Journal of Catalysis 340 (2016) 49–59

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Controlled synthesis and catalytic properties of supported In–Pd intermetallic compounds

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ARTICLE INFO

Article history:
Received 24 March 2016
Revised 10 May 2016
Accepted 10 May 2016
Available online 6 June 2016

Keywords:
InPd
In_3Pd_2
In_7Pd_3
In_2O_3
MSR
CO_2 selective
Methanol steam reforming

ABSTRACT

DTA/TG/MS measurements were used to investigate the temperature-dependent and successive phase formation of different intermetallic In–Pd compounds by controlled reduction of PdO/In_2O_3 with hydrogen. Reduction procedures were developed to obtain supported intermetallic InPd and In_3Pd_2 particles by reactive metal–support interaction (RMSI) without detectable amounts of other compounds. In_7Pd_3 could only be obtained in admixture with elemental indium due to the direct reduction of the In_2O_3 support at temperatures above 350 °C.

All materials exhibit catalytic activity for methanol steam reforming and exhibit high CO_2 selectivities up to 98%. Long-term measurements proved the superior stability of the $In–Pd/In_2O_3$ materials in comparison with Cu-based systems over 100 h times on stream with high selectivity.

1. Introduction

The depletion of fossil energy carriers as well as the increasing demand of energy worldwide led to an intensification in the research for alternative energy sources. Renewable energies and secondary energy carriers such as hydrogen have gained much attention in the recent years especially with the advances of fuel cell technology [1–5].

Hydrogen is today mainly produced by reforming hydrocarbons [6–8]. Another possibility intensively studied momentarily is the development of better electrodes for electrochemical water splitting [9,10]. Hydrogen itself has a relatively low volumetric energy density (0.0107 MJ/L [11]). Therefore it has to be compressed or liquefied to improve the transportation efficiency. Besides the physical storage of hydrogen the chemical storage in the form of metal hydrides or small chemical compounds, e.g. methanol, is likely to be of great importance and is studied broadly [12]. Up to now, the storage capacity in metal hydrides is too low and lacks materials exhibiting easy and fast hydrogen charging and discharging [3,4]. Compared to gasoline (34.2 MJ/L [11]), methanol has a relatively high energy density per volume (16 MJ/L [13]) and is a liquid, easing handling and transport. The often discussed drawback of the toxicity of methanol relativizes comparing the $LD50_{oral}$ values of methanol (rat ~ 5600 mg/kg [14]) and gasoline (rat ~ 15,000 mg/kg [15]) and considering the carcinogenic effects of the latter. This makes methanol a promising hydrogen storage candidate with high potential in a future hydrogen-based energy infrastructure.

Methanol steam reforming (MSR) is a smart method to release the chemically stored hydrogen from methanol and water mixtures [16]. Thereby methanol is reacting with one water molecule forming three molecules of hydrogen and the by-product CO_2 according to reaction Eq. (1).

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (1)$$

$$CH_3OH \rightarrow 2H_2 + CO \quad (2)$$

Besides this preferred reaction, decomposition of methanol can take place (Eq. (2)) leading to a lower hydrogen content in the product stream and, more importantly, to the formation of CO. To ensure most efficient use of hydrogen in PEM fuel cells, the CO concentration has to be lower than 10–30 ppm since higher contents

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http://dx.doi.org/10.1016/j.jcat.2016.05.006
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lead to strong deactivation of the PEM fuel cell [17]. Therefore a high selectivity toward steam reforming instead of methanol decomposition has to be ensured. To complicate things, both reaction pathways are linked by the water gas shift reaction (Eq. (3)).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

$Cu/ZnO/Al_2O_3$ catalysts can be applied to methanol steam reforming, showing high activity and selectivity [16]. The major drawback of these catalysts is a high deactivation rate, especially at temperatures above 300 °C due to sintering of the copper particles [18]. Materials circumventing deactivation were found by Iwasa et al. who investigated several noble metal-based catalytic systems with easily reducible oxides as support [19–21]. After reduction at elevated temperatures intermetallic compounds, i.e. compounds having a different and ordered crystal structure than the constituting elements, such as ZnPd (from Pd/ZnO) or InPd (from Pd/In_2O_3) are formed by reactive metal–support interaction (RMSI [22]) reaction of palladium with the reduced metal atoms from the oxide. Since then several studies have been published on In–Pd-based catalysts and their physical and catalytic properties [23–27]. The presence of intermetallic compounds improved the CO_2-selectivity of the catalysts to above 95%. These materials are also much more resistant against sintering, showing higher stability at temperatures above 300 °C compared to Cu-based systems [18,28,29]. Up to now most effort has been put into investigating the roles of the different phases in ZnPd/ZnO catalysts [30–33] revealing an interplay between ZnO and ZnPd being responsible for the observed excellent selectivity – and not the sheer presence of the intermetallic compound ZnPd [34]. At 300 °C pre-reduced Pd/In_2O_3 samples showed up to 95.5% selectivity for MSR [20,35]. Men et al. prepared $In–Pd/Al_2O_3$ samples with various In–Pd ratios. They found that the CO_2-selectivity is increasing with higher In/Pd ratios. After catalytic testing up to 450 °C the supported samples contained InPd [25]. Lorenz et al. obtained different In–Pd intermetallic compounds during stepwise reduction of Pd/In_2O_3 exhibiting high selectivities for MSR. At reaction temperatures above 400 °C the intermetallic compounds were encapsulated with an In_2O_3 shell reducing the accessible surface [23]. Rameshan et al. investigated near-surface intermetallic In–Pd phases (NSIPs [36]) in MSR by near-ambient pressure XPS (NAP-XPS) measurements. They supposed the interplay between the oxide and the intermetallic compound also to play a crucial rule on the selectivity in methanol steam reforming on In–Pd materials [36]. Although there are several publications on $In–Pd/In_2O_3$ materials, there is no detailed investigation available dealing with the successive formation of In–Pd intermetallic compounds. Therefore the aim of this work was to close this gap by investigating the processes occurring during reduction of PdO/In_2O_3 by *in situ* differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA/TG/MS) measurements, NAP-XPS as well as powder X-ray diffraction (XRD) to identify crystalline phases. In addition, this study gives detailed insight into the catalytic activity and selectivity in the steam reforming of methanol of the respective intermetallic compounds supported on In_2O_3.

2. Experimental

2.1. Catalyst preparation

10 wt% Pd/In_2O_3 was prepared by wet impregnation using $Pd(NO_3)_2{\cdot}2\ H_2O$ (Sigma Aldrich, ~40% Pd) on In_2O_3 (Chempur, >99.99%) according to procedures described in the literature [23]. For a typical impregnation 3.5 g In_2O_3 was suspended in a solution of 1.042 g $Pd(NO_3)_2{\cdot}2\ H_2O$ in 20 mL deionized water with 2–3 drops of concentrated nitric acid (Sigma–Aldrich, >65%). Subsequently, 200 mL of deionized water was added and the resulting mixture was stirred for 30 min prior to the removal of the water in vacuum at 70 °C. The impregnated sample was calcined at 400 °C for three hours in synthetic air (Air Liquide, 20.5% O_2 in N_2). A 10 wt% Pd/SiO_2 sample (SiO_2: Wacker, HDK-N20) was prepared using the same procedure.

For comparison a conventional $Cu/ZnO/Al_2O_3$ catalyst with a molar composition of the metal oxides of 67.5/22.5/10 was prepared by co-precipitation from the respective nitrates according to the literature [37]. 20.667 g $Cu(NO_3)_2{\cdot}3\ H_2O$ (Merck, 99.5%), 23.522 g $Zn(NO_3)_2{\cdot}4\ H_2O$ (Merck, 98.5%) and 26.079 g $Al(NO_3)_3{\cdot}9\ H_2O$ (Grüssing, 98%) were dissolved in 500 mL of a 1:1 ethanol–water mixture (v/v) (ethanol: Roth, 99.8%) and quickly added to a solution of 52.99 g Na_2CO_3 (Grüssing, 99.5%) in 500 mL 1:1 ethanol–water mixture (v/v). The resulting gel was aged for 1.5 h at 40 °C. Subsequently the precipitate was filtered and washed several times with deionized water. The product was dried at 90 °C for five hours prior to calcination in synthetic air with a heating-rate of 3 °C/min and holding for 12 h at 400 °C.

2.2. Characterization

Chemical composition of the materials was obtained by ICP-OES (*Vista RL*, Varian). All samples were dissolved in aqua regia and measured in triplicate. Oxygen content of the samples was determined by carrier gas hot extraction (*TCH 600*, Leco). DTA/TG/MS measurements were conducted in a Netzsch *STA 448 F3 Jupiter*® combined with a Pfeiffer *Omnistar* quadrupole mass spectrometer on approximately 80 mg samples. The high resolution of 1 µg makes the TG measurements a valuable method for the investigation of small mass changes in reactive atmosphere and the rather high amount of sample results in a standard deviation of less than 0.01 wt%. For the DTA/TG/MS measurements the samples were heated with 5 °C/min to 200 °C and cooled down to room temperature again to desorb moisture and other volatile compounds prior to the reductive treatment. Gas flows during the measurements (10 vol% hydrogen in helium for reduction) with a total flow of 50 mL/min were provided by mass flow controllers (Bronkhorst). All DTA/TG/MS measurements are corrected by blank measurements to account for any non-sample effects. Low temperature-programmed reduction (TPR) was measured in the range of −80 °C up to 550 °C with a Thermo *TPDRO 1100* in 10 vol% hydrogen in argon (total flow 20 mL/min). Prior to reduction, samples were pretreated in 5 vol% oxygen in helium (total flow 20 mL/min) heating with 5 °C/min and holding 1 h at 400 °C. All samples were characterized by powder X-ray diffraction (XRD) with a *Huber G670* (Guinier geometry, Cu $K\alpha_1$ radiation $\lambda = 1.54060$ Å, quartz monochromator, image plate detector) to identify crystalline phases during reduction and catalytic measurements. XRD patterns were fitted using the program PowderCell to estimate the content of the phases and their crystallite size [38].

2.3. Near-ambient pressure XPS measurements

NAP-XPS measurements of supported PdO/In_2O_3 were recorded at the ISISS-PGM beamline at BESSY II (Helmholtz Zentrum Berlin für Materialien und Energie GmbH) to give detailed insight into the formation of intermetallic In–Pd species during reduction and under MSR conditions. The experimental setup is described in the literature [39]. For the NAP-XPS measurements, samples were prepared as thin disks (with a diameter of 8 mm) using 1 g PdO/In_2O_3 pressed with 1.5 tons in air. Samples were first measured as prepared under UHV conditions before being reduced in 0.5 mbar H_2 up to 390 °C. Methanol steam reforming conditions were subsequently applied (total pressure of 0.2 mbar, water-to-methanol ratio 2:1) while heating the samples up to 360 °C.