In situ study of the formation and stability of supported Pd$_2$Ga methanol steam reforming catalysts

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ABSTRACT

Pd/Ga$_2$O$_3$ methanol steam reforming (MSR) catalysts were characterized in detail by utilizing a range of *in situ* techniques of varying surface sensitivity. Correlating the nature of the intermetallic Pd–Ga compound (IMC; formed upon reduction) with the corresponding activity/selectivity revealed pronounced differences. Generally, a dynamic response of the catalyst surface to the surrounding gas environment was observed. Special attention was paid to the bulk and surface stability of the Pd–Ga IMCs. Whereas the bulk was stable in O$_2$, decomposition of the surface occurred resulting in a partial coverage by Ga$_x$O$_y$ islands. In addition, the main formation mechanism of undesired CO and therefore the reason limiting the selectivity to MSR were identified. CO was shown to have a detrimental effect on the selective Pd–Ga intermetallic compound, causing partial decomposition of the IMC to metallic Pd at the surface. Consequently, patches of Pd metal are present under reaction conditions, catalyzing the unwanted parallel methanol decomposition reaction.

1. Introduction

Hydrogen is considered as one of the most promising and clean energy carriers of the future, especially in combination with fuel cells. It can be produced from a variety of resources including bio-feedstock. One of the major processes for hydrogen production is steam reforming of hydrocarbons or oxygenates. Among the latter, methanol is especially interesting for on-board production of hydrogen [1–5], since it is easy to store, transport, and handle.

Cu-based catalysts are highly active and selective for methanol steam reforming [2,6–9]. High selectivity to CO$_2$ and H$_2$ production is crucial due to the poisoning effect of CO on fuel cell anodes in polymer electrolyte membrane fuel cells (PEMFC), requiring <20 ppm CO in the H$_2$ fuel [10]. Pd supported on ZnO has attracted much attention due to its superior stability compared with Cu/ZnO [3,11,12]. In contrast to Pd on inert supports such as SiO$_2$ or active carbon, which catalyzes methanol decomposition to CO and H$_2$ [13], Pd on ZnO, Ga$_2$O$_3$, and In$_2$O$_3$ can show high activity and selectivity for steam reforming to CO$_2$ and H$_2$ [14,15].

Several explanations were proposed for the remarkable alteration in the catalytic properties on certain supports, such as the formation of Pd–Zn, Pd–Ga, and Pd–In alloys. By XPS and UPS valence band studies, it was found that the electronic properties of the 1:1 PdZn alloy resemble those of metallic Cu [16,17], which was confirmed by DFT density of states calculations [18,19]. Using DFT, Neyman et al. [18] calculated reaction barriers for methoxy dehydrogenation to CO and H$_2$ on Pd, PdZn, and Cu surfaces and found similar barriers for the dehydrogenation of intermediate formaldehyde to CO on Cu and PdZn, which are both notably higher than on Pd. These findings could explain the excellent selectivity of PdZn to MSR, similar to Cu.

While several research groups studied Pd/ZnO MSR catalysts, less work was dedicated to Pd/Ga$_2$O$_3$. Pd and Ga can form a number of intermetallic compounds (IMC) and/or alloys; e.g., Pd$_2$Ga, PdGa, Pd$_3$Ga$_7$, and PdGa$_5$ were reported in literature [20]. Metallurgically prepared, unsupported intermetallic bulk materials have been studied in recent years, showing excellent catalytic properties for selective hydrogenation of acetylene in excess ethylene [21–24].

Ga$_2$O$_3$ on its own exhibits interesting catalytic properties as well, e.g., Ga$_2$O$_3$ supported on zeolites is active in the dehydrogenation and aromatization of light alkanes [25–28]. Recently, the

influence and role of oxygen defects on β-Ga$_2$O$_3$ samples was investigated for the (reverse) water–gas shift reaction [29,30] by systematically studying the interaction with H$_2$, CO$_2$, CO, and H$_2$O after different pretreatments. In another work, Ga$_2$O$_3$ supported on TiO$_2$ showed remarkable activity for steam reforming of dimethylether [31]. Bonivardi and coworkers [32] studied the interaction of Ga$_2$O$_3$ and Pd/Ga$_2$O$_3$ with H$_2$ and CO$_2$ for methanol synthesis. In contrast to Iwasa's work, they did not observe Pd–Ga alloy formation [33]. They attributed the catalytic activity for methanol synthesis to the reaction of polydentate carbonates with dissociatively adsorbed hydrogen on the Ga$_2$O$_3$ surface, while the addition of Pd only accelerates the reaction by spillover of hydrogen [32]. Penner et al. [34] and Lorenz et al. [35], however, did observe Pd–Ga alloying and improved selectivity in steam reforming in a study focusing on Pd/Ga$_2$O$_3$ thin-film model catalysts, but identified different intermetallic compounds than Iwasa's group.

By utilizing a range of in situ techniques with varying bulk and surface sensitivities, we have explored in detail the structure, electronic properties, available surface sites, and catalytic properties of Pd/Ga$_2$O$_3$ MSR catalysts under pretreatment and reaction conditions. Questions that were addressed include which phase forms during H$_2$ reduction as well as under actual MSR conditions and what is the stability of the intermetallic phases formed in different atmospheres. Special attention was paid to combining information on surface and bulk properties of the materials. The characterization and stability data were correlated with the catalytic properties to identify the pathways leading to the formation of residual unwanted CO.

2. Experimental

2.1. Materials

Ga$_2$O$_3$-supported Pd catalysts were prepared by incipient wetness impregnation of commercial β-Ga$_2$O$_3$ (Alfa Aesar, 99.99% purity, particle size <250 μm). The Ga$_2$O$_3$ surface area was determined by the adsorption of N$_2$ according to BET and amounted to 7 m^2/g. Metal loadings of 2 and 5 wt.% were prepared by varying the amount of palladium(II) acetate (Fluka) precursor dissolved in toluene (Merck, p.a.). After impregnation, the catalysts were dried at 373 K for 48 h and subsequently calcined at 773 K for 4 h in static air. Reduction of the catalysts was performed in situ, except for transmission electron microscopy measurements for which samples were reduced externally.

2.2. In situ X-ray diffraction (XRD)

In situ XRD experiments were performed on a STOE Theta/Theta diffractometer (Cu Kα radiation, secondary monochromator, and scintillation counter) operating in reflection scan mode. The diffractometer is equipped with an Anton Paar XRK 900 high-temperature gas cell. In situ diffraction patterns were recorded in a 2θ range from 32.5° to 47.5° with a step size of 0.02° and a time per step of 2 s. The calcined sample (5 wt.% Pd/Ga$_2$O$_3$) was preoxidized at 773 K in a 20% O$_2$/He mixture, then cooled to 303 K, and flushed in He. The atmosphere was then changed to a flow of 25% H$_2$ in He, and the diffraction pattern was recorded. To check for the presence of Pd–hydride, the cell was subsequently flushed in He once more before starting the temperature-programmed reduction in H$_2$/He from 303 K to 773 K with diffractograms being recorded at temperature plateaus in steps of 25 K. An analogous temperature-programmed experiment was performed in the absence of H$_2$, i.e., in a flow of pure He. All experiments were performed at ambient pressure at a total flow of 100 ml/min.

2.3. Transmission electron microscopy (TEM)

Transmission electron micrographs were acquired with a 200 kV FEI TECNAI F20 S-TWIN analytical transmission electron microscope, equipped with a field emission source. TEM specimens were prepared by dipping a holey carbon–coated copper grid into the fine sample powders. Before microscopy, catalyst samples were reduced (ex situ) in a H$_2$ flow for 120 min. Reduction temperatures were 303 K and 673 K.

2.4. In situ X-ray photoelectron spectroscopy (XPS)

In situ XP-spectroscopy experiments were performed at the ISISS beamline at BESSY II (Helmholtz-Zentrum Berlin) at photon energies between 160 and 1120 eV and normal electron emission. The setup allows for in situ photoemission studies in the mbar range and has been described in detail, e.g., in [36]. Hydrogen and oxygen gas were introduced into the system by calibrated mass flow controllers. All spectra were corrected for synchrotron beam current, incident photon flux, and energy-dependent photoionization cross sections [37]. Binding energy calibration, to account for small shifts due to sample charging, was done by keeping the main Ga^{3+} signal originating from the bulk Ga$_2$O$_3$ support at 20.55 eV and additionally recording valence band spectra at the same excitation energy. Peak deconvolution was performed using the software XPSPeak 4.1 by fitting symmetric Gauss–Lorentz sum functions with the exception of Pd metal for which an asymmetric peak shape was used (described by the parameters TS (peak shape asymmetry) and TL (tail extension asymmetry)).

2.5. In situ FTIR spectroscopy

FTIR spectra were recorded in transmission mode on a Bruker IFS 28 spectrometer using an MCT detector at a resolution of 4 cm^{-1}. The calcined samples were pressed into self-supporting wafers (6 mm in diameter, $m \approx 10$ mg) and placed into a small transmission flow cell with CaF$_2$ windows, equipped with a ring-shaped furnace and a type-K thermocouple mounted to the sample holder. A spectrum recorded without sample in a flow of He was used as a background that was subtracted from all spectra. Typically, about 100 scans were summed up, so that recording an IR spectrum took less than 1 min. All pretreatments were performed in situ inside the cell using gas flows introduced via calibrated mass flow controllers.

In the temperature-programmed reduction experiment, the sample was reduced for 60 min in 25% H$_2$/N$_2$ at each temperature ranging from 303 K to 673 K (the maximum temperature in the current cell construction), flushed, and cooled to room temperature in pure N$_2$ before switching to the 5% CO/He mixture (p_{CO} = 50 mbar) used for adsorption. Before reduction at the next (higher) temperature, CO was removed from the surface by heating to 673 K in a flow of N$_2$.

In the in situ experiment performed under methanol steam reforming turnover, the sample was reduced at 303 K and 673 K in an analogous way, then flushed in pure N$_2$ at 673 K, and cooled to the desired reaction temperature before switching to the steam reforming feed containing CH$_3$OH and H$_2$O at a molar ratio of 1:1 (p_{CH3OH} = p_{H2O} = 10 mbar).

2.6. Catalytic measurements

Methanol steam reforming (MSR) and reverse water–gas shift (RWGS) studies were carried out in a continuous fixed-bed flow reactor (d = 4 mm) at reaction temperatures between 493 and 573 K and atmospheric pressure. All gases were introduced via calibrated mass flow controllers. In MSR, separate He flows were