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CO oxidation as a test reaction for strong metal–support interaction in nanostructured Pd/FeO_x powder catalysts

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ABSTRACT

A series of differently loaded palladium–iron catalysts was prepared by a controlled co-precipitation method of the nitrate precursors, in order to ensure homogeneous Pd particle size-distribution. After characterization of the pre-catalysts by various techniques, different controlled reduction conditions were applied to investigate the interactions within the Pd–iron system, containing reversible and irreversible processes like phase transformations, SMSI, sintering and alloying. Strong indications for the reversible surface decoration of the Pd nanoparticles with iron oxide species via strong metal–support interaction were found by the combined results of DRIFTS, CO-chemisorption, TEM and XPS measurements. This SMSI state was found to be unstable. It was observed independent of bulk phase or palladium particle size. Catalytic CO-oxidation was found to be a suitable test reaction for the study of the phenomenon: higher activity as well as oxidative deactivation of the SMSI state was observed by investigating the light-off behavior in repeated, temperature-programmed cycles as well as by isothermal measurements. The instability was found to be higher in case of higher Pd dispersion. In addition, bulk properties of the Pd–Fe system, like alloying, were investigated by detailed XRD measurements.

1. Introduction

Recently, iron oxide supported noble metal catalysts have been intensively studied as model systems for the effect of strong metal–support interaction (SMSI) in CO oxidation. For example, the group of Freund studied well-defined Pt-nanoparticles on Fe_3O_4(1 1 1)/Pt(1 1 1) [1–3]. The authors were able to generate SMSI (encapsulation) at elevated temperatures and to study its structure-function relationship. The support overlayer wetting the Pt-particles was identified by STM as a FeO(1 1 1) monolayer, because of a characteristic Moiré superstructure. In that state, a strongly enhanced CO oxidation activity was observed that was attributed by the authors to an oxygen-induced formation of a catalytically active O—Fe—O trilayer (Mars–van Krevelen type reaction mechanism). No such effect was observed so far for Pd/FeO_x model systems. Schalow et al. [4–7] studied the surface chemistry and reported the formation of different oxygen species on Pd/Fe_3O_4/Pt(1 1 1) model catalysts as well as their influence on CO-oxidation activity. By combining surface sensitive IR-spectroscopy, XPS and molecular beam experiments, they found a reversible formation of Pd-oxide species at $T > 500$ K. It was dependent on the metal–support interface and occurred preferentially on Pd particles of about 7 nm in diameter. With regard to CO-oxidation kinetics, the Pd-oxides were found to suppress the reaction rate, when compared to adsorbed oxygen species. At $T > 450$ K the oxidation state of the Pd-species was found to be subject to dynamic changes, in dependence of the reaction gas composition. Wang et al. [8] reduced Pd/Fe_3O_4 with different reagents (H_2 or CO) and did not find any hints for encapsulation, but for the formation of bimetallic PdFe alloys, which have been characterized earlier by Felicissimo et al. [9].

These UHV-studies have been recently complemented by investigations in our group on more realistic catalysts [10,11]. Post-synthesis treatment of co-precipitated Pd/iron oxide catalysts was found to be crucial for the induction of phase-transition in the supporting iron oxide (from Fe_2O_3 to Fe_3O_4 polymorph). We were able to evidence the decoration of the palladium particles via SMSI upon reduction at 523 K by different techniques.

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The CO-chemisorption capacity of Pd in that decorated state was reduced and the reversibility of the overlayer formation was confirmed by in-situ XPS experiments. Activity studies of CO revealed an enhanced CO-oxidation rate in the state of decoration of the noble metal particles (E_a determined to 33 kJ/mol), as well as the instability of this SMSI state leading to fast deactivation during reaction (E_a = 70 kJ/mol) [11]. A possible explanation for the different behavior of the co-precipitated Pd/Fe_2O_3 catalysts, compared to the Pd/Fe_3O_4 model system could be release of oxygen during the phase transformation of the iron oxide support, which might facilitate the palladium encapsulation, as proposed by Wang et al. [8].

Other CO-oxidation studies on Pd/Fe systems like Pd/Fe_3O_4 core-shell particles [12], $Pd/\alpha\text{-}Fe_2O_3$ [13] or evaporated model system [14] showed moderate catalytic activity with T_{50} values between 363 K [12] and 453 K [13] as well as a change of the crystal structure during reaction. The model system showed an E_a of 136 kJ/mol, decreasing with increasing reduction temperature. Much lower E_a (about 34 kJ/mol) and full conversion already at around 273 K was reported in studies using uncalcined, co-precipitated $Pd/Fe(OH)_x$ systems [15–19].

The target of the present work was to get a deeper understanding of the formation, the reversibility and the stability of the decorated SMSI state during CO oxidation reaction, with a focus on the influence of the gas composition during reduction and during reaction. For this purpose, the analytical methods described previously [11] were applied and complemented by additional CO-infrared studies (DRIFTS) to probe the surface properties in different reduction states.

We present a multi-technique analysis to better understand the interaction of bulk and surface chemistry with the catalytic behavior in this complex catalytic system. We focus on the prehistory of the system that determines the nature of the active sites (chemical memory). Besides SMSI and PdFe alloy formation, processes like Pd particle sintering, Pd restructuring (by reversible hydride formation), Pd re-oxidation or poisoning by carbon species might play a role.

2. Experimental

2.1. Catalyst synthesis

The catalyst precursors were synthesized by co-precipitation from Fe- and Pd-nitrate solutions in an automated laboratory reactor and under controlled conditions. The details of the synthesis are presented as Supporting information (SI). The precipitate precursor was dried in air for 24 h, mortared and calcined in 20% O_2/Ar atmosphere (2 h at 823 K, 2 Kpm heating rate). The product consists of PdO supported on $\alpha\text{-}Fe_2O_3$ (hematite). The palladium loading was varied to yield 1, 2 and 5 wt.% Pd/Fe_2O_3 catalysts. The calcined samples were reduced for microscopy studies in 5% H_2–Ar (100 ml/min) at different temperatures and with a heating rate of 2 Kpm and 30 min of holding time.

2.2. Catalyst characterization

Elemental composition of the samples was verified by optical emission spectroscopy (ICP–OES) and energy-dispersive X-ray spectroscopy (EDX). The specific surface area was investigated by nitrogen physisorption (BET). Scanning electron microscopy (SEM) was used to check the morphology, whereas transmission electron microscopy (TEM) was used to investigate the Pd particle distribution and monitor structural changes after treatments or reactions. The reduced samples were transferred to the microscope without air contact. X-ray diffraction (XRD) was used for analysis of the bulk structure/phase analysis. CO-chemisorption was performed to measure the active surface area. CO-IR measurements (DRIFTS), X-ray photoelectron spectroscopy (XPS) and thermogravimetry coupled with differential scanning calorimetry (TG-DSC) were applied to investigate surface and bulk properties during reduction and/or CO-oxidation. The equipment used and the detailed procedures are described in the SI.

2.3. Catalytic testing

The CO-oxidation as catalytic test reaction was carried out in a self-constructed catalytic reactor setup which is equipped with an on-line gas analyzer (X-Stream, Emerson/Rosemount) to quantify O_2, CO, CO_2 and H_2O. The temperature in the catalyst bed can be directly monitored by an analog connection to the gas analyzer. The setup is equipped with a switch-board for mixing the carrier gas (He 5.0) with CO (3.7), O_2 (5.0) or H_2 (5.0) with the help of 6-port switching valves (Valco, Vici). Every gas line is equipped with a filter, a mass-flow controller (E1-flow, Bronkhorst), a check valve and a shut-off valve. The CO-gas line is equipped with a carbonyl remover, consisting of a tube filled with inert SiC and heated to 573 K. The carrier gas line is equipped with a water and oxygen filter. The reactor itself is a U-tube reactor with an inner diameter of 5 mm, made of glass-lined steel (SGE). It is put inside a Cu-block oven for a maximum temperature of about 773 K, controlled by a Watlow thermo-controller unit and offering an isothermal zone of about 4 cm (±1 K). The oven is equipped with a pressured-air connection to make faster cooling possible. Usually, 25 mg of the catalyst, diluted by 250 mg of inert SiC (particle diameter: 250–355 μm) were weighed out and reduced in 5% H_2–He or in 2% CO–He (100 ml/min) at different temperatures (2 Kpm, holding time 30 min). For the subsequent CO-oxidation, normally three repeated light-off conversion cycles were measured (100 ml/min, 0.5% O_2, 1% CO, 98.5% He) from 323 to 523 K (2 Kpm heating rate, 15 min. holding). The TPR experiments were performed in the same setup using 5% H_2–He and a heating rate of max. 5 Kpm. About 150 mg of undiluted catalyst were used for TPR.

3. Results

3.1. Synthesis and characterization of calcined pre-catalysts

Three Pd/Fe_2O_3 catalysts have been prepared by co-precipitation in the described synthesis reactor. For the surface study of SMSI, lower Pd loaded samples (1 and 2 wt.%) were favored due to a more narrow Pd particle size distribution and to exclude particle size effects. A higher loaded 5 wt.% sample was prepared in order to better investigate structural–chemical bulk effects during temperature programmed reduction.

Table 1 summarizes selected parameters of the pre-catalysts after calcination at 823 K. While the specific surface area of the lower loaded samples, which have been precipitated at pH = 4, were similar at about 35 m^2/g, the higher loaded sample, prepared at pH = 9 as in Ref. [11], showed a value of 61 m^2/g after calcination. All samples contained meso-pores with an average pore volume of 0.18 cm^3/g and an average pore diameter of 22 nm according to BJH analysis. After calcination, the samples were investigated by SEM–EDX and XRD. EDX at different locations showed that the palladium distribution in case of all investigated samples was homogeneous. A porous structure was observed by microscopy, as shown in Figs. S2b and S3a. The iron oxide support phase consisted of crystallites of about 50 nm in diameter and was identified as the hematite polymorph, $\alpha\text{-}Fe_2O_3$, as it can be seen in the XRD (Figs. S2 and S3 in Supporting information). In the 5 wt.% Pd/Fe_2O_3 catalyst, broad XRD peaks of PdO can be identified by Rietveld refinement