Hydrogen induced spreading of CeO$_2$ on SiO$_2$

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Interaction of small (~5 nm) CeO$_2$ particles with silica catalyst carrier in hydrogen at 570–970 K was studied by XRD and TEM. It was found that, at 770 K, CeO$_2$ began to redisperse and spread onto silica and at 970 K its complete amorphization occurred. Addition of 0.4 wt% Pd had a small promoting effect on the process.

Keywords: Ceria–silica interaction; CeO$_2$ spreading; XRD; TEM

1. Introduction

Systems composed of rare-earth oxide dispersed on main group oxides (Al$_2$O$_3$, SiO$_2$) have gained considerable importance because of their potential applications in catalysis. Cerium oxide is a widely used additive in noble metal–alumina automotive catalysts owing to its ability to store and release oxygen and to improve thermal stability of alumina and dispersion of the metal [1]. On silica, addition of Ce to platinum improves the selectivity and activity of the catalyst in CO hydrogenation reactions [2,3].

At elevated temperatures CeO$_2$ interacts strongly with Al$_2$O$_3$ and SiO$_2$ and in a reducing atmosphere cerium aluminate (CeAlO$_3$) [4,5] or cerium silicate (Ce$_2$Si$_2$O$_7$) [6] is formed. Presence of a platinum metal (Pd, Pt, Rh) increases the rate of aluminate formation [7–9]. Very recently Krause et al. [10] showed that in a model, thin film Rh–Ce/SiO$_2$ catalyst the temperature of cerium silicate formation is a few hundred degrees lower than in an CeO$_2$–SiO$_2$ physical mixture.

In this work we present results of XRD and TEM studies on the interaction between ceria and silica in powder CeO$_2$/SiO$_2$ and Pd–CeO$_2$/SiO$_2$ samples prepared by a chemical method.
2. Experimental

CeO$_2$/SiO$_2$ sample containing 25 wt% CeO$_2$ was prepared by impregnation of SiO$_2$ (Degussa Carrier No. 310) with an appropriate amount of a 20 wt% colloidal dispersion of CeO$_2$ in aqueous solution of acetic acid (Aldrich). The slurry was dried overnight in air at 350 K and finally ground into a mortar. In the case of Pd–CeO$_2$/SiO$_2$ sample, a small amount of PdCl$_2$ solution (to get 0.4 wt% Pd) was added to the CeO$_2$ dispersion. Controlled (SiO$_2$ free) CeO$_2$ and 0.4 wt%Pd/CeO$_2$ samples were prepared by evaporation and drying of the CeO$_2$ colloidal dispersion alone or mixed with an appropriate amount of PdCl$_2$ solution.

The samples were reduced in a hydrogen flow at 570, 770 and 970 K for 20 h. The gas was purified by passing it over Pd/asbestos catalyst kept at 450 K, NaOH, P$_2$O$_5$ and finally zeolite promoted with Co.

Structural changes occurring in the samples were monitored after each step of reduction by X-ray diffraction (XRD) (Siemens D 5000 diffractometer, Bragg-Brentano geometry, Cu K$_\alpha$ radiation), transmission electron microscopy (TEM) and electron diffraction (ED) (Tesla BS 613).

To each sample studied by XRD some corundum (α-Al$_2$O$_3$) powder was added as an internal standard so that the ratio of volume fractions of CeO$_2$ and Al$_2$O$_3$ was constant. This allowed for the precise determination of the CeO$_2$ lattice parameter, the true peak widths and the amount of CeO$_2$ present as a crystalline phase. Samples for TEM and ED were prepared by ultrasonic dispersion of some powder in methanol and putting a droplet of the suspension on a copper microscope grid covered with carbon.

3. Results and discussion

Figs. 1 and 2 show X-ray diagrams of CeO$_2$/SiO$_2$ and Pd–CeO$_2$/SiO$_2$ samples “as prepared” (a) and heated in H$_2$ at 570 (b), 770 (c), and 970 K (d) for 20 h. Additionally in figs. 1 and 2, diagrams of the control CeO$_2$ and 0.4 wt%Pd/CeO$_2$ samples heated in H$_2$ at 970 K for 20 h are included and marked (e). In the 40°–60° range of 2θ angles close but not overlapping (113), (024), (116) corundum and (220), (311) CeO$_2$ reflections occur. No reflections from any other phase could be found in any sample, even if additional, 70 h, heating of the samples in H$_2$ at 970 K was applied.

Parameters describing the evolution of CeO$_2$ phase in the samples treated in H$_2$ are given in table 1. In column 2 the ratio of intensities of CeO$_2$ (220) and Al$_2$O$_3$ (113) reflections is presented. Its decrease with temperature of H$_2$ treatment indicates the decline of the amount of crystalline CeO$_2$. Column 3 contains the measured widths (FWHM) of the CeO$_2$ (220) reflection corrected for the instrumental broadening (assumed to be equal to the FWHM of the