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_2O_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_2O_3 and SiO_2 and in a reducing atmosphere cerium aluminate ($CeAlO_3$) [4,5] or cerium silicate ($Ce_2Si_2O_7$) [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.

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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_2O_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 Kα radiation), transmission electron microscopy (TEM) and electron diffraction (ED) (Tesla BS 613).

To each sample studied by XRD some corundum (α-Al_2O_3) powder was added as an internal standard so that the ratio of volume fractions of CeO_2 and Al_2O_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_2O_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

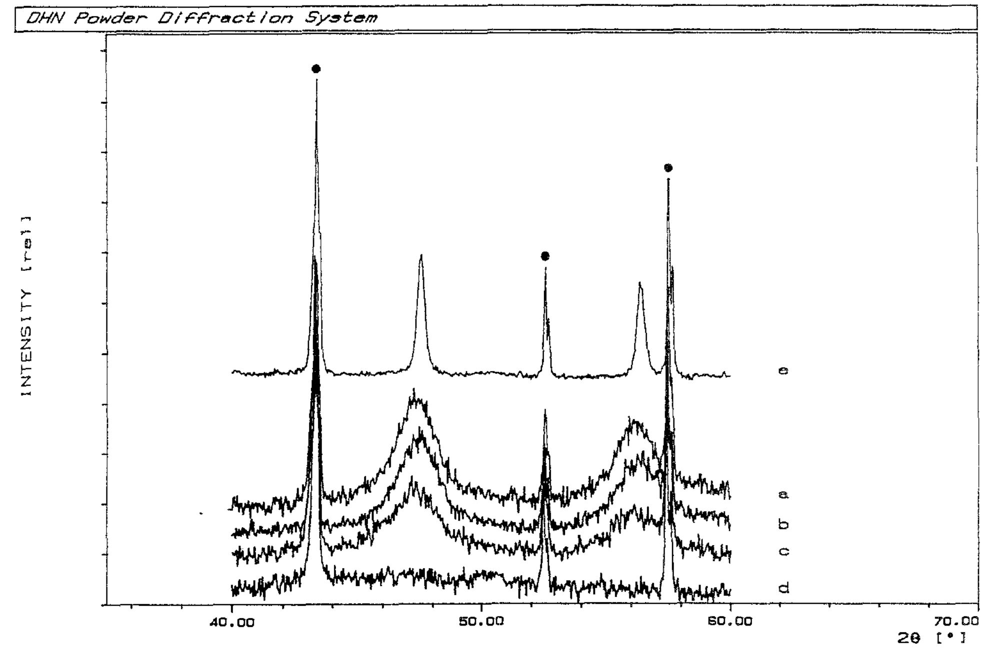

Fig. 1. XRD diagrams of 25 wt%CeO_2/SiO_2 powder sample "as prepared" (a) and heated in H_2 at 570 (b), 770 (c) and 970 K (d) for 20 h. For comparison, a diagram of the control 100% CeO_2 sample heated at 970 K for 20 h is shown (e). Reflections of the corundum standard are marked with dots.

Al_2O_3 (113) reflection): $B_{\mathrm{corr}} = (B^2_{\mathrm{CeO_2}} - B^2_{\mathrm{Al_2O_3}})^{1/2}$. Column 4 shows average size of CeO_2 crystallites determined by using the Scherrer formula,

$$L = \lambda \cdot K / B_{\mathrm{corr}} \cdot \cos \Theta,$$

where λ is the wavelength of X-ray (here 0.15405 nm), K is a constant (we assume $K = 1$), Θ the angle of reflection (in our case 23.65°), B_{corr} the corrected FWHM of the reflection (in radians).

It appears from figs. 1 and 2 and table 1 that fine crystalline CeO_2 particles supported on SiO_2 disappear gradually when heated in H_2 at 770 K or above. Heating at 970 K for 20 h completely removes the CeO_2 reflections and no other phase is formed, even if the heating time is increased to 90 h. The presence of Pd (0.4 wt%) does not change qualitatively this process, though it accelerates it (the amount of crystalline CeO_2 starts to decrease already at 570 K). The lattice constant of CeO_2 supported on SiO_2 is expanded by approximately 0.4% and does not change upon the heat treatment.

The control CeO_2 and Pd–CeO_2 samples (without SiO_2) behaved in a quite opposite way, i.e. sintering of CeO_2 instead of its amorphization occurred at 970 K (X-ray characteristics of the "as prepared" CeO_2 and Pd/CeO_2 samples were very close to those of the respective CeO_2/SiO_2 and Pd–CeO_2/SiO_2 ones). Additionally, the lattice constant of CeO_2 changed after heating to the value

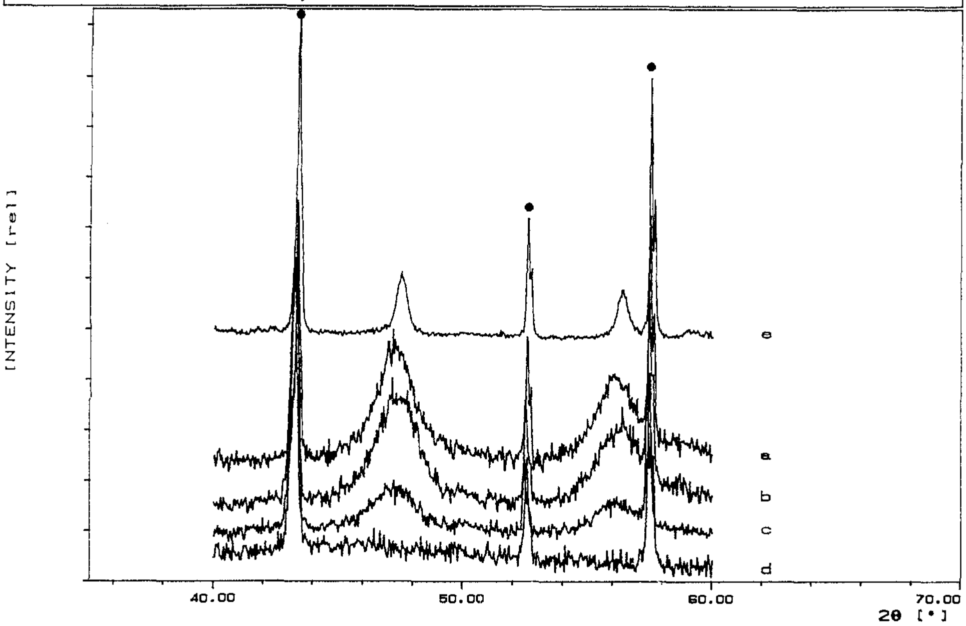

Fig. 2. XRD diagram of 0.4 wt% Pd–25 wt% CeO_2 /SiO_2 powder sample "as prepared" (a), and heated in H_2 at 570 (b), 770 (c) and 970 K (d) for 20 h. For comparison, a diagram of the control 0.4 wt% Pd/CeO_2 sample heated at 970 K for 20 h is shown (e). Reflections of the corundum standard are marked with dots.

0.541 nm, characteristic for the crystalline CeO_2 [11]. For the Pd/CeO_2 sample, however, the intensity of CeO_2 reflections decreased upon heating at 970 K, indicating that at this temperature reduction of some CeO_2 into an amorphous phase occurred.

The XRD results for CeO_2/SiO_2 and Pd–CeO_2/SiO_2 samples were confirmed by TEM and ED studies. Fig. 3 shows electron micrographs and electron diffractograms of the CeO_2/SiO_2 sample "as prepared" (a), then heated in H_2 at 570 (b), 770 (c) and 970 K (d) for 20 h. The results for Pd–CeO_2/SiO_2 were indistinguishable and are not shown here. In samples "as prepared" and reduced at 570 and 770 K (figs. 3a–3c), CeO_2 particles are clearly visible as black dots with sizes ≈ 5 nm, corresponding nicely with the XRD value (see table 1). In the sample heated at 970 K (fig. 3d) the contrast between CeO_2 and SiO_2 is much weaker and the number of CeO_2 particles that can be discriminated is greatly reduced. Some sintering of the SiO_2 support is also seen in the micrograph. Electron diffractograms of the samples presented in fig. 3 contain only lines from CeO_2, which fade slowly with increasing temperature. Only very diffuse rings appear in the sample treated at 970 K indicating complete amorphization of CeO_2. Prolonged heating (90 h) at this temperature did not cause visible crystallization of any new phase.

Table 1
XRD results for CeO_2/SiO_2 and Pd–CeO_2/SiO_2 samples heated in hydrogen

Sample	I_{ceria}/I_{silica} [a]	$CeO_2(220)$ peak width [b] (nm)	CeO_2 particle size [c] (nm)	CeO_2 lattice constant (nm)
CeO_2/SiO_2				
air, 350, 20 [d]	0.48	1.86	5.3	0.543
H_2, 570, 20	0.48	1.94	5.0	0.543
H_2, 770, 20	0.29	2.51	3.8	0.543
H_2, 970, 20	0.0	–	–	–
CeO_2				
H_2, 970, 20	0.49	0.34	28.4	0.541
Pd–CeO_2/SiO_2				
air, 350, 20	0.46	1.70	5.7	0.543
H_2, 570, 20	0.40	1.72	5.6	0.543
H_2, 770, 20	0.21	2.02	4.8	0.543
H_2, 970, 20	0.0	–	–	–
Pd/CeO_2				
H_2, 970, 20	0.20	0.46	21.0	0.541

[a] Ratio of intensities of CeO_2 (220) and Al_2O_3 (113) peaks.

[b] FWHM (full width at half maximum) corrected for an instrumental broadening.

[c] Calculated by using the Scherrer formula.

[d] Denotes sample treatment: in air at 350 K for 20 h.

The solid state reaction between CeO_2 and SiO_2 was studied by Felsche and Hirsiger [6] who established that in an inert atmosphere or under vacuum a temperature 1770 K was necessary for the $Ce_2Si_2O_7$ silicate to be formed. According to the authors, the thermodynamically difficult reduction $CeO_2 \rightarrow Ce_2O_3$ was the determining step in the silicate formation and it occurred at 1770 K at the presence of SiO_2 only.

For CeO_2 supported on Al_2O_3, Shyu et al. [5] showed that in H_2 small CeO_2 crystallites reacted with alumina to form $CeAlO_3$ aluminate above 870 K. Large CeO_2 particles required much higher temperature ≈ 1070 K, to form the aluminate [5]. Very recently Krause et al. [10] studied the interaction between CeO_2 and SiO_2 in a Rh–Ce/SiO_2 thin film, model catalyst by a number of methods including XPS, HREM and EELS. They found that annealing of the preoxidized samples in H_2 at 870 K caused the partial reduction of Ce^{4+} to Ce^{3+} and its strong interaction with SiO_2, leading to redispersion and complete disappearance of small CeO_2 crystallites (below 20 nm). Larger CeO_2 crystallites redispersed much slower and eventually formed very stable, flat (up to 5 nm thick) crystals of $Ce_2Si_2O_7$ silicate. No such phase was formed in CeO_2/SiO_2 sample (without Rh) at this temperature, indicating that Rh catalyzed the process.

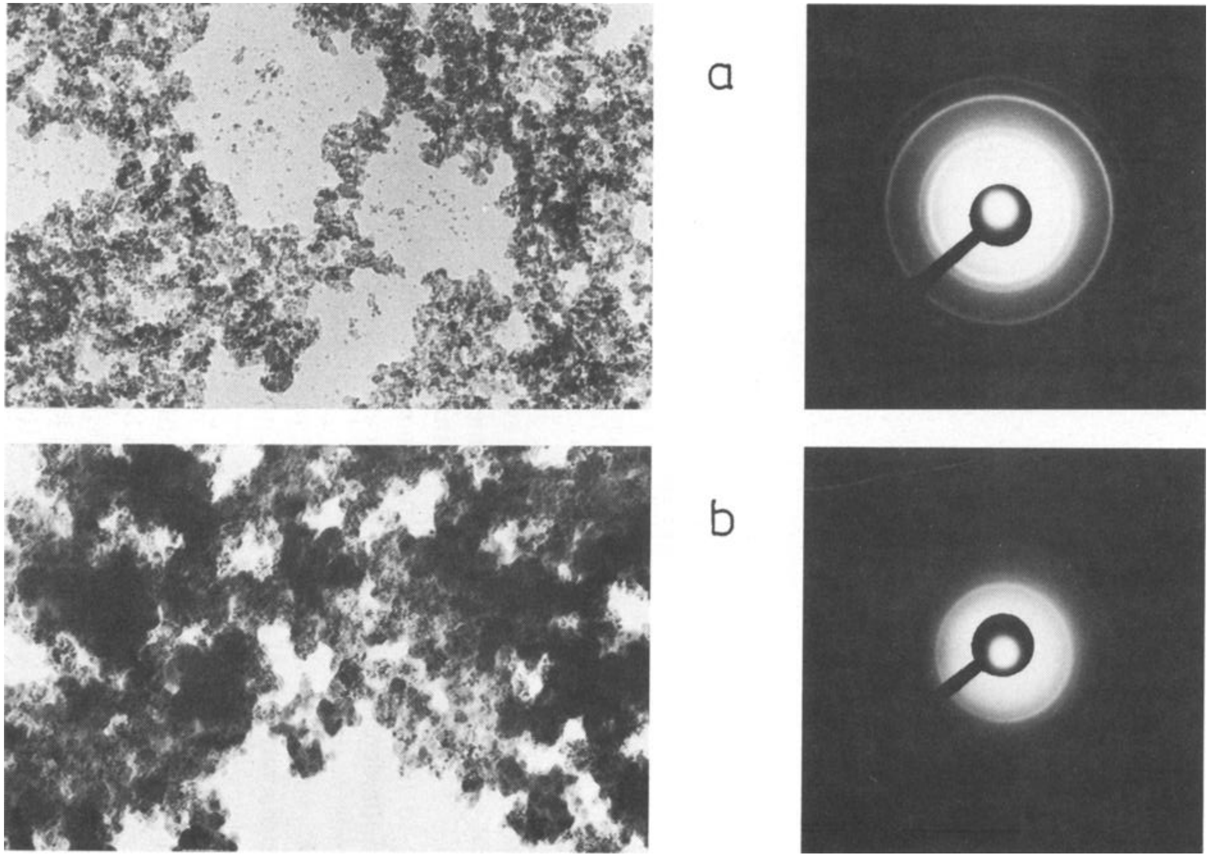

Fig. 3. Electron micrographs and electron diffractograms of 25 wt% CeO_2/SiO_2 sample "as prepared" (a) and heated in H_2 at 570 (b), 770 (c) and 970 K for 20 h.

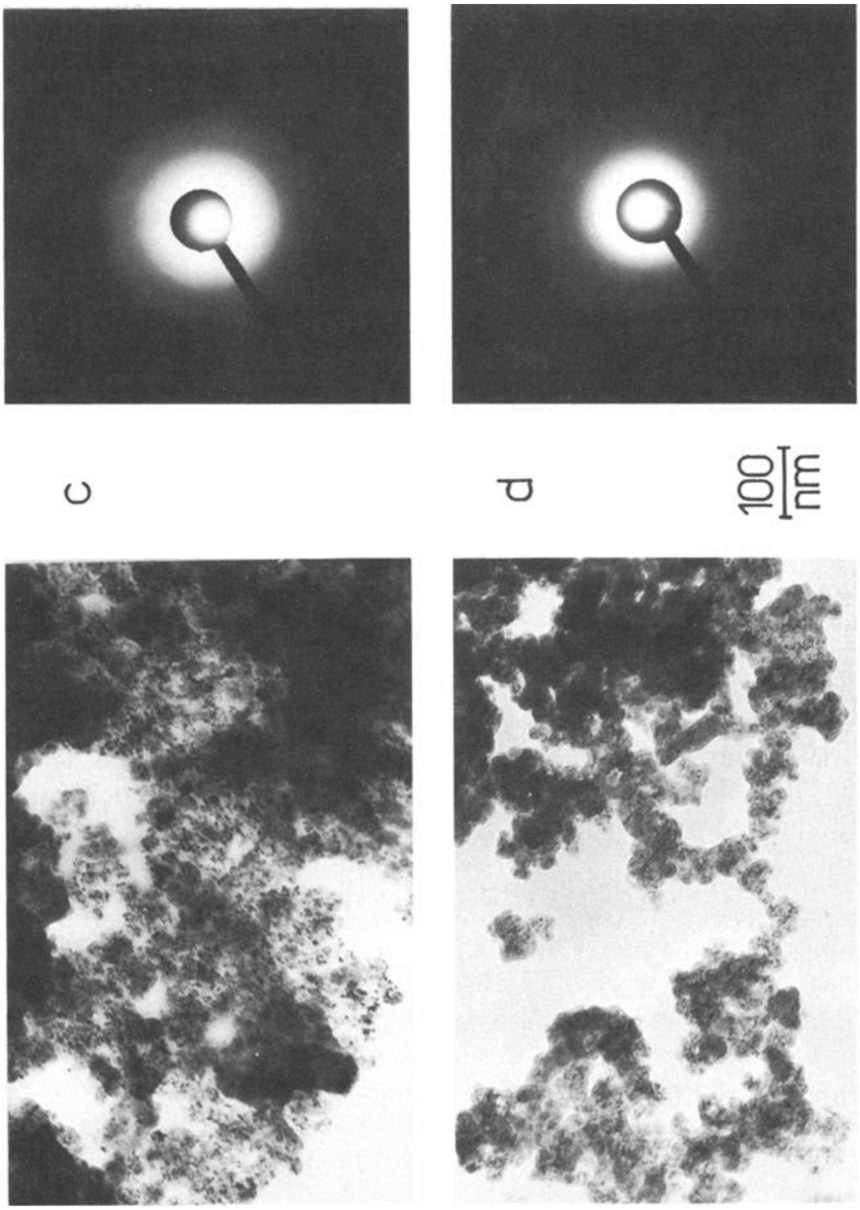

Fig. 3 (continued).

Our results for CeO_2/SiO_2 and Pd–CeO_2/SiO_2 powder samples agree with those of Krause et al. [10], concerning the complete redispersion of small CeO_2 particles in H_2 at 870 K in contact with SiO_2. The lack of $Ce_2Si_2O_7$ lines in our XRD and electron diffractograms also confirms the statement of Krause et al. [10], that the $Ce_2Si_2O_7$ phase grows only from relatively large CeO_2 crystallites (> 20 nm) attached to Rh particles and may be visualized in this initial stage of formation only by HREM.

It seems to us, however, that the role of the metal is two-fold. In addition to the promoting effect on CeO_2 reduction claimed by Krause et al., Rh particles serve as nucleation centers for $Ce_2Si_2O_7$ crystallization in an amorphous matrix of SiO_2. The rather small influence of the metal (Pd, Pt) on the aluminate formation in the CeO_2/Al_2O_3 system [7,8] can be explained by the fact that the aluminate can easily crystallize at alumina grains having very similar structure.

The strong interaction of transition metal oxides with SiO_2 leading to their spreading on the support occurs also in oxidized atmosphere and has been observed, e.g., for Nb_2O_5 [12], CrO_3 [13], TiO_2 [14] and Co_3O_4 [15]. The behavior of CrO_3/SiO_2 is particularly interesting, since upon annealing in air CrO_3 phase became amorphous at about 380 K and at ≈ 570 K diffraction lines of Cr_2O_3 appeared. It seems that only intermediate (non-stoichiometric) oxides wet SiO_2.

4. Summary and conclusions

Small CeO_2 particles (≈ 5 nm) supported on SiO_2 interact strongly with the support in H_2 at temperatures above 770 K, and redisperse on it completely at 970 K, forming an amorphous layer, probably chemically bound to SiO_2. Addition of Pd (0.4 wt%) accelerates the rate of CeO_2 amorphization but does not change the process qualitatively. In particular, we did not observe the formation of $Ce_2Si_2O_7$ silicate, reported by Krause et al. [10] in Rh–Ce/SiO_2 system at 870 K, despite prolonged heating of our Pd–CeO_2/SiO_2 samples in H_2 at 970 K for 90 h.

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