The catalytic properties of thin film Pd-rich GaPd$_2$ in methanol steam reforming

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Abstract

An unsupported Pd-rich GaPd$_2$ sample in form of a thin film has been prepared by alternating layer deposition of Pd and Ga metal and was subsequently used as a structurally and chemically stable model system to clarify the catalytic properties of the unsupported intermetallic compound GaPd$_2$ in methanol steam reforming (MSR). The sample revealed a slightly Pd-richer GaPd$_2$ bulk composition of Ga$_{28}$Pd$_{72}$, as evidenced by EDX analysis, low-energy ion scattering, X-ray diffraction measurements and depth profiling by *in-situ* X-ray photoelectron spectroscopy. The latter additionally showed a high stability of GaPd$_2$ both under methanol and oxidative methanol steam reforming conditions. No active redox chemistry of Ga species or other reaction-induced oxidative Ga surface segregation have been detected during catalytic MSR reaction. Corroborating these observations, corresponding catalytic experiments under methanol steam reforming conditions revealed only a, in comparison to elemental Pd, very small activity in methanol dehydrogenation (CO formation rate at maximum 0.019 mbar min^{-1}; 0.08 site^{-1}s^{-1}). Unsupported thin film Pd-rich GaPd$_2$ with the given surface and bulk stoichiometry must therefore be considered a poor methanol steam reforming/dehydrogenation catalyst. In oxidative steam reforming experiments, only total oxidation without significant H$_2$ formation has been observed.

1. Introduction

Recently, catalysts comprising the intermetallic compound $GaPd_2$ have evoked a lot of interest in the selective hydrogenation of acetylene as well as in the steam reforming of methanol reaction [1-6]. The first reaction conditions are strongly reducing, while the second ones are likely to be more oxidizing, especially at low conversion and high temperature. While the unsupported compound has been investigated concerning its stability under reducing atmospheres [3,7], the question of its behavior under methanol steam reforming conditions has only been recently addressed in the form of nano-particulate systems on supported material [5,6,8].

Since the observation that the intermetallic compound $GaPd_2$ is formed under reductive conditions at high temperatures on Pd/Ga_2O_3 (~770 K [4]), a variety of different materials have been used to increase the knowledge and understanding of the ongoing processes. Besides studying Pd supported on different gallia polymorphs [6], model systems of small Pd-particles covered by a thin layer of Ga_2O_3 have been used to study the formation mechanism of the intermetallic compound during reduction [9]. Surface alloys, prepared by deposition of a thin Ga layer on Pd single crystals under ultra-high vacuum conditions and subsequent annealing, have been explored to monitor the electronic and compositional changes occurring during formation of the intermetallic compound and to correlate these changes to the catalytic properties [10]. The catalytic role of the oxidic constituent of the usually studied $GaPd_2/Ga_2O_3$ catalyst system, namely Ga_2O_3, has been scrutinized in recent publications [4, 9]. However, up to now, no reports are available on the catalytic properties of single-phase, unsupported bulk $GaPd_2$, although its presence has been crucially linked to high CO_2-selectivity already by Iwasa et al. [11]. It is also known, that intermetallic Ga-Pd compounds with higher Ga content (precisely GaPd), although Ga_2O_3-supported, are less CO_2-selective [4].

GaPd$_2$ itself crystallizes in the Co$_2$Si type of crystal structure [12] (Pearson symbol oP12, space group *Pnma*) and its crystal structure has been studied in detail, also taken into consideration compositional influences [13,14]. While the homogeneity range does not allow a Ga-enrichment of more than x = -0.05 for Ga$_{1-x}$Pd$_{2+x}$ (the Ga-rich border of the homogeneity range is temperature independent from 400 to 1030 °C), it is possible to accommodate a significantly higher fraction of Pd – up to x = 0.20 at 1030 °C – in the compound [14]. The additional Pd atoms are located on the crystallographic Ga sites in the structure. The shortest Pd-Pd distances are 2.808(5) Å for x = 0 and 2.752(5) Å for x = 0.17 [14].

Within this study we, for the first time, provide a direct comparison between the structural and catalytic properties of unsupported, structurally and chemically stable, Pd-rich GaPd$_2$ in MSR. These studies are aimed at a more detailed understanding of the complex GaPd$_2$/Ga$_2$O$_3$ catalyst system, since they essentially show that the presence of the supposedly catalytically active and selective intermetallic GaPd$_2$ alone is not sufficient to explain the high CO$_2$-selectivity of the above-discussed catalyst system. Rather, the results prove that a bi-functional synergism between GaPd$_2$ and the supporting Ga$_2$O$_3$ (as it is the case for nano-particulate systems [4]) is most likely prevalent – similar to the system ZnPd/ZnO [15-18]. The thermodynamically stable intermetallic compound GaPd$_2$ is synthesized as a bulk film model system and its surface and bulk structure thoroughly characterized. A large fraction of this characterization is devoted to *in situ* X-ray photoelectron spectroscopy (XPS) studies to monitor temperature- and atmosphere- initiated near-surface changes of GaPd$_2$. These studies are complemented by catalytic studies to unambiguously correlate the composition of the surface/bulk structure with the observed catalytic properties.

2. Experimental

Preparation of the GaPd₂ thin film

Thin film $GaPd_2$ was prepared by alternating layer deposition of Pd and Ga in a PVD-dedicated HV apparatus [10]. The film was deposited at 573 K onto a Ta metal sheet (18 x 20 x 0.125 mm), which was pre-cleaned with abrasive paper and cleaned in boiling hot water and hot ethanol. To stimulate formation of the intermetallic compound, the alternating layer setup was chosen to induce preliminary intermixing of the Pd and Ga layers. Pd and Ga were both thermally evaporated from either a W crucible (Pd) or a Ta crucible (Ga) in a background pressure of $5x10^{-6}$ mbar. To prepare the $GaPd_2$ film, in sum 21 layers at a mass ratio Ga:Pd = 1:3.1, corresponding to an atomic ratio of 1:2, were deposited. Start and end layer was half of a Pd layer. Subsequently, the $GaPd_2$ film was transferred to the UHV chamber and post-annealed at 673 K. Surface composition and cleanliness of the sample was checked by X-ray photoelectron spectroscopy and low-energy ion scattering (LEIS), confirming a clean surface after a mild sputter-anneal cycle sufficient to remove ambient-induced carbonaceous deposits. The resulting film had a thickness of 400 nm.

X-ray Diffraction (XRD)

Powder X-ray diffraction was conducted on a STOE-STADIP-MP powder diffractometer in Bragg-Brentano geometry (Cu $K_{\alpha1}$-radiation, Ge(111) monochromator) from $2\theta = 5$ to $100°$. To increase the surface sensitivity of the measurements, the sample was measured under grazing incidence conditions, using 5° between the surface and the incoming beam.

Energy-dispersive X-ray spectroscopy

Surface morphology and chemical homogeneity of as-prepared thin film $GaPd_2$ flakes have been investigated by scanning electron microscopy (JEOL 6610, W-cathode) equipped with

silicon drift detector (SDD) for energy dispersive X-ray spectroscopy (Noran 7 system, ThermoFisher).

The HZB/Bessy II setup

The HZB/BESSY II system [19] (at beamline ISISS-PGM) allowed us to perform *in-situ* photoelectron spectroscopy up to 1 mbar total reactant pressure. It is equipped with differentially-pumped electrostatic lenses and a SPECS hemispherical analyzer. The sample is positioned inside the high-pressure/analysis chamber ~2 mm away from a 1 mm aperture, which is the entrance to the lens system separating gas molecules from photoelectrons. Binding energies (BE) were generally referred to the Fermi-edge recorded after each core level measurement. Samples were mounted on a transferable sapphire holder. The temperature was measured by a K-type Ni/NiCr thermocouple spot-welded to the side of the sample and temperature-programmed heating was done by an IR laser from the rear. Sample cleaning by a mild Ar^+ sputter treatment (1.5 min at 5 µA, 10^{-4} mbar) is sufficient to remove the ambient-induced carbonaceous/Ga(ox) layer. Mild conditions are needed in order to avoid major loss of film thickness. Subsequent annealing up to 673 K restores the clean surface. The sensitivity of the simultaneous MS detection of the reaction products at HZB/BESSY II was not sufficient to extract reliable reaction rate and selectivity data for $H_2/CO/CH_2O/CO_2$, mainly because of an unfavorable ratio of the large total reactant flow through the XPS high pressure cell (which is generally operated in constant flow mode) relative to the minor amounts of products formed on the low surface area and low activity catalyst. However, "connecting" experiments performed in the setup in Innsbruck (see below) using the same conditions with respect to initial reactant pressures and reaction temperature range, allowed to assess a possible "pressure gap" effect and provided a reliable connection between the data obtained in either experimental setup. The thickness of the Ga_2O_3 layer was calculated using the SRD 82 NIST database for estimating the electron attenuation lengths (EAL) for Ga_2O_3 and $GaPd_2$.

On the basis of the density of both $GaPd_2$ (10.89 g cm^{-3}) and Ga_2O_3 (6.4 g cm^{-3}) and the asymmetry parameter for the Ga 3d peak (taken from the ELETTRA-Database; 0.8485 for a photon energy of 170 eV) electron attenuation lengths of 5.1 Å for $GaPd_2$ and 4.1 Å for Ga_2O_3 resulted. The Ga_2O_3 thickness was subsequently calculated using the program XPS Thickness Solver [20].

The Innsbruck UHV setup and catalytic measurements in methanol steam reforming

The UHV system (base pressure low 10^{-10} mbar range) with attached all-glass high-pressure reaction cell is designed for catalytic studies up to 1 bar and has been described in detail elsewhere [21].

Characterization of the catalysts was performed using a Thermo Electron Alpha 110 XPS/Auger/LEIS spectrometer and a standard double Mg/Al anode X-ray gun (XR 50, SPECS), an Omicron ISE 100 ion gun to provide the focused 1 keV He$^+$ ions for LEIS, an electron beam heater, an ion sputter gun and a mass spectrometer (Balzers). All the LEIS experiments were performed at an angle of beam incidence $\Psi = 45°$ and a scattering angle of $\theta = 90°$. After correction for the different cross sections, intensity normalization of the Pd and Ga signals was performed relative to the total backscattering yield, that is I_{Ga}(normalized) = $I_{Ga}/(I_{Pd} + I_{Ga})$ and I_{Pd}(normalized) = $I_{Pd}/(I_{Pd} + I_{Ga})$. The Pd and Ga scattering cross-sections valid for our specific setup were determined by measurement of clean Pd foil and a sufficiently thick pure Ga metal surface layer covering all Pd under identical experimental conditions.

Regarding catalytic characterization in methanol steam reforming, we present here only the most important facts and for details refer to previous publications [10]. Detection of reaction products and even minor intermediates with high sensitivity is possible either by discontinuous sample injection into the gas chromatography-mass spectrometry (GC-MS)

setup (HP G1800A) or by direct online MS analysis of the reaction mixture via a capillary leak into the GC-MS detector. UHV-prepared samples can be transferred by means of a magnetically coupled transfer rod from the UHV sample holder to a Pyrex glass sample holder used inside the all-glass reaction cell (60.6 mL, no hot metal components). With this all-glass setup of the ambient-pressure reaction cell, no wires or thermocouples are connected to the sample during catalytic measurement (thermocouple mechanically contacted at the outside). Accordingly, background (blind) activity of the reaction cell is routinely checked and was found to be negligible for all tests. Apart from the UHV pumping system, the high-pressure cell is evacuated sequentially by a rotary pump (via liquid nitrogen cooled zeolite trap) and then via the main chamber down to UHV base pressure, and can be heated from outside to 723 K with an oven covering the cell. For better mixing of the reactants, the high-pressure cell is operated in circulating batch mode. By using an uncoated GC capillary attached to the high-pressure cell, the reaction mixture in the close vicinity of the sample is analyzed continuously by the electron ionization detector (EID) of the GC-MS system and in-parallel by a Balzers QMARS analyzer to quantify H_2 formation. EID and QMS signals of methanol, CO_2, CO, H_2 and CH_2O were externally calibrated and corrected for fragmentation (that is, CO and CH_2O fragments for methanol, CO fragment for CO_2). Methanol and methanol/water mixtures were degassed by repeated freeze-and-thaw cycles. All MSR reactions were conducted with methanol/water mixtures of a 1:10 composition of the liquid phase. This corresponds to a room temperature partial pressure ratio of methanol:water = 1:2, as verified by mass spectrometry. This procedure has been followed to provide excess of water in order to avoid unwanted methanol dehydrogenation due to lack of water in the reaction mixture.

The catalytic methanol steam reforming experiments were performed in a temperature-programmed manner, i.e. the reaction cell was heated at a constant linear rate of ~ 8 K min^{-1} to the final temperature of 623 K, and then kept isothermal at this temperature for ~ 20 min. Experimental details will be given in context with the individual reaction runs. The advantage of the TPR (temperature-programmed reaction) runs is that pronounced selectivity changes can be monitored via the partial pressure changes as a function of the reaction temperature, yielding useful qualitative information about changes of the reaction mechanism and the catalyst state. From the product partial pressures vs. time plots the reaction rates were obtained by differentiation and are usually given in partial pressure change per minute [mbar min^{-1}]. From the partial pressure change, the turnover frequency (TOF, given in site^{-1}s^{-1}) can be calculated by multiplication of the partial pressure change with a conversion factor f = 4.3, i.e. a reaction rate of 1 mbar min^{-1} corresponds to a TOF of 4.3 site^{-1}s^{-1}. The TOF calculation was based on an estimation of the surface sites of the GaPd$_2$ compound. Starting from the density of GaPd$_2$ (10.89 g cm^{-3}) and the molecular weight (282.52 g mol^{-1}), the number of atoms per cm^2 was calculated as 8.2×10^{14}, finally resulting in 5.7×10^{15} atoms on a 7 cm^2 GaPd$_2$ foil. Considering the reactor volume of 60.6 mL, a conversion factor of 4.3 resulted. As the TOF values have been estimated exactly as for similar Pd-based systems [15], both internal comparison to other Pd-based systems (especially NSIP's and particulate systems [15]), as well as comparison to other systems, thereby representing the lower limits of the TOF, is possible (under the assumption of equal activity of all surface GaPd$_2$ ensembles). True surface area determination (e.g. by BET) of this particular material is not possible, since the sample is a thin film of 400 nm thickness. The total surface of the sample is 7 cm^2, with surface roughness contributing only a few % of the total area increase (like foil vs. single crystal). Thus, we have the advantage of a "flat" bulk film sample. This error in surface area is much smaller than the error induced by the "structure sensitivity" of the reaction rates, which is unknown in all published cases (e.g. in ref. [4, 11]). As outlined above, our

estimation of the number of active sites, following similar arguments like on ZnPd or InPd, allows for estimating the TOF values from simple geometric arguments [15].

Correction for the steady removal of a fraction of the reaction mixture through the capillary leak has been achieved by adding 30 mbar Ar inert gas at the beginning of the reaction run and monitoring the $m/z = 40$ Ar intensity throughout the whole experiment. The Ar intensity over time then was used to recalculate the changes of the molar amounts of all products and reactants as referred to the initial state (before TPR start, reactor volume 60.6 mL and 300 K in the whole re-circulating batch system).

Catalytic measurements in oxidative methanol steam reforming

Catalytic measurements in oxidative methanol steam reforming were performed in an NI Labview-automatized recirculating batch reactor of about 13 mL volume [22]. The system allows automated pre-treatment cycles (oxidative and reductive) and reaction sequences. A quadrupole mass spectrometer (Balzers QMG 311) attached to the circulating batch Duran glass reactor via a capillary leak was used for continuous detection of the reaction components. All oxidative methanol steam reforming reactions were also conducted with methanol/water/oxygen mixtures of a gas phase composition of 1:2:0.5 = methanol:water:oxygen (12:24:6 mbar) at room temperature. All methanol/water mixtures were degassed by repeated freeze-and-thaw cycles. For each catalytic oxidative methanol steam reforming experiment, to about 50 mbar methanol/water mixture, 7.5 mbar Ar (to be measured at $m/z = 40$) was added to account for the decrease of the mass spectrometer signal due to the continuous gas withdrawal through the leak. Finally, He was added to 1 bar total pressure. In order to account for the partial adsorption of methanol and water on the stainless steel parts of the reaction system and to achieve a constant signal level, all catalytic measurements include a 15 minute equilibration period in the starting mixture prior to each measurement. All the catalytic experiments were also corrected for the activity of the catalyst

holder containing only quartz glass wool (almost negligible, at maximum 1% conversion based on CO_2 formation after 1 h). For data evaluation, the relative intensities of the mass spectrometer signals were converted into partial pressures via external calibration using gas mixtures of defined partial pressures and subsequently given in mbar min^{-1} vs. time.

A brief account of the mass and heat transport limitations should be given at this point. Regarding mass transport limitation, this appears to be less of an issue, since the sample does not represent a porous material (see the SEM image presented below in Figure 2). Limitation by pore diffusion can therefore be excluded. Note that this is the same catalyst setup that has been used for the studies on the NSIP Pd-Ga system [10], where much higher reaction rates were measured. To estimate if mass transport limitations play a role, we compared the collision number Z (via Z= p/(2πmkT)$^{1/2}$; 2.1 x10^{21} cm^{-2} sec^{-1}) and the maximum CO reaction rate (as given in the MSR experiment of this paper, 5.3x10^{15} cm^{-2} sec^{-1}) and it turned out that the collision rate is orders of magnitudes larger than the reaction rate. Hence, limitation by diffusion is not relevant. As for the heat transfer limitation, this is also thought to play a minor role since local temperature effects are excluded due to the low reaction rates (and the bimetallic thin film prepared on the metal foil) and generally, heat transfer via the gas phase is enhanced due to the deliberate admission of He to the reaction mixture.

3. Results

3.1. Characterization

To verify that the sample shows the GaPd$_2$ bulk structure after synthesis, it was subjected to X-ray diffraction using small incident angles. The presence of the GaPd$_2$ structure in the bulk is essentially verified. As a representative example, Figure 1 highlights an X-ray diffraction pattern of the post-annealed film, confirming the presence of the orthorhombic GaPd$_2$ structure as main phase (space group *Pnma* [13]). The lattice parameters were determined

from the XRD measurement as $a = 7.814$ Å, $b = 5.477$ Å, $c = 4.058$ Å. Due to the small sample amount no internal standard could be added, thus no reliable standard deviation could be determined. Beside the reflections of $GaPd_2$, only two very weak additional reflections were detected (marked by asterisks). Ga-, Pd- or Ta-oxides as well as elemental palladium or tantalum can be excluded as source for the additional reflections. A unique assignment was not possible, but the reflection may indicate the presence of very minor traces (less than 3 mol-%) of the intermetallic compound Ga_5Pd_{13}.

While XRD results in the aimed-for crystal structure, the chemical composition of the sample was investigated using energy-dispersive X-ray spectroscopy (EDX). Due to the morphology (brittle flake-like pieces), hindering wave-length dispersive analysis, and some charging of the sample (~0.5 keV), the analysis totals only 90 wt.% of the sample. Nevertheless, this did not importantly affect the final matrix correction, i.e. its influence is estimated to be 1 to 2 at.%. The EDX analysis (spot mode) resulted in significant higher palladium content − in accordance with the possible detection of Ga_5Pd_{13} in the XRD patterns. Instead of the aimed for 1:2 composition, the analysis showed a composition of $Ga_{28(1)}Pd_{72(1)}$, indicating a Pd-rich sample. Figure 2a shows a secondary-electron (SE) contrast image of one of the obtained thin film $GaPd_2$ flakes after catalytic measurements. Strikingly, well defined grains possessing different surface morphologies are observed. EDX-mapping using the Ga-L and the Pd-M lines shows a weak variation of intensity in both images (Figures 2b and 2c). This behavior is mainly due to the morphology (surface roughness and inclination) of the sample. In general, a homogeneous Ga and Pd distribution is revealed (the EDX analysis was performed at 10 different spots of the sample. In the EDX maps intensities that are directly related to the relative mass concentration of the elements present in the sample are shown. For the mapping we used the Ga-L and the Pd-M lines, which are lower in energy, thus retrieving the highest resolution possible for our setup. On the basis of the analysis of the relative intensities in these 10 chosen spots, no significant changes were observed). Another rarely observed feature in

the elemental maps is the occurrence of small areas significantly enriched in palladium (see circles in Fig. 2b and 2c). These may be assigned to small particles of a Pd-richer phase, e.g. Ga_5Pd_{13}.

Regarding a possible size effect in catalytic performance, we note that the average crystallite size of the initial $GaPd_2$ bulk film is 29 nm and thus, in the range of the oxide-supported $GaPd_2$ particles (also in the low nm-range; ~ 10-20 nm [4, 11]). Note, however, that the thin film in essence is a bulk material (as e.g. a foil or a single crystal).

As for the resolution of the EDX maps, considering the ideal sample composition $Ga_{25}Pd_{75}$ and the used beam acceleration voltage (20 or 25 KeV), the penetration depth of the beam is estimated to be ~300 nm for the Ga-L line and ~40 nm for the Pd-M line, with an estimated cross-section of ~100 nm². Thus, the resolution is higher than the crystallite size of 29 nm. Nevertheless, the grains of the sample are much larger than the crystallites, thus enabling a meaningful analysis.

To learn about the electronic state of gallium and palladium as well as to detect impurities, depth profiling measurements by XPS have been carried out. Figure 3, highlighting the Pd $3d_{5/2}$, Ga 3d and valence band regions measured between 150 eV (most surface sensitive) and 750 eV (most bulk sensitive) kinetic energy of the photoelectrons, clearly show that no substantial spectral changes for any of the spectra occur. We note that the Pd $3d_{5/2}$ signal exhibits a slight shoulder on the right, which in principle implies that a second component might be present. Taking into account the binding energy of that shoulder (335.3 eV), we might explain it with the presence of the Pd-richer intermetallic compound Ga_5Pd_{13} within the bulk film corroborating the results from EDX and XRD analysis. A short comment on the shape of the Ga peak at the highest photon energies should be added. Although it is clear, that no second component or shift in binding energy is present, the Ga peak at 750 eV photon energy merges almost to a single peak - accordingly also the valance band region appears to exhibit a worse signal-to-noise ratio. This is a feature that has also been observed in the

corresponding foil experiments [15] and appears to be an intrinsic feature of the Ga peak at the highest photon energies, possibly also influenced by the decreased photon flux at higher photon energies.

To gain further insight into the surface composition, the chemical composition of the surface and near-surface layers was determined by low-energy ion scattering (LEIS) analysis. Figure 4 shows a representative LEIS spectrum of the Pd-rich GaPd$_2$ thin film after post-annealing at 673 K. The scattering peaks of both Ga and Pd are well resolved and on the basis of the sensitivity factor relation between Ga and Pd (4.5:1 for Ga:Pd, from ref. [10]), a surface composition of ~ 1:2 Ga:Pd results.

3.2. Behavior under methanol steam reforming conditions

Figure 5 shows the *in situ* XPS spectra (Pd 3d$_{5/2}$, Ga 3d and valence band region) of the thin film Pd-rich GaPd$_2$ collected under methanol steam reforming conditions at various temperatures (reaction mixture: 0.12 mbar methanol + 0.24 mbar water). As it is evident, hardly any spectral changes are visible, neither in the Pd 3d$_{5/2}$, Ga 3d nor valence band region. The Ga 3d spectrum exhibits a small oxidic peak, Ga(ox), at 20.3 eV, which nevertheless appears constant during heating in the MSR reaction mixture. Note that the peaks are generally larger at higher temperatures, which might be associated with a cleaner surface at these temperatures (this also applies to the discussion of Figure 10 below). The same trend has also been observed for the PdGa NSIP (cf. Figure 9 of ref. [10]). Note that in this Figure 9 of ref. [10], the Ga 3d doublet is of about the same size than in our spectra, but clearly also an oxidized Ga component is visible. Hence, if such a pronounced oxidized component would be present in this case, it would be also visible.

To clarify this issue, as highlighted in Figure 6, a detailed analysis of this Ga(ox) species has been carried out. As can be clearly seen, the oxidic Ga component hardly changes as a function of temperature (two representative peak deconvolutions are shown for the spectra

taken at 323 and 573 K; the signals have been fitted by two separate Ga 3d doublets; the right panel shows the entire temperature-dependence of the intermetallic Ga species and the Ga(ox) component, plotted as temperature vs. fraction of intermetallic Ga metal or Ga(ox), as deduced from the areas of the fitted peaks). In essence, the Ga(ox) species does not change during MSR. The thickness of the oxide as a layer was determined to be only 0.075 nm – well below a monolayer. This confirms the outstanding thermo-chemical stability of the Pd-rich $GaPd_2$ thin film under close to real catalytic conditions as well as the presence of intermetallic surface under reaction conditions, since full oxidation does not occur. The $GaPd_2$ bulk material, at least in its Pd-rich state, therefore appears to be also stable under the more oxidizing (as compared to a hydrogenation reaction) methanol steam reforming conditions, since diffusional loss of the surface atoms in deeper layers, as it was the case for the near-surface intermetallic Ga-Pd phases at $T > 573$ K [10], is excluded.

To further confirm the stability of the Pd-rich $GaPd_2$ thin film under characteristic steam reforming conditions, depth profiling at a temperature of 500 K, corresponding to the onset of catalytic activity, has been carried out. Figure 7 reveals the thermo-chemical bulk stability of the intermetallic compound $GaPd_2$ and confirms by absence of substantial binding energy shifts for any of the Pd $3d_{5/2}$, Ga 3d and valence band peaks the chemical homogeneity of the sample. Most important, no reaction-induced segregation of either Pd or Ga, except the already present invariant Ga(ox) intensity at 20.3 eV, has been observed at low photon energies. This component, however, is absent in deeper sample regions, as can be clearly seen by comparison of the spectra taken at higher kinetic energies of 350, 550 and 750 eV. Obviously, this component represents some residual Ga(ox) species induced by partial oxidation of the surface layer during transport in air, which was not removed by the sputtering.

Regarding the catalytic experiments, as shown in Figure 8, Pd-rich $GaPd_2$ does not show appreciable catalytic selectivity for CO_2 (about 20% at 623 K), but only a very small CO_2

formation rate (at maximum 0.006 mbar min^{-1}; 0.025 site^{-1}s^{-1}) in comparison with the higher CO formation rate (at maximum 0.019 mbar min^{-1}; 0.08 site^{-1}s^{-1}). It is worth noting, that this CO formation rate is still very small in comparison with clean elemental Pd (up to 0.6 mbar min^{-1}; 2.6 site^{-1}s^{-1}) and also with respect to the GaPd near-surface intermetallic phase (NSIP) [10], since the latter decomposes at higher reaction temperatures toward metallic Pd, in turn favoring methanol dehydrogenation on an increasing Pd metal fraction of the surface. In contrast, the Pd-rich GaPd$_2$ thin film is stable under MSR conditions, thus apart from the low MSR activity, also substantial methanol dehydrogenation toward CO does not occur. The formation rate of formaldehyde amounts to 0.009 mbar min^{-1} (0.038 site^{-1}s^{-1}) at maximum. At the maximum temperature (623 K), a methanol conversion of less than 2% is obtained indicating the very low overall activity of Pd-rich GaPd$_2$ in methanol conversion. Subsequently, Figure 9 shows the analysis of the apparent activation energy, yielding an activation energy of 110 kJ mol^{-1} on the basis of an Arrhenius plot. As the linearized Arrhenius plot (see inset in Figure 9) obeys linear behavior, changes in the activation energies during reaction are clearly absent.

Hence, basically a very small overall activity in methanol conversion is observed on the Pd-rich GaPd$_2$ thin film, rendering the latter obviously a bad choice as a steam reforming catalyst. A high CO$_2$-selectivity, as observed e.g. on GaPd$_2$/β-Ga$_2$O$_3$ [4,11], is most likely only observed once a bi-functional synergism between the intermetallic compound and the (supporting) oxide is established. The activation of water, a prerequisite for efficient CO$_2$ formation, therefore seems to be most favorable at interfacial regions or the Ga$_2$O$_3$. A comparison with the 1:1 GaPd near-surface intermetallic phase (NSIP) reveals very similar selectivity patterns, apart from a much lower CO activity of the GaPd$_2$ bulk film [10]. This basically can be referred to a higher thermal stability, because the near-surface intermetallic phase shifts to a Pd-like state due to dilution of Ga into the bulk already at 623 K [10].

3.3. Behavior under oxidative methanol steam reforming conditions

The oxidative steam reforming experiments are performed to elucidate, if the $GaPd_2$ sample is in principle capable of oxygen activation, which could help optimizing the CO_2 selectivity also over unsupported $GaPd_2$ and to subsequently efficiently suppress the CO content of the reformate gas also under continuous flow reaction conditions.

Also under oxidative steam reforming conditions (0.12:0.24:0.6 mbar methanol:water:oxygen) the Pd-rich $GaPd_2$ thin film is stable up to 523 K (Figure 10). Starting at ~ 523 K, an additional oxidized Ga species is visible at 20.3 eV, but that does not induce a shift of the "Cu-like" Pd 4d density of states to a more "Pd-like" intensity at the valence band, as it was observed for the 1:1 GaPd near-surface intermetallic phase [10]. This means that, except some additional surface-limited oxidative Ga segregation, the geometric and electronic Ga-Pd arrangement of the intermetallic compound remains mostly unaltered. Figure 11 highlights the corresponding catalytic oxidative steam reforming experiments. The CO_2 formation rate exhibits a clear rate maximum at 504 K (~ 0.3 mbar min^{-1}; 1.3 site^{-1}s^{-1}), decreases and re-increases again starting at 577 K. The total methanol conversion is under these conditions close to 50%. The CO rate smoothly increases at 435 K, exhibits an almost flat rate maximum at 520 K (maximum ~ 0.07 mbar min^{-1}; 0.3 site^{-1}s^{-1}) and starts to increase again in-parallel with CO_2 formation. Interestingly, also formic acid is formed starting at ~ 500 K, going through a rate maximum at 577 K (~ 0.2 mbar min^{-1}; 0.86 site^{-1}s^{-1}) and finally being totally consumed (negative rate maximum). The question now arises how to interpret this rather peculiar selectivity pattern. Obviously, the intermetallic compound $GaPd_2$ or the Ga(ox) species are indeed capable of efficient oxygen activation and thus of total oxidation of methanol, leading to the observed maximum in the CO_2 formation rate. CO formation could not be totally suppressed. In general, the methanol conversion is one order of magnitude higher than without the presence of O_2. The selectivity pattern above 520 K very much resembles the one observed for pure Ga_2O_3 [4] and is further complicated by the thermal

decomposition of formic acid above 573 K, leading to the observed negative formation rate. However, as formic acid has only been observed over pure Ga_2O_3, but never over small $GaPd_2$ particles supported on β-Ga_2O_3, the selectivity pattern can only consistently be interpreted by the presence of oxidized Ga species formed during the oxidative steam reforming reaction. This is in good agreement with the appearance of reaction-induced oxidized Ga species in the Ga 3d spectra (cf. Figure 10), indicating that the surface regions are oxidized, and above 573 K, only the catalytic activity and selectivity pattern of the pure oxidized Ga species, presumably Ga_2O_3, are measured. As the decrease of the HCOOH partial pressure coincides with the increase of CO_2 and CO, HCOOH is likely the central intermediate of both total oxidation toward CO_2 and CO formation, as already shown for β-Ga_2O_3 [4]. The catalytic pattern in oxidative steam reforming therefore seems to consist of two mechanistic regimes: total oxidation of methanol on $GaPd_2$ and unselective methanol reforming on H_2O/O_2-induced segregated Ga_2O_3. The H_2-mass balance in oxidative steam reforming (OSR) up to ~ 540 K yields a very similar pattern as the one observed for the Ga-Pd near-surface intermetallic phase, where the overwhelming fraction of methanol was totally oxidized to CO_2 and water (~87%) and only a minor fraction partially oxidized to CO_2 and H_2 (13%) [10].

4. Discussion

Based on previous experiments on Ga_2O_3-supported small intermetallic GaPd particles and studies on a surface-near intermetallic 1:1 GaPd phase, we aimed at an understanding of the catalytic properties of the unsupported Pd-rich intermetallic compound $GaPd_2$. Reviewing the previous experiments, we observed that supported $GaPd_2$ particles were very CO_2-selective in methanol steam reforming (> 95%), but turned out to be less sinter-stable than their ZnPd counterparts [4]. Also the 1:1 GaPd surface-near intermetallic phase was found to be thermally unstable and, due to the missing Ga_2O_3 interface, hardly any CO_2-selectivity/activity was observed [10]. Assuming that a realistic model of the $GaPd_2$ bulk

material could be obtained, two features were anticipated: In the first place, the $GaPd_2$ bulk film should not be CO_2-selective/active, as the interaction with the Ga_2O_3 support is missing. Secondly, the $GaPd_2$ bulk material should be thermally stable, since a diffusion of Ga into deeper layers of the Pd bulk, as it was the case for the thermodynamically metastable surface-near intermetallic phase [10], is not possible. In fact, both assumptions were proven by the results presented in the preceding chapter. With these results in hands, a clearer picture of the catalytic action of $GaPd_2/\beta$-Ga_2O_3 in methanol steam reforming evolves. Regarding the explanation of the overall CO_2-selectivity of this catalyst, there is common agreement, that - although the intrinsic catalytic property of unsupported $GaPd_2$ was not known - the presence of $GaPd_2$ is a must to obtain a high CO_2-selectivity. In contrast, although previously neglected, the catalytic capabilities of β-Ga_2O_3 in methanol steam reforming have also been worked out in detail. Pure β-Ga_2O_3, without contact to $GaPd_2$, is a poor methanol steam reforming catalyst. Together, $GaPd_2$ and β-Ga_2O_3 form a highly selective catalytic entity. With highlighting the unquestionably poor performance of a Pd-rich $GaPd_2$ thin film in methanol steam reforming, the last, but nevertheless highly important piece of information has been added: $GaPd_2$, at least in its Pd-enriched state, itself is also a poor methanol steam reforming catalyst, as has been shown for ZnPd [16-18]. This of course renders a scenario of a bimetal-oxide bi-functional synergism highly likely. Having said that, such a synergism has also been proposed in a recent paper by Haghofer et al., who highlighted the important role of β-Ga_2O_3 in contact with $GaPd_2$ [23]. In short, the entire catalytic process was ascribed to proceed on the defective Ga_2O_3 surface after high-temperature reduction in hydrogen, with the intermetallic compound $GaPd_2$ essentially supplying methoxy groups (via decomposition of methanol), which are converted via monodentate formate species and OH to CO_2 and H_2. Note that this pathway is crucially different from what was observed on oxidized β-Ga_2O_3, for which no pronounced CO_2-selectivity has been detected [4].

The catalytic differences between the single constituents and the synergistically acting complex catalyst system are also reflected in a comparison of the CO_2-TOF related values and the corresponding apparent activation energies. For better comparison, TOF values – derived as described in the Experimental Section – extrapolated to 500 K are reported. The Pd-rich $GaPd_2$ thin film exhibits a CO_2-TOF of $\sim 10^{-3}$ s^{-1} at 500 K, which is considerably higher than pure β-Ga_2O_3, for which 6×10^{-6} s^{-1} is estimated from measurements at higher temperatures [4], but well below the CO_2-TOF of the corresponding $GaPd_2/\beta$-Ga_2O_3 system (0.01 s^{-1}) [4]. The same trend is also visible in the apparent activation energies: 130 kJ mol^{-1}, 110 kJ mol^{-1} and 61 kJ mol^{-1} are reported for pure β-Ga_2O_3 [4], Pd-rich $GaPd_2$ and $GaPd_2/\beta$-Ga_2O_3 [4], respectively. A synergistic action of both constituents is therefore evident. Quite recently, such a bi-functional synergism has also been established for the methanol synthesis reaction from CO_2 and H_2 over Ga_2O_3-supported Pd-Ga nanoparticles. Bonivardi and co-workers clearly showed that the stepwise hydrogenation of (bi)carbonate to formate and then to methoxy groups on Ga_2O_3 took place via a bi-functional pathway and that the sole role of the Ga-Pd intermetallic particles was the provision of activated hydrogen, in turn spilling over to the oxidic surface for further reaction [24]. Another important prerequisite for CO_2-selective MSR is moreover the capability of the dopant Ga to block "full dehydrogenation" of methanol via formaldehyde toward CO. We regard also this property proven by the presented study, as bulk $GaPd_2$ exhibits a 30 times lower TOF of CO formation, as compared to clean Pd. This "bimetal-intrinsic" residual CO activity may explain the remaining 5% of CO in the reformate obtained on the supported catalyst. On the other hand, intermediate formaldehyde was never observed on supported $GaPd_2/\beta$-Ga_2O_3, indicating fast conversion of the latter assisted by the bimetal-oxide synergism toward CO_2 [4]. Thus, the overall mechanistic picture necessarily comprises blocking of the "full dehydrogenation" pathway to CO along with optimized water activation and thus accelerated conversion of e.g. HCHO to CO_2. The latter total oxidation mechanism is inhibited on unsupported Pd-rich $GaPd_2$, thus this system remains at low

activity without opening of this crucial reaction channel. Finally, the detailed mechanism of the conversion of formaldehyde toward CO_2 needs further clarification. There is a broad range of mechanistic possibilities between the purely H_2-associated role of Ga_xPd_y [25] and the formation of intermediates such as dioxomethylene [26] or hydroxymethoxy [26], which may occur on the electronically "Cu-like" intermetallic $GaPd_2$ surface once water activation at the phase boundary region can supply oxygen-containing species such as $-OH_{ads}$ to the bimetallic surface (which for itself is obviously not capable of efficient water activation). In essence, a complex spillover/reverse spillover scenario of different intermediates is conceivable, minimizing not only the desired reaction pathway barriers, but also selectively increasing those of the unwanted elementary reaction steps.

5. Conclusion

The presented results represent a considerable step closer to the full understanding of the Ga_2O_3-supported system, and moreover, the impact on the understanding of the other members of the group of CO_2-selective, oxide-supported Pd-based intermetallic compounds cannot be underestimated. Since Pd/ZnO, Pd/Ga_2O_3 and Pd/In_2O_3 all exhibit a similar catalytic performance in CO_2-selective methanol steam reforming after entering the oxide-supported bimetallic state [11], it is tempting to transfer the mechanistic implications obtained for $GaPd_2$/Ga_2O_3 results also to the corresponding Pd/ZnO and Pd/In_2O_3 systems. In fact, for ZnPd bulk [16], pure ZnO [17] and ZnPd/ZnO [17, 27] exactly the same trend in apparent activation energies has been observed. These activation energies increase from 69-93 kJ mol^{-1} [17,27] for ZnPd/ZnO over 120 kJ mol^{-1} [16] for ZnPd bulk materials to > 130 kJ mol^{-1} for pure ZnO [17]. Hence, a bi-functional synergism may also be prevalent in the Pd/ZnO system, which has been recently also made visible by aberration-corrected HRTEM measurements, clearly showing the presence of oxidized Zn patches on top of the ZnPd particles in the CO_2-selective state of the catalyst during MSR [18]. The CO_2-TOF values of bulk ZnPd still

remain to be determined, although recent experiments on near-surface intermetallic Pd:Zn 1:1 phases could point to a synergistic action, because the CO_2-TOF values of that phase at 500 K with $2 \cdot 10^{-3}$ s^{-1} [28] is placed exactly in-between those of pure ZnO ($5 \cdot 10^{-6}$ s^{-1}) [17] and ZnPd/ZnO (0.8 s^{-1}) [17]. The Pd/In_2O_3 system is somewhat placed out of line, since its CO_2-selective oxide-supported representative (InPd/bcc-In_2O_3) is strongly prone to enter a state of strong-metal support interaction at high reduction temperatures and is correspondingly deactivated with respect to the InPd near-surface intermetallic phase, which makes a clear correlation not straightforward [29, 30].

The logical extension to fully resolve the influence of the intermetallic/oxide phase boundary on the catalytic performance of the entire CO_2-selective catalytic entity of small oxide-supported intermetallic particles would hence require the preparation of small $GaPd_2$ (or ZnPd and InPd) *particles* on an inactive (e.g. SiO_2 or Al_2O_3) support. Using this approach, also the catalytic properties of the isolated nanoparticle-sized intermetallic particles could finally be elucidated and compared to the corresponding Ga_2O_3-, ZnO- and In_2O_3-supported intermetallic particles, representing the vast majority of studied systems.

References

[1]   L. Shao, W. Zhang, M. Armbrüster, D. Teschner, F. Girgsdies, B. Zhang, O. Timpe, M. Friedrich, R. Schlögl, D. S. Su, Angew.Chem.Intl.Ed. 50 (2011) 10231-10235.

[2]   A. Ota, M. Armbrüster, M. Behrens, D. Rosenthal, M. Friedrich, I. Kasatkin, F. Girgsdies, W. Zhang, R. Wagner, R. Schlögl, J.Phys.Chem.C 115 (2011) 1368-1374.

[3]   M. Armbrüster, K. Kovnir, M. Behrens, D. Teschner, Yu. Grin, R. Schlögl, J.Am.Chem.Soc. 132 (2010) 14745-14747.

[4]   H. Lorenz, S. Penner, W. Jochum, C. Rameshan, B. Klötzer, Appl.Catal.A 358 (2009) 203-210.

[5]   A. Haghofer, K. Föttinger, F. Girgsdies, D. Teschner, A. Knop-Gericke, R. Schlögl, G. Rupprechter, J.Catal. 286 (2012) 13-21.

[6]   L. Li, B. Zhang, E. Kunkes, K. Föttinger, M. Armbrüster, D. S. Su, W. Wei, R. Schlögl, M. Behrens, ChemCatChem 4 (2012) 1764-1775.

[7]   H. Kohlmann, J.Solid State Chem. 183 (2010) 367-372.

[8]   A. Haghofer, K. Föttinger, M. Nachtegaal, M. Armbrüster, G. Rupprechter, J. Phys. Chem. C 116 (2012) 21816-21827.

[9]   S. Penner, H. Lorenz, W. Jochum, M. Stöger-Pollach, D. Wang, C. Rameshan, B. Klötzer, Appl.Catal.A 358 (2009) 193-202.

[10] C. Rameshan et al. J. Catal. 290 (2012) 126-137

[11] N. Takezawa , N. Iwasa, Catal. Today 36 (1997) 45-56

[12] K. Schubert, H. L. Lukas, H.-G. Meißner, S. Bhan, Z.Metallk. 50 (1959) 534-540.

[13] K. Kovnir, M. Schmidt, C. Waurisch, M. Armbrüster, Yu. Prots, Yu. Grin, Z.Kristallogr.- NCS 223 (2008) 7-8.

[14] C. Wannek, B. Harbrecht, J.Alloys Compd. 316 (2001) 99-106.

[15] H. Lorenz, C. Rameshan, T. Bielz, N. Memmel, W. Stadlmayr, L. Mayr, Q. Zhao, S. Soisuwan, B. Klötzer, S. Penner, ChemCatChem 5 (2013), doi: 10.1002/cctc.201200712

[16] M. Friedrich, D. Teschner, A. Knop-Gericke, M. Armbrüster, J.Catal 285 (2012) 41-47

[17] H. Lorenz, M. Friedrich, M. Armbrüster, B. Klötzer, S. Penner, J.Catal. 297 (2013) 151-154

[18] M. Friedrich, S. Penner, M. Heggen, M. Armbrüster, Angew.Chem.Int.Ed. 52 (2013) 4389-4392

[19] H. Bluhm, M. Havecker, A. Knop-Gericke, E. Kleimenov, R. Schlögl, D. Teschner, V. I. Bukhtiyarov, D. F. Ogletree and M. Salmeron, J. Phys. Chem. B 108 (38), (2004) 14340-14347

[20] RAPPTURE, NIST Database #71 and #82, CasaXPS. Refer to manual for detailed citations; K. Smith, D. A. Saenz, D. Zemlyanov, A. A Voevodin (2012), "XPS Thickness Solver," https://nanohub.org/resources/xpsts. (DOI: 10.4231/D3N29P603)

[21] W. Reichl, G. Rosina, G. Rupprechter, C. Zimmermann and K. Hayek, Rev. Sci. Instr. 71 (3) (2000) 1495-1499

[22] C. Zimmermann, K. Hayek, Chem. Ing. Tech. 63 (1991) 6-10

[23] A. Haghofer, D. Ferri, K. Föttinger, G. Rupprechter, ACS Catalysis 2 (11) (2012) 2305-2315

[24] S. E. Collins, J. J. Delgado, C. Mira, J. J. Calvino, S. Bernal, D. L. Chiavassa, M. A.

Baltanas, A. L. Bonivardi, J. Catal. 292 (2012) 90-98

[25] D. L. Chiavassa, J. Barrandeguy, A. L. Bonivardi, M. A. Baltanas, Catal. Today 133-135 (2008) 780-787

[26] C. Rameshan, W. Stadlmayr, S. Penner, H. Lorenz, M. Hävecker, R. Blume, T. Rocha, D. Teschner, A. Knop-Gericke, R. Schlögl, N. Memmel, D. Zemlyanov, B. Klötzer Angew. Chemie 124 (2012) 3057-3061

[27] Y. Chin, R. Dagle, J. Hu, A. Dohnalkova, Y. Wang, Catal. Today 77 (2002) 79-88

[28] C. Rameshan et al. J. Catal. 276 (2010) 101-113

[29] H. Lorenz, O. Lebedev, S. Turner, B. Klötzer, S. Penner, Appl. Catal. A 374 (2010) 180-188

[30] C. Rameshan, H. Lorenz, L. Mayr, S. Penner, D. Zemlyanov, R. Arrigo, M. Haevecker, R. Blume, A. Knop-Gericke, R. Schlögl, B. Klötzer, J. Catal. 295 (2012) 186-194

Figure captions

Figure 1: XRD pattern of the initial $GaPd_2$ thin film after background correction. All major reflections can be assigned to the orthorhombic $GaPd_2$ structure (grey). Two reflections, possibly attributable to a very small amount of Ga_5Pd_{13}, are marked by asterisks.

Figure 2: a) Secondary-electron contrast image of the thin film $GaPd_2$ sample (flake-like piece). b) and c) show the EDX-mapping of a region of the sample using the Ga-L and Pd-M lines, respectively. Images were obtained at beam acceleration voltage of 20 keV.

Figure 3: Depth profiling of the $GaPd_2$ thin film. Pd $3d_{5/2}$ (left), Ga 3d (middle) and valence band region (right), measured at resulting kinetic energies of 150, 350, 550 and 750 eV.

Figure 4: Low energy ion scattering profile of the $GaPd_2$ thin film. The peak at 835 eV is associated with Ga, the one at 890 eV with Pd.

Figure 5: Pd $3d_{5/2}$ (left), Ga 3d (middle) and valence band region (right), taken during a methanol steam reforming reaction (0.12 mbar methanol+0.24 mbar water) starting from the $GaPd_2$ sample prepared by alternating layer deposition of Pd and Ga. For maximum surface sensitivity, the Pd $3d_{5/2}$ signal has been measured at 470 eV photon energy, the Ga 3d and valence band signals with 170 eV.

Figure 6: Deconvoluted Ga 3d XPS spectra of the top-most (cf. 573 K) and bottom-most (cf. 323 K) spectra shown in the central panel of Figure 5 (left panel). The right panel shows the temperature-dependent fraction of Ga metal and Ga(ox) species, as deduced from the areas of the respective deconvoluted Ga 3d components. Both components have been fitted by individual 3d doublets. Photon energy: 170 eV.

Figure 7: Depth profiling of the $GaPd_2$ thin film under steam reforming conditions at a reaction temperature of 500 K. Pd $3d_{5/2}$ (left), Ga 3d (middle) and valence band region (right), measured at at resulting kinetic energies of 150, 350, 550 and 750 eV.

Figure 8: Temperature-programmed methanol steam reforming reaction on the $GaPd_2$ thin film sample. Reaction conditions: 12 mbar methanol, 24 mbar water, 1000 mbar He. Linear ramp (8 K/min) up to 623 K, subsequent isothermal reaction at 623 K for 25 min.

Figure 9: Turnover frequencies for CO_2 as a function of reaction temperature. The experimental curves have been fitted by an Arrhenius function to determine the apparent activation energy. The inset shows a linearized Arrhenius plot.

Figure 10: Pd $3d_{5/2}$ (left), Ga 3d (middle) and valence band region (right), taken during an oxidative methanol steam reforming reaction (methanol 0.07 mbar, water: 0.14 mbar, oxygen: 0.035 mbar, total pressure 0.25 mbar) starting from the $GaPd_2$ thin film. For maximum surface sensitivity, the Pd $3d_{5/2}$ signal has been measured at 470 eV photon energy, the Ga3d and valence band signals with 170 eV.

Figure 11: Temperature-programmed oxidative methanol steam reforming reaction on the $GaPd_2$ thin film sample. Reaction conditions: 50 mbar methanol/water/oxygen mixture (ratio 1:2:0.5 at room temperature in the gas phase, including 7.5 mbar Ar to correct for the gas withdrawal due to mass spectrometry, He added to 1 bar total pressure). Linear ramp up to 623 K (5 K/min).