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Formation of Pd-Ce intermetallic compounds by reductive metal-support interaction

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ABSTRACT

The intermetallic compound (IC) formation between Pd and Ce *via* reductive metal-support interaction (RMSI) has been studied using two different Pd/CeO_2 materials: A thin film of Pd particles embedded in fluorite-type CeO_2, grown on vacuum-cleaved NaCl(001) facets and CeO_2 powder impregnated with small Pd particles. The reduction of CeO_2 and formation of different Pd-Ce intermetallic compounds has been monitored by diffraction in an electron microscope and synchrotron-based *in situ* X-ray diffraction, and is complemented by density functional theoretical calculations (DFT) of the formation enthalpies to judge the relative stabilities of the formed intermetallic compounds. On both studied materials, the formation of similar ICs, namely $CePd_3$ and $CePd_5$, has been observed for the first time at temperatures of 1100 K following RMSI and, thus, indicates that any catalytic pre-treatment in hydrogen, provided the reduction temperature is high enough, must also be considered for the Pd-CeO_2 system. The studies are complemented by a brief review of the Pd-Ce phase diagram to discuss the potential pathways of Pd-Ce intermetallic compound formation.

1. Introduction

Intermetallic compounds and alloy phases play an ever increasing role in various areas of catalytic research [1]. The former, through covalent bond formation, is usually preferred if a knowledge-based approach to tailored physico-chemical and catalytic properties is followed. Depending on the system, application in *e.g.* CO oxidation, benzene hydrogenation, hydrocarbon isomerization, CO methanation, aldehyde and alcohol dehydrogenation, water synthesis as well as methanol steam reforming has been reported [2]. Apart from the deliberate use of stoichiometrically prepared single-phase and single-structure intermetallic compounds, a large and important research field within heterogeneous catalysis is devoted to the "accidental" formation of such compounds *via* reactive metal-support interaction during reductive catalyst activation of oxide-supported (noble) metal particles [2]. So far, more than 60 intermetallic compounds have been detected using this routine, highlighting its paramount importance [2]. As reduction of the oxide naturally precedes the diffusion of reduced oxide (or even metal) entities to the noble metal, such reactive metal-support interaction is mostly found for, but not limited to, easy-to-reduce oxides such as In_2O_3 or TiO_2. One important oxide, which is considered one of the archetypal reducible oxides, is CeO_2—partly because metal-support interaction effects are especially pronounced for metal-CeO_2 systems [3]. Intermetallic compound formation through reactive metal-support interaction has thus far resulted in the formation of $CePt_5$ [3–5] and $CePt_3$ [6], CeNi and $CeNi_2$ [7], as well as $CeRh_3$ intermetallic compounds [8], starting from Pt/CeO_2, Ni/CeO_2 and Rh/CeO_2 catalysts, respectively. One particular class of materials, however, has only been covered unsatisfactorily by experiments: reductive activation of the corresponding Pd/CeO_2 materials could not be observed to lead to intermetallic compound formation so far. This system is particularly interesting since Pd-based intermetallic compound catalysts and oxide-supported intermetallic particles have been in a special research focus and showed tremendous capabilities in *e.g.* methanol steam reforming regarding CO_2 selectivity [9,10]. Detection of a Pd-Ce intermetallic compound or alloy phase, nevertheless, remained ambiguous. No direct structural confirmation either by electron microscopy or X-ray diffraction has been delivered, even after prolonged hydrogen treatments at 1100 K for 20 h [3,11]. The only hint towards Pd-Ce alloy formation was given by a small expansion of the

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Pd lattice by approximately 2.1% after hydrogen treatment, accompanied by Pd overgrowth of reduced CeO_x layers [11,12]. However, the Pd-Ce binary phase diagram is well developed and currently comprises at least eight different compounds ($CePd_3$, $CePd_5$, $CePd_7$, Ce_3Pd_5, Ce_3Pd_4, CePd, Ce_3Pd_2, Ce_7Pd_3), with $CePd_3$ and $CePd_5$ being the expected phases due to their high thermodynamic stabilities, featuring distinct dystectic and peritectic points [13]. Hence, the necessary reduction treatment provided, formation of distinct intermetallic compounds can be expected.

To close this knowledge gap, we in this work provide direct evidence by electron microscopy and *in situ* X-ray diffraction for the formation of Pd-Ce intermetallic phases with distinct stoichiometries following reduction in hydrogen. To increase the likelihood of Pd-Ce interaction, we primarily follow an already well-developed thin film model approach: the contact area between Pd and CeO_2 is increased by embedding the particles into a CeO_2 matrix, thus facilitating both reduction of CeO_2 and consequently, diffusion of reduced Ce species into the Pd lattice. This pathway has already proven its strengths upon inducing the intermetallic compound formation of Pt with oxides such as SiO_2 or Al_2O_3, which are considered to be hard to reduce [6,8]. As templates, single crystal facets of NaCl(001) are exploited, which might act as structural mediator leading to well defined or even epitaxially stabilized structures. In addition, we complement these studies by similar investigations on a Pd/CeO_2 powder material prepared by an impregnation technique since this system represents real catalysts, where the phase boundaries between Pd and CeO_2 are smaller than in the case of the embedded Pd particles in the thin film model system. Thus, it is expected that it is more difficult to induce any reactive metal-support interaction in the powder samples.

2. Experimental

2.1. Thin Film Deposition

The thin films were prepared on freshly cleaved NaCl(001) single crystal substrates in a modular high vacuum chamber, which is pumped by a turbomolecular pump and a liquid-nitrogen-filled baffle acting as a cryo pump, enabling a base pressure of 1×10^{-4} Pa. The palladium nanoparticles were first deposited using electron beam evaporation (at substrate temperatures of approximately 620 K), which was achieved by winding a Pd wire (0.25 mm diameter, 99.99% purity, manufactured by Goodfellow) around a tungsten rod to form the anode that was subsequently bombarded by 1.4 keV electrons emitted from a W stripe acting as the cathode filament (with a bombardment current of 60 mA). The CeO_2 (Alfa Aesar, 99.99%) was subsequently evaporated onto the Pd particles by means of thermal evaporation (*via* resistive heating), where an oxygen pressure of 2×10^{-2} Pa was used to ensure fully oxidized films. The substrate temperature was kept at 620 K in order to yield well defined crystalline cerium oxide samples. For both the electron beam and the thermal evaporation, the deposition rates were monitored using a quartz microbalance.

The specimens were reduced in flowing, dry hydrogen ($1\ mL\ s^{-1}$) at different temperatures up to 873 K, with heating rates of $10\ K\ min^{-1}$. The gold grids were supported by glass wool inside a quartz tube to form a large contact area with the gas phase.

2.2. Preparation of the powder materials

The investigated catalyst consisting of 8 wt% PdO on CeO_2 was prepared by a wet-impregnation technique. 0.0874 g $Pd(NO_3)_2 \cdot 2H_2O$ (Sigma-Aldrich, ≈40% Pd basis) were dissolved in 20 mL of deionized water. This solution was added dropwise to a stirred suspension of 0.4601 g CeO_2 (Alfa Aesar, 99.9%) in 35 mL of deionized water over the course of 15 min. The stirred liquid was removed overnight by evaporation at elevated temperature with a water bath heated to 60 °C. Finally, calcination at 600 °C for 2 h in air yielded 0.4478 g of 8 wt% PdO on CeO_2. The PdO is readily reduced to metallic palladium during the reduction treatments at low temperatures.

2.3. Characterization

For the recording of the transmission electron microscopy (TEM) images and diffraction patterns, a Zeiss EM10C (operated 100 kV), as well as a FEI Tecnai F20 S-TWIN analytical (high-resolution) transmission electron microscope (200 kV) were used.

In situ X-ray diffraction (XRD) was performed at beamline 12.2.2 at the Advanced Light Source using an incident photon energy of 25 keV, corresponding to a wavelength of 0.4959 nm. The sample was contained in quartz capillaries (with an inner diameter of 700 µm), and the gas injection was enabled by a 500 µm capillary [14,15].

2.4. Density functional calculations

In order to assess the relative stabilities of the different intermetallic compounds, density functional theory (DFT) was employed. This was done using the ABINIT code [16,17], with projector-augmented waves [18]. PBE functionals at the GGA level were utilized [19]. In order to account for the localized f states of cerium, the computations were performed within the DFT+U formalism. The Hubbard U is determined using a linear response approach as proposed by Cococcioni et al. [20] leading to a value of about 3.15 eV. The enthalpies of formation, $\Delta_f H$, were calculated as the differences between the total energies, E, of the products minus those of the reactants for a reaction in the form of $x\text{Ce} + y\text{Pd} \rightarrow \text{Ce}_x\text{Pd}_y$, normalized to the formula units in the primitive cells:

$$\Delta_f H(\text{Ce}_x\text{Pd}_y) = E(\text{Ce}_x\text{Pd}_y) - (xE(\text{Ce}) + yE(\text{Pd})) \quad (1)$$

To remove the dependency of the enthalpies on the number of atoms in the compound, the $\Delta_f H$ values were divided by $n_{\text{atoms}} = x + y$ to form a new figure of merit, $\Delta_f H/n_{\text{atoms}}$, that allows the comparison of the different intermetallic phases.

Prior to the calculation of the total energies, convergence studies of the cutoffs for the coarse and fine grids, as well as the number of k points that were sampled, were conducted to obtain an accuracy better than 1 MeV. The cutoffs were consequently set to 1600 eV and 2700 eV for the coarse and fine grids, respectively, and $10 \times 10 \times 10$ k point grids were employed.

3. Results and discussion

3.1. Thin film model systems

The bright field TEM image in Fig. 1a) shows the Pd/CeO_2 thin film after deposition. The contrast in the micrograph is characteristic of polycrystalline materials. Since palladium has a higher mass than the average mass of cerium dioxide, and consequently scatters more strongly, the darker particles correspond to Pd, with the lighter contrast being the ceria. However, since the CeO_2 is crystalline as well, Bragg contrast can also lead to dark cerium oxide crystallites. After reduction in dry, flowing hydrogen at 873 K for one hour (this procedure is labelled as H600 throughout this work), the contrast changes drastically (Fig. 1b)). Most of the Pd particles contain contrast within them, which is especially visible as dark regions at their edges (as highlighted by the arrows in the inset in panel b)). This could either be the result of mass contrast due to cerium uptake by the particles (because of Ce having a larger atomic mass than Pd), or it could indicate a recrystallization due to a possible formation of alloys or intermetallic phases. Since the corresponding high angle annular dark field (HAADF) image of the reduced specimen in Fig. 1c), showing primarily thickness and mass contrast, does not show any bright edges of the Pd particles (bright contrast), the dark edges in the bright field