In situ Studies of Alloy Formation on a Pd/Ga\textsubscript{2}O\textsubscript{3} Methanol Steam Reforming Catalyst

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Introduction

Methanol steam reforming is a promising reaction in terms of hydrogen production for use in PEM fuel cells. Catalyst research has focused mainly on Cu/ZnO formulations, because of their superior selectivity to CO\textsubscript{2} and H\textsubscript{2}. The common byproduct CO is problematic due to its poisoning effect on the anode of a downstream fuel cell. Some years ago it was shown that palladium supported on certain reducible oxides (ZnO, Ga\textsubscript{2}O\textsubscript{3}, In\textsubscript{2}O\textsubscript{3}) matches the copper based catalysts in selectivity while providing a higher thermal stability [1]. As a reason for the improved selectivity the formation of an alloy or intermetallic compound (IMC) between Pd and the reduced support has been suggested. The aim of this work was the investigation of alloy formation on a 5 wt% Pd/Ga\textsubscript{2}O\textsubscript{3} powder catalyst under reducing conditions. The bulk information obtained by in situ XRD was complemented by the surface sensitive information from IR spectroscopy and in situ XPS.

Experimental

Experimental methods in this work were IR spectroscopy, in situ XRD and in situ XPS. IR spectra were recorded in transmission on a Bruker IFS28 spectrometer. CO was adsorbed at room temperature after reducing the catalyst at different temperatures. In situ XRD in different atmospheres (H\textsubscript{2}/He, He, O\textsubscript{2}/He) was performed on a STOE Theta/theta Bragg-Brentano diffractometer equipped with an Anton Paar XRK 900 reactor chamber. The temperature was raised in steps of 25 K to follow alloy/IMC formation. In situ XPS was performed at the ISSIS beamline at BESSY in Berlin, with the possibility of working at mbar pressures and at varying information depth. Ga3d signals were recorded at a hydrogen pressure of 0,25 mbar and temperatures of 448, 523 and 623 K.

Results and discussion

In situ XRD measurements show the onset of alloy formation at 548 K in a flow of 25 % H\textsubscript{2} in He. Analogous measurements in a flow of pure He showed no alloying thereby excluding a pure thermal effect. Selected diffractograms are shown in Fig. 1(a). An unambiguous identification of the compound formed on the powder catalyst is difficult, likely candidates are Pd\textsubscript{2}Ga, PdGa and PdGa\textsubscript{5}. IR spectroscopy of room temperature CO adsorption after H\textsubscript{2} reduction temperatures of 303, 423, 523 and 623 K are shown in Fig. 1(b). Reduction at room temperature leads to the typical spectrum of CO on metallic Pd particles. Increasing reduction temperatures lead to a decreased amount and at T\textsubscript{reduction} ≥ 423 K to a total disappearance of bridge- and multiply bonded CO, indicating an isolation of Pd atoms by alloy/IMC formation. At the same time the intensity of linearly adsorbed CO decreased pointing to a reduced Pd surface area. In situ XPS showed an increasing amount of reduced Ga species at increased
temperature in 0.25 mbar H₂. Metallic Gallium forms above 523 K on the Pd/Ga₂O₃ catalyst, in contrast to pure Ga₂O₃ under the same conditions.

Figure 1. (a) Selected x-ray diffractograms recorded in H₂/He at the indicated temperatures (b) IR spectra of CO adsorbed at 303K after reduction at the indicated temperatures.

Conclusions

The formation of a bulk alloy/intermetallic compound between Pd nanoparticles and reduced Ga from the support set in at a T_{\text{reduction}} of 548 K. IR spectroscopy indicated a site isolation at the surface, possibly accompanied by a decreased Pd surface area at higher T_{\text{reduction}}. In situ XPS showed increasing amounts of metallic Ga during H₂ treatments in the temperature region where bulk alloying was shown to set in by XRD. Reactivity studies in methanol steam reforming are currently being performed.

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References