$) and ethane ($m/e = 30$) were monitored. For the evaluation, the ion currents of ethylene and ethane were normalized to the acetylene signal and plotted versus time of the experiment. The normalization was performed to account for possible pressure fluctuations.

2.9. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was performed with a Hitachi S4800 with a cold FEG (Field Emission Gun). The setup was equipped with an Energy Dispersive X-ray system EDAX Genesis 4.52, the EDX detector consist of Si(Li) crystal and a SUTW (Super Ultra Thin Window). Samples were mounted on Al-holder with conducting carbon tape.

2.10. Catalysis

A detailed description of the catalysis experiments has been published elsewhere [4]. Catalytic investigations of the selective hydrogenation of acetylene were performed within a plug flow reactor (30 mL/min) with high excess of ethylene: 0.5 % acetylene, 5 % hydrogen (99.999%) and 50 % ethylene (99.95%) in helium (99.999%). Pre-mixed acetylene in helium (2%) (C₂H₂: 99.6%, He: 99.996%) was used. All gases were supplied by Westfalen Gas (Germany). A Varian CP 4900 MicroGC (Gas Chromatograph) was used for the exhaust gas analysis during isothermal experiments. As reference, commercial Pd/Al₂O₃ (5 wt.-%, Aldrich) with a BET surface area of 114 m²g⁻¹ and an active metal surface of 5.6 m²g⁻¹ (determined by CO chemisorption) was used [3-4]. Selectivity and conversion were calculated by the following formulas [4]:

$$\text{conversion} = \frac{C_{\text{feed}} - C_x}{C_{\text{feed}}}; \text{selectivity} = \frac{C_{\text{feed}} - C_x}{C_{\text{feed}} - C_x + C_{\text{ethane}} + 2C_{C_4H_x}}$$

where C_{feed} is the acetylene concentration in the feed, C_x is the acetylene concentration after the reactor, C_{ethane} is the ethane concentration and $C_{C_4H_x}$ is the total concentration of the different C₄H_x hydrocarbons detected. To measure the selectivity at similar conversion, different amounts of

catalyst were used according to their specific activity determined in previous experiments. The activity of the samples was calculated using the following equation:

$$\text{activity} = \frac{\text{conversion} \cdot C_{\text{feed}} \cdot C_{\text{ex}}}{m_{\text{cat}}}$$

where m_{cat} is the amount of catalyst in gram and C_{ex} is 1.904 g/h. The latter was introduced to convert the acetylene flow from [ml/min] to [g/h] and is based on the ideal gas model:

$$C_{\text{ex}} = \frac{M_{\text{acetylene}} \cdot p \cdot F}{R \cdot T}$$

where $M_{\text{acetylene}}$ is the molar weight of acetylene (26 g/mol), p the pressure (1.013 bar), F the total gas flow through reactor at room temperature (1.8 l/h at 300 K), R the universal gas constant R (8.3144 Jmol⁻¹K⁻¹) and T the temperature (300 K).

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3. Results and discussion

3.1. Milling

During this work it was established that the milling procedure has significant influence on the catalytic activity of the investigated compounds. Milling of the intermetallic compounds PdGa and Pd₃Ga₇ was performed with the aim to increase the catalysts surface area. Initially the milling was performed in air. Afterwards, significant covering of the surface of the catalyst milled in air by gallium oxides was detected by XPS and SEM [4-5]. Since all the syntheses were performed in a glove box (O₂ and H₂O contents lower than 1 ppm), it is very unlikely that the oxygen contamination was caused by the preparation. Although gallium oxides were detected, the activity was considerably increased after milling the samples, e.g. by a factor of 20 for PdGa.

To avoid oxide formation, the milling procedure was performed in inert argon atmosphere. Surprisingly, samples milled under argon showed negligible activity compared to the ones milled in air. Moreover, the particles after milling in Ar stuck to each other, which hindered regrinding of the samples in a mortar, while air-milled samples could easily

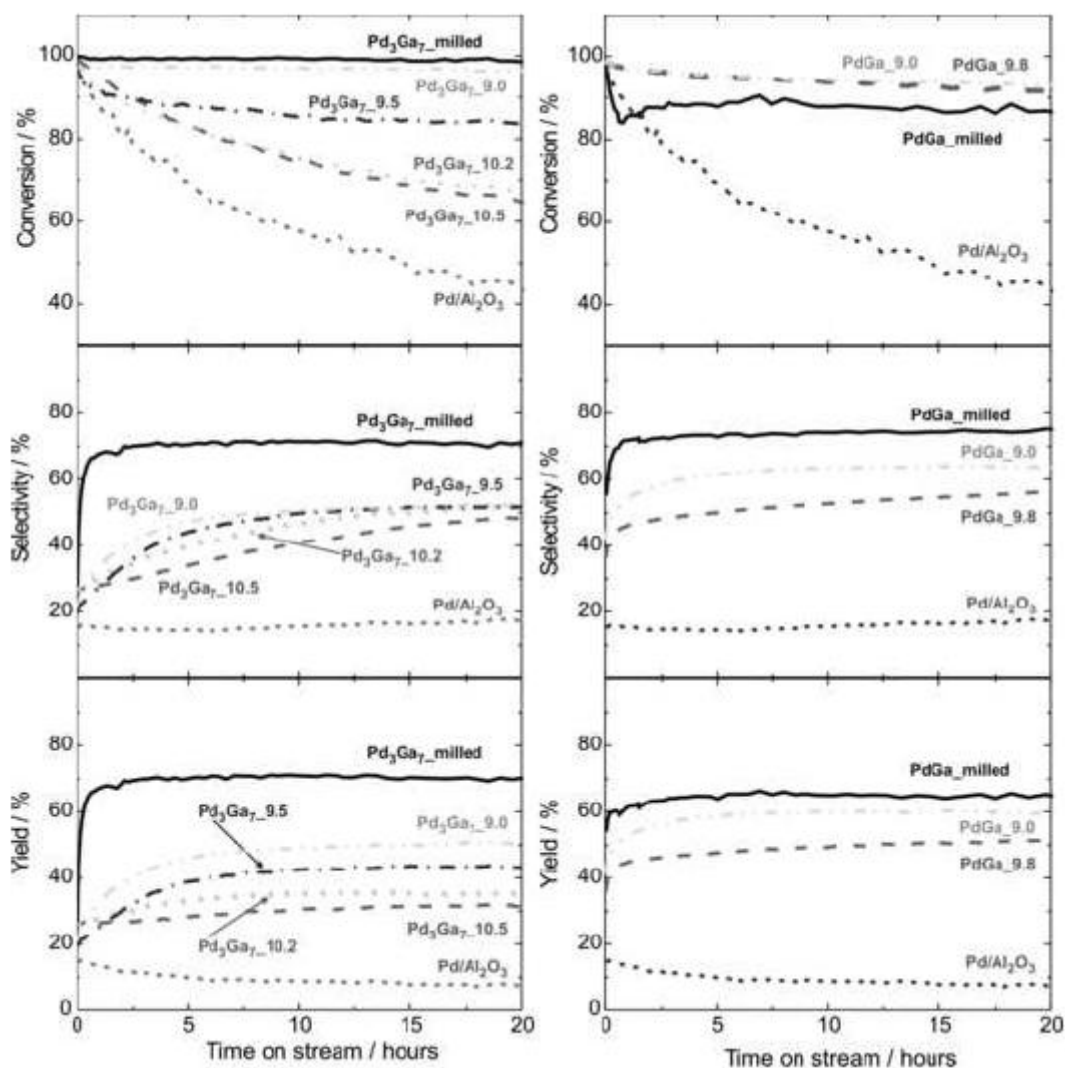


Fig. 2: Acetylene conversion (top), selectivity (middle) and ethylene yield (bottom) for milled and etched samples of Pd₃Ga₇ (left) and PdGa (right). Samples weights: **Pd₃Ga₇_milled** – 100 mg, **Pd₃Ga₇_10.5** – 1 mg, **Pd₃Ga₇_10.2** – 0.8 mg, **Pd₃Ga₇_9.5** – 5.5 mg, **Pd₃Ga₇_9.0** – 13 mg; **PdGa_milled** – 40 mg, **PdGa_9.8** – 1.5 mg, **PdGa_9.0** – 5 mg. For comparison the data of a commercial 5 wt.% Pd/Al₂O₃ (0.15 mg) is also shown. Feed composition: 0.5% C₂H₂ + 5% H₂ + 50% C₂H₄ + 44.5% He; isothermal experiments at 473 K.

Table 1: Acetylene conversion, selectivity and activity of milled and chemically etched PdGa, Pd₃Ga₇ and the reference catalyst Pd/Al₂O₃ after 20 hours time on stream in a mixture of 0.5% C₂H₂ + 5% H₂ + 50% C₂H₄ in helium at 473 K.

Sample	Sample mass (mg)	Conversion (%)	Selectivity (%)	Activity (g _{C₂H₄} /g _{cat} h)
Pd₃Ga₇_milled	50	69	79	0.3
Pd₃Ga₇_9.0	13.0	97	52	1.8
Pd₃Ga₇_9.5	5.50	84	52	3.7
Pd₃Ga₇_10.2	0.80	68	52	20.5
Pd₃Ga₇_10.5	1.00	65	48	15.7
PdGa_milled	40.0	86	75	0.3
PdGa_9.0	5.00	93	64	2.9
PdGa_9.8	1.50	91	56	9.6
Pd/Al₂O₃	0.15	43	17	545.8

be reground. Apparently, during the argon milling a partial destruction of the surface occurred and segregation of gallium (melting temperature 303 K) took place, thus leading to sticking of the particles. Milling the samples in air leads to a partial oxidation of the surface gallium and the formed gallium oxides prevent the particles from sticking together.

Because of their higher catalytic activity, the following investigations were carried out on air-milled samples.

Chemical etching with ammonia solution was employed to remove the gallium oxide overlayer from the surface of the intermetallic particles. Ammonia solutions are well known for chemical etching of semiconductor surfaces like GaAs [18-20]. Chemical etching of PdGa and Pd₃Ga₇ was per-

formed at room temperature with an aqueous ammonia solution at pH values as indicated. After drying, the samples were catalytically characterized (Figure 2 and Table 1).

3.2. Catalysis

First we will discuss the influence of the etching on Pd₃Ga₇ before turning our attention to PdGa. As reference, the sample **Pd₃Ga₇_milled** with a mass of 100 mg was measured and showed a stable conversion of 99% during 20 hours time on stream, as well as a selectivity towards ethylene of 70% (activity 0.09 g_{C₂H₂}/g_{cat}·h). The activity of the samples etched at high pH values after 20 hours time on stream was significantly increased: 8.09 and 6.19 g_{C₂H₂}/g_{cat}·h for **Pd₃Ga₇_10.2** and **Pd₃Ga₇_10.5**, respectively. The employed mass could significantly be reduced by a factor of 125 and 100, compared to **Pd₃Ga₇_milled**, still revealing high conversion levels of 97% and 94%, respectively, after the first 30 minutes. In contrast to the milled sample the long-term stability was reduced. Nonetheless, after 20 hours time on stream the etched samples still revealed higher conversion (65%) than Pd supported on alumina (43%, see Figure 2). Concerning the selectivity, the samples etched at high pH values did not reach a steady-state. During 20 hours of experiment, their selectivity continuously increased – a process that seems to be closely related with the deactivation of these catalysts. Catalysts etched at low pH values (**Pd₃Ga₇_9.5** and **Pd₃Ga₇_9.0**) were less active but more stable than the ones etched at high pH values. **Pd₃Ga₇_9.0** showed a stable conversion level of 97% during the 20 hours time on stream, while the activity increased by a factor of eight (0.71 vs. 0.09 g_{C₂H₂}/g_{cat}·h for **Pd₃Ga₇_9.0** and **Pd₃Ga₇_milled**, respectively). The samples etched at low pH values 9.0 and 9.5 reached a steady-state selectivity of 50–55% after the first 5–8 hours (Figure 2), which is significantly higher than the selectivity of the reference catalyst Pd/Al₂O₃ -17 %.

Similar results were obtained for the intermetallic compound PdGa (Figure 2). **PdGa_9.8** and **PdGa_9.0** showed high activity (5.78 and 1.77 g_{C₂H₂}/g_{cat}·h, respectively) compared to the milled sample (0.20 g_{C₂H₂}/g_{cat}·h). In contrast to Pd₃Ga₇, etching of PdGa has minor impact on the long-term stability of the compounds. The selectivity of the PdGa samples decreases in the sequence **PdGa_milled** (74%) – **PdGa_9.0** (64%) – **PdGa_9.8** (56%), viz. with increasing pH.

The activity-selectivity relationship for the intermetallic catalysts PdGa and Pd₃Ga₇ is presented in Figure 3. Both compounds exhibit a performance outside the parameter range given by the reference catalysts – unsupported Pd₂₀Ag₈₀ [4] and 5 wt.% Pd/Al₂O₃. PdGa and Pd₃Ga₇ found families of catalysts characterized by conversion-selectivity trends running in parallel to that of the reference Pd catalysts but with intrinsically higher selectivity.

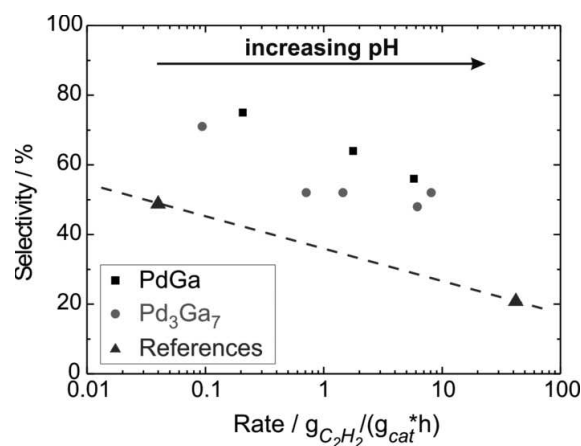


Fig. 3: Selectivity to ethylene in % vs. the rate of acetylene hydrogenation. Data for milled and differently etched PdGa (squares) and Pd₃Ga₇ (circles) catalysts are shown together with two reference catalysts (triangles): unsupported Pd-Ag alloy (left) and 5 wt.% Pd/Al₂O₃ (right) [4]. Damaging the intermetallic compounds is expressed in the reduction of the maximum performance when the etching solution becomes too strong resulting in an Pd-enrichment of the surface.

Table 2. ICP-OES analysis of the filtered solution after etching of PdGa and Pd₃Ga₇.

Sample	Pd (mg/L)	Ga (mg/L)	Corresponds to	
			mol% Pd	mol% Ga
Initial NH ₃ solution	<0.1	<0.02	–	–
PdGa_9.0	<0.1	1.0(1)	–	0.4
PdGa_9.8	~0.06	5.5(2)	0.02	2.1
Pd ₃ Ga ₇ _9.0	<0.1	1.2(1)	–	0.3
Pd ₃ Ga ₇ _10.5	0.35(6)	46.6(5)	0.13	11.6

To summarize, chemical etching significantly enhanced the catalytic activity of Pd-Ga intermetallic compounds. While soft etching increased the activity of PdGa and Pd₃Ga₇ by a factor of 9 and 8 respectively, strong etching resulted in an increase of up to 90 times. In addition, soft etched intermetallic catalysts showed high stability – similar to milled samples – while strong etched samples experienced significant deactivation. After 20 hours time on stream all intermetallic samples were still much more active and selective than Pd supported on alumina, which only showed a selectivity of 15% and significant deactivation from 97% to 43% conversion. The following XPS, XRD, BET, SEM, EDX and *in situ* XPS measurements as well as the chemical analysis of the etching solution were performed to understand the ongoing processes during the chemical etching.

3.3. Analysis after chemical etching

The ammonia solution after the etching procedure was filtered and palladium and gallium concentrations were determined by ICP-OES (Table 2). The amount of dissolved gallium strongly depends on the pH value of the etching solution, while palladium is practically not dissolved. Strong etching dissolves more than 10 mol-% of the

gallium, while soft etching leaches significantly lower amounts of gallium (around 0.4 mol-%).

3.4. XPS

To determine the near-surface composition, XPS measurements were performed on milled, strong etched (pH = 10.5 and 9.8 for Pd₃Ga₇ and PdGa, respectively) and soft etched samples (pH = 9.0 for both compounds). The results of the XPS investigations are collected in Table 3. In the case of PdGa etching leads to the expected decrease of gallium and oxygen contents, while the relative palladium content in the near-surface region increases. It should be noted that for strongly etched PdGa samples the Pd/Ga ratio was close to 2:1, which does not correspond to the bulk composition, verifying the partial dissolution of gallium from the intermetallic compound. In addition, the surface concentration of carbon increased with increasing pH of the etching solution. This indicates the formation of a significant amount of fresh and reactive palladium sites on the surface, which readily adsorbed carbon-containing species from the air. The removal of the gallium oxide coating during the etching procedure results in a lower oxygen concentration for the etched samples.

For Pd₃Ga₇ the general tendency is similar: the strongly etched sample **Pd₃Ga₇-10.5** showed less gallium and oxygen and more palladium in the near-surface region compared to the milled samples. As in the case of PdGa, the palladium content on the surface was higher than expected from the bulk composition: the Pd/Ga ratio was ~4:7 instead of 3:7. For the soft etched sample (**Pd₃Ga₇-9.0**) this effect is not so pronounced, particularly the oxygen and palladium concentrations in the near-surface region were similar to **Pd₃Ga₇-milled**, while the etching resulted in a decrease of the gallium and an increase of the carbon concentration.

The amount of gallium dissolved during strong etching (10 at.%) can not originate solely from dissolving the surface gallium oxides. XPS clearly reveals that strong etching leads not only to the dissolution of gallium oxides from the catalyst surface but also to a partial destruction of the intermetallic surface resulting in a palladium enrichment, thereby locally disrupting the well-ordered crystal structure. In the case of soft etching the surface gallium oxide layers are preferentially dissolved, while the intermetallic structure is only little affected.

These results are in excellent agreement with the observed catalytic behavior of the investigated samples. The decreasing selectivity of etched PdGa and Pd₃Ga₇ with increasing pH values of the etching solution can be explained by partial leaching of gallium from intermetallic compound. This caused the partial destruction of the crystal structure, thus partly annihilating the isolation of active Pd sites and leading to the formation of palladium ensembles on the surface. Accordingly, this results in a decreased selectivity as well as reduced long term stability. Increasing

Table 3. Near-surface concentration (at.%) for milled and etched samples of PdGa and Pd₃Ga₇ obtained by XPS analysis. Estimated relative error of the concentrations is in the region of 20%.

Sample	Ga	O*	C	Pd
PdGa_milled	32	57	5	6
PdGa_9.0	26	48	14	12
PdGa_9.8	14	36	17	32
Pd ₃ Ga ₇ _milled	36	58	4	2
Pd ₃ Ga ₇ _9.0	26	56	17	2
Pd ₃ Ga ₇ _10.5	27	48	10	16

* Although the values for the oxygen content may not be absolute accurate, they should be sufficient to evaluate the trends since the same fitting procedure was applied for all investigated samples.

Table 4. Specific surface areas obtained from nitrogen (etched samples) and krypton(milled samples) adsorption BET measurements.

Sample	Surface area (m ² /g)
PdGa_milled	0.41(2)
PdGa_9.0	~0.5(2)
PdGa_9.8	1.0(2)
Pd ₃ Ga ₇ _milled	0.37(2)
Pd ₃ Ga ₇ _9.0	~0.5(2)
Pd ₃ Ga ₇ _10.5	2.2(2)

the pH of the etching solution causes stronger destruction of the intermetallic surface and more pronounced palladium agglomeration. The extreme case of palladium clustering results in formation of metallic Pd which possesses low selectivity and strong deactivation, as in the case of Pd/Al₂O₃.

3.5. XRD, SEM and BET

Comparison of the powder X-ray diffraction patterns of as-synthesized, milled and etched samples revealed clearly that milling leads to a significant decrease of the crystallite size (from 60 nm to 14 nm), as can be seen from the broadening of the diffraction peaks (Figure 4). In turn, diffraction patterns of the etched samples revealed a slightly higher crystallite size as the milled samples (22

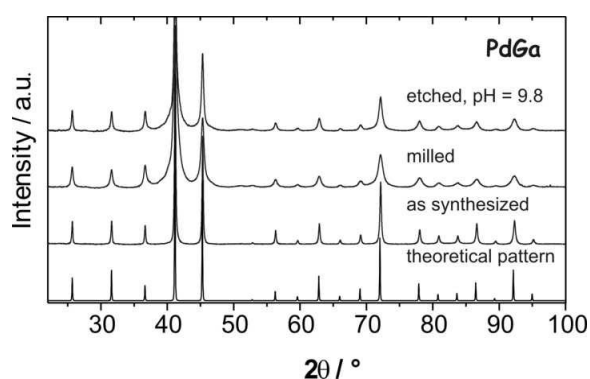


Fig. 4: X-ray diffraction patterns of as synthesized, milled and chemically etched (pH= 9.8) PdGa. The theoretical pattern is shown for comparison.

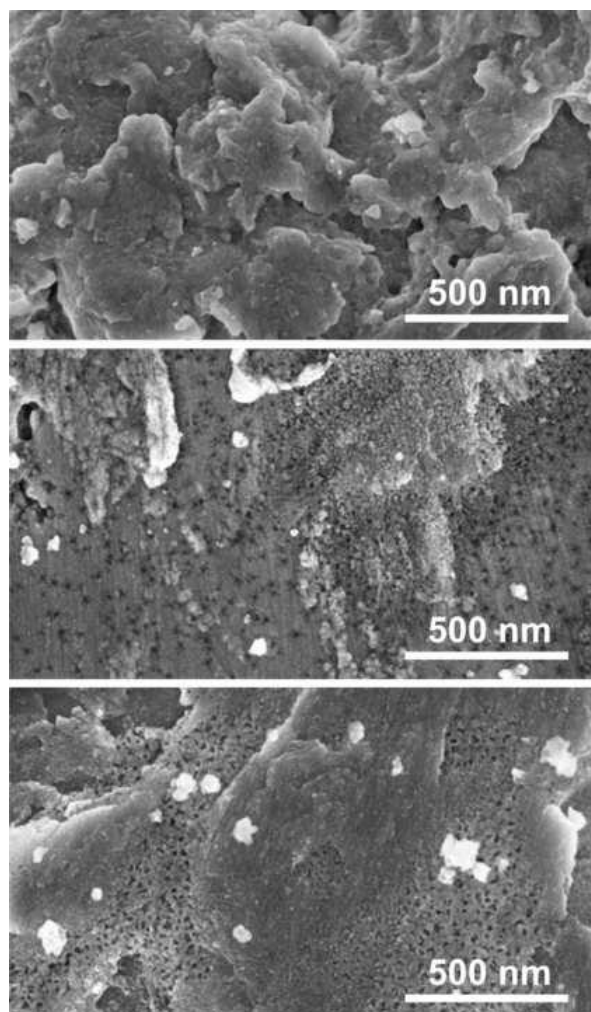


Fig. 5: High resolution SEM pictures (5 keV, SE) of the surface of PdGa: milled (top),chemically etched at pH = 9.0 (middle) and at pH = 9.8 (bottom).

nm). Thus, chemical etching did not lead to a further decrease of the crystallite size. However, BET measurements showed a significant gain in surface area of strongly etched samples, compared to the milled samples (Table 4).

To understand the reason for the surface area increase, the particle morphology was investigated by high resolution SEM. No substantial changes in particle size distribution or shape took place and no agglomeration of the particles occurred for the etched samples. Conventional EDX analysis revealed a stoichiometric composition for the milled and soft etched samples, while strong etched samples possessed a slight palladium excess in agreement with the chemical analysis of the etching solution. High resolution SEM showed a strong influence of the chemical etching procedure on the particle surface. Comparison of images of milled, soft and strong etched samples of PdGa and Pd₃Ga₇ clearly revealed the formation of small pores with a diameter of 20-50 nm after the etching (Figures 5

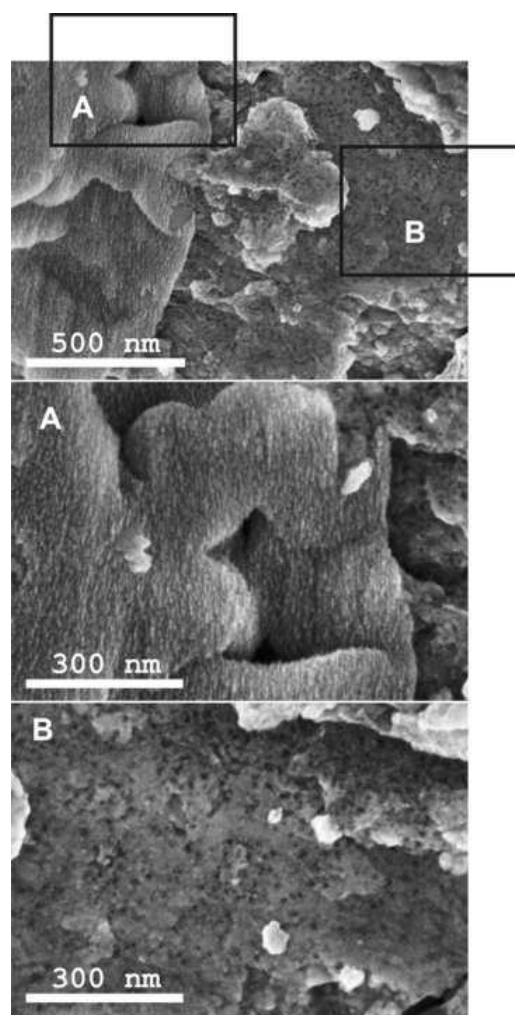


Fig. 6: High resolution SEM picture (5 keV, SE) of the surface of Pd₃Ga₇, chemically etched at pH = 9.0 (top) where two different kinds of areas were detected. Increased view of the rough area of the top picture corresponds to frame A (middle), increased view of the smooth area of the top picture corresponds to frame B (bottom).

and 6), which was more pronounced in the case of strong etching. The relatively small increase of specific surface area (2-4 times, Table 4) and absence of hysteresis loop on the isotherms for etched samples indicated that the formed pores are not infinite, they rather corresponded to some kind of closed caverns formed during the etching. Thus, instead of decreasing the particle size, a system of caverns was created, leading to higher surface area while at the same time gallium oxides were partly removed. Upon increasing the pH of the etching solution the gain in surface area increased.

While activities calculated per gram of catalyst showed a strong increase for the etched samples (Table 1) it is more meaningful to compare the activity per active Pd surface. Unfortunately, the absence of detectable CO chemisorption on the milled samples did not allow to determine the concentration of active Pd surface atoms [4]. However, a rough estimate can be made by using the BET surface area and the XPS Pd near-surface concentration

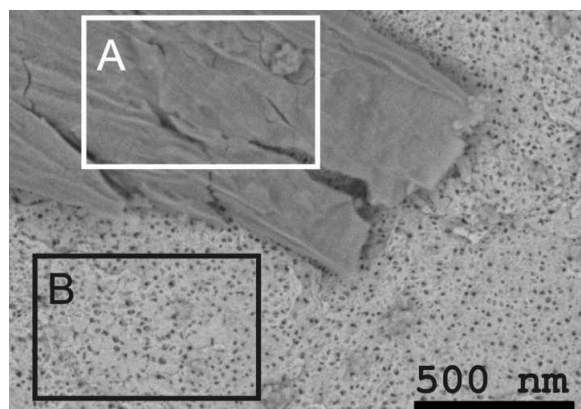


Fig. 7: High resolution SEM picture (1.5 keV, SE/BSE) of the surface of Pd₃Ga₇ chemically etched at pH = 10.5, where two different kinds of areas can be seen (A: dark grey, no caverns; B: light grey, caverns).

(Tables 3 and 4). For milled samples of PdGa and Pd₃Ga₇, the activities per “surface Pd” are $8 \text{ g}_{\text{C}_2\text{H}_2} \text{ m}_{\text{Pd}}^{-2} \text{ h}^{-1}$ and $12 \text{ g}_{\text{C}_2\text{H}_2} \text{ m}_{\text{Pd}}^{-2} \text{ h}^{-1}$, correspondingly. For strongly etched samples the activity indeed increases up to $18 \text{ g}_{\text{C}_2\text{H}_2} \text{ m}_{\text{Pd}}^{-2} \text{ h}^{-1}$ for both PdGa_{9.8} and Pd₃Ga_{7_10.5}. This clearly shows that the increasing activity of the etched samples is mainly caused by a combination of the higher surface area and the higher surface Pd concentration. However, an intrinsic activity increase, e.g. by forming more active Pd ensembles can not be excluded.

Detailed investigations were performed with Pd₃Ga₇ for the two extreme pH values of the etching solution: 10.5 and 9.0. The micrographs shown on Figures 5 and 6 were taken with an accelerating voltage (V_{acc}) of 5 kV in SE (Secondary Electrons) mode to get information of the surface region of the catalysts. SE information depth is generally about 10 nm. Image shown on Figure 7 was taken with $V_{\text{acc}} = 1.5 \text{ kV}$ in a mixed SE/BSE (Back Scattered Electrons) mode to get information of the near surface and additional of the element contrast. BSE information depth adds up to about 35 nm under these terms.

High-resolution SEM investigations of the surface of the sample Pd₃Ga_{7_9.0} revealed that soft etched samples contain two different types of surface: more smooth ones containing caverns and more rough ones without them (Figure 6). EDX analysis performed (information depth ~200 nm) indicated that the smooth areas are richer in palladium and carbon, while the rough areas contain more gallium and oxygen (Table 5). Accordingly to the EDX analysis, smooth areas correspond to intermetallic surface with relatively high palladium and additional carbon content, while the rough areas correspond to a remaining gallium oxide overlayer.

Investigations of the strong etched sample Pd₃Ga_{7_10.5} by high-resolution SEM also revealed the presence of two different surface types (Figure 7): dark-gray ones, and light-gray areas containing caverns. For the dark-gray areas EDX analysis revealed a composition close to the smooth areas of the sample Pd₃Ga_{7_9.0}. In turn,

Table 5. Atomic concentration (at.%) obtained from EDX analysis ($V_{\text{acc}} = 5 \text{ kV}$, information depth ~200 nm) for the different areas of the samples Pd₃Ga_{7_9.0} and Pd₃Ga_{7_10.5} corresponding to the frames marked in Figures 6 and 7. Estimated relative error of the concentration is in the region of 20%.

Frame	Ga	O	C	Pd	Ratio Pd:Ga
Pd₃Ga_{7_9.0}					
Rough area (Fig. 5, frame A)	41	40	11	8	1:5
Smooth area (Fig. 5, frame B)	30	21	25	24	1:1
Pd₃Ga_{7_10.5}					
Dark-gray area (Fig. 6, frame A)	27	30	16	26	1:1
Light-gray area (Fig. 6, frame B)	13	7	32	47	4:1

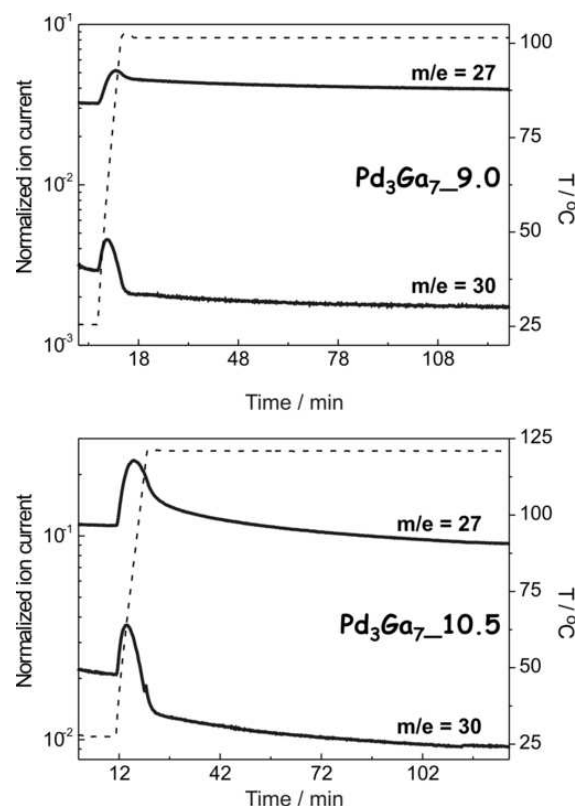


Fig. 8: Results of mass-spectrometry during *in situ* XPS: evolution of ethylene ($m/e = 27$) and ethane ($m/e = 30$) as well as the sample temperature (dashed line) are shown for Pd₃Ga_{7_9.0} (top panel) and Pd₃Ga_{7_10.5} (bottom panel). Presented ethylene and ethane ion currents are normalized to the acetylene signal ($m/e = 26$).

light-gray porous areas showed an excess of palladium and carbon (Table 5), indicating the formation of a palladium-rich overlayer on the surface of intermetallic compound.

It should be noted that the results presented in Table 5 are only semi-quantitative as no standards were applied. However, comparing results obtained from different areas and samples is still useful. Furthermore, the SEM results correlate well with the XPS data – strong etching leads to a significant disturbance of the catalyst surface and accumulation of carbon on the surface, while the intermetallic surface was less affected by soft etching. In both cases the gallium oxides coatings was not fully removed.

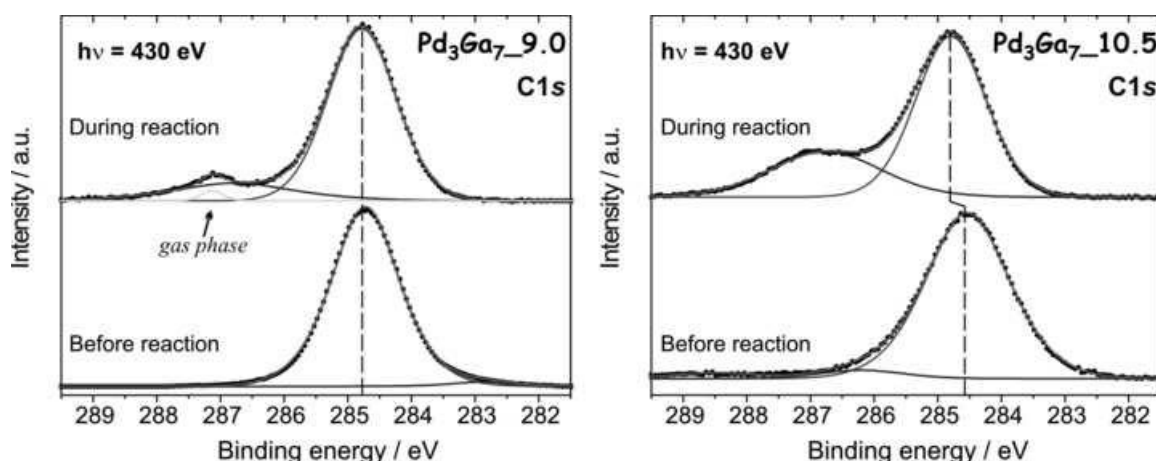


Fig. 9: C1s region of Pd₃Ga_{7_9.0} (left) and Pd₃Ga_{7_10.5} (right) before and during the hydrogenation of acetylene. In the upper left spectrum the contribution of gas phase acetylene is exemplified.

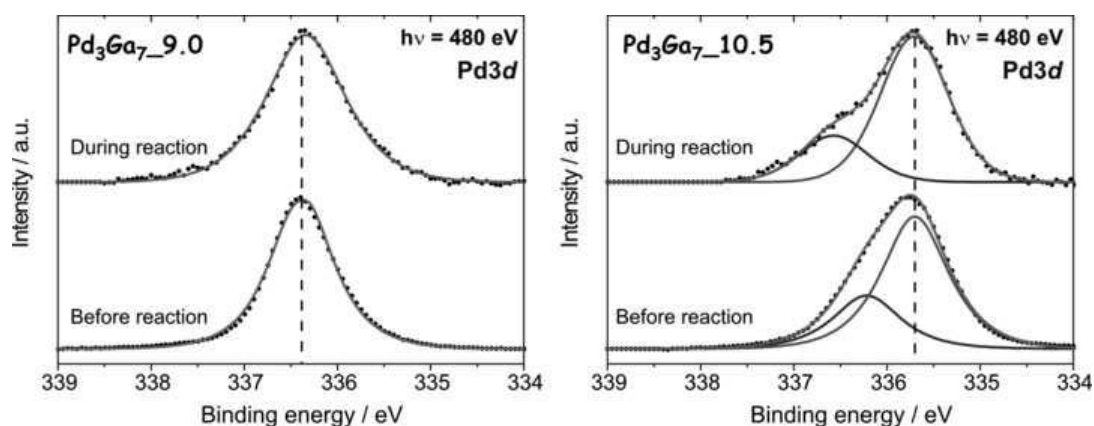


Fig. 10: Pd3d region for the etched samples Pd₃Ga_{7_9.0} (left) and Pd₃Ga_{7_10.5} (right) before and during the hydrogenation of acetylene.

3.6. *In situ* XPS

The same two samples (Pd₃Ga_{7_9.0} and Pd₃Ga_{7_10.5}) investigated by SEM were chosen for a detailed *in situ* synchrotron-based XPS investigation. This technique allows monitoring the chemical composition of the surface with higher surface sensitivity and the introduction of gas phase during surface analysis. A significant amount of carbon was detected on the surface of each compound in UHV conditions, which is typical for active Pd catalysts investigated in this setup [21]. The detected carbon might originate from the residual pressure of hydrocarbons present in the cell used for *in situ* investigations at mbar conditions. XP spectra were collected prior to and during the reaction semi-hydrogenation of acetylene. The gas composition was monitored by mass-spectrometry and the plots of the normalized ion currents during the experiments are presented in Figure 8. The desired product of the reaction is ethylene ($m/e = 27$), while the main by-product is ethane ($m/e = 30$). As can be seen both investigated samples are active and selective for the hydrogenation of acetylene.

C1s spectra before and during the reaction for both investigated samples are shown in Figure 9. The binding energy of the main carbon peak (at 284.5–284.7 eV) changed slightly when switching from UHV to reaction conditions and can be assigned to graphitic carbon [21, 22]. During reaction an additional carbon component appeared at higher binding energy, fitted as a broad peak with a maximum at 288.6 eV and a FWHM > 2 eV. Contribution of the gas phase carbon in both cases was significantly smaller (less than 2%), as indicated on the upper-left plot on Figure 9. The high binding energy carbon components corresponded to a mixture of the aliphatic hydrocarbon polymers (CH₂)_n (~285 eV) and, mainly, oxygenated carbon species, containing C–O bonds (286–288 eV) [22, 23]. Apparently, C–O bonds were formed due to the reaction of the feed with Ga-oxides (see below description of Ga3d spectra). The amount of aliphatic and oxygenated hydrocarbons was significantly higher for the strongly etched sample (Pd₃Ga_{7_10.5}), demonstrating its higher ability to produce such carbonaceous deposits – most probably due to higher

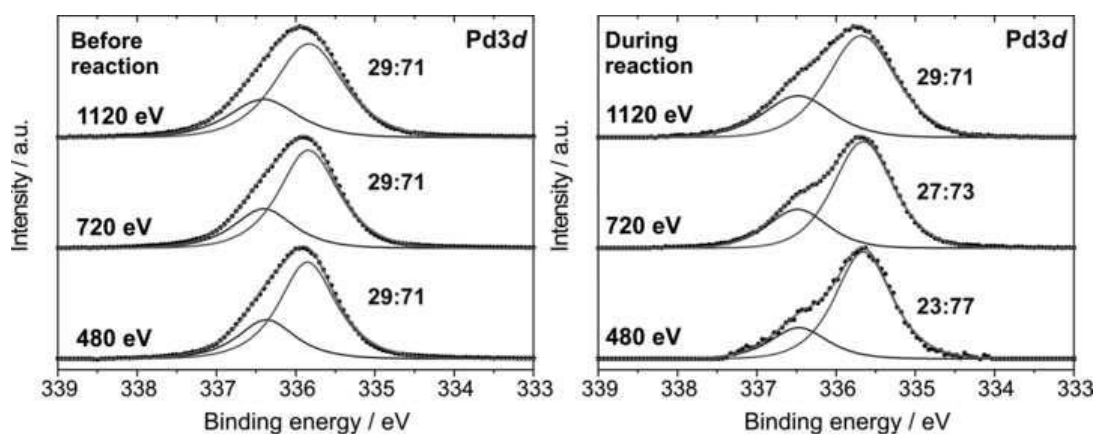


Fig. 11: Non-destructive depth profiling Pd3d XPS of **Pd₃Ga_{7_10.5}** before (left) and during (right) the hydrogenation of acetylene. The ratios of the different components are also given in the figure.

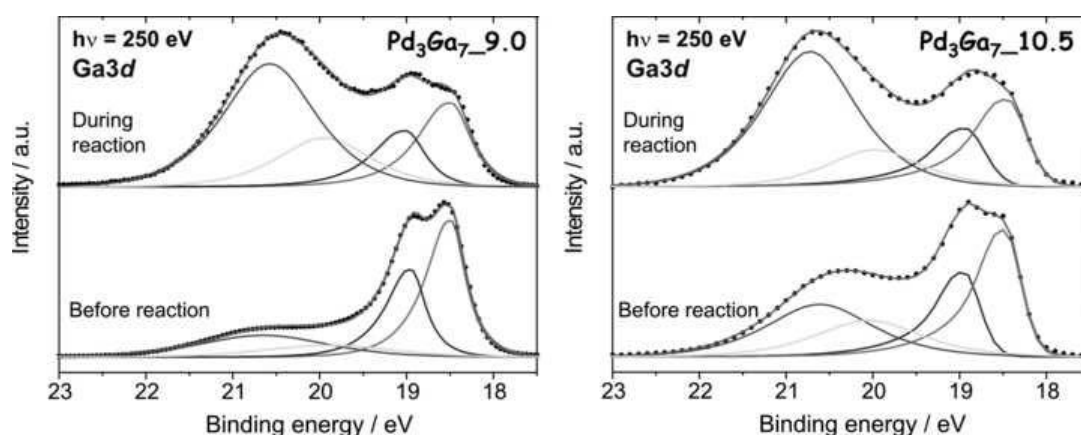


Fig. 12: XPS Ga3d region for etched samples **Pd₃Ga_{7_9.0}** (left) and **Pd₃Ga_{7_10.5}** (right), before and during the hydrogenation of acetylene.

content of non-isolated Pd atoms on the surfaces. This finding explains why the strongly etched samples do not possess high long-term stability: here, as in the case of elemental palladium, the accumulation of polymerized carbon leads to covering of the surface, thus deactivating the catalyst.

A significant difference between strongly and softly etched samples can be observed when examining the Pd3d spectra (Figure 10). The UHV spectrum of **Pd₃Ga_{7_9.0}** shows a narrow (FWHM = 0.77 eV) single peak with a binding energy of 336.4 eV which corresponds to the binding energy of the Pd3d peak (336.4 eV) for the as-synthesized Pd₃Ga₇ intermetallic compound, measured as reference. During hydrogenation the Pd3d peak became broader (FWHM = 0.94 eV) but remained at the same binding energy. On the other hand, the UHV Pd3d spectrum of the strongly etched **Pd₃Ga_{7_10.5}** is a superposition of two components with binding energies of 336.3 eV (30%) and 335.7 eV (70%, Figure 10). The first one corresponds to the intermetallic compound Pd₃Ga₇, while the second component can be attributed to a more Pd-rich phase, for example Pd₂Ga [25, 26]. It should be noted that the binding energy

is still higher than for elemental Pd with 335.0 eV [21, 24]. Thus, in the near-surface region of **Pd₃Ga_{7_10.5}** two different kinds of Pd are present: isolated and mainly non-isolated ones. In the depth profiling experiment the variation of the incoming radiation wavelength allowed to receive information from different penetration depth (see experimental section 2.8.). Depth profiling of **Pd₃Ga_{7_10.5}** revealed that the additional component is not only present in the topmost layers but also in the deeper layers (Figure 11).

Both investigated samples revealed a high stability of the surface under reaction conditions. Even in the case of strongly etched **Pd₃Ga_{7_10.5}**, containing two different kinds of Pd species on the surface, the surface seemed to be preserved during acetylene hydrogenation (Figure 11). Neither additional components, nor significant changes of binding energies or component ratios were detected. The same high stability was observed for **Pd₃Ga_{7_9.0}**, which allows to differentiate between etched Pd-Ga intermetallic compounds and Pd metal. The latter forms an additional Pd component during alkyne hydrogenation, which was attributed to the formation of a carbon-containing palladium

surface phase stable only *in situ*, i.e. in presence of the alkyne feed [27–29]. Formation of this Pd-C phase provided the specificity of Pd being selective in alkyne hydrogenations. The Pd-C component possesses a higher binding energy (335.6–335.7 eV) than metallic Pd (335.0 eV). In the case of Pd-Ga intermetallic compounds the palladium 3d core level is already strongly modified: for the as-cast samples of PdGa and Pd₃Ga₇ binding energies of Pd3d_{5/2} were 336.0 [1, 30] and 336.4 eV, respectively. Thus, no further modification of Pd states by subsurface chemistry is necessary to obtain a selective catalyst. For **Pd₃Ga₇_10.5** the binding energy of the lower energy component is close to the binding energy of the Pd-C phase. Additionally, the covalent bonding between Pd and Ga makes the intermetallic compounds much more resistant against the incorporation of carbon or hydrogen atoms [1, 3, 30].

The investigation of the Ga3d region allows to determine gallium oxidation states and the presence of Ga oxides on the surface (Figure 12). The spectra show a resolvable Ga3d doublet at 18.5 and 19.0 eV and a broad component at higher binding energies. The binding energy of unresolved Ga3d doublet for metallic gallium is 18.5 eV, while for gallium intermetallic compounds slightly higher binding energies were reported: 18.7 eV for GaInSn [31] and 18.6 for Ni₂MnGa [32]. This allows us unambiguously assign the observed doublet to Ga in an intermetallic compound. During the fitting of the spectra the ratio of Ga3d_{3/2}:Ga3d_{5/2} was fixed to the theoretical value of 40:60 [15]. A successful fitting of the spectra was only possible when two additional components were introduced with binding energies of 20.0 eV and 20.7 eV. Since the area ratio as well as the energy difference of these components does not fit the spin-orbit split components of Ga3d, we attribute them to two different kinds of Ga-oxides (two unresolved Ga3d doublets). Indeed, for Ga₂O and Ga₂O₃ similar binding energies of 20.0 eV and 21.0 eV, respectively, were reported [31, 33, 34]. Comparison of the samples revealed that the strongly etched sample contain more Ga oxides on the surface. Apparently, oxide layers are readily formed during contact of the freshly etched surface of Pd₃Ga₇ with air. During the reaction the relative concentration of oxidized gallium species increased. This can be explained by taking into account that the pressed samples were made from powders. The surface of the pill was cleaned by Ar⁺ sputtering prior to XPS measurements, however grain boundaries may contain significant amounts of oxygen, which can diffuse to the surface at 400 K. The surface Ga oxides overlayer is stable, even under much stronger reduction conditions (500 mbar of hydrogen at 573 K [4]), which explains why the surface Ga oxides were not reduced during the conditions applied in this studies. The segregation of the oxygen may lead to the observed increase in Ga oxide coverage as well as the formation of oxygenated carbon species on the surface as was mentioned above.

The *in situ* XPS results are in good agreement with SEM/EDX data. The Pd3d XP spectra revealed that soft etching dissolves preferably Ga oxides preserving the in-

termetallic structure, while strong etching leads to the partial destruction of the intermetallic compound and to the formation of a new surface phase with higher Pd-agglomeration. This surface phase readily accumulates carbon, thus reducing the long-term stability during acetylene hydrogenation. As expected, oxygen on the surface of Pd-Ga intermetallic compounds is bound to gallium and not to palladium.

3.7. Discussion

Intermetallic compounds exhibit high potential as selective hydrogenation catalysts. PdGa and Pd₃G₇ were selected based on knowledge of their crystal and electronic structures, applying the active-site isolation approach. Presence of the covalent bonding between gallium and palladium in these compounds was expected to diminish the subsurface chemistry, known for elemental Pd [27–29], and to suppress the segregation phenomena, common for alloys [35]. Both chosen intermetallic compounds exhibit isolation of Pd atoms due to well-ordered crystal structure. It was shown that bulk structures of PdGa and Pd₃G₇ are stable during the reaction of acetylene hydrogenation and no incorporation of C and/or H atoms occurred (*in situ* XRD, *in situ* EXAFS and *in situ* Prompt Gamma Activation Analysis) [1, 3, 26]. XPS revealed that the electronic structures of the surface of PdGa and Pd₃Ga₇ are close to the electronic structures of the bulk, e.g. Pd d-band and corresponding adsorption properties are strongly modified compare to elemental Pd [1, 26, 30].

Current study shows that gallium atoms on the surface of the intermetallic compounds PdGa and Pd₃Ga₇ are easily oxidized, and milling of the intermetallic compounds in air leads to the formation of a gallium oxides overlayer. This overlayer neither completely covers the surface, nor affects the Pd atoms, since the catalytic properties (high selectivity and long-term stability) of PdGa and Pd₃Ga₇ are preserved after milling [4]. We have demonstrated that chemical etching can be successfully applied to remove the gallium oxides overlayer partly, thus increasing the activity of the investigated intermetallic compounds. According to our results soft etching with ammonia solution (pH ≤ 9.0) is well suited for the removal, retaining the electronic structure of intermetallic compound as well as the isolation of palladium atoms on the surface. *In situ* XPS revealed perfect surface stability of the etched compounds during reaction, thus, excluding sub-surface chemistry, like segregation and/or incorporation of C/H atoms. In turn, strong etching (pH ≥ 10.0) leads to a significant destruction of the intermetallic surface and, therefore, to the breaking apart the active-site isolation. The strong etching results in palladium-rich surfaces which are less selective than soft etched intermetallic compounds, but still more selective and stable than supported palladium catalysts in the hydrogenation of acetylene.

It was shown that full removal of gallium oxides from the intermetallic surfaces can not be achieved by

chemical etching independent of the pH of the ammonia solution. Surface gallium oxides may play a role in hydrogen spillover as it was demonstrated for the supported Ga₂O₃-Pd/SiO₂ system [36]. In the case of Pd-Ga intermetallic compounds, surface palladium atoms are isolated from one another not only by gallium atoms but also by surface gallium oxides. Thus, hydrogen being dissociated on one Pd active site can become close to an acetylene molecule adsorbed on another Pd active site due to hydrogen spillover on the oxides. UHV single-crystal studies are expected to shed some light on the role of gallium in the semi-hydrogenation of acetylene catalyzed by Pd-Ga intermetallic compounds.

4. Conclusions

The drawback of the low surface area of PdGa and Pd₃Ga₇ intermetallic compounds – both perspective catalysts for the selective hydrogenation of acetylene – can be overcome by milling and chemical etching. Milling experiments showed that the presence of oxygen during the milling is necessary to prevent agglomeration of the particles. After milling, an etching procedure with ammonia solution was applied to increase the active surface area of

the catalysts by removing the inactive gallium oxide overlayer. The chemical etching led to considerable, but not complete removal of the oxides as well as to the formation of nanosized caverns. This process optimizes the catalyst active surface by a combination of higher surface area, higher surface Pd concentration and, possible, by forming more active Pd ensembles. Etching at high pH values is accompanied with a partial destruction of the intermetallic crystal structure and the enrichment of the surface by palladium as detected by *in situ* XPS and SEM. This leads to a decrease in selectivity and long-term stability of the etched catalyst as is expected from the active-site isolation concept. Nonetheless, all etched PdGa and Pd₃Ga₇ catalysts still possess a significantly higher selectivity and long-term stability than Pd/Al₂O₃ after 20 hours time on stream.

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References

- [1] K. Kovnir, M. Armbrüster, D. Teschner, T. Venkov, L. Szentmiklósi, F.C. Jentoft, A. Knop-Gericke, Yu. Grin, R. Schlögl, *Surf. Sci.* (2008) in press.
- [2] J. Osswald, R. Giedigkeit, M. Armbrüster, K. Kovnir, R.E. Jentoft, T. Ressler, Yu. Grin, R. Schlögl, European Patent EP/1834939A1 (2006); R. Giedigkeit, M. Armbrüster, K. Kovnir, Yu. Grin, R. Schlögl, J. Osswald, T. Ressler, R.E. Jentoft, International Patent WO/2007/104569 A1 (2007).
- [3] J. Osswald, R. Giedigkeit, R.E. Jentoft, M. Armbrüster, F. Girgsdies, K. Kovnir, T. Ressler, Yu. Grin, R. Schlögl, *J. Catal.* 258 (2008) 210.
- [4] J. Osswald, K. Kovnir, M. Armbrüster, R. Giedigkeit, R.E. Jentoft, U. Wild, Yu. Grin, R. Schlögl, *J. Catal.* 258 (2008) 219.
- [5] K. Kovnir, J. Osswald, M. Armbrüster, R. Giedigkeit, T. Ressler, Yu. Grin, R. Schlögl, *Stud. Surf. Science Catal.* 162 (2006) 481.
- [6] 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.
- [7] A. Borodziński, G.C. Bond, *Catal. Rev.* 48 (2006) 91.
- [8] A.N.R. Bos, K.R. Westerterp, *Chem. Eng. Process.* 32 (1993) 1.
- [9] P. Albers, J. Pietsch, S.F. Parker, *J. Mol. Catal. A* 173 (2001) 275.
- [10] A.M. Doyle, Sh.K. Shaikhutdinov, H.-J. Freund, *J. Catal.* 223 (2004) 444.
- [11] W.T. Tysoe, G.L. Nyberg, R.M. Lambert, *J. Phys. Chem.* 90 (1986) 3188.
- [12] W. Palczewska, in: Z. Paal, P.G. Denon (Eds.) *Hydrogen Effects in Catalysis*, Marcel Decker, New York, 1988, p. 372.
- [13] E. Hellner, F. Laves, *Z. Naturforsch. A* 2 (1947) 177.
- [14] K. Khalaff, K. Schubert, *J. Less-Common Met.* 37 (1974) 129.
- [15] D. Briggs, M.P. Seah, *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Wiley, Chichester, 1988.
- [16] 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.
- [17] NIST Electron Inelastic Mean Free Path Database, version 1.1, <http://www.nist.gov/srd/nist71.htm>.
- [18] C. Bryce, D. Berk, *Ind. Eng. Chem. Res.* 35 (1996) 4464.
- [19] M.V. Lebedev, D. Ensling, R. Hunger, T. Mayer, W. Jaegermann, *Appl. Surf. Sci.* 229 (2004) 226.
- [20] C.C. Chang, P.H. Citrin, B. Schwartz, *J. Vac. Sci. Technol.* 14 (1977) 943.
- [21] D. Teschner, A. Pestryakov, E. Kleimenov, M. Hävecker, H. Bluhm, H. Sauer, A. Knop-Gericke, R. Schlögl, *J. Catal.* 230 (2005) 186.
- [22] N.M. Rodriguez, P.E. Anderson, A. Wootsch, U. Wild, R. Schlögl, *Z. Paál. J. Catal.* 197 (2001) 365.
- [23] Z. Paál, U. Wild, R. Schlögl, *Phys. Chem. Chem. Phys.* 3 (2001) 4644.
- [24] D. Teschner, A. Pestryakov, E. Kleimenov, M. Hävecker, H. Bluhm, H. Sauer, A. Knop-Gericke, R. Schlögl, *J. Catal.* 230 (2005) 195.
- [25] a) K. Kovnir, M. Schmidt, C. Waurisch, M. Armbrüster, Yu. Prots, Yu. Grin, *Z. Kristallogr. NCS.* 223 (2008) 7
- [26] K. Kovnir, D. Teschner, M. Armbrüster, P. Schnörch, M. Hävecker, A. Knop-Gericke, Yu. Grin, R. Schlögl, *BESSY Highlights* (2007) 22.

- [27] 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
- [28] D. Teschner, J. Borsodi, A. Wootsch, Zs. Révay, M. Hävecker, A. Knop-Gericke, S. David Jackson, R. Schlögl, *Science*, 320 (2008) 86
- [29] D. Teschner, Zs. Révay, J. Borsodi, A. Knop-Gericke, R. Schlögl, D. Milroy, S.D. Jackson, D. Torres, P. Sautet, *Angew. Chem. Int. Ed.* (2008) DOI: 10.1002/anie.200802134.
- [30] K. Kovnir, M. Armbrüster, D. Teschner, T.V. Venkov, F.C. Jentoft, A. Knop-Gericke, Yu. Grin, R. Schlögl, *Sci. Technol. Adv. Mater.* 8 (2007) 420
- [31] F. Scharmann, G. Cherkashinin, V. Breternitz, Ch. Knedlik, G. Hartung, Th. Weber, J.A. Schaefer, *Surf. Interface Anal.* 36 (2004) 981.
- [32] C. Biswas, S.R. Barman, *Appl. Surf. Sci.* 252 (2006) 3380.
- [33] R. Carli, C.L. Bianchi, *Appl. Surf. Sci.* 74 (1994) 99.
- [34] C.C. Surdu-Bob, S.O. Saied, J.L. Sullivan, *Appl. Surf. Sci.* 183 (2001) 126.
- [35] J.S. Sinfelt. *Bimetallic Catalysts*, Wiley, New York, 1983.
- [36] S.E. Collins, D.L. Chivassa, A. L. Bonivardi, M.A. Baltanás, *Catal. Lett.* 103 (2005) 83.