Pt/CERIA THIN FILM MODEL CATALYSTS AFTER HIGH TEMPERATURE REDUCTION: A (HR)TEM STUDY

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Abstract

Well-facetted Pt particles, epitaxially grown on (001) NaCl single crystal surfaces, were supported by thin films of crystalline ceria. Structural and morphological changes due to calcination and reduction have been studied after treating in oxygen (673K, 1h) and hydrogen exposure at increasing temperatures from 673 to 1073K. These changes were followed by (HR)TEM, electron diffraction and EELS, and possible structures were selected with help of density functional calculations. Reduction at 723K causes the transformation of the initially half octahedral Pt particles into cube or platelet shapes with a double lattice periodicity in both HRTEM image and electron diffraction pattern. This can be attributed to the hydrogen-influenced topotactic formation of a Pt_3Ce alloy phase of high thermodynamic stability as confirmed by DFT calculations. Further heating of the ceria-based catalyst in hydrogen up to 1073K results in clustering of metal particles on large flat areas of the sintered support with lattice periodicities between 0.8 and 1.2 nm. EELS and X-ray diffraction both confirm partial reduction of ceria and indicate the formation of chemically stable Ce suboxides.

Introduction

Ceria supported noble metals are widely used as valuable catalysts in deNOx and combustion

technology. However, like most noble metal-reducible oxide combinations they are subjected to strong metal-support interaction upon high temperature reduction, resulting in a change of structure, catalytic properties [1] and eventually deactivation. Investigation of these phenomena is greatly facilitated by the properties of the studied thin film model catalysts: They are characterised by a narrow size distribution and defined particle shapes and well suited for plan view lattice imaging by HRTEM [2]. As SMSI-like behaviour usually starts to develop under hydrogen treatment at elevated temperatures, the present work focuses on the

changes in both structure and morphology of ceria-supported Pt particles subjected to varying reduction procedures in the temperature range between 673K and 1073K. The results are compared to experiments on "non-SMSI" systems (especially Pt/silica and Pt/alumina), where similar observations were made under identical experimental conditions [3]. (HR)TEM, electron diffraction and EELS were used to monitor the resulting changes and assisted by density functional calculations performed with the VASP code.

Experimental

Pt particles were deposited by electron-beam evaporation at 623K on a fresh vacuum-cleaved NaCl (001) single crystal surface. Subsequently, they were covered by a layer of crys-

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talline ceria (~ 25 nm). Ceria was prepared by thermal evaporation of CeOx in 10-5 mbar oxygen. The resulting thin films were put into distilled water in order to remove the NaCl, dried and finally mounted on gold grids for electron microscopy. After an oxidising treatment (1 bar O_2, 673K, 1h), the films were exposed to hydrogen at varying temperatures up to 1073K for one hour, either in a flow system or a circulating batch reactor. Their morphology and structure were examined by HRTEM and EELS and compared to the as-grown state. The images were taken with a Zeiss EM 10C, a Philips CM 200 FEG and a JEOL 4000 microscope. EELS measurements were performed at the Philips CM 200 FEG equipped with a Gatan energy filter.

Results and Discussion

The as-grown state of the ceria-supported Pt particles is shown in Fig 1: In this low-magnification TEM image the Pt particles (mean diameter: 10 nm) can be identified as dark and grey spots of square or rectangular shape, the black ones being aligned in perfect Bragg orientation, the latter more or less tilted out of the respective Bragg position. Weak-beam dark field images of the corresponding alumina-based catalysts reveal the half-octahedral habit of most metal particles [2]. Their almost perfect orientation with respect to the original NaCl substrate is confirmed by the SAED pattern (insert a). HRTEM images of octahedral particles show (200) lattice fringes of the Pt fcc structure (d_{200}(Pt)=1.96Å), including an angle of 45° with the particle edges (attachment b). Thus, most of the Pt particles exhibit (001) base planes perpendicular to the electron beam. They are surrounded by grains of fluorite type ceria. The SAED patterns reveal a partial epitaxial correlation between Pt particles and ceria, but most ceria grains are not well oriented with respect to each other. Ceria exhibits mainly (111) lattice fringes in HRTEM images (d_{111}(ceria)=3.12Å).
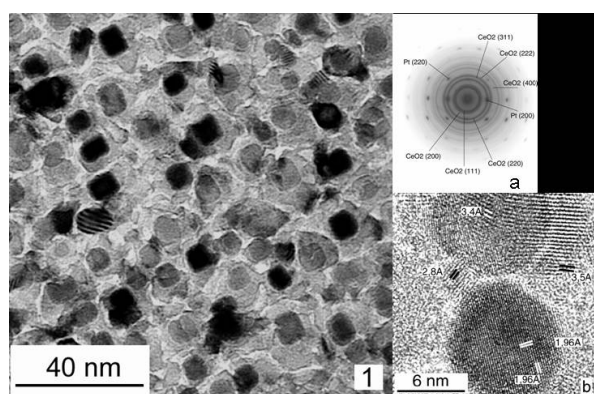

Fig. 1: As-grown Pt particles supported by crystalline ceria. Attachments: selected area electron diffraction (SAED) pattern (a) and HRTEM image of a half-octahedral Pt particle (b).

Low-temperature reduction (1 bar H_2, T ≤ 723K, 1h) leads to a slight sintering of the ceria support (as indicated by the closing of the grain boundaries) and to the appearance of

higher-indexed facets on the metal particles, generally explained in terms of a hydrogen-induced equilibrium shape. However, after reduction at 723K these particles are transformed into a new cube or platelet like structure. Their cube shape is compatible with the absence of the characteristic contour lines in weak-beam dark field images of silica supported Pt particles under similar reduction conditions [3]. Fig. 2 shows that the recrystallised particles are still well
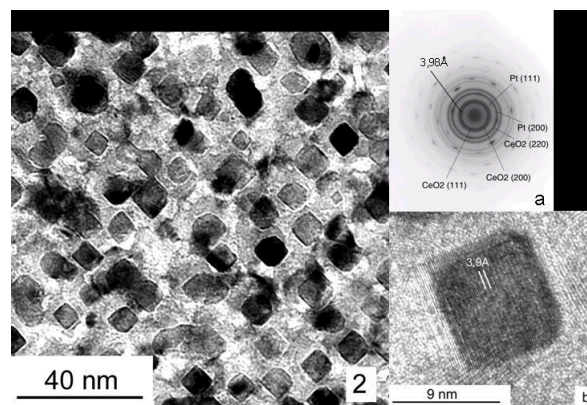

Fig. 2: Pt particles supported by ceria after hydrogen reduction at 723K for one hour. Attachments: corresponding SAED pattern (a) and HRTEM image of a recrystallised particle (b).

oriented to each other and probably pinned to the former steps of the NaCl substrate. The corresponding SAED pattern (attachment a) reveal also Pt (111) reflections indicating a change of metal-support interface of some particles. Nevertheless, most of the particles keep in [001] zone, changing only their azimuthal orientation. At d = 3.98 ± 0.1 Å four additional distinct spots coinciding with the forbidden (100) reflection of fcc Pt are detected. Similar periodicities are also found in HRTEM images (attachment b), revealing the corresponding lattice fringes as *parallel* to the particle edges. This "doubling of the Pt (200) distance" ($2 \times d_{200}$(Pt) = 3.92Å) might be explained by a particle reconstruction under hydrogen, but recent studies on the corresponding silica and alumina based catalysts proved the formation of a Pt_3Me (Me = Si, Al) alloy phase of simple cubic Cu_3Au structure with a lattice constant only slightly differing from the Pt value (a(Pt) = 3.92Å, a(Pt_3Si) = 3.89Å and a(Pt_3Al) = 3.87Å) [3]. A bulk Pt_3Me phase is also known for the Pt/Ce system [4], with a lattice constant of 4.16Å slightly larger than that of Pt_3Si and Pt_3Al. Further weak reflections in the SAED pattern can also be attributed to this Pt_3Ce phase (see Table 1) while most other possible PtCe alloys [5,6] can be excluded. The new cube-like structure persists up to reduction in hydrogen at 973K.

As the observations on Pt/ceria are very similar to those on Pt/silica and Pt/alumina, the formation of a Pt_3Ce alloy is considered most likely to occur under the given experimental conditions. The formation of sharp-edged particles upon high-temperature reduction of (silica) supported Pt particles has been reported previously [7,8] and has been explained

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by a surface reconstruction under the influence of hydrogen, leading the system to a minimum surface energy [8]. However, alloy formation has also been reported, e.g. Pt_3Si by Lamber et al. [10] and Pt_5Ce, with larger lattice parameters, by Bernal et al. [5] and Abid et al. [11] on Pt/ceria. In addi-

Table 1: Experimentally measured interplanar distances d_{hkl} [Å] and their assignment

Experimental d_{hkl} of Pt_xCe_y [Å]	Assignment
3.98	Pt_3Ce (100)
3.17	CeO_2 (111)
2.95	Pt_3Ce (110)
2.74	CeO_2 (200)
2.41	Pt_3Ce (111)
2.23	Pt (111)
2.10	Pt_3Ce (200)
1.95	Pt (111) and CeO_2 (220)
1.67	CeO_2 (311)
1.57	CeO_2 (222)
1.49	Pt_3Ce (220)
1.37	Pt (220) and CeO_2 (400)

tion, density functional calculations using the VASP code [12] show a remarkable stability of the Pt_3Ce phase compared to Pt_3Si and Pt_3Al (Table 2). We have previously explained the formation of Pt_3Si and Pt_3Al alloy phases upon

Table 2: VASP calculated formation energies [eV] of different Pt_3Me compounds

Phase	E_{form} [eV]	E_{form} per atom [eV]
Pt_3Ce	- 3.888	- 0.972
Pt_3Si	- 1.201	- 0.300
Pt_3Al	- 2.754	- 0.689

high-temperature reduction by a surface reconstruction of the Pt particles under hydrogen followed by topotactic growth of the alloy at the metal-support interface. On Pt/ceria the alloying process starts at slightly lower temperature (723K) than on Pt/silica and Pt/alumina (T ≥ 773K) which may be explained by the better epitaxy of crystalline ceria and Pt, facilitating the topotactic growth of the alloy in the proper structure and orientation. The observed disagreement between the experimentally determined lattice constant (HRTEM 3.9Å, electron diffraction 3.98 Å) and the expected bulk value of Pt_3Ce (4.16Å) could be due to the fact that at this growth stage the incorporation of Ce into the former Pt lattice is not yet completed. It must be pointed out that the probability of formation of a specific alloy and the onset temperature of formation will depend on the experimental conditions (contact area between metal and oxide, crystallinity of the oxide, possibility of topotactic growth etc.) which may also explain the different results obtained by other authors [5,6,13,14].

Further heating of the Pt/ceria catalyst in hydrogen at 1073K leads again to a different picture. Clustering of metal particles is observed together with a structural change of the ceria support. Widespread periodic patterns with lattice periodicities between about 4 and 12 Å appear on large flat areas of partly reduced, sintered ceria (Fig. 3). HRTEM images (attachment a) reveal that the larger lattice fringes are often three- or fourfold subdivided. The corresponding
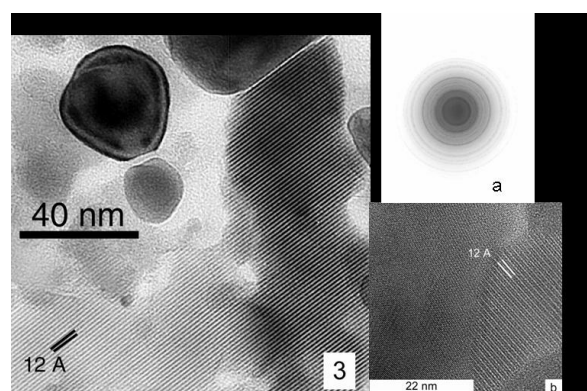

Fig. 3: The Pt/ceria thin film after hydrogen reduction at 1073K for one hour. Attachments: SAED pattern (a) and HRTEM image (b).

electron diffraction patterns (attachment b) show series of additional sharp rings, although it is still possible to detect Pt and fluorite-type CeO_2. The same HRTEM images and diffraction patterns are also obtained upon reducing a bare ceria film. Similar patterns have been reported by Krause et al. [15] after high-temperature reduction of a Pt/ceria/silica system and attributed to the formation of cerium silicate ($Ce_2Si_2O_7$), but the presence of Si could be excluded by EELS in the present case. Furthermore, X-ray diffraction of thicker ceria films after high-temperature reduction shows an overall decrease of diffracted intensities from fluorite type ceria and the appearance of new reflections which arise very likely from reduced ceria phases. On the other hand,

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EELS measurements on the reduced ceria support reveal that the structural change is accompanied by a change of the oxidation state from Ce^{4+} to Ce^{3+}, so that most likely a defect superstructure with a distorted fluorite lattice is formed. CeO_2 is very-well known to form a large number of sub-stoichiometric phases CeO_x ($1.714 \leq x \leq 2$) upon high-temperature reduction, most being characterised by an ordering of the formed oxygen vacancies and a fluorite-related lattice [16]. Although most of these structures are reported to be easily reoxidised under atmospheric conditions their kinetic stability may be enhanced by a surrounding thin layer of cerium hydroxide. Density functional calculations and additional EELS measurements are presently carried out in order to determine the possible atomic arrangement in this superstructure, but of course in-situ experiments will also be needed to prevent reoxidation under ambient conditions.

Conclusions

After reduction of a Pt/ceria thin film catalyst SAED analysis and HRTEM images reveal the formation of a Pt_3Ce alloy compound crystallising in the simple cubic Cu_3Au structure. After reduction at 1073K striking structural changes of the ceria support occur and enable the Pt particles to coalesce to large aggregates. These changes are most likely due to a bulk reduction of ceria and the formation of a defect superstructure, exhibiting the observed lattice periodicities. Presently, VASP calculations and EELS measurements are carried out in order to determine the origin of this defect structure.

Acknowledgement

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