Surface Dynamics of the Intermetallic Catalyst Pd_2Ga, Part II – Reactivity and Stability in Liquid Phase Hydrogenation of Phenylacetylene

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Abstract

The catalytic properties of unsupported Pd_2Ga for the liquid phase hydrogenation of phenylacetylene are investigated after different pre-treatments with focus on the stability of the catalyst during reaction. The surface of as prepared Pd_2Ga consists mainly on Pd and oxidized Ga species. Under the conditions of the liquid phase hydrogenation of phenylacetylene the intermetallic surface cannot be re-formed *in situ* by reduction of Ga oxide. After a reductive pre-treatment in 5% H_2/Ar at 400 °C, an almost clean Pd_2Ga surface can be obtained. Its hydrogenation activity is significantly lowered compared to elemental Pd, which is due to the intrinsic adsorption properties of the intermetallic surface. However, residues of H_2O or O_2 lead to oxidation of this surface. Excluding these impurities the decomposition can be suppressed. In this case, the bulk material of Pd_2Ga gets cracked by phenylacetylene during reaction. The controlled modification of the crystal and the electronic structure of Pd by formation of the intermetallic compound Pd_2Ga is accompanied with a decreased stability.

Keywords: selective hydrogenation, phenylacetylene, Pd_2Ga, intermetallic compound, d-band shift, stability, Lindlar's catalyst

1. Introduction

Liquid phase hydrogenations of C-C triple bonds is widely used in the industrial synthesis of fine chemicals[1] and pharmaceuticals for example during the synthesis of Vitamin K or as final step in the Linalool synthesis[2]. After C-C-coupling by alkynylation of an organohalide or ketone the resulting alkyne is semi-hydrogenated to the corresponding alkene, while the full hydrogenation to the alkane is undesired. Another process is the semi-hydrogenation of phenylacetylene, which must be removed from styrene feeds, for the usage in the production of polystyrene[3].

Various catalysts e.g. Raney-nickel[4], so called "amorphous Ni-B alloys"[5] or Fe based[6,7] catalysts are reported to show good catalytic properties for the liquid phase alkyne hydrogenation but generally require harsh conditions, i.e. high temperature and pressure. In particular in fine chemical syntheses mild conditions are desired and thus Pd is usually the metal of choice for alkyne hydrogenation[8]. Using Pd, reactions can be carried out under batch conditions with temperatures far below 100 °C and H_2 pressures of 1 bar or slightly above usually in presence of a solvent. However, beside over-hydrogenation and oligomerization[9] Pd can catalyze further side-reactions, when substituted alkynes are hydrogenated. That is e.g. the cis-trans isomerization[10], double bond migration[11] and reduction of other easily to reduce functional groups. The reaction scheme for the hydrogenation of phenylacetylene (Figure 1) is comparably simple as stereo-selectivity need not to be considered and double bond migration cannot occur.

To suppress the side-reactions Pd is usually further modified. The most prominent catalyst for the selective liquid phase hydrogenation of C-C triple bonds is Lindlar's catalyst[12] consisting of Pd supported on $CaCO_3$ and poisoned with $Pb(OAc)_2$ showing in many cases very high (Z)-alkene yields and low isomerization rates (for more information see comments

in SI). However, a considerable H_2 consumption due to total hydrogenation of styrene to ethylbenzene was noticed using Lindlar's catalyst[13,14]. Further efficient modifications of Pd for the hydrogenation of phenylacetylene were achieved by using bimetallic system, e.g. Pd-Mg, Pd-Fe, Pd-Ni[15], Pd-Zn[16], Pd-Si[17], Pd-Cu[18] where high selectivities between 85 and 95% at full conversions are frequently observed. Generally, the addition of organic nitrogen bases, e.g. quinoline, often further enhances the yield of the desired olefin[19]. For example, N-doped polymers as additional modifiers for Lindlar's catalyst gave excellent yields (~98% selectivity at 100% phenylacetylene conversion)[20]. However, Molnar et al.[21] found a comparably high selectivity of ~94% at 100% phenylacetylene conversion for an unsupported Pd catalyst without any modification. Kinetic studies of phenylacetylene hydrogenation reveal a zero order kinetics with respect to the alkyne and first order with respect to H_2[22,23,24] and the apparent activation energies are in the range between 22 and 46 kJ/mol. Unfortunately, oligomers are hard to detect directly and are generally not quantified.

In this part, the resulting change of the electronic structure of the surface of an unsupported Pd_2Ga model catalyst after different pre-treatments is correlated with its properties for the hydrogenation of phenylacetylene in the liquid phase. Compared to elemental Pd, intermetallic catalysts in the Pd-Ga systems have shown high selectivities and stability in the gas phase hydrogenation of acetylene at high temperatures [25,26,27,28]. The high stability and selectivity of these catalyst materials was explained by their intrinsically modified crystal and electronic structure, which addresses three critical factors for selectivity: 1) the (partial) isolation of Pd atoms by Ga reduces the ensemble size of Pd or separates them, respectively 2) the d-band shifts away from the Fermi level, leading to reduced heats of adsorption, in particular favoring alkene desorption 3) the covalent bonds hinder diffusion of C or H in the subsurface and stabilize the intermetallic structure. However, our first results for the liquid phase hydrogenation of phenylacetylene with unsupported Pd_2Ga and PdGa did not reveal

significant differences in the catalytic properties compared to monometallic Pd[29]. Pd_5Ga_2/SiO_2 prepared by impregnation was tested for the liquid phase hydrogenation of tolane by Komatsu et al.[30]. Its selectivity to stilbene was rather low and falls below 70% at tolane conversions above 90%.

In part I of this work[31], highly dynamic changes of the surface of Pd_2Ga have been found to contrast the stability of the intermetallic compound in the bulk. Milled Pd_2Ga was single phase according to XRD and no phase transformation, e.g. formation of hydride, was detected during long-time treatment in a 10% H_2/He atmosphere. The bulk remained stable until about 300 °C in O_2 atmosphere. On the other hand the surface of the sample is, according to XP spectra and HR-TEM images, almost completely decomposed: Ga segregation due to mechanical treatment leads to an inhomogeneous over-layer of oxidized Ga species, where nanoparticles of mainly elemental Pd, Pd oxide and undefined Pd species as well as some Pd_2Ga are embedded. A metallographic specimen, polished under Ar, was adopted as reference material for XP spectroscopy, since its comparably marginally disturbed surface could be easily reformed by heating to 400 °C in dynamic vacuum (~10^{-7} mbar) in the *in situ* XPS chamber. This procedure was insufficient for the powdered materials and led only to a partial reversal of the decomposition. An almost clean surface of the powder could be achieved after treatment for 4 h at 400 °C in 5% H_2/Ar and subsequent cooling in this reducing atmosphere. Within the scope of the detection limit of XPS, Pd was solely intermetallic when analyzing the Pd 3d core level spectra. However, the Ga 3d spectra still reveal some oxidized Ga at the outermost surface, which necessarily involves a Pd enrichment in the near surface. This enrichment might be balanced by the intermetallic compound due to its broad homogeneity range[32] but the presence of small amounts of elemental Pd agglomerates could not be excluded. As consequence of the high oxophilicity of Ga on the one hand and the ability of Pd to activate H_2 on the other hand we found a high

dynamic of the surface, whose structure strongly depends on the pre-treatment and the actual chemical environment.

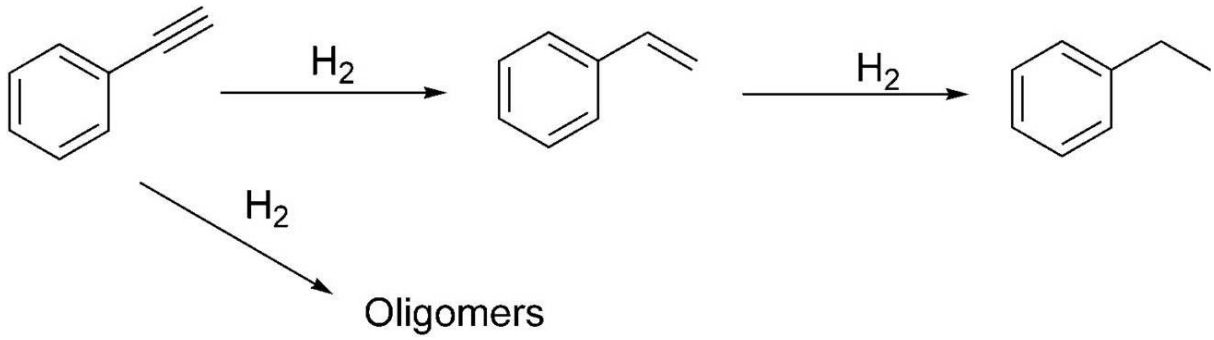

Figure 1: Reaction scheme for the hydrogenation of phenylacetylene

Based on the characterization results presented in part I[31] we address in this part of the work how Pd_2Ga with its strong shift of the d-band compared to elemental Pd performs under the conditions of a liquid phase hydrogenation.

2. Materials and Methods

2.1 Synthesis of Pd_2Ga

Pd_2Ga was synthesized as described in part I[31] by melting stoichiometric amounts of palladium granules (Chempur, 99.95%) and Ga pellets (Chempur, 99.99%) in a glassy carbon crucible in a high frequency induction furnace under Ar atmosphere. The obtained regulus was annealed at 800 °C in an evacuated quartz glass ampoule for three days. To get a fine powder of Pd_2Ga, the material was powdered in a swing mill (*Retzsch*, MM 200, 4 ml WC pot with two WC balls, 25 Hz) two times for 30 min. The absence of any additional phases was verified by powder X-ray diffraction.

2.2 X-ray diffraction

For *ex situ* powder X-ray diffraction the sample was placed on a 3 μm Kapton TM foil covered with vaseline. The measurement was performed on an image plate Guinier camera (G670, Huber, Cu $K\alpha_1$ radiation, $\lambda = 1.54056$ Å, curved Ge monochromator, $3° < 2\Theta < 100°$, CCD detector).

2.3 X-ray photoelectron spectroscopy

Near ambient pressure X-ray photoelectron spectroscopy[33] was performed at the ISISS beamline at Bessy II, Helmholtz Zentrum Berlin. Approximately 250 mg of powdered samples where pressed in air to a pill with 8 mm diameter and about 1 mm thickness. For the XPS investigation of a spent sample 300 mg catalyst were used for the hydrogenation procedure described below. After reaction the organic phase was decanted in air and the catalyst was washed three times with n-hexane and dried in vacuum at about 1 mbar. Ga 3d, Pd 3d and C 1s core levels as well as the valence band region were recorded. Spectra were taken with various excitation energies corresponding to kinetic energies of the photoelectrons of 145 eV, 385 eV or 785 eV. Using 3-times the inelastic mean free path given for elemental Pd[34], these kinetic energies refer to an information depth of 1.3, 2.0 and 3.4 nm as a rough estimation. Analysis of the spectra was performed by the software CASA XPS.

2.4 HR-TEM

A Philips CM200FEG microscope operated at 200 kV and equipped with a field emission gun, Gatan imaging filter and an energy-dispersive X-ray (EDX) analyzer was used. The coefficient of spherical aberration was Cs = 1.35 mm and the information limit was better than 0.18 nm. High-resolution images with a pixel size of 0.016 nm were taken at the magnification of 1.083.000 × with a CCD camera, and selected areas were processed to

obtain the power spectra (square of the Fourier transform of the image), which were used for measuring interplanar distances (+/- 0.5 %) and angles (+/- 0.5 deg) for phase identification.

2.5 Catalytic hydrogenation

The following reagents were used: n-hexane (Roth > 99%), n-octane (Acros Organics 99%+), n-decane (Acros Organics, 99+%), phenylacetylene (Aldrich, >98%), styrene (Merck, 99%, stabilized), ethylbenzene (Aldrich, anhydrous, 99.8%), Lindlar's catalyst (Aldrich, 5 wt% Pd on $CaCO_3$, poisoned with Pb, used without further poisoning by nitrogen bases), Pd/Al_2O_3 (5 wt% Pd, Aldrich), Pd powder (< 20 μm Aldrich, 99.9%) and H_2 (Westfalengas, 99.999%). Liquids beside n-octane, n-decane and n-hexane were distilled under Ar before use. n-Octane, n-decane and phenylacetylene were optionally stored under Ar adding a 4 Å molecular sieve (Roth).

Most hydrogenation reactions were carried out using a commercial autoclave (*Büchi AG*, Switzerland, 100 ml glass vessel) equipped with a heating jacket and a hydrogen dosing system. In a typical run the catalyst powder is added to a mixture of 80-100 ml n-octane, 1 ml n-decane as internal standard and ~3 ml (27 mmol) substrate. The mixture is purged with Ar and heated to the reaction temperature, usually 40 °C, under stirring (1250 rpm). The reaction system is flushed with H_2 (total pressure 1-4 bar), which is the starting point of the reaction.

For reactions under very inert conditions a reduction tube can be transferred and connected to a Schlenk line after high temperature reduction of the catalyst. A small part of the catalyst containing tube can be sealed off at $\sim 10^{-5}$ mbar avoiding additional contact with gaseous atmospheres. The ampoule is put in a custom-made glass reactor (~ 200 ml total volume) (an image is shown in Figure 2 SI). A magnetic stirring bar and three glass-baffles ensure turbulent flow during hydrogenation reaction. H_2-supply, thermocouple and the sample taking system were connected via KF-flanges. The setup allows a bake-out under high vacuum (~10^{-}

^{4} mbar). Two spindle valves were attached as inlet for the liquids and for the connection to the Schlenk line, equipped with an oil diffusion pump. The reaction can be started as the stirrer is turned on and the catalyst containing ampoule breaks. Thus the surface of the catalyst contacts immediately the alkyne. For analyses, either an *Agilent* 7820A GC equipped with a FID detector and a DB-WAX column or an *Agilent* GC-MS 5975B equipped with a MS and FID detector and a DB-1 column were used. Conversion X_{PA} and selectivity to styrene S_{Sty} for the hydrogenation of phenylacetylene were calculated using the following formula, where c_{Sty}, c_{EB} and c_{PA} are the concentrations of styrene, ethylbenzene and phenylacetylene and c^0 are the initial concentrations:

$$X_{PA} = \frac{c_{Sty} - c_{Sty}^0 + c_{EB} - c_{EB}^0}{c_{Sty} - c_{Sty}^0 + c_{EB} - c_{EB}^0 + c_{PA}} \qquad (1)$$

$$S_{Sty} = \frac{c_{Sty} - c_{Sty}^0}{c_{Sty} - c_{Sty}^0 + c_{EB} - c_{EB}^0} \qquad (2)$$

The carbon balance was obtained by:

$$CB = \frac{c_{Sty} + c_{EB} + c_{PA}}{c_{Sty}^0 + c_{EB}^0 + c_{PA}^0} \qquad (3)$$

Blindtests of phenylacetylene hydrogenation as well as all hydrogenation reactions using styrene as reactant show a constant carbon balance close to 100% with a scattering of max. ±2%. However, a slight decrease of the carbon balance during phenylacetylene hydrogenation was frequently observed. Temporary adsorption[23], oligomer formation or formation of carbonaceous deposits may account for this behavior. Unfortunately we were not able to quantify oligomers, but even a full literature survey was unsuccessful providing any description to it. These effects are not considered in formulas (1) and (2), but they will be discussed separately by means of carbon balances.

The initial activity towards styrene formation A_{Sty}, normalized to the catalyst mass, was calculated by the formula:

$$A_{Sty} = \frac{A_0 \cdot V_{Total}}{m_{Cat}} \qquad (4)$$

V_{Total} represents the total volume of the solution during reaction and m_{Cat} is the mass of utilized catalyst for the catalytic run. A_0 is the slope of the plot of styrene concentration versus time at t = 0. It was determined by the derivative of a numerical approximation of the concentration plot by a 4th order polynomial, yielding satisfying fits to the experimental data. Investigations for mass transport influence were performed for hydrogenation of phenylacetylene at 4 bar and 40 °C with milled Pd_2Ga. The initial activity was independent of the stirring rate when using a minimum of 750 rpm (Figure SI I), excluding external mass transport limitation. The corresponding Arrhenius-plot (see Figure SI 1) shows a linear dependency and the calculated apparent activation energy was 35.8 kJ/mol. This is in the order of magnitude of reported values and would be significantly lower (0-15 kJ/mol) in the case of film diffusion limitation, e.g. reported in [35]. Due to the absence of pores in the unsupported intermetallic catalyst, internal mass transport limitations are not considered. The initial activity increases proportional with applied H_2 pressure, whereas the selectivity did not changed significantly. Similar activities were detected for the commercial as well as for the custom-made reactor.

3. Results and Discussions

3.1 Hydrogenation of phenylacetylene with as prepared milled Pd_2Ga, Pd powder, Pd/Al_2O_3 and Lindlar's catalyst

The catalytic results for hydrogenation of phenylacetylene at 4 bar at 40 °C using the as prepared milled powder of Pd_2Ga were compared with different reference catalysts. The observed concentration profiles using Pd/Al_2O_3, Lindlar's catalyst and unsupported elemental

Pd powder are shown in Figure 2 and Table 1. The corresponding conversion, selectivity and carbon balance plots are shown in Figure SI 4. n-Octane was chosen as solvent to minimize possible solvent effects on the reaction behavior due to the presence of additional functionalities. Pd/Al_2O_3 is a commercial catalyst which was used in earlier work as reference in the acetylene hydrogenation reaction[26]. With this catalyst, a relatively high selectivity to the semi-hydrogenated product styrene (96.5%) can only be achieved at low conversions, which is typical for a supported monometallic Pd catalyst in this type of reaction. At full conversion the selectivity is lowered to 82.5%. In contrast, Lindlar's catalyst with its effective modification of the active Pd species provides the highest selectivity to styrene at low and still 94.5% selectivity at full conversion. The selectivity of Pd_2Ga is the lowest at ~10% conversion (95%). At full conversion it is intermediate between the commercial catalysts (88.5%), but very similar to that observed for pure Pd powder (90.5%). Similar observations were obtained in the hydrogenation of 1-hexyne and 2-methyl-3-butyn-2-ol (not further discussed here) indicating that the comparable properties of Pd and Pd_2Ga are not significantly substrate dependent. Apart from the selectivity towards over-hydrogenation to ethylbenzene we observed a spontaneous decrease in the carbon balance as soon as the reaction starts and it continuously decreases slightly in all cases, being most pronounced for the Pd/Al_2O_3 catalyst. Jackson et al.[23] also observed during their analysis that the carbon balance in the beginning of the reaction rapidly decreases, but increases to a certain value during reaction. Adsorption, oligomer formation or carbonaceous deposits are the most likely reasons for this behavior.

The XP spectra of spent Pd_2Ga (see Figure SI 3) reveal only the reduction of Pd oxide, which readily occurs under the hydrogenation conditions, while the amount of oxidized Ga is essentially the same and the majority of the Pd remains in elemental state. This suggests that the intermetallic surface cannot be re-formed *in situ* in liquid phase hydrogenation. This can

be understood by taking into consideration that the onset reduction temperature of the oxidic overlayer is 180 °C in 10% H_2/He as shown in part I[31] , whereas the reaction temperature in the liquid phase was only 40 °C.

The activities and selectivities summarized in Table 1 illustrate, that a direct comparison of the catalysts is rather difficult. The dispersion of the bulk catalysts is extremely low demanding a high amount of catalyst as clearly visible by means of the specific activities in Table 1. The low specific surface area makes the application of chemisorption methods difficult which unfortunately impede the determination of the active surface area and thus the determination of a reliable turnover frequency. As the specific activity is low, the selectivity towards over-hydrogenation is considerably suppressed even with unmodified Pd powder, which might be related to the unusual dispersion of all of our model catalysts. Additionally, compared to acetylene hydrogenation in earlier studies[25], conclusions on the selectivity behavior in the liquid phase hydrogenation of phenylacetylene are handicapped by a lack of exact quantification of potentially formed oligomers. Nevertheless, the carbon balance of usually 95% and above suggest, that any oligomers are rather minority products. The big advantage of using bulk model catalysts is, that their characterization with XPS and XRD is straightforward and more reliable compared to supported systems. Simultaneously, the absence of any support or modifier allows studying the intrinsic properties of the materials. It was shown in part I[31] that the surface and the electronic structure of Pd_2Ga is highly dynamic and strongly depending on the pre-treatment. The main focus of this study lies on the comparison of the catalytic behavior of Pd_2Ga after different pre-treatments and the resulting surface state. Comparing finally the rate of ethylbenzene formation in presence of phenylacetylene and the initial rate of ethylbenzene formation from pure styrene allows revealing qualitative differences in the operation mode of the different catalysts.

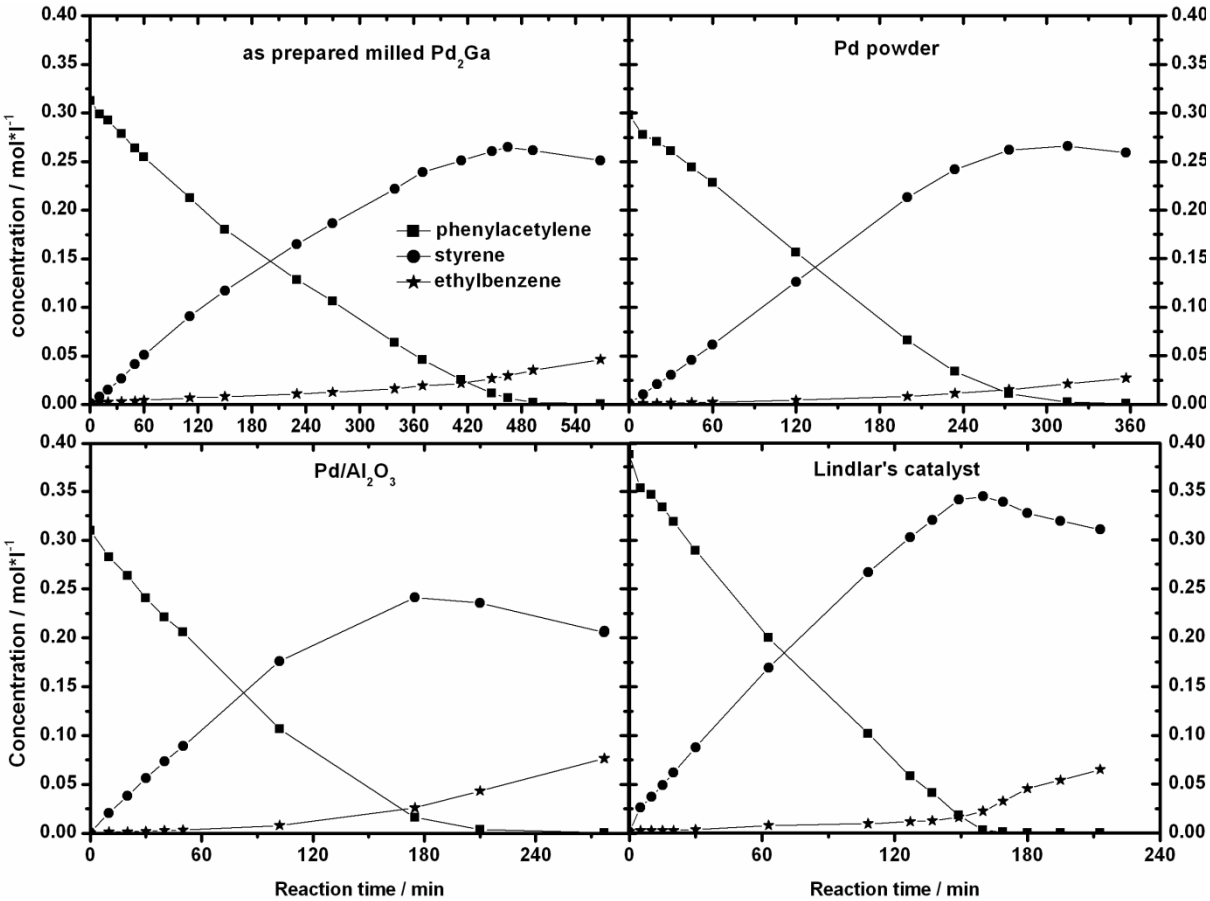

Figure 2: Concentration profiles during the hydrogenation of phenylacetylene at 4 bar, 40 °C in octane using Pd_2Ga (10 mg), Pd powder (10 mg), Lindlar's catalyst (3.5 mg, 5 wt-% Pd) and Pd/Al_2O_3 (0.8 mg, 5 wt-% Pd). Note the different scales of the x axis.

Table 1: Comparison of initial activity and selectivity towards styrene S_{Sty} at low and full conversion and the carbon balance CB of as prepared, milled Pd_2Ga with Pd, Pd/Al_2O_3 and Lindlar's catalyst in the hydrogenation of phenylacetylene at 4 bar, 40 °C in octane in a commercial autoclave.

Catalyst	A_{Sty} / (mmol/(g_{Cat}*h)	S_{Sty} ($X_{PA} \approx 10\%$)	S_{Sty} ($X_{PA} \geq 99\%$)	CB ($X \geq 99\%$)
milled Pd_2Ga - as prepared	478	95.0	88.5	94.5
Pd powder	417	97.0	90.5	96
Pd/Al_2O_3	9828	96.5	82.5	91
Lindlar's catalyst	4939	98	94.5	96.5

3.2 Hydrogenation of phenylacetylene with Pd_2Ga after different pre-treatments

A reductive pre-treatment at 400 °C is sufficient to heal structural disturbances in the bulk and to regenerate the intermetallic surface to a large extent. Thus, the catalysts were submitted to a corresponding pre-treatment to study the catalytic properties of the intact

intermetallic surface. As a first attempt to avoid the re-oxidation of the freshly reduced powder, it was transferred into a glove box without contact to air immediately after reduction and covered with degassed octane, used as solvent in the reaction. The suspension was transferred in a wet state without air-contact into the commercial setup which was baked out at 100 °C and purged with Ar directly before the experiment. This level of effort is appropriate for many air and/or water sensitive reactions. When the reaction is performed after such a pre-treatment, a considerably lower initial reaction rate but a strong increase over time was observed as visible in Figure 3 (the corresponding plots for conversion, selectivity and carbon balance are shown in Figure SI 5). This is a clear indication that the surface undergoes modifications during reaction and that the catalyst is not stable. The activating behavior can be understood considering the significant d-band shift of Pd_2Ga compared to Pd. Due to the significantly lower density of states at the Fermi level one would expect, that the intermetallic compound provides a lower intrinsic activity than Pd. In part I[31] we have shown that the oxophilicity of intermetallic Ga is still high leading easily to surface oxidation even at very low partial pressures (< 100 ppb) of oxidants similar to elemental Ga. It is likely that the small residues of water or oxygen – hardly avoidable in such a reactor – attack the surface even under these reductive conditions forming a more Pd enriched surface embedded in Ga oxide leading to the increasing activity.

In a further attempt to study the intrinsic catalytic properties of the intermetallic surface and, in turn, to diminish further the influence of residues of water and oxygen, the reaction was performed under even more inert conditions using a tight glass reactor and Schlenk techniques. The freshly pre-reduced catalyst was sealed directly in the glass reduction tube, connected to a Schlenk line. The catalyst-containing ampoule and a magnetic stirring bar were placed in the reactor and subsequently subjected to a thorough bake-out at ~ 100 °C and dynamic vacuum (10^{-4} mbar). The dried liquids were then filled inside the reactor using

Schlenk technique. For degassing, the liquids were frozen in liquid nitrogen and degassed under high vacuum at 10^{-4} mbar before defrosting. The sequence was repeated four times. The reaction was started when the atmosphere was changed from Ar to H_2 after the stirrer was turned on and the catalyst-containing ampoule was broken. This procedure provides the advantage that the catalyst does not come into contact with any gaseous atmosphere and is immediately covered by the solved alkyne – the latter binds strongly to the surface of the catalyst and might protect it from oxidation. Under these conditions a more stable initial reaction rate could be achieved (Figure 3). Nevertheless, also in this case the reaction rate slowly increased with time indicating instability of the catalyst. The specific activity is significantly lowered by a factor of about 20, compared to the as prepared Pd_2Ga at least at the beginning of the reaction.

The milled Pd_2Ga was also treated in 100% Ar at 400 °C for 4 h but the activity was only slightly lower without an activation period (compare Table 2). This indicates that the lower activity of the pre-treated catalyst does not originate from changes in surface area during the heat-treatment. The specific surface area was determined before (0.27±0.01 m^2/g) and after pre-reduction at 400 °C (0.28±0.01 m^2/g), revealing no significant change. The increase in reaction rate is furthermore not due to a possible mechanical split of slightly agglomerated particles after high temperature treatment. Such an artifact was excluded by an experiment where an ultra-sonic treatment after breaking the ampoule and before switching to H_2 atmosphere had no influence on the observed activation behavior. Taking into account that the total concentration of Pd on the outermost surface increases after pre-reduction[31] we can also exclude that the lower activity originates from a significantly lower Pd surface concentration.

In contrast to the pre-treatment at 400 °C in Ar, a pre-treatment at the same temperature in a static vacuum (14 h in static vacuum in a quartz glass ampoule at $p \leq 1 \cdot 10^{-3}$ mbar, then stored

in air), showed a very small activation in the beginning of the hydrogenation reaction (Figure 3) but yields essentially a stable catalyst afterwards. The reaction rate is ~ 5.7 times lower compared to the sample as prepared or pre-treated in 100% Ar at 400 °C. This result is in agreement with the observation that 400 °C and (dynamic) vacuum is sufficient for a partial reduction of Ga oxide accompanied with an almost symmetric but still relatively broad Pd 3d peak, shifted to 335.6 eV as shown in part I[31]. After this procedure a passivation layer still exists and the sample is stable even after long time air-contact without mechanical load.

Taking these experiments into account it is most likely that the strongly decreased activity originates from the modified electronic structure of the intermetallic compound, which is expected due to the significantly shifted d-band of Pd_2Ga compared to Pd. However, we are not able to decide unambiguously, whether only Pd_2Ga or very small amounts of probably highly dispersed Pd on top of (inactive) Pd_2Ga catalyzes the reaction.

For the still existing increase in reaction rate with reaction time, leaching of Pd and thus contribution of homogeneous catalysis during the reaction might be responsible. To verify the absence of a homogeneous contribution, the catalyst was separated from the solution. After adding fresh phenylacetylene to this solution, no further catalytic activity was observed, which clearly rules out a homogeneous contribution to the catalytic activity. A more likely scenario is that traces of O_2 or H_2O, which cannot be avoided *completely* even with the precautions taken in the Schlenk reactor, lead to advancing decomposition of the surface and surface enrichment of elemental Pd with higher activity. Thus, the intermetallic surface could function like a getter-material for oxygen even in apparently inert atmospheres.

XRD analysis of the spent sample (mixed with borosilicate glass, which originates from the broken glass ampoule) revealed a strong broadening of the reflections compared to the freshly reduced Pd_2Ga (Figure 4 b). The positions of the reflections do not significantly

change and within the detection limit of this method other crystalline phases are absent. The reason for the broadening is visible in TEM images. While the freshly reduced samples show large domains of crystalline Pd_2Ga[31] with smooth surfaces, the samples after catalysis show ensembles of nanoparticles (Figure 5). Also the bulk of the particles exhibits contrast fluctuations indicating that the crystallites have been broken into smaller domains. At the edges of the particles also amorphous material is present between the metallic nanoparticles. The amorphous material is likely related to Ga oxide and also carbon depositions, the latter could partially explain the notably decrease in the carbon balance. However, it is not possible to decide whether Ga oxide is formed already during reaction or by unavoidable contact with air during sample recovery after reaction. Attempts to identify the nature of the metal nanoparticles by HR-TEM did not result in a clear indication for the presence of elemental Pd. Unfortunately, an analysis by XPS was not possible due to strong charging of the glass containing sample. The formation of cracks and small domains might induce the formation of pores, which would certainly enhance the surface area during reaction and thus the reaction rate. This change in the microstructure of the whole catalyst particles and the observed increase in reaction rate can certainly not be explained only by the attack of oxygen or water impurities. Phenylacetylene seems to chemically attack the material.

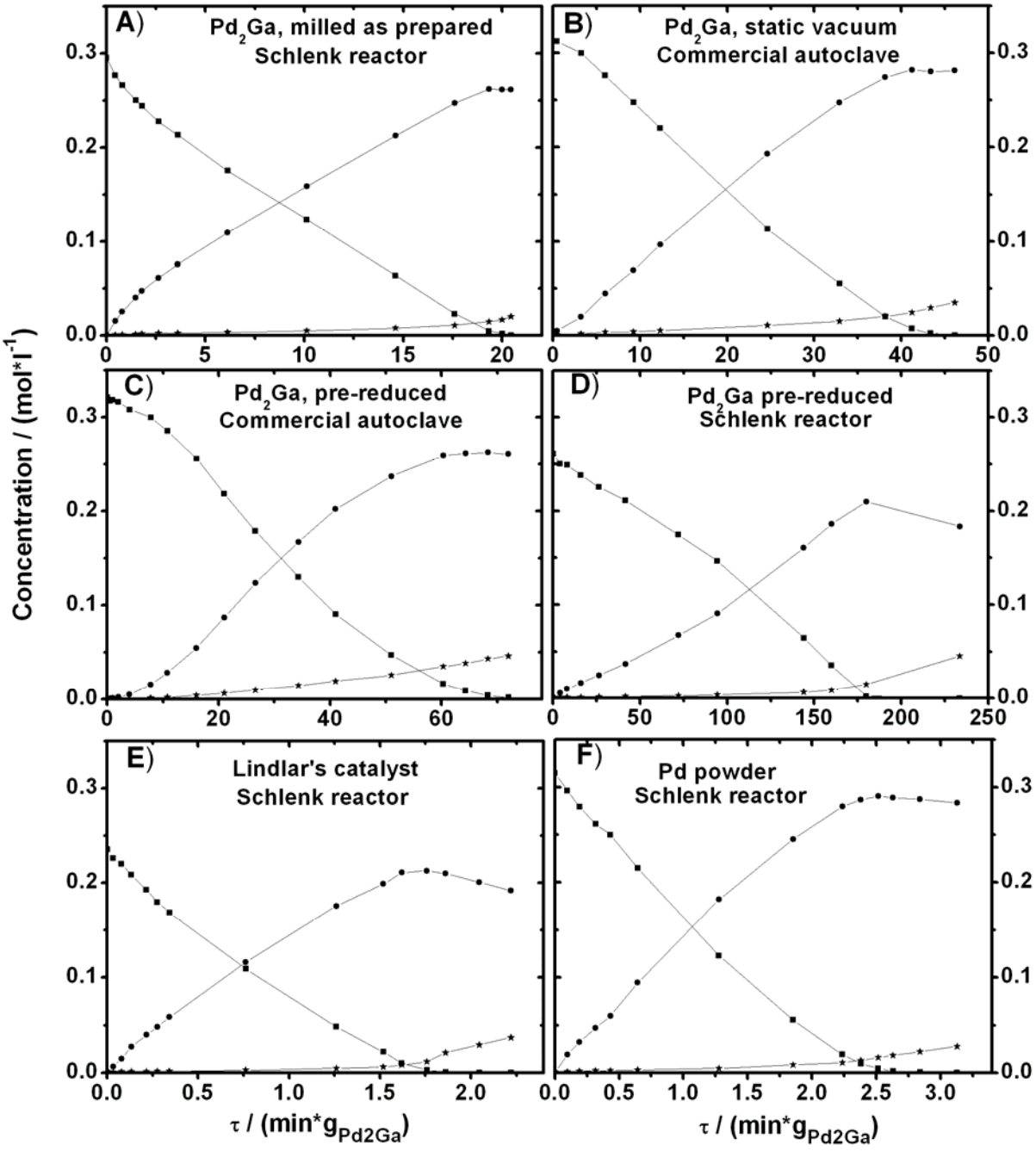

Figure 3: Concentration profiles of phenylacetylene hydrogenation for Pd_2Ga after different pre-treatments as well as Pd powder and Lindlar's catalyst as reference catalysts. For better visualization of the strongly different activity of the Pd_2Ga catalyst after the pre-treatments, the reaction time was multiplied by the catalysts mass on the x axis. Note their very different scales. All reactions were carried out at 40 °C in octane at ~ 1 bar, except Pd_2Ga pre-treated in static vacuum (4 bar, compare Table 2).

Table 2: Initial activity towards styrene formation (A_{Sty}) and selectivities to styrene (S_{Sty}) as a function of the pre-treatment and the used reactor for hydrogenation of phenylacetylene. Pre-reduction was 5% H_2/Ar for 4 h at 400 °C. ~ 3 ml phenylacetylene were solved in octane (80-100 ml). The reaction temperature was always 40 °C.

Catalyst	Pre-treatment	Reactor (p / bar)	A_{Sty} / (mmol / (g_{cat} · h))	S_{Sty} / % $X_{PA} \approx 10\%$	S_{Sty} / % $X_{PA} \geq 99\%$	CB / %
Pd_2Ga	None	Commercial (1.1)	121	96	88.5	96
Pd_2Ga	None	Schlenk (1.3)	136	97	93	95
Pd_2Ga	400°C, ~$1 \cdot 10^{-3}$mbar,	Commercial (4)	84	95.5 ($X_{PA} \approx 20\%$)	89	99.5
Pd_2Ga	pre-reduced	Commercial (1.1)	~5 (rapidly increasing)	(93)	(85)	96
Pd_2Ga	pre-reduced	Schlenk (1.3)	7.1	97	(94)	86.5
Pd_2Ga	400 °C , 100% Ar,	Schlenk (1.3)	121	96.5	n.d.	n.d.
Pd powder	None	Schlenk (1.3)	641	97.5	93.5	98
Lindlar's catalyst	None	Schlenk (1.3)	1154	99	95.5	96

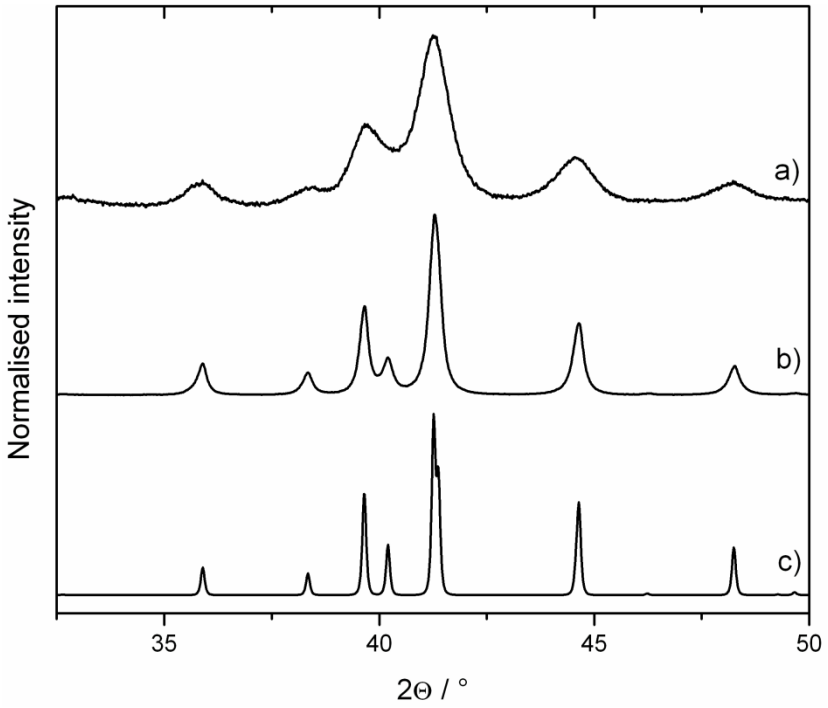

Figure 4: X-ray diffraction pattern of pre-reduced Pd_2Ga (a) after liquid phase hydrogenation of phenylacetylene under inert conditions; (b) after styrene hydrogenation. c) represents the calculated pattern according to [36].

Table 3: Lattice parameters and FWHM of the (203) reflection of pre-reduced Pd_2Ga used for hydrogenation of a) phenylacetylene and b) styrene. The values for a fresh sample pre-reduced at 400 °C are given for comparison (c).

Sample preparation	*a*	*b*	*c*	FWHM / °

a)	5.4715(2)	4.0582(1)	7.7849(2)	1.2
b)	5.4799(2)	4.0550(1)	7.7835(3)	0.27
c)	5.4815(1)	4.05556(3)	7.7859(1)	0.23

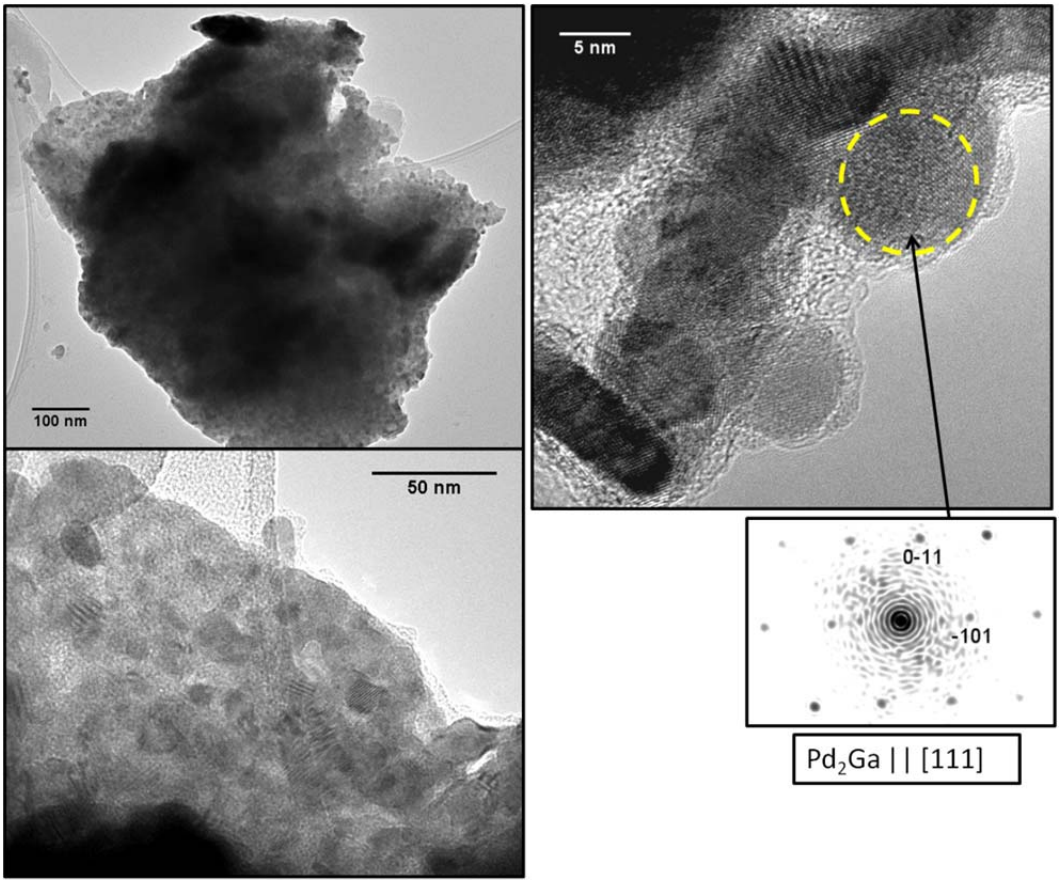

Figure 5: HR-TEM of a sample spent for phenylacetylene hydrogenation. In contrast to a pre-reduced fresh sample, the particles are cracked in smaller domains. According to Fourier analysis the surface consists of Pd_2Ga nanoparticles. An amorphous phase is also detected, which can be related either to carbon or Ga oxide. The sample was exposed to air after reaction and before TEM imaging.

It is noted that according to the necessary reduction temperature for the oxidized layer of 180 °C as determined on the unsupported particles, a stable catalytic reaction on the clean intermetallic surface might be possible in gas phase hydrogenation at considerably higher temperatures than usually applied in triple bond hydrogenation reactions as reported earlier. Indeed, at 200 °C and without reductive pre-treatment a clear selectivity difference between Pd_2Ga and a commercial Pd/Al_2O_3 catalyst was achieved and a stable reaction rate was observed[25]. However, concerning supported Pd_2Ga nanoparticles a remarkably similar

activation behavior during acetylene hydrogenation with time on stream has been observed after pre-reduction at high temperatures[25]. Like the gradual increase in reaction rate in the liquid phase, a long activation period without major changes in the selectivity has been reported. It seems likely that this behavior is also related to a gradual decomposition of the intermetallic surface liberating highly active Pd species from the less active intermetallic compound. Partial surface decomposition of supported Pd_2Ga nanoparticles has also been reported for application in methanol steam reforming, however, under more oxidizing conditions[37].

3.3 Activity of styrene hydrogenation with pre-reduced Pd_2Ga, Pd powder and Lindlar's catalyst

The loss in the initial activity of pre-reduced Pd_2Ga under inert conditions is not accompanied by an intrinsic gain in selectivity. Compared to reactions carried out in the commercial reactor the selectivity does increase from 88.5% to 93% at full conversion, but such higher selectivity was also obtained with all reference catalysts (Figure 3, Table 2) in the custom-made reactor and is probably an effect of using distilled and dried phenylacetylene. However, determining the selectivity at 100% conversion for the pre-reduced catalysts is not very meaningful, since the catalyst in this state is already partly decomposed. A clear difference can be seen in the carbon balance, which decreases to ~86%, which is significantly lower than in the case of all other catalysts and further lowers the overall yield of styrene. We therefore had a closer look on the initial activity in styrene hydrogenation. Using phenylacetylene as educt the initial rate of styrene hydrogenation is very low compared to styrene formation for Pd, Pd_2Ga as well as Lindlar's catalyst. Using pure styrene as educt leads in all cases to a significant enhancements of the initial rates of ethylbenzene formation, see Table 4. The carbon balance remains constant, close to 100%, indicating that

carbonaceous species and oligomers originate from phenylacetylene. Contrariwise to the phenylacetylene hydrogenation, no increase in reaction rate, was observed over time for pre-reduced Pd_2Ga if very inert conditions were applied (Figure 6), which suggests that the increase in reaction rate in phenylacetylene hydrogenation is not only caused by O_2 or H_2O impurities, but is a complex convolution of different influences, including the chemical interaction with phenylacetylene, possibly promoted by mechanical load due to stirring. The XRD pattern of such a spent sample revealed only marginal reflection broadening (Figure 4). The crucial role of oxidizing impurities was proven during styrene hydrogenation by adding 50 µl H_2O during the reaction in H_2 atmosphere, which corresponds to a total water concentration of about 500 ppm. We observed a spontaneous sharp increase in reaction rate, indicating oxidative decomposition of the catalyst (Figure 6).

Comparing the ratio of the initial activities of the phenylacetylene hydrogenation and the hydrogenation of pure styrene, the Pd, pre-reduced Pd_2Ga and Lindlar's catalyst show differences. It is 0.58 for pure Pd powder, meaning that double hydrogenation occurs clearly faster than triple bond hydrogenation. This is typically for Pd catalysts, e.g. in the gas phase hydrogenation of acetylene[38], and was also reported for the liquid phase hydrogenation of phenylacetylene[39]. The ability to form hydrides makes Pd highly reactive towards alkene hydrogenation[40]. The low selectivity towards styrene hydrogenation (see Table 4) with pure Pd in phenylacetylene hydrogenation is likely related to the modification of the surface by the alkyne. Irreversible carbon deposits and an *in situ* formed subsurface Pd-C phase[41,42] reduces the availability of surface hydrogen and suppresses Pd hydride formation. The stability of the Pd-C phase decreases as the chemical potential of the alkyne decreases, which occurs continuously in a batch reaction. Thus at high conversions of phenylacetylene the Pd-C phase vanishes and the reaction becomes unselective.

The ratio is 0.94 for pre-reduced Pd_2Ga, thus there is, compared to Pd, a lowered ability for styrene hydrogenation, while no clear difference in ethylbenzene selectivity at low conversions is observed when phenylacetylene is hydrogenated. The explanation is likely the inability of the almost clean intermetallic (sub)-surface to form highly reactive hydrides, which is intrinsic and does not depend on the presence of an alkyne. However, the electronic effect indeed significantly lowers the activity of Pd_2Ga but does apparently not have a clear influence on the selectivity in phenylacetylene hydrogenation.

In the case of Lindlar's catalyst the initial activity towards styrene formation from phenylacetylene is slightly higher (1.16) than the initial activity towards ethylbenzene formation from pure styrene. In agreement with the literature, there is still a considerably ability for styrene hydrogenation if Lindlar's catalyst[13,14] is not additionally poisoned with nitrogen bases. However, the rate of ethylbenzene formation from styrene in presence of phenylacetylene is still the lowest compared to the other catalysts. Lindlar's catalyst has a characteristic, which clearly distinguishes it from the other catalysts. There is a short but resolvable increase in rate of ethylbenzene formation when phenylacetylene is completely consumed followed by a sudden decrease at a certain point in time leading finally to a "s"-shape of the ethylbenzene concentration-profile, visible in Figure 2 as well as in Figure 3 E. A geometric effect of Pb[43] by site-blocking can be considered here. Pb blocks the active sites necessary for alkene hydrogenation but alkynes with their higher heat of adsorption are able to compete for active sites, forcing Pb to restructure. They will be readily hydrogenated over the liberated sites. At the point where the phenylacetylene concentration becomes zero, free active sites are exposed leading to enhanced rates of ethylbenzene formation. Simultaneous restructuring of Pb can occur, which will lead to blockage of these sites diminishing again ethylbenzene formation. The ratio of the velocities of Pb restructuring and

ethylbenzene formation determines the degree of over-hydrogenation at 100% conversion using Lindlar's catalyst.

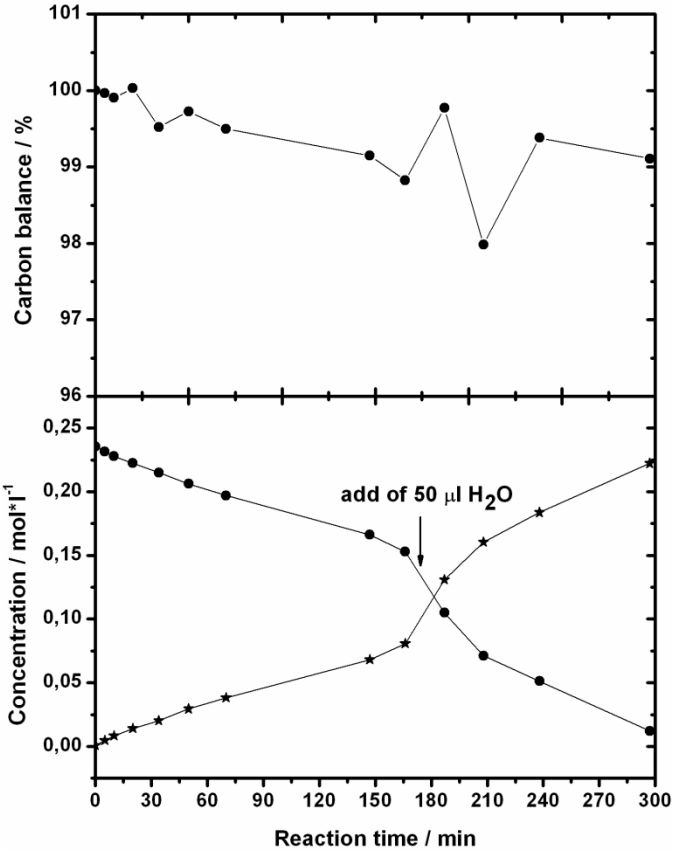

Figure 6: Hydrogenation of styrene (circles) with pre-reduced Pd_2Ga to ethylbenzene (stars). Adding small amounts of H_2O under H_2 atmosphere result in spontaneous increase in reaction rate when Pd_2Ga is used.

Table 4: Initial reaction rate of ethylbenzene formation (A_{EB}) for Pd, pre-reduced Pd_2Ga and Lindlar's catalyst. All reactions were carried out in the Schlenk reactor and the reaction conditions for styrene hydrogenation are similar to that described for phenylacetylene hydrogenation. A_{Sty} is given for comparison. The ratio between both activities is calculated for the catalysts.

catalyst	Substrate	A_{EB} / (mmol/(g_{cat}*h)	A_{Sty} / (mmol/(g_{cat}*h)	A_{Sty} : A_{EB}
Pd powder	phenylacetylene	16.9	641	37.9
Pd powder	styrene	1096	-	0.58
Pd_2Ga pre-reduced	phenylacetylene	0.2	7.1	37.5
Pd_2Ga pre-reduced	styrene	7.6	-	0.94
Lindlar's catalyst	phenylacetylene	19.5	1154	59.2
Lindlar's catalyst	styrene	991.2	-	1.16

4. Summary

The catalytic properties of Pd_2Ga after different pre-treatments for the hydrogenation of phenylacetylene were investigated in the present study. Based on the results of part I[31] we focused on the stability of this catalyst as function of the pre-treatment with special focus on residual oxidants. The surface of as prepared Pd_2Ga consists mainly of Pd, Pd oxide, Pd_2Ga and Ga oxide (Figure 7 a). Despite the reduction of Pd oxide this catalyst is stable under hydrogenation conditions and behaves very similar to the elemental Pd powder used as reference here (Figure 7 B). An *in situ* re-formation of a clean intermetallic surface (Figure 7 D) does not occur. The powder must be subjected to an *ex situ* pre-reduction in 5% H_2/Ar at 400 °C (Figure 7 C). After this treatment the catalyst provides a considerable lower initial activity, which is likely due to the filled valence d-band of Pd_2Ga, shifted away from the Fermi level. However, the contribution of traces of highly dispersed elemental Pd to the activity cannot be excluded (compare also part I of this work [31]). The activity increases quickly over time during reaction and suggests the enrichment of Pd by *in situ* decomposition of the IMC. By applying very inert conditions the increase in activity can be delayed, indicating that the intermetallic surface can be easily oxidized even under reducing conditions in the liquid phase if traces of O_2 or H_2O are present. HR-TEM images as well as XRD of a spent sample show that, independent of the oxidative decomposition of the surface, the bulk gets affected probably by a chemical attack of phenylacetylene (Figure 7 E). In no case Pd was leached and thus no homogeneous hydrogenation occurs. The selectivity towards styrene is high even if pure Pd is used and cannot be outperformed by any Pd_2Ga catalyst. This behavior is certainly not comparable to supported systems. Differences in ethylbenzene formation activities are visible when pure styrene is converted to ethylbenzene in terms of a lower initial activity for double bond hydrogenation of Pd_2Ga compared to Pd. That suggests that the resulting surface provides an intrinsically lower ability for double bond hydrogenation, which originates from the suppressed subsurface chemistry. Lindlar's catalyst

still performed slightly better; here the selectivity control is likely a geometric effect due to an *in situ* restructuring of Pb, which competes with alkenes for surface Pd.

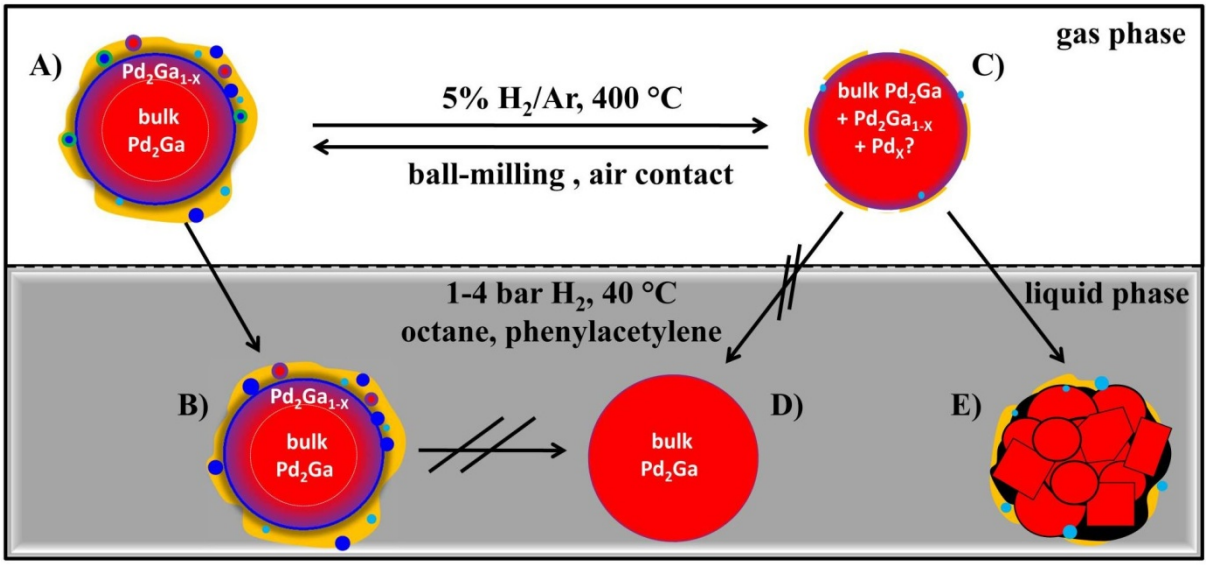

Figure 7: Schematic sketch of the structure of a microcrystalline Pd_2Ga particle before and after liquid phase hydrogenation and subsequent air contact. Red: Pd_2Ga, purple: Pd_2Ga_{1-x} (within the homogeneity range), yellow: surface Ga oxide, black: carbon, dark blue: elemental Pd, green: Pd oxides, light blue particles represent the presence of undefined Pd species. However, the exact nature and morphology of the Pd species is not known.

5. Conclusion

In this study we investigated the reactivity and stability of unsupported Pd_2Ga in the liquid phase hydrogenation of phenylacetylene. We observed a strongly reduced hydrogenation activity for Pd_2Ga when exposing an almost clean intermetallic surface, which originates from the valence d-band of Pd, shifted away from the Fermi level, in agreement with the d-band theory[44,45]. However, the obtained results during phenylacetylene hydrogenation confirm the high surface dynamics and the tendency for oxidative decomposition of Pd_2Ga at the surface, which was observed in UHV and gaseous atmosphere in part I of this work. Under the mild conditions of the liquid phase hydrogenation this oxidation is not reversible. Besides the surface dynamics, the observed decay of the bulk structure during phenylacetylene hydrogenation is an additional upcoming issue.

The spectroscopic and catalytic results of part I and of this study hold an important aspect for the general concept of modifying catalytic properties by d-band manipulation. In order to take practical advantage of this significant electronic modification by alloying or formation of intermetallic compounds, not only the electronic structure itself, but also its stability needs to be carefully investigated in particular at the surface. The targeted strong electronic modification can be achieved using chemically different metals, e.g. a noble and non-noble component[46,47]. For instance, compared to Pd the d-band of Pd_2Ga is significantly more shifted than in a Pd-Ag alloy. However, the present results show that for catalytic application one is not completely free in choosing a suitable combination within this concept. The strong modification might be accompanied by an increased instability and tendency towards surface reactions or relaxation that reverses the aimed effect. Covalent interactions between Pd and Ga in Pd_2Ga, lead to a strong electronic modification, but unfortunately not to a sufficient stability. It is the strong oxophilicity of Ga that handicaps practical application in liquid phase hydrogenation catalysis. Intermetallic compounds with their different crystal and electronic structures has been shown to offer interesting potential for various reactions e.g. methanol steam reforming with Pd_2Ga[48] or PdZn[49,50,51] or acetylene hydrogenation with $Al_{13}Fe_4$[52] as noble metal free catalyst. However, despite a stable bulk, the IMC surface might rather act as a precursor for the formation of the truly active surface as it is the case for PdZn in methanol steam reforming. The less noble metals like Ti, Zn, Al or In face the same issues like Ga. The surface structure and their electronic structure are dynamic and difficult to control and can get modified by forming a contingent passivation layer with a provisory stability. Thus the catalytic properties will strongly depend on the preparation, pre-treatment and the reaction conditions. For the special case of Pd_2Ga in liquid phase hydrogenation of phenylacetylene we found indications, that the almost clean intermetallic surface without passivation does not protect the surface or the bulk from decomposition. Thus, when making theoretical

predictions based on the electronic structure or crystal structure of an intermetallic compound or alloys, chemical dynamics and instabilities need to be considered for application as catalysts. In this case, the price for a concerted d-band manipulation was a practically insufficient stability.

Acknowledgement

The authors thank Ulrich Burkhardt, Monika Eckert and Gisela Weinberg for the metallographic and microscopic analysis, Horst Borrmann, Yuri Prots and Steffen Hückmann for the XRD measurements. We thank the Helmholtz-Zentrum Berlin for providing the beam time and for the continuous support. Timur Kandemir, Edward Kunkes and Yuan Luo are acknowledged for giving fruitful discussions and support during laboratory work.

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