Relationships between Structural/Morphological Modifications and Oxygen Storage–Redox Behavior of Silica-Doped Ceria

Eliana Rocchini,* Alessandro Trovarelli,*.¹ Jordi Llorca,† George W. Graham,‡ Willes H. Weber,‡ Marek Maciejewski,§ and Alfons Baiker§

* Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, via Cotonificio 108, 33100 Udine, Italy; †Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain; ‡Ford Research Laboratory, P.O. Box 2053, Dearborn, Michigan 48121-2053; and §Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

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The reduction/oxidation and oxygen storage behavior of silicadoped ceria is described with particular attention to structural transformation occurring under these conditions. It is shown that the reduction properties of CeO₂ are strongly dependent on the amount of silicon. In particular, the use of silicates during the preparation of ceria endows the material with remarkable reduction behavior. TPR studies and thermogravimetric analysis of ceria under H₂ show a promotion of reduction, especially after thermal redox cycles at high temperature. This is correlated to the formation upon reduction of a Ce_{9.33}(SiO₄)₆O₂ phase, which was detected by XRD and HREM-EDX studies. Reoxidation of this phase in the range of temperatures between 773 K and 1073 K gives a mixture of amorphous silica and small ceria crystallites which are responsible for the enhancement of oxygen storage behavior, measured by alternately pulsing CO and O₂ over the catalysts. © 2000 Academic Press

Key Words: automotive exhaust catalysts; ceria; CeO₂; mixed oxides; oxygen storage; TPR; redox behavior; TWC; CeO₂-SiO₂; ceria-silica.

INTRODUCTION

The study of the redox behavior of CeO₂ has been the subject of thorough investigation in recent years (1–5). These studies have been prompted mainly by the use of CeO₂ in three-way catalysts (TWC) for it is well known that the structural and morphological modifications which occur on CeO₂ under reducing and oxidizing conditions strongly affect the performance of auto exhaust catalysts. It is also known that CeO₂, at high temperatures and reduced oxygen partial pressures or in the presence of reductants (CO, hydrocarbons, H₂), can easily deviate from a stoichiometric composition to give a continuum of oxygen-deficient, non-stoichiometric CeO_{2-x} ($0 \le x \le 0.28$) oxides. These suboxides have a strong tendency to remain in their fluorite struc-

tured lattice even after a considerable amount of oxygen has been lost, thus stabilizing a structure with an elevated number of oxygen vacancies. The reoxidation of these suboxides by oxygen or by other oxidizing species (H₂O, NO) easily restores stoichiometric CeO₂. If the atmospheric environment in which CeO₂ operates changes continuously from a net oxidizing to a net reducing composition, as in TWCs, the Ce cation in CeO_2 shifts alternately from a 4+ to a 3+ oxidation state, thus enhancing the conversion of the main pollutants present in the exhaust. The unique features of ceria arise from the thermodynamics and kinetics of the redox processes, which allow a perfect fit between the extent and the rate of reduction/oxidation processes on the ceria surfaces and the time scale of fluctuation of composition in the exhaust stream. Additional benefits derive from the presence of noble metals, which allow a certain degree of metal-support interaction to develop over time (6) and help the transfer of oxygen from the bulk to the surface under oxygen-deficient conditions (7).

It is therefore clear that modification of catalyst redox behavior is a key to the preparation of advanced materials for the treatment of auto exhaust and similar processes. A number of different approaches have recently been developed to increase the redox features of CeO₂, including the doping of ceria with rare-earth or transition metals (8, 9) and the development of novel methodologies of preparation (5, 10, 11). In the first approach, the enhancement of redox properties is achieved mainly by structural modifications which induce an increase in the diffusion rate of oxygen through the lattice whereas the second approach focuses on the preparation of materials with enhanced textural properties. It is recognized that the texture of cerium oxide has a great impact on the interaction of CeO_2 with H_2 or CO, leading to the formation of different CeO_{2-x} species, depending on the initial ceria surface area (2). One problem which still needs to be solved is the loss of ceria surface area after treatment at high temperature, which is one of the main causes of deactivation (12).



 $^{^1}$ To whom correspondence should be addressed. Fax: ++39-0432-558803. E-mail: trovarelli@dstc.uniud.it.

TABLE 1

Some of us have recently reported the preparation of mesoporous ceria using template-assisted synthesis (13). With this methodology, surface areas in excess of 200 m^2/g are obtained after calcination at 723 K. In addition, improved thermal resistance was observed and surface areas in excess of 40 m^2/g were obtained after treatment at 1173 K under air. Our preliminary results have shown that this cerium oxide exhibits an unusual behavior pattern under reducing atmospheres, especially after treatment at high temperature (11). However, it was also shown that small amounts of SiO₂ (1-4% wt) can be easily incorporated within the oxide during the synthesis, particularly when working at high pH with glass apparatus (14b). The presence of SiO₂, which escaped our earlier investigations (11, 14a), can be responsible during reduction for the formation of reduced phases containing Ce and Si, and thus it can explain the enhancement of the reduction properties previously observed.

Several studies have been carried out on the CeO₂-SiO₂ system, especially with ceria supported on silica (15-18). These studies were mainly focused on the behavior of supported ceria and its interaction with the support. A few studies were also concentrated on the thermal stabilization of ceria with silicon compounds (19, 20). However, the redox properties of ceria-silica mixtures and their morphological features were not covered in the literature. The present study was carried out to investigate the behavior of mixed ceria-silica oxides under reducing and oxidizing conditions, with particular attention to structural and morphological modifications originating after high-temperature treatment. The implications of these transformations in the oxygen storage ability of the catalysts are discussed, partly in view of the application of this material as a support for noble metal deposition. An evaluation of the effect of Si on the reduction properties of ceria is also necessary for a critical comparison with our previous preliminary investigation (11, 14a), where the presence of Si was not detected.

EXPERIMENTAL

Materials

The materials, corresponding to a CeO₂/SiO₂ weight ratio varying in the range 87.2/12.8–100/0, were obtained by coprecipitation after hydrothermal synthesis in a Nalgene autoclave. An aqueous solution of sodium silicate (Riedel-De Haën) of the appropriate concentration (0–0.05 M, depending on the desired composition), containing a SiO₂ amount of 63% by weight, was mixed with a 0.13 M aqueous solution of CeCl₃ · 7H₂O (Aldrich). A solution of concentrated ammonia was then slowly added to reach a pH of 11.5 followed by vigorous stirring at 363 K for 24 h. The yellow precipitate was filtered, washed with water and acetone, and dried for 24 h at 333 K.

Sample	Composition (%wt)	Si (%wt) nominal (found)	Surface area (m²/g)
CS0	CeO ₂ 100%, SiO ₂ 0%	0 (0.02)	77
CS0.2	CeO2 99.6%, SiO2 0.4%	0.2 (0.33)	117
CS1	CeO ₂ 97.9%, SiO ₂ 2.1%	1 (1.18)	131
CS3	CeO2 93.6%, SiO2 6.4%	3 (3.17)	155
CS6	CeO ₂ 87.2%, SiO ₂ 12.8%	6 (5.49)	168

Calcination and thermal treatments were carried out in a tubular oven ($\phi_{\text{int.}} = 50 \text{ mm}$, l = 900 mm) by placing the material in a quartz crucible and heating for 2 h at the required temperatures (from 723 to 1173 K at a heating rate of 10 K/min) with an air flow of 0.2 Nl/min (STP) passing over the sample.

The specific surface areas of the oxide powders were measured by the BET method using N_2 adsorption at 77 K with a Sorptomatic 1990 apparatus (Carlo Erba). Table 1 reports for clarity the characteristics of the different samples.

Redox Properties

Investigation of the redox properties was carried out using quantitative temperature-programmed reduction (TPR), thermal analysis, and measurements of oxygen storage capacity. TPR was carried out in a conventional, Ushaped, quartz microreactor (i.d. = 6 mm, l= 200 mm) using a 5% H₂-in-argon mixture flowing at 35 ml/min (STP). For TPR measurements, the temperature range investigated was 298–1400 K and the heating rate was invariably 10 K/min. Measurement of hydrogen consumption was carried out with a thermal conductivity detector and a quadrupole mass spectrometer (Balzers QMS 422). Reduction of CuO to metallic copper was used to calibrate TPR apparatus for H₂ consumption.

Oxygen-storage capacity was measured by pulse chromatography following a method similar to that reported by Kacimi *et al.* (21). The sample of the catalyst (10–30 mg) was placed in a stainless steel microreactor heated to 763 K under a He atmosphere. During measurement, the sample was first oxidized with five pulses of oxygen (0.5 ml of a 2% O₂/He mixture) and was then treated with CO pulses (0.25 ml of 4% CO/He mixture) injected every 2 min. We took the amount of CO₂ produced from the first pulse as an estimate of the fast oxygen storage capacity of the sample.

In the thermoanalytical studies, oxidation and reduction of ceria samples were carried out on a Netzsch STA 409 thermoanalyzer equipped with a pulse device (Netzsch) and combined on-line with a Balzers QMG 420 quadrupole mass spectrometer connected to the thermoanalyzer by a heated capillary. Before reduction, samples were oxidized at a heating rate of 5 K/min under a 60% O₂-in-He mixture in the range 303-1200 K. Oxidation was stopped when the samples reached constant mass. Samples were then cooled and reduced by a 20% H₂-in-He mixture while the temperature was raised from 302 K to 1373 K at a heating rate of 5 K/min. After reduction, samples were cooled to room temperature under the same reducing atmosphere to prevent uncontrolled oxidation by traces of oxygen present in the system. At room temperature, the atmosphere was changed and oxidation was investigated.

An additional investigation of sample redox properties was carried out by the PulseTA method (22). The method is based on the injection of a specific amount of gaseous reactant into the inert carrier gas stream and monitoring the changes in mass, enthalpy, and gas composition which result from the incremental extent of the reaction. Onemilliliter pulses of hydrogen and oxygen were injected into the helium stream during heating at a rate of 1 K/min. The results were compared with the isothermal PulseTA experiments carried out from 773 to 1173 K at 50-degree steps. After each pulse of hydrogen leading to the reduction of the material, two pulses of oxygen were injected in order to re-establish the original degree of oxidation of the sample before the next hydrogen pulse. Sample mass monitored on-line indicated that before the subsequent reduction process, the sample was always in the same, maximally oxidized state. Some partial reoxidation of the reduced sample took place before the injection of oxygen owing to the presence of traces of O_2 in the carrier gas.

Structural and Morphological Studies

Structural and morphological studies were carried out by *ex situ* and *in situ* powder X-ray diffraction (XRD), Raman spectroscopy, and high-resolution transmission electron microscopy coupled with selected area electron diffraction (HRTEM–SAED). The XRD equipment consisted of a Siemens D-500 θ –2 θ powder diffractometer equipped with a flow-through, Anton-Paar HTK-10 hot stage and position-sensitive detector. Cu $K\alpha$ radiation and a graphite filter were used in all experiments. A thin sample of powdered catalysts of about 100 mg was placed on a platinum strip which was electrically heated. Temperature monitoring was performed directly on the sample with a thermocouple attached to the strip. XRD profiles were collected at a step width of 0.025 degrees by counting 15 s at each step in the range of interest.

External morphologies and textures of catalysts were studied by scanning electron microscopy (SEM) using a Leica LC-360 instrument working at 10 kV. Samples for the SEM were mounted on aluminum stubs. Detailed microstructural characteristics were obtained from highresolution transmission electron microscopy studies (HRTEM) performed in a Philips CM-30 microscope operating at 300 kV and equipped with a LaB₆ source and an ultrahigh-vacuum system to achieve an ultimate spatial resolution of less than 0.2 nm. Samples for HRTEM studies were taken from ultrasonically dispersed methanol suspensions and placed onto copper grids with perforated carbon films. The experimental image was digitalized on a high-resolution scanner, and the digital processing was performed with a local software package. Conventional transmission electron microscopy combined with energydispersive X-ray microanalysis (EDX) was performed using a Hitachi MT-800 electron microscope working at 200 kV and equipped with a Kevex analytical system and a built-in CCD camera.

The Raman spectra were obtained using a Renishaw System 1000 Raman microscope with a 633-nm HeNe laser. This instrument uses holographic optics to couple the laser light into the microscope onto the sample and to reject the Rayleigh scattered light, while passing the Raman-shifted spectrum onto the single-stage spectrometer. Typical exposure times were 150 s using about 3 mW of laser power focused with a $50 \times$ microscope objective.

RESULTS

Redox Behavior

We will consider first the results from TPR measurements. Figure 1 shows a series of TPR experiments carried out on the fresh samples calcined at 923 K for 2 h. In trace a (CS0) the consumption of H_2 starts at 600 K to continue over 1300 K and the majority of H_2 is consumed in two steps. The low-temperature step consists of two poorly resolved peaks, one centered at ca. 750 K and the other at around



FIG. 1. Temperature-programmed reduction profiles of fresh samples calcined at 923 K: (a) CS0, (b) CS0.2, (c) CS1, (d) CS3, and (e) CS6.

820 K, while at high-temperature a peak is centered at ca. 1115 K. This profile is characteristic of pure CeO₂ and the peak's position and intensity change slightly depending on the previous history of the sample. For example, the intensity of the low-temperature signals is influenced by the texture of the oxide, and is almost proportional to the surface area (2). These signals are generally attributed to the reduction of surface and bulk Ce^{4+} respectively although other phenomena, like adsorption of H₂ and/or formation of reduced CeO_x phases, were also considered in the rationalization of the reduction profile of ceria (6). Trace b (CS0.2) shows a profile similar to that of undoped ceria (a), with a first group of peaks centered at 750 and 820 K indicative of the surface reduction and a second peak observable at 1080 K due to the bulk reduction. Traces c (CS1), and especially d (CS3) and e (CS6), show a very different profile. The two separate reduction steps become almost indistinguishable and merge in a broad region of H₂ consumption upon an increase in the silicon content. In trace e the H₂ consumption begins at 550 K and two maxima can be evidenced at ca. 840 K and 970 K. The calculated reduction degree of ceria is 50, 51, 61, 74, and 80% respectively in profiles a, b, c, d, and e corresponding to a final stoichiometry CeO_x -SiO₂ with 1.75 > x > 1.60.

Figure 2 (profiles a and d) compares the reduction profiles of CS6 and CS0 calcined at 923 K. The TPR behavior of CS6 is substantially different from that exhibited by CS0,



FIG. 2. Temperature-programmed reduction profiles of (a) fresh CS6 calcined at 923 K, (b) CS6 after first TPR and reoxidation at 773 K, (c) sample b subjected to another redox cycle, (d) CS0 calcined at 923 K, (e) CS0 after first TPR and reoxidation at 773 K, (f) CS6 after first TPR and reoxidation at 1073 K, (g) sample f after reoxidation at 773 K, (h) sample g after reoxidation at 1073 K, and (i) sample h after reoxidation at 773 K.

as previously seen. There are two points which deserve to be highlighted: (i) although two poorly resolved peaks can be identified on the first TPR trace of CS6, their position is shifted if compared with those of CS0; the first peak is centered at around 840 K whereas the high-temperature peak is shifted to ca. 970 K; (ii) the background signal at high temperature does not show any residual H₂ consumption, indicating that the reduction process was completed at approximately 1200 K. This stands in sharp contrast with the behavior of CS0, where the reduction process still proceeds even at 1400 K (see the background line in Fig. 2d). The degree of reduction, calculated by integrating the TPR curve with CuO as standard (23), is 50% with CS0 and 80% with CS6. The former value is in agreement with previous studies (24) and, if H₂ consumption can be entirely associated to Ce⁴⁺ reduction, the results suggest a much lower reducibility of undoped ceria compared to CS6.

Another interesting finding in the reduction behavior is observed when CS0 is subjected to a redox cycle. In this case after a first TPR, the sample is reoxidized at 773 K and a second TPR is run with the same sample. Generally, the high-temperature treatment under H₂/Ar during the first TPR strongly modifies the surface properties of CeO₂ (the surface area drops to very low values, $<2 \text{ m}^2/\text{g}$), and the reduction behavior of the reoxidized sample changes correspondingly (25). Specifically, it has been reported that the first low-temperature peak disappears and the reaction proceeds at a much higher temperature, where bulk reduction occurs. We confirmed this behavior with the TPR trace of the reoxidized sample CS0 where only one peak is centered at ca. 1150 K (Fig. 2e). A totally different and in some respects interesting behavior pattern is observed with CS6 (Fig. 2b). The second TPR profile shows a major sharp peak at an intermediate temperature centered at ca. 890 K, followed by a small peak centered at ca. 1000 K. This profile remains unmodified after the following redox cycle (Fig. 2c), indicating that the procedure (reduction plus oxidation) does not lead to changes of the ceria reducibility even though the surface area drops to lower values (see next section). The integration, after the second TPR, corresponds to a global reduction degree of 60%, and the value remains substantially unchanged during successive cycles (a total of six cycles were tested). A similar pattern is shown by the CS3 sample, while CS1 has a behavior intermediate between those of CS6 and CeO₂. For lower SiO₂ content (CS0.2), the TPR traces after redox treatment are almost equivalent to those of pure ceria.

To obtain the promotion of the reduction behavior, the first reduction must be carried out at a temperature of at least 1073 K. Below this reduction temperature, the TPR profile remains almost unaffected (Fig. 3A), exhibiting the two broad and poorly resolved peaks. The reoxidation temperature also affects the reducibility (Fig. 3B). An optimum reduction profile is obtained after reoxidation at 773–873 K,



FIG. 3. (A) Temperature-programmed reduction profiles of (a) CS6 calcined at 923 K, and (b–f) after a redox cycle (reduction at the temperature indicated and reoxidation at 773 K): (b) reduced at 673 K, (c) 873 K, (d) 1073 K, (e) 1273 K, and (f) 1373 K. (B) Temperature-programmed reduction profiles of CS6 (a) calcined at 923 K, and (b–f) after a redox cycle: reduced at 1273 K and reoxidized at (b) 773 K, (c) 923 K, (d) 1073 K (e) 1173 K, and (f) 1273 K.

whereas reoxidation at T > 923 K causes a progressive shift of the reduction peak to higher temperature and under these conditions, the TPR profiles of CS6 and CS0 samples become similar.

In order to study the effect of the reoxidation temperature, further redox cycles were investigated on sample CS6 (Fig. 2f–i). The following treatments were performed sequentially: TPR of the fresh sample (Fig. 2a); oxidation at 1073 K for 1 h under air and reduction, TPR (f); oxidation at 773 K for 1 h under air and reduction, TPR (g); oxidation at 1073 K for 1 h under air and reduction, TPR (h); oxidation at 773 K for 1 h under air and reduction, TPR (i). The oxidation at 773 K promotes the successive reduction which occurs at lower temperature, while reoxidation at 1073 K shifts the successive reduction to higher temperature and the effects are fully reversible. It is interesting to note that hydrogen consumption for ceria reduction in profiles a, f, and h is the same (about 2100 μ mol/g), while in traces g and i it diminishes to ca. 1500 μ mol/g.

There are several artifacts which can invalidate TPR measurements especially when quantitative estimations are made (26, 27), such as the presence of carbonates and nitrates or adsorption/desorption of H₂. TPR alone cannot therefore give a complete, conclusive picture of the reduction behavior of ceria-containing samples. It has been reported that formation of ceria bronzes like CeO_2H_x occurs when ceria is treated under hydrogen (28). If this is the case here, part of the hydrogen adsorbed in the TPR profile should not be used for reduction immediately but stored by ceria and eventually desorbed or utilized for reduction at higher temperatures. We carried out analysis of hydrogen stored in CS6 during a TPR run at different temperatures and the results showed that only a negligible amount is present. It probably originates from adsorbed water and is certainly not responsible for the main peak of the TPR profile. In addition, TPR analysis carried out using a quadrupole mass spectrometer shows that water immediately desorbs following H₂ consumption, indicating that a pure reduction process is taking place. Therefore, TPR traces of ceria-silica are indicative of a promotion of the reduction properties induced by the presence of SiO₂.

To further corroborate these results, reduction/oxidation was carried out by monitoring weight changes on a representative sample using a thermobalance. Figure 4 shows the weight changes of CS3 and CS0 during reduction (A) and subsequent oxidation (B). Reduction of CS3 occurs at lower temperatures, beginning under the conditions applied at ca. 723 K and being complete at 1200 K, in agreement with TPR analysis. The weight loss due to the oxygen removal indicates that the product of reduction has a composition of CeO_{1.67}, which is similar to the CeO_{1.65} obtained by quantitative TPR analysis. The reduction of CS0 starts at higher temperature (ca. 873 K) and it is not complete at 1353 K, where the TG still shows weight changes. Weight loss at 1353 K indicates that the composition of the sample after the reduction process is close to $CeO_{1.77}$, which is in agreement with TPR results (where x = 1.75 in CeO_x). Oxidation of the reduced samples was carried out immediately after cooling under the reducing atmosphere. In the case of the CS0 sample the beginning of oxidation is very fast and almost 60% of the total weight gain is reached below 473 K. However, total oxidation of this sample is barely achieved



FIG. 4. Reduction (A) and oxidation (B) of CS0 and CS3 samples. Weight changes expressed in wt% are marked on curve.

even at temperatures as high as 1353 K. The silicon-doped sample behaves differently: the oxidation is slower at low temperatures but is already complete at ca. 1000 K.

To study the redox behavior in incremental steps at different temperatures and the same degree of oxidation or reduction, the Pulsate method described above was applied; i.e., pulses of hydrogen followed by pulses of oxygen were injected into the carrier gas He. The results presented in Fig. 5 indicate that after each hydrogen pulse there is a distinct weight loss due to ceria reduction. The sample is then partly oxidized by traces of oxygen in the carrier gas, a process that takes place much faster in the case of the CS0 sample, as in the case of the CS3 sample (see Fig. 5B). Both samples behaved differently during the oxygen pulse. In the case of the CS3 sample, a distinct oxygen uptake is observable, leading to a weight gain greater than the weight loss that occurs during reduction. After ca. 15 min, the excess oxygen is desorbed from the ceria and the mass of the sample returns to its initial value. The maximal weight gain caused by the transient oxygen uptake is marked as ΔO_2 in Fig. 6A. For the oxidized CS0 sample, interaction with oxygen did not lead to weight uptake and only minor buoyancy effects (an apparent change of the sample mass due to variation of the density of the surrounding gas) were observed after an oxygen pulse on the TG curve.

The extra oxygen uptake observed with CS3 may be due to some adsorption of O2 on stoichiometric ceria. The difference between the two samples indicates that CS3 interacts easily with O₂/H₂. Figure 6 presents the weight losses for both samples caused by a 1-ml pulse of hydrogen (part A) as a function of the temperature of the injection and weight uptake after oxygen pulses for the CS3 sample (part B). It is shown that in the temperature range 873-1173 K the CS3 sample is more easily reduced than CS0; e.g., the reduction from the composition $CeO_{2.00}$ to $CeO_{1.99}$ occurs with a 1-ml pulse of hydrogen at ca. 983 K for CS3 while for CS0 it takes place at ca. 1062 K. Oxygen uptake is observable only for the CS3 sample and the maximal ability of ceria for short adsorption of oxygen is observed at ca. 1123 K. At higher temperatures, the amount of oxygen uptake decreases. From this experiment it can be clearly seen that under applied conditions there is no H₂ adsorption on ceria. All H_2/O_2 consumption is due to the redox processes. There is only some extra oxygen uptake on CS3 sample, which may be due to simple O₂ adsorption/desorption on the surface of ceria (29).



FIG. 5. One milliliter pulses of hydrogen and oxygen over CS3 (A) and CS0 (B) samples during heating under helium at a rate of 1 K/min. Weight loss due to ceria reduction is marked as ΔH_2 and weight gain due to oxygen pulses as ΔO_2 .



FIG. 6. (A) Weight loss due to reduction of ceria caused by hydrogen pulses (marked as ΔH_2 in Fig. 5) for CS0 and CS3 samples. Weight losses characteristic of certain degrees of reduction (CeO_{1.99} and CeO_{1.98}) are marked in the figure. (B) Oxygen uptake during O₂ pulses (ΔO_2 in Fig. 5) over CS3 sample.

Oxygen Storage Behavior

The oxygen storage capacity (OSC) of the CS0 and CS6 samples was also evaluated by measuring CO conversion to CO_2 under pulsed dynamic conditions. Under these conditions, the ability of the catalyst to rapidly undergo changes in the oxidation states by converting reagents into products was evaluated. Fresh catalyst and catalyst subjected to a redox cycle were compared. It was shown that whereas fresh CS0 ceria has a better OSC than CS6 (35 μ mol of CO₂ per gram with CS0 compared to 27 μ mol with CS6 sample for the first CO pulse), the situation is reversed after a redox cycle, where CS6 ceria has a superior OSC (10 vs 2 μ mol). This is in agreement with TPR and TG results, which evidence an enhancement of the reduction behavior after a redox cycle only for the silica-doped sample.

Oxidation at different temperatures after reducing treatment at 1273 K dramatically changes OSC in the silicondoped material (Fig. 7). CO conversion to CO_2 reaches a maximum after oxidation at 773 K, where the CS6 sample has an efficiency 5 times higher than that of the CS0 sample. On increasing the oxidation temperature to 1073 K, there is a progressive decrease in CO_2 production and the exchange capacities of the materials become similar. This highlights a situation of strong promotion of OSC behavior of silicon-doped ceria compared to pure CeO_2 sample. The decrease of OSC efficiency with increasing oxidation temperature is in agreement with the lower reducibility of samples detected by TPR at the higher oxidation temperatures (Fig. 3B).

Structural Characterization

A combined XRD-TEM analysis was undertaken in order to obtain more information on the structural and morphological modifications which occur on silica-doped ceria following reduction and oxidation treatments. Structural characterization was carried out mainly on CS0 and CS6 samples for comparison. XRD of CS6 calcined at 1273 K is shown in Fig. 8a. It shows typical diffractions corresponding to pure ceria, and there is no evidence for the presence of crystalline SiO₂. A similar pattern is shown by the other samples with intermediate composition. This indicates that fresh sample is probably made up of separate domains of crystalline ceria and amorphous silica, as will be shown later. XRD patterns of CS0, CS3, and CS6 after reduction under a 5% H₂/Ar mixture at 1273 K are also presented in Fig. 8. Reductive treatments were carried out in a U-shaped quartz microreactor; the samples after reduction were cooled to 250 K under a H₂/Ar atmosphere and transferred into a glovebox for storage. Reduction of CeO₂ at 1273 K results in the formation of a deep-blue-colored powder; the XRD pattern shows the characteristic peaks of a reduced fluorite phase (Fig. 8b). The positions of the main peaks are shifted to the left indicating a modification of the cell parameters. It is generally reported that during reduction a progressive depletion of oxygen from ceria lattice



FIG. 7. Oxygen storage capacity of CS6 (\Box) and CS0 (\bigcirc) measured at 673 K after redox cycle. Reduction under H₂ (5%)/Ar at 1273 K for 1 h and oxidation under air for 1 h at the temperature indicated.

FIG. 8. X-ray powder diffraction patterns of (a) CS6 calcined at 1273 K, (b) CS0 reduced at 1273 K, (c) CS3 reduced at 1273 K, (d) CS6 reduced at 1273 K, and (e) $Ce_{9.33}(SiO_4)_6O_2$ prepared from a stoichiometric mixture of SiO₂ and CeO₂.

takes place with formation of substoichiometric fluoritestructured CeO_{2-x} (30). At high degrees of reduction, the hexagonal and cubic, A- and C-type sesquioxides have also been observed (2, 31, 32). In our case no evidence for segregation of the hexagonal or cubic sesquioxide Ce₂O₃ is observed. The shift of the position of the peaks to lower values of 2θ originates from the presence of Ce^{3+} ; in this case a lattice expansion of the fluorite structure is expected, owing to the difference in the ionic dimensions of Ce^{3+} and Ce^{4+} (1.012 vs 0.97 Å) (33). The difference in the XRD patterns of fresh and reduced ceria suggests that reoxidation of ceria at room temperature is slow under these conditions, probably due to the formation of a thin layer of oxidized ceria which prevents further reoxidation of the reduced sample (32), which is known to oxidize easily under air (2, 34). From the XRD, only small signals originating from oxidized ceria are observed on the right side of the main diffraction peaks.

Reduction of CS6 under identical conditions gives a lightblue powder. The XRD profile recorded at room temperature shows the presence of peaks assigned to the fluorite phase plus a series of peaks not belonging to a reduced fluorite phase or to a C- and A-type sesquioxide (Fig. 8d). These peaks are present also in the reduced CS3 sample (Fig. 8c), although with a lower intensity. The position of diffraction lines and their relative intensities calculated for CS6 are reported in Table 2. Satisfactory agreement for all the experimental lines is obtained for an hexagonal unit cell, space group $P6_3/m$, with a=9.583(4) and c=7.086(3) Å. The Miller indices and the corresponding interplanar spacings calculated on the basis of the parameters of this cell are also reported in Table 2. The position of the observed peaks and their relative intensities are well accounted for by the hexagonal cell reported for $M_{9,33}(SiO_4)_6O_2$ with M = La, Pr (35). We suggest that the phase reported here is $Ce_{9.33}(SiO_4)_6O_2$ (36) which forms by interaction of SiO₂ and CeO₂ under H₂. The same phase has been recently observed by Kepinski and Wolcyrz studying the spreading and interaction of CeO₂ supported on SiO₂ under an H₂ atmosphere (15). To support these findings a sample of $CeO_2(82\%)$ -SiO₂(18%) containing the stoichiometric amount of the two oxides to give $Ce_{9,33}(SiO_4)_6O_2$ has been prepared. The mixed oxide was subjected to reduction under TPR conditions and the Xray diffraction of the resulting white-light gray powder is included in Fig. 8. It is shown that under these conditions there are no traces of the presence of the fluorite structure after reduction, indicating that complete reaction between CeO_2 and SiO_2 to form $Ce_{9.33}(SiO_4)_6O_2$ has occurred.

The stability of the $Ce_{9.33}(SiO_4)_6O_2$ phase in CS6 on reoxidation under air was followed by *in situ* temperatureprogrammed XRD experiments. The XRD profiles

TABLE 2

Analyzed Powder Spectrum of Ce_{9.33}(SiO₄)₆O₂ Phase

$d_{ m obs}$ /Å	I/I_0	$d_{ m calc}$ /Å	hkl
4.786	4	4.791	110
4.145	22	4.149	200
3.964	19	3.969	111
3.543	12	3.543	002
3.259	32	3.258	102
3.135	28	3.137	210
2.864	100	2.868	211
2.766	24	2.766	300
2.697	3	2.694	202
2.304	6	2.302	310
2.271	4	2.270	221
2.184	5	2.180	302
2.123	9	2.119	113
2.077	5	2.075	400
1.988	22	1.985	222
1.934	13	1.930	312
1.907	6	1.904	320
1.891	25	1.887	213
1.842	13	1.839	321
1.814	18	1.811	410
1.794	20	1.790	402
1.776	10	1.772	004
1.562	6	1.558	331
1.547	7	1.543	214
1.507	9	1.503	502
1.496	6	1.491	510
1.488	6	1.492	304
1.461	9	1.459	511
1.310	4	1.306	521
1.296	6	1.292	215
1.270	10	1.266	414
1.248	8	1.244	522
1 202	3	1 198	440
1.202	3	1.198	440





FIG. 9. Powder X-ray diffraction pattern of (a) CS6 reduced at 1273 K, and reoxidized at (b) 773 K, (c) 873 K, (d) 1073 K.

obtained at 773, 873, and 1073 K are illustrated in Fig. 9. As the oxidation temperature increases, the relative intensities of all the peaks belonging to the cerium silicate decrease while maintaining their relative proportions, which provides additional evidence that all the indexed lines correspond to the same phase. At ca. 1073 K complete reoxidation takes place, and this phase is totally transformed to cubic ceria and amorphous silica. It can be clearly seen that at the end of the experiment (after treatment at 1073 K), the intensity of the peaks belonging to cubic ceria has increased. However, between 773 and 873 K the oxidation of $Ce_{9,33}(SiO_4)_6O_2$, evidenced by the progressive disappearance of its reflections, is not accompanied by an increase in CeO₂ peak intensity. Increasing amorphization of the Ce-Si-O phase is observed in the profiles recorded at these temperatures, as evidenced by an anomalous background adsorption. This is in agreement with the transformation of the silicate first to amorphous silica and ceria, which at higher temperatures originates crystalline cubic ceria. The nature of the crystallites of this cubic ceria is different from that of pre-existing ceria. Profile analysis of individual CeO₂ peaks permits the deconvolution of each signal into two components centered at the same 2θ value but with different width values. The narrow component corresponds to pre-existing CeO_2 , and the broad component to much smaller CeO_2 crystallites resulting from Ce_{9.33}(SiO₄)₆O₂ oxidation. Crystallite dimensions measured by TEM go from an average value of ca. 90 nm for the sample after TPR to ca. 62 nm

for the sample reoxidized at 873 K. However, most of the small ceria crystallites are embedded within amorphous silica, and this makes it difficult to obtain a good correlation also for surface areas. Values in the range of $2-4 \text{ m}^2/\text{g}$ are obtained after reoxidation.

The structural features of the fresh CS6 sample and the transformation that occurs after reduction and oxidation treatments were also monitored in detail by electron microscopy. Selected-area electron diffraction performed in the fresh CS6 sample after calcination at 923 K shows rings corresponding to cubic, pure CeO₂ and amorphous SiO₂, which is visible as a diffuse background near the transmitted spot at the center. Energy-dispersive X-ray microanalysis demonstrates the presence of both cerium and silicon in this sample. Figure 10 depicts a single CeO₂ crystallite embedded in amorphous SiO₂ and its associated Fourier transformed image. The crystal shows (111) planes. There is a sharp interface between the two oxides, thus indicating the absence of any apparent interaction between CeO₂ and SiO_2 at this stage in the sample. The sample comprises a physical mixture of amorphous SiO₂ and well-defined crystallites of cubic CeO2 of about 15-30 nm in agreement with XRD results.

When the calcined sample is subjected to a reduction treatment at 1273 K there is the formation of a ternary Ce-Si-O phase, with a larger particle size with respect to preexisting CeO₂ crystals. Energy-dispersive X-ray microanalysis performed over different areas of this sample mostly indicates the common presence of cerium and silicon. However, some minor, smaller particles constituted only by CeO₂ remain. No amorphous or segregated SiO₂ is present. On the other hand, the resulting ternary compound is perfectly crystalline. As an example, Figure 11 shows a single crystal of this phase and its experimental electron diffraction pattern. It is concluded that the ternary compound belongs to the hexagonal crystallographic system with lattice parameters (as deduced from electron diffraction studies) a = 9.60 and c = 7.12 Å, which are in close agreement with those obtained by XRD for $Ce_{9.33}(SiO_4)_6O_2$.

When $Ce_{9.33}(SiO_4)_6O_2$ is subjected to an oxidation treatment at 773 K strong changes take place at the microstructure level. First, the resulting crystals are covered by a ca. 4-5 nm thick, amorphous layer of SiO₂, which has exsolved from the $Ce_{9.33}(SiO_4)_6O_2$ phase. Second, and as a consequence of this exsolution of SiO₂, the size of the resulting particles decreases. These facts are nicely seen in Fig. 12. Third, the overall crystallinity of the sample is gradually lost and small domains of pure CeO₂ do appear. A close view of one particle of this sample is depicted in the lattice fringe image of Fig. 13. Besides the fringes of the particle, which still contains cerium and silicon as determined by EDX, several small domains of CeO_2 of about 4 nm are seen (indicated by arrows). It is very interesting to note that all the small CeO₂ crystallites grown from the same $Ce_{9,33}(SiO_4)_6O_2$ particle show (200) planes at 2.7 Å in a



FIG. 10. CeO_2 crystal embedded in a SiO₂ matrix in the CS6 sample calcined at 723 K. The inset corresponds to the Fourier-transformed image of the CeO₂ particle. The crystal shows (111) planes at 3.1 Å.

similar orientation, thus indicating that the formation of CeO₂ is a structure-dependent process. On the other hand, a detailed analysis of the remaining Ce_{9.33}(SiO₄)₆O₂ phase indicates that its initial crystallinity has been lost. As an example, Fig. 14 shows the high degree of disorder in one particle containing Ce, Si, and O. In the same figure is included the corresponding Fourier-transformed image, which deserves additional comments. Three different phases can be identified in the FT image. First, there are spots corresponding to $(3\bar{2}\bar{1}\bar{2})$ and $(\bar{1}10\bar{1})$ planes at 2.4 and 5.4 Å, respectively, of the hexagonal $Ce_{9.33}(SiO_4)_6O_2$ phase. Second, there are spots corresponding to (200) planes of the cubic CeO₂ crystals. Third, there is an inhomogeneously distributed, diffuse ring, which corresponds to the partial amorphization of $Ce_{9.33}(SiO_4)_6O_2$. It is also interesting to highlight that the ring of amorphization is preferentially intense in precisely the same direction of CeO_2 (200) planes (perpendicular to the CeO_2 (200) spots in the FT image). From that, it can be concluded that cubic CeO₂ crystallites form through partial amorphization of hexagonal $Ce_{9,33}(SiO_4)_6O_2$ particles following the same crystallographic direction.

When the reoxidation is carried out at higher temperatures, i.e., at 1073 K, the effects observed above take place to a large extent. Now the exsolution of SiO₂ from $Ce_{9.33}(SiO_4)_6O_2$ is complete and the sample comprises two phases: small CeO₂ crystallites embedded in amorphous SiO₂. This is observed for example in Fig. 15. Now, the crystallization of CeO_2 is complete, in accordance with XRD results, and chaotic; no preferred orientation of the resulting CeO_2 crystallites is visible.

The microstructure of pure ceria after the same reduction/ oxidation treatment differs completely from the microstructure exhibited by the silica-doped sample. The CS0 sample after redox treatment comprises exclusively crystallites in the range of 20–65 nm. The micrograph in Fig. 16a represents a general view of this sample and, for comparison, Fig. 16b shows under the same magnification an image of the CS6 sample. At the microstructure level, and in complete contrast with what was observed in the CS6 sample, the CS0 sample is completely free from any paracrystalline structure or layer. All the particles in the sample look like the one depicted in micrograph 16a, that is, crystals with clean ends and free from any covering layer.

Figure 17 shows Raman spectra, recorded at room temperature, of the $Ce_{9,33}(SiO_4)_6O_2$ sample and its transformation into CeO_2 and SiO_2 induced by heating in air for 30 min intervals at successively higher temperatures. Spectrum a, taken from the silicate under an inert-gas atmosphere, reveals peaks at 128, 171, 223, 285, 389, 446, 522, 737, and 856 cm⁻¹. There is little change after oxidation at 473 K, other than a slight broadening of the peaks, but by 673 K all of these peaks have disappeared, a broad band below 600 cm⁻¹ has developed, and the 465-cm⁻¹



FIG. 11. Lattice-fringe image and its associated experimental electron diffraction pattern of $Ce_{9.33}(SiO_4)_6O_2$ present in the CS6 sample resulting from temperature-programmed reduction. The particle is perfectly crystalline and oriented along the [1 2 3 2] crystallographic direction. Closest planes are (1 0 1 2) at 3.3 Å and (2 2 0 1) at 3.6 Å.



FIG. 12. Sample CS6 oxidized at 773 K after TPR. The particles are covered by a 4-5 nm thick layer of amorphous SiO₂ (see areas enclosed by arrows).



FIG. 13. Sample CS6 oxidized at 773 K after TPR. Big particles corresponding to hexagonal $Ce_{9.33}(SiO_4)_6O_2$ are seen along with small crystallites of cubic CeO_2 (marked by white arrows). CeO_2 crystallites exhibit (200) planes at 2.7 Å.



FIG. 14. High-magnification image corresponding to a selected area of Fig. 13 and the associated Fourier-transformed image. The particle has lost crystallinity, but it is possible to obtain the crystallographic orientation along the $[1 \ 2 \ 3 \ 1]$ direction. Planes close to the origin are $(3 \ 2 \ 1 \ 2)$ at 2.4 Å and $(1 \ 1 \ 0 \ 1)$ at 5.4 Å. Spots corresponding to CeO₂ (200) planes are visible in the Fourier-transformed image as well as a poorly defined ring corresponding to the partial amorphization of the Ce_{9.33}(SiO₄)₆O₂ phase in the same direction (marked by arrows in the image) as the CeO₂ (200) planes.



FIG. 15. Sample CS6 calcined at 1073 K after TPR treatment. Small CeO_2 crystallites are surrounded by amorphous SiO_2 . Inset: High-magnification image of a selected portion where CeO_2 particles are randomly oriented.

peak from fluorite-structured CeO₂ (37) has appeared. The broad band, reflecting the phonon density of states (37), is characteristic of Raman scattering from amorphous materials. This band continues to grow with further oxidation at 873 K as the CeO₂ line narrows and strengthens. Finally, by 1073 K, the usual Raman spectrum of well-crystallized CeO₂ is obtained. This series of spectra closely parallels the XRD results shown in Fig. 9.

Morphological Characterization

Morphological investigations on CS6 and CS0 samples after redox treatment were also performed by scanning electron microscopy. In both cases, the reduced samples exhibit typical features of an agglomerated powder. However, after reoxidation, the CS6 sample shows an important rearrangement in its external morphology (Fig. 18a), which is highly porous and consists of homogeneous spherical aggregates of ca. 0.1 μ m in diameter. In contrast, the calcined CS0 sample does not show this structure (Fig. 18b). It appears that amorphization of the CS6 sample at the microstructure level during the redox cycle, as revealed by TEM studies, is also accompanied by a change of morphology, which results in a morphological homogeneization of the sample and a

higher degree of porosity, which in turn is responsible for the different surface area observed in the CS6 sample after a redox cycle compared to ceria ($3 vs 1 m^2/g$). A high degree of porosity has been observed on ceria and ceria–zirconia samples subjected to redox cycles (25), and has been attributed to stress and coalescence of dislocations induced by the expansion and shrinkage of the lattice during the cycles. In our case, in addition to this possibility, the formation of the silicate, which on oxidation gives amorphous ceria, can contribute to the enhancement of the degree of porosity and surface area.

DISCUSSION

The results presented in this paper show unambiguously that high-surface-area silica-doped ceria exhibits superior reduction behavior, leading to an enhancement of the oxygen storage/release capacity as shown in pulse and temperature-programmed experiments. These characteristics are especially important if the materials are subjected to a redox cycle at high temperatures. In this case bulk reduction is strongly promoted in contrast to what happens with undoped ceria. The main issue which needs to be



FIG. 16. (a) Representative high-resolution transmission electron micrograph corresponding to the CS0 sample after reduction–oxidation treatment. Only the presence of pure cubic CeO_2 is evidenced. (b) High-resolution transmission electron image obtained from the CS6 sample after the same redox cycle. Here cubic crystalline CeO_2 particles are covered by an amorphous layer of SiO₂.

addressed here is to understand the reasons for this peculiar behavior, and to know why cerium oxide doped with silica develops these interesting reduction features.

Let us first analyze the reduction/oxidation behavior studied by TPR and TG. Stepwise reduction is often considered as a fingerprint to identify the characteristics of bare CeO_2 (6) or CeO_2 supported and/or included in a different matrix (6, 9, 25, 38). Despite the apparent simplicity of the TPR profile, several interpretations have been put forward to explain the origin of the two peaks in TPR traces. One of the most reliable explanations hypothesizes the reduction of CeO_2 in two stages. First, surface Ce^{4+} is reduced at low temperature, generating the peak at around 770 K. This process is then followed by bulk reduction at higher temperatures (39). A second interpretation of the results is based on the formation of intermediate stoichiometries in the course of reduction (40), for it is known that several CeO_{2-x} suboxides can be formed under reducing conditions. These explanations however do not exclude that both phenomena might contribute to the reduction process. Generally, when studying the effect of surface area on the reduction of CeO_2 , a series of homologous ceria samples are used, all of which originate from the same material calcined at different temperatures. In these cases it is clearly



FIG. 17. Raman spectra of (a) the $Ce_{9.33}(SiO_4)_6O_2$ sample and (b–e) its transformation into fluorite-structured CeO_2 and SiO_2 upon reoxidation performed by heating in air for 30 min intervals at successively higher temperatures: (a) 298 K, (b) 473 K, (c) 673 K, (d) 873 K, and (e) 1073 K.

seen that there is a linear dependence between the amount of H_2 consumed in the first peak and surface area (2). It is known that several other variables can affect initial CeO₂ reduction, including the presence of doping cations and adsorbed molecules (8, 26), crystallite dimensions and shape (41, 42), and different reactivity of the exposed planes (43, 44). These factors could explain why the reduction profile of fresh ceria differs from that of ceria-doped silica, especially when dopant concentration reaches values of 3-6% wt (Fig. 1). In addition the presence of SiO₂ promotes the reduction of ceria with formation of $Ce_{9.33}(SiO_4)_6O_2$, and this strongly affects the bulk reduction temperature. Correspondingly, and in agreement with the presence of separate domains of ceria and silica in the fresh material, the onset of Ce⁴⁺ reduction in the TPR of silica-doped samples and pure ceria is similar, and occurs at a temperature of ca. 600 K. At higher temperatures the TPR traces of CS3 and CS6 consist of a series of broad, poorly resolved peaks in a position which is intermediate between the lowand high-temperature peaks of CS0. This corresponds to the anticipated reduction of the bulk of ceria, driven by the formation of cerium silicate. The interesting issue which deserves to be investigated is the change of reduction behavior of ceria–silica after a redox treatment, even when the surface area is low. This behavior is evident especially in the CS6 sample and indicates a promotion of oxygen diffusion in the bulk at moderate temperatures compared to the case with CS0 (Fig. 2). It has been observed for example on doping CeO₂ with ZrO_2 (8, 25) and it was associated with the enhancement of ion mobility due to the presence of structural defects created by the smaller Zr^{4+} inside CeO₂ lattice.

The reduction of ceria occurs by progressively abstracting oxygen from the lattice and forming a fluorite-structured oxygen-deficient ceria CeO_{2-x} at increasing Ce^{3+} concentration there is a corresponding increase of charged defects. In fluorite-type oxides, for degrees of reduction higher than 15% (CeO_{2-x} with x > 0.08), these defects tend to cluster, making ionic transport more difficult (45). Consistently in the reduction profile of ceria, when a degree of reduction of x = 0.08 - 0.16 is reached, the reduction process is decelerated and further reduction requires more energy. Another limitation for the reduction of ceria in these temperature ranges is the drop of surface area which occurs under hydrogen during TPR, which consequently affects the reduction rate. The discrepancies noted in the literature on the extent of reduction at low temperature for pure ceria can be related to the intimate nature of this process which does not allow under these conditions the formation of an equilibrium structure of definite composition. In addition, for the hightemperature region here investigated, the thermodynamics of ceria/hydrogen system does not allow more than 50-60% reduction (46). However, if there is a transformation of a fluorite-structured anion-deficient CeO_{2-x} into a hexagonal silicate phase, these limitations are no longer present and reduction can proceed, leading to the formation of the silicate. Under these conditions only one peak should be observed and the reduction should proceed rapidly to the formation of the new phase. The difference between the first and the successive reduction profiles can be explained on the basis of the better homogeneity of CeO₂-SiO₂ after a redox cycle. As evidenced by HRTEM, fresh material consists mainly of large separated domains of CeO₂ and SiO₂ (Fig. 10). After the first reduction/oxidation cycle small ceria crystallites form from the silicate and by oxidation of reduced ceria. This allows a higher degree of homogeneity between the two oxides, which increases the reduction rate in a narrow temperature range.

Oxidation experiments have shown that with pure ceria the reoxidation process is faster at lower temperatures compared to that of silica-doped samples (Fig. 4). The reoxidation of hexagonal $Ce_{9.33}(SiO_4)_6O_2$ to cubic ceria does not occur simply by refilling of oxygen vacancies, and more energy ought to be involved to allow the transformation of a hexagonal phase to cubic. This process takes place in the range of temperature between 573 K and 873 K through the



FIG. 18. Scanning electron microscopy images corresponding to CS6 (a, top) and CS0 (b, bottom) samples after redox treatment.

intermediate formation of an amorphous phase, which then transforms to cubic ceria. The oxygen storage features measured by cycling both O_2/H_2 and O_2/CO show a maximum exactly when oxidation is carried out in this temperature range (Fig. 7). The importance of reoxidation temperature in the development of oxygen storage properties is well highlighted in Figs. 2, 3B, and 7.

A summary of the structural transformation occuring with silica-doped ceria is given in Scheme 1. It is suggested that formation of a Ce–Si–O phase enables participation of the bulk oxygens in the redox processes. Under these conditions, the window of stability for reduced ceria (especially in an oscillating environment, such as auto exhaust catalysis) is widened and the reduction process becomes faster. This allows improved oxygen storage behavior since it is known that it is the reduction step which is energetically demanding, reoxidation being energetically favorable (9). Therefore, the overall redox process can benefit from the increase of the reduction rate and the stability of a reduced phase. Moreover, as suggested by XRD and



SCHEME 1

HRTEM studies, reoxidation of the silicate gives amorphous, small ceria crystallites, which possess higher reactivity toward O_2/H_2 and O_2/CO . It is known that CeO_2 nanocrystallites show enhanced electronic and ionic transport properties (47), which might also be dependent on the surfaces exposed and on the presence of grain-boundary defects, and these transport properties govern the kinetic of oxygen exchange. The recent observation of nanoscale segregation of ceria from ceria-zirconia solid solutions (48) strongly supports this view and the deduction that nanoscale segregation of CeO₂ must be a crucial factor in increasing the OSC of our samples. The extent to which this occurs is the key factor in the overall performance of the catalyst and that may depend on the way catalysts are processed. This situation of high reactivity linked to the presence of amorphous/nanocrystalline ceria is operative only in a limited temperature range. Reoxidation carried out at T > 1073 K inevitably causes transformation of the small ceria crystallites into bulk ceria, thus reducing its oxygen storage and redox properties.

If we bear in mind that the oscillation of CeO_2-CeO_{2-x} under real auto exhaust conditions is limited to a few percent (x < 0.02) of the total degree of reduction, because of kinetic constrains (6), an increase in reduction efficiency and rate can lead to a substantial improvement in redox behavior under operating conditions, at least up to when Ce– Si–O/amorphous ceria/ceria crystallites are present. Therefore, the stabilization of these domains in a wider temperature range may be one of the keys in the development of better CeO_2 -based redox catalysts.

CONCLUSIONS

In summary, the doping of ceria with silica induces important structural and morphological modifications which depend on the amount of dopant and on the thermal history of the sample. For a Si content greater than 3 wt%, the reducibility of the material is positively affected, especially after thermal treatment under redox conditions, in a fashion similar to that previously observed in ZrO_2 (8). However, the origin of this phenomenon does not depend on structural perturbations in the lattice of ceria induced by the dopant (25), as in the case of zirconia, but on the formation of a silicate phase under reducing conditions. Evidence for the formation of $Ce_{9.33}(SiO_4)_6O_2$ is obtained by quantitative TPR and combined powder XRD analysis and HRTEM. This phase, on reoxidation, decomposes giving amorphous silica and small ceria crystallites which are more reactive toward reduction and oxidation. The dynamics of these transformations is strongly dependent on the degree of homogeneity of the two oxides and on the temperature of the redox treatment. Presently, an important limitation is the upper limit of the reoxidation temperature (T < 1073 K) which causes growth of ceria crystallites with a resulting drop of oxygen storage activity.

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