

## Unusual Oxygen Storage/Redox Behavior of High-Surface-Area Ceria Prepared by a Surfactant-Assisted Route

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The preparation and characterization of high-surface-area, thermally resistant, transition-metal oxides has been the focus of an intense scrutiny in recent years. This is particularly evident in the field of catalysis and adsorption, where the careful control of textural and morphological properties has always been the key to successful applications. Recently, much interest has been focused on the preparation of high-surface-area, structurally ordered oxides using small organic molecules as templates, or structure-directing agents.<sup>1</sup> Employing this approach, a wide range of transition-metal oxides with potential applications in catalysis were prepared, including alumina,<sup>2</sup> titania,<sup>3</sup> zirconia,<sup>4</sup> and cromia.<sup>5</sup> A few of them showed an ordered, well-defined pore size, even after calcination.<sup>6</sup> Others had a high surface area but did not possess a regular pore system, in either the as-synthesized or calcined form.<sup>4a</sup> The difficulty of obtaining regular mesophases is consistent with the thermal instability of the mesostructured transition-metal oxide and their different oxo chemistry in comparison with silicon. It is only recently that stable transition-metal oxide "molecular sieves" have been described.<sup>7</sup>

As a part of a more general project aimed at developing catalysts containing ceria with improved textural, structural, and redox properties for catalytic applications, we investigated the possibility of preparing high-surface-area (HSA) cerium oxide using a series of cationic surfactants as *pseudo-templating* agents. In addition to our interest in this surfactant-assisted route, we have also concentrated on the potential use of high-surface-area ceria as a catalyst or catalyst support.<sup>8</sup> In particular, the textural properties and redox/oxygen-

storage features of CeO<sub>2</sub> (i.e.- the ability of ceria to be reduced easily and to shift rapidly between the +3 and +4 state and vice versa) play a key role in the development of the so-called three-way catalysts (TWCs) for auto-exhaust treatment.<sup>9</sup>

Here we found for the first time that use of a surfactant-assisted route, employing cationic surfactants and hydrous cerium oxide, although failing to provide an ordered pore structure, is necessary to prepare a material that shows enhanced surface area and exceptionally high redox behavior.

The procedure we used to prepare HSA cerium(IV) oxide exploits the interaction of hydrous cerium oxide with cationic surfactants under basic conditions, where the organic molecule can be easily incorporated within the hydrous oxide by ion exchange with hydroxy groups, at a pH well above that of the isoelectric point of the oxide (6.75).<sup>10</sup> For the preparation, an aqueous solution of the appropriate cationic surfactant (we used cetyltrimethylammonium bromide (C<sub>16</sub>), myristyltrimethylammonium bromide (C<sub>14</sub>), or octadecyltrimethylammonium bromide (C<sub>18</sub>), 0.1 M Aldrich) was added to a solution of CeCl<sub>3</sub>·7H<sub>2</sub>O (0.1 M Aldrich), and the ratio Ce/C<sub>n</sub> was varied in the range 0.6–1.25. After stirring the mixture for 30 min, ammonia was added very slowly with vigorous stirring until the pH reached 11.4. This caused the precipitation of hydrous cerium oxide as a gelatinous yellow-brown solid. The mixture was then sealed and placed in a thermostatic bath maintained at 363 K under stirring for 5 days. The mixture was subsequently cooled and the precipitate filtered and washed several times with water and acetone. The yellow powder was then dried at 333 K for 1 day and calcined at different temperatures in the range 723–1173 K for at least 2 h.

After reaction the incorporation of the surfactant through cation exchange with surface hydroxy groups was detected by combined FTIR TG/DTA measurements. The FTIR spectrum of CeO<sub>2</sub> before calcination shows adsorption bands in the region 2800–2900 cm<sup>-1</sup> associated with the C–H stretching mode of the surfactant hydrocarbon chain. These bands disappear after calcination as the temperature increases, indicating a progressive loss of surfactant on heating. This is also evidenced by thermogravimetric analysis, which shows weight loss from ca. 400 to 870 K, which corresponds to the elimination of water and of the organic moieties in different stages. Carbon/nitrogen atomic ratios, measured by elemental analysis, are consistent with the presence of surfactant which remains intact during synthesis. Quantitative analysis indicates that the composition of the dried material, when using C<sub>16</sub>, is close to CeO<sub>x</sub>(O–C<sub>19</sub>H<sub>42</sub>N)<sub>y</sub>·0.9H<sub>2</sub>O with 0.06 < y < 0.15, depending on the initial concentration of the organic and the pH. The maximum amount of incorporated surfactant being approximately one molecule for every 6–7 cerium atoms.

X-ray diffraction patterns of the as-synthesized material and the material calcined at 723 K did not exhibit a clear reflection at low 2θ values. Only a single broad reflection was observed. This corresponded to a d

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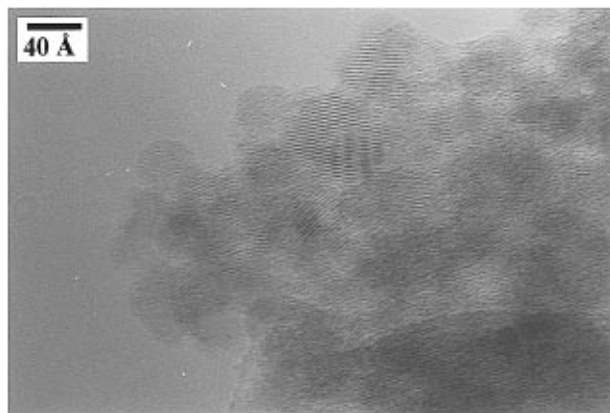
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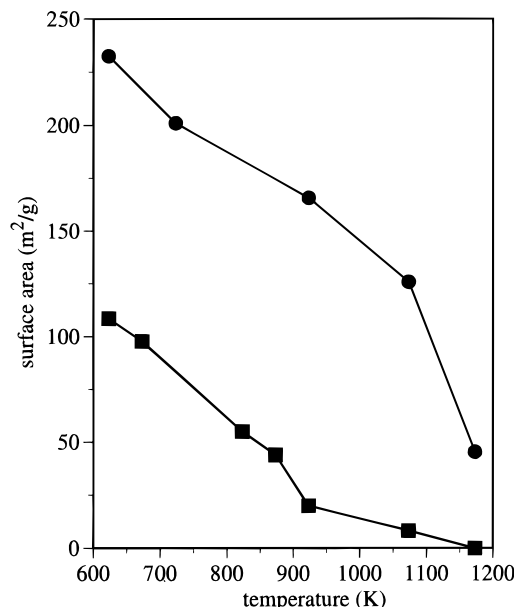


**Figure 1.** Representative HRTEM image of fresh  $\text{CeO}_2$  prepared using surfactants.

spacing of 20.5 Å, which is only slightly dependent on the chain length of the surfactant used.<sup>11</sup> The observation indicates the absence of a long-range order in the structure, which was also evidenced by HRTEM studies. Figure 1 illustrates a representative high-resolution electron micrograph of the sample as synthesized, which exhibits an atomic assembly ordered only at a microdomain level (from ca. 20 to 50 Å), with a characteristic cluster-of-grapes morphology, and in some regions highly disordered. Pores are irregularly spaced. The presence of mesopores in the range 20–50 Å with a maximum at around 37 Å was also detected by nitrogen adsorption studies. Isotherms of type IV, typical of mesoporous materials, were obtained for all samples. Efforts in order to increase the degree of ordering were done by varying the amount of surfactant incorporated into the oxide.<sup>12</sup> This did not produce any appreciable variation in the degree of ordering.

The surface areas of  $\text{CeO}_2$  at increasing calcination temperatures are shown in Figure 2 and compared with those from a sample of  $\text{CeO}_2$  obtained without surfactant. The data presented highlight two main observations: the first is that the use of organic agents considerably increases the surface area of the oxides (230 vs 110  $\text{m}^2/\text{g}$  after calcination at 623 K); the second is that this preparation method shifts the limit of stability of ceria to a higher temperature. Generally, a drop in surface area is observed at around 900–1000 K with conventionally prepared  $\text{CeO}_2$ ,<sup>13</sup> whereas the use of surfactant-assisted synthesis allows the upper temperature limit to be raised to 1173 K, where a surface area of ca. 40  $\text{m}^2/\text{g}$  can still be obtained. These surface area values compare favorably with the highest values observed for  $\text{CeO}_2$  and, to the best of our knowledge, are among the highest reported for this oxide at the calcination temperature investigated.

The high surface area is probably related to the modification of water surface tension produced by the surfactant at the oxide pore during the drying and calcining procedure. Surfactants can be added to reduce



**Figure 2.** Surface area of  $\text{CeO}_2$  vs calcination temperature: (■)  $\text{CeO}_2$  prepared by conventional precipitation and (●)  $\text{CeO}_2$  prepared by a surfactant-assisted synthesis.

the interfacial energy and thereby decrease the surface tension of water in the pores; this will reduce the shrinkage and collapse of the network during drying and calcination.<sup>14</sup> Similar findings were observed for  $\text{ZrO}_2$  obtained by cation exchange on hydrous zirconium oxide gel.<sup>4a</sup> In that case, however, it was observed after calcination a partial ordering, which was attributed to a “scaffolding-type mechanism” rather than a true templating effect. This difference can be attributed to the existence of various stable oxidation states of cerium. During calcination, reduction of  $\text{Ce}^{4+}$  operated by the surfactant and/or adsorbed  $\text{CO}_2$  (giving carbonates) and reoxidation by oxygen could occur, thus preventing ordering of the structure or at least limiting it to only a few regions. Alternative approaches must therefore be utilized, like those recently described,<sup>7</sup> when looking at long-range, structurally ordered mesophases, especially when dealing with elements with variable oxidation states. There is no description of the preparation of  $\text{CeO}_2$ -based, structurally ordered mesoporous oxides in the open literature.

An important requirement of  $\text{CeO}_2$ -based materials, especially when used in catalyst formulations for auto-exhaust treatment, is the ability to undergo rapid cycling between +3 and +4 oxidation states.<sup>8,9</sup> An indirect measurement of this ability can be accomplished by monitoring the interaction of  $\text{CeO}_2$  with  $\text{H}_2$  at various temperatures by temperature-programmed reduction (TPR) followed by reoxidation.<sup>15</sup> The reduction profile of  $\text{CeO}_2$  consists of two peaks located at ca. 770 K and 1100 K (see Figure 3a). The first peak originates from reduction of easily reducible surface cerium and the second is due to reduction of the innermost layer of  $\text{CeO}_2$  to  $\text{Ce}_2\text{O}_3$ .<sup>16</sup> The TPR profile of

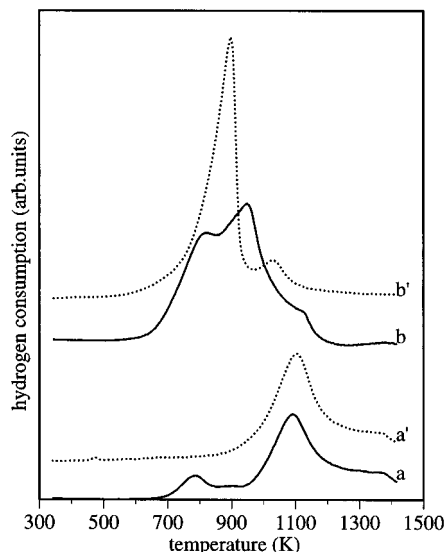
(11) After calcination at  $T > 923$  K, the XRD pattern typical of a fluorite structured material is obtained. This was indexed as cubic  $\text{CeO}_2$  (fcc with  $a = 0.5410$  nm).

(12) To increase the amount of the incorporated surfactant, we acted on the pH ( $9 < \text{pH} < 13$ ), the ratio  $\text{Ce}/\text{C}_p$ , the reaction temperature, and time. While these considerably affected surface area, the degree of ordering remained low.

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**Figure 3.** TPR profiles of  $\text{CeO}_2$  prepared by conventional precipitation (a) and by a surfactant assisted synthesis (b); TPR of sample a after a redox cycle, i.e., an oxidation following the first TPR (a'); TPR of sample b after a redox cycle (b').

$\text{CeO}_2$  prepared with and without surfactants is shown in Figure 3. The a, b traces are the TPR performed on the fresh sample and the a', b' traces refer to the recycled samples.<sup>17</sup> The most remarkable difference is shown after high-temperature cycling. While conventionally prepared  $\text{CeO}_2$  completely lost its low-temperature  $\text{H}_2$ -uptake/reduction characteristics, a promotion of  $\text{Ce}^{4+}$  reduction was observed with surfactant-prepared  $\text{CeO}_2$ . A quantitative evaluation of hydrogen consumed after the first and second TPR (corresponding to sample b and b') indicates that a ceria reduction degree of 75 and 70% is reached which is in agreement with formation of  $\text{CeO}_x$  with  $x$  respectively 1.625 and

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(17) Recycled sample is obtained after a redox cycle (reduction at 1273 K and reoxidation at 773 K). This procedure provides a useful test to check for the sensitivity of the material to cycling (successive reduction/reoxidation cycles).

1.65.<sup>18</sup> Correspondingly, an increase in oxygen uptake was observed when reoxidizing reduced ceria. It is important to note that the surface area of ceria prepared in both ways after a redox cycle drops to less than  $6 \text{ m}^2/\text{g}$ , thus evidencing that the reduction behavior is not directly dependent on surface area. This unprecedented behavior leads to some important considerations: (i) by careful design of synthesis procedure,  $\text{CeO}_2$  reduction at low temperatures can be promoted with no need to structurally dope  $\text{CeO}_2$  with different cations and with no need to have high surface areas;<sup>15c,19</sup> (ii) the mechanisms leading to low-temperature  $\text{CeO}_2$  reduction should be reevaluated to explain this behavior. The question is why and how ceria prepared using surfactants show enhanced interaction with  $\text{H}_2$ , especially after high-temperature cycling. The answer is likely to be found in the different morphology and stability of the material prepared using surfactants that can influence the reduction process. For example, preferential exposure of more reactive surfaces<sup>20</sup> or the formation of  $\text{CeO}_x$  suboxide with different stoichiometries<sup>21</sup> may explain the high degree of reduction of these ceria at low temperatures. In addition, some contribution to hydrogen adsorption due to the stabilization of ceria hydrides<sup>22</sup> cannot be ruled out at this stage, although we have no direct evidence to support an enhanced dissolution of hydrogen within the ceria lattice.

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(18) These results were tested through several repeated preparation of  $\text{CeO}_2$ . The values of total hydrogen consumed and temperature of the maximum are contained within a deviation of respectively 9 and 2%.

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