

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

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Ceria-supported noble metals are widely used as valuable catalysts in deNO_x 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 changing catalytic properties [1] and eventually deactivation. An investigation of these phenomena and of structure-activity correlations is greatly facilitated by model systems with planar thin supports. In the present work, well-faceted Pt particles, obtained by epitaxial growth on (001) NaCl surfaces, were supported by thin films of crystalline ceria. These model catalysts are well suited for characterisation by electron microscopy and provide a defined reference state for studies of structural changes during catalyst treatment and reaction. Catalyst changes due to calcination and reduction have been studied after treating the samples in oxygen (673K, 1h), and after hydrogen exposure at increasing temperatures from 673K to 1073K for 1h, either in a flow system or in a circulating batch reactor. The morphology and composition were followed by (HR)TEM, electron diffraction and EELS.

In their initial state, most Pt particles are truncated half octahedra with (001) faces perpendicular to the electron beam, exhibiting square or rectangular shapes at lower magnification [2]. They are surrounded by grains of CeO₂, partly in epitaxial correlation to the metal. In contrast, after a reductive treatment at 723 K, Pt particles embedded in ceria recrystallise into a cubic or platelet-like structure, thereby losing in part their original azimuthal orientation. Some particles exhibit round edges but have increased in size, obviously due to agglomeration. At this reduction stage the bulk stoichiometry of the ceria support is still unchanged. With rising reduction temperature the average particle size increases but the platelet or cube like structure persists. On Pt/silica and Pt/alumina a similar transformation of the Pt particles was observed to occur at higher temperature and possibly connected with alloy formation [3]. These phase transformation are reversible by low-temperature oxidation and can be repeated by subsequent reduction. At present, HREM, image simulations and EELS measurements are carried out in order determine the origin of this effect.

Further heating of the ceria-based Pt catalyst in hydrogen up to 1073K results in clustering of the Pt particles on large flat areas of a sintered support of partly reduced ceria, exhibiting large lattice periodicities between 0.8 and 1.2 nm. EELS measurements confirm the formation of a chemically stable Ce (III) oxide.

These structural changes are connected to changes of the catalytic properties [4], as will be exemplified and discussed for the CO hydrogenation.

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