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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 has been detected during catalytic MSR reaction. Corroborating these observations, corresponding catalytic experiments under methanol steam reforming conditions revealed only a, in comparison with 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 the 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 Takezawa and Iwasa [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].

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$GaPd_2$ itself crystallizes in the Co_2Si type of crystal structure [12] (Pearson symbol *oP*12, 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 $GaPd_2/Ga_2O_3$ 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_2O_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 are 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 in $GaPd_2$. These studies are complemented by catalytic studies to unambiguously correlate the composition of the surface/bulk structure with the observed catalytic properties.

2. Experimental

2.1. Preparation of the $GaPd_2$ 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 × 20 × 0.125 mm), which was pre-cleaned with abrasive paper and cleaned in boiling hot water and hot ethanol. To stimulate the 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 5×10^{-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 layers were 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 were 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.

2.2. X-ray diffraction (XRD)

Powder X-ray diffraction was conducted on a STOE-STADIP-MP powder diffractometer in Bragg–Brentano geometry (Cu $K_{\alpha 1}$-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.

2.3. 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).

2.4. 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].

2.5. 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, $I_{Ga}(\text{normalized}) = I_{Ga}/(I_{Pd} + I_{Ga})$ and $I_{Pd}(\text{normalized}) = I_{Pd}/(I_{Pd} + I_{Ga})$. The Pd and Ga scattering cross sections valid for our specific setup were determined by measurement of clean