PLATINUM NANOCRYSTALS SUPPORTED BY SILICA, CERIA AND ALUMINA: METAL-SUPPORT INTERACTIONS DUE TO HIGH-TEMPERATURE REDUCTION IN HYDROGEN

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Regular Pt nanoparticles, obtained by epitaxial deposition on (001) NaCl surfaces, were supported by thin films of amorphous silica, amorphous alumina and crystalline ceria, respectively, and subjected to reductive treatments in flowing hydrogen (1 bar) at increasing temperature up to 1073 K. The changes in morphology and composition were followed by (HR)TEM, electron diffraction and EELS, and possible structures were checked by image simulation. After reduction above 773 K similar structural changes are observed on all supports, despite their differing chemical properties. The observed platelet- and cube-like structures, some exhibiting double lattice periodicities in diffraction patterns and high resolution images, arise in part from surface reconstruction in the hydrogen and in part from alloy formation. Reduction of the ceria support above 973 K leads to stable Ce suboxide films with large periodicities.

Introduction

In heterogeneous catalysis, model systems are indispensable to elucidate the mechanism of structure-sensitive reactions. Regular metal particles on planar thin supports greatly facilitate the characterisation by electron microscopy, and provide a defined initial state for subsequent structural alterations due to oxidation and reduction. Noble metal particles grown epitaxially on NaCl and thereafter transferred to different supporting films are ideally suited to study the influence of different supports on identical nanoparticles. Lately, they have been extensively studied as model systems for supported catalysts [1,2].

Experimental

Pt particles epitaxially grown on (001) NaCl single crystals were covered with a supporting film of amorphous silica. Subsequently, the NaCl was dissolved in water and the films were mounted on gold grids [1]. After an oxidising treatment (O_2, 673K, 1h) the samples were exposed to H_2 at temperatures varying from 673 to 1073 K for 1h, either in a flow system or in a circulating batch reactor. The morphology and structure of the samples were examined by HRTEM and compared to the as-prepared state. The images were taken with a Zeiss EM 10C, with a Philips CM FEG 200 and with a JEOL 4000 microscope.

Results and Discussion

Fig. 1a shows a low-magnification image of the "initial state" of the Pt particles (which is identical in all catalysts) in the as-prepared Pt/SiO_2 sample, together with the corresponding diffraction pattern. Most of the as-grown Pt particles exhibit square or rectangular outlines and were identified as truncated half octahedra with (001) faces perpendicular to the electron beam [1] (insert). In contrast, after a reductive treatment at 873 K a considerable number of Pt particles have undergone a change in either shape or orientation (Fig. 1b). Those with round edges also have increased in size, obviously due to agglomeration. Particles with sharp edges

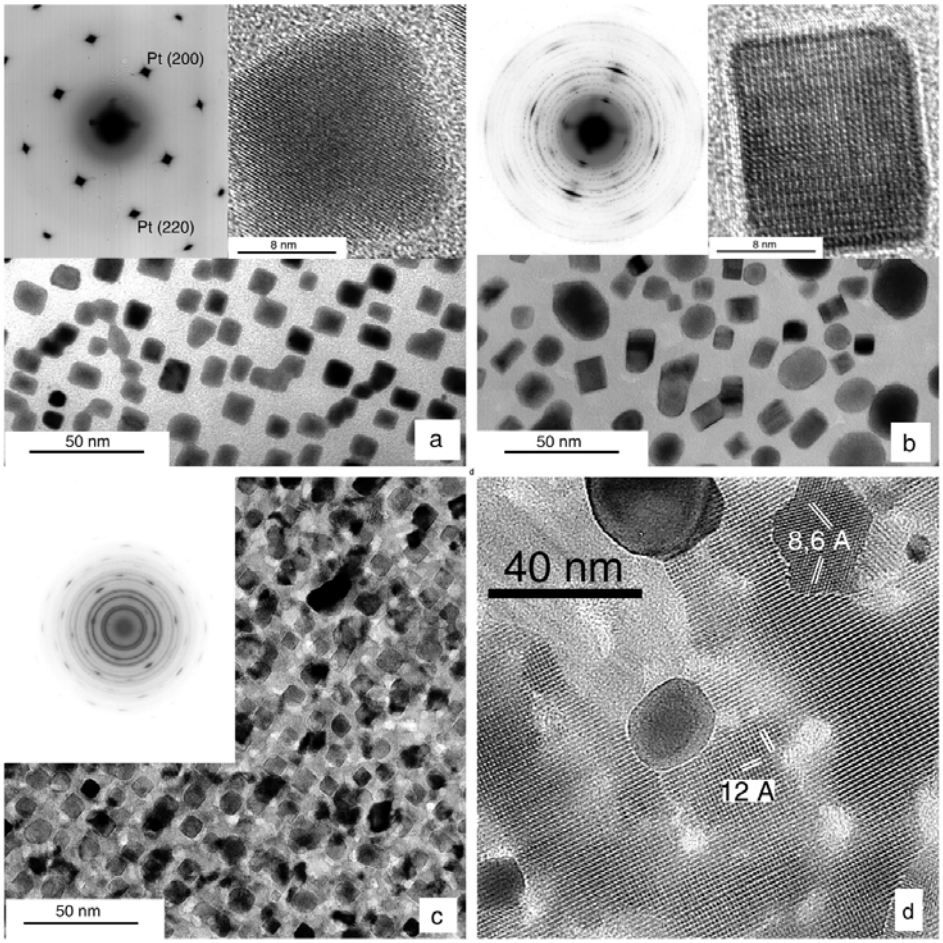

Fig. 1 a) Pt nanocrystals supported by SiO_2, as grown with SAED pattern and HR image of a selected particle; b) after a 1 bar hydrogen treatment at 873 K for 1 h; c) ceria-supported Pt particles after the same treatment as in b); d) ceria-supported Pt after hydrogen treatment at 1073 K, with large lattice spacings of CeO_x.

are cube-or platelet-like and double periodicities are observed in both the diffraction pattern and the lattice fringes at high resolution (inserts in Fig. 1b). At the same time the formerly amorphous silica support has crystallised whereby the Pt particles possibly act as nuclei. Under the given experimental conditions silicide formation [3] must be taken into account, at least to some extent, but it does not explain all features of the diffraction patterns. Moreover, very similar results were obtained when Pt nanocrystals supported on alumina were reduced under identical conditions. Again, sharp edged platelet and cube-like structures were formed while amorphous alumina had crystallised (not shown here). Finally, platelets and cubes were also formed upon reduction from Pt particles in contact with crystalline ceria already upon hydrogen treatment at 773 K and above (Fig. 1c), whereby the epitaxial relation between the Pt particles and the ceria grains was retained. Upon further reduction the support is reduced to a chemically stable CeIII oxide with large lattice periodicities (Fig.1 d).
At present, image simulation and EELS measurements are carried out in order to discriminate between alloy phases and superstructures due to surface reconstruction under hydrogen [4].

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