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Surface Characterization and Properties of Ordered Arrays of CeO₂ Nanoparticles Embedded in Thin Layers of SiO₂

J. Y. Chane-Ching, a,† M. Airiau, ‡ A. Sahibed-dine, § M. Daturi, § E. Brendlé, || F. Ozil, || A. Thorel, ⊥ and A. Corma†

Rhodia Recherches, 52 rue de la Haie Coq, 93308 Aubervilliers, France, Faculté des Sciences, Université Chouaïb Doukkali, B.P. 20, El Jadida, Morocco, Laboratoire de Catalyse et Spectrochimie, ENSICAEN, 6 Bd Maréchal Juin, 14050 Caen Cedex, France, IGCLab, Carreau Rodolphe, Route de Guebwiller, 68480 Pulversheim, France, ENSMP, Centre des Matériaux, BP 87, 91003-Évry, France, and Instituto de Tecnología Química, UPV-CSIC, Auv de Los Naranjos, 46022 Valencia, Spain.

We demonstrated the surface composite character down to the nanometer scale of SiO₂–CeO₂ composite high surface area materials, prepared using 5 nm colloidal CeO₂ nanoparticle building blocks. These materials are made of a homogeneous distribution of CeO₂ nanoparticles in thin layers of SiO₂, arranged in a hexagonal symmetry as shown by small-angle X-ray scattering and transmission electron microscopy. Since the preparation route of these composite materials was selected in order to produce SiO₂ wall thickness in the range of the CeO₂ nanoparticle diameter, these materials display surface nanoroughness as shown by inverse chromatography. Accessibility through the porous volume to the functional CeO₂ nanoparticle surfaces was evidenced through an organic acid chemisorption technique allowing quantitative determination of CeO₂ surface ratio. This surface composite nanostructure down to the nanometer scale does not affect the fundamental properties of the functional CeO₂ nanodomains, such as their oxygen storage capacity, but modifies the acid–base properties of the CeO₂ surface nanodomains as evidenced by Fourier transform IR technique. These arrays of accessible CeO₂ nanoparticles displaying high surface area and high thermal stability, along with the possibility of tuning their acid base properties, will exhibit potentialities for catalysis, sensors, etc.

Introduction

Optical,† electrical,‡ magnetic,§ and catalytic objects have been tuned by varying their sizes in the nanometer size regime. Considerable efforts have been devoted to manipulate nanosize objects to exploit their beneficial properties.5,6,7 Ordered nano-object assemblies can enhance some of their properties and widen their range of applications.8–11 For instance, controlled structuring through the control over interparticle separation could provide a means for controlling both quantum and classical coupling interactions.12 Strong magnets with excellent coupling interactions were fabricated through the self-assembly of mixtures of magnetic nanoparticles.13 The effort to understand the physics of ordered arrays of nano-objects has been paralleled by attempts to construct arrays with controlled composition and architecture.14–17

These arrays are usually induced by slow evaporation of the carrier solvent after ultrasonic agitation of the solvent dispersions.8,10 Ligand exchange of the long chain surface capping group allowed the interparticle distance to be adjusted. Self-assembly alone however produces simple close packed arrays of colloidal particles. To generate more complex crystal lattices, one should create periodic potentials for self-assembly of colloidal spheres.6,10 Recently emulsion droplets were used to template self-assembly of colloidal spheres of 844 nm polystyrene (PS) spheres.17 During the evaporation of the toluene droplets, the PS spheres strongly bound to the toluene droplets packed by capillary forces to form colloidal assembly with a sequence of symmetric patterns. However there are relatively few methods to control the fabrication and arrangement of nanoparticles in three-dimensional (3D) arrays which display high surface area and physical integrity under attrition conditions and sustain high-temperature regimes. A need exists for producing arrays of individual nanoparticles displaying mechanical and high-temperature stability, useful for a variety of applications such as sorption, catalysis, etc.

Our approach involves the use of nanoparticle building blocks and their self-assembly using a mineral binder.

[References and footnotes]

1 Rhodia Recherches.
2 Université Chouaïb Doukkali.
3 Laboratoire de Catalyse et de Spectrochimie, ISMRA.
4 IGCLab, Carreau Rodolphe.
5 ENSMP, Centre des Materiaux.
6 Instituto de Tecnología Química, UPV-CSIC.
Since mesoporous SiO$_2$ material was largely developed,$^{18}$ a co-template method involving both the precipitation of silica into ordered thin layers in the presence of CeO$_2$ nanoparticles as functional building blocks is proposed. In this approach, the challenge is to minimize the coverage of the CeO$_2$ functional nanoparticle by the silica binder allowing significant accessibility to the functional nanoparticle building blocks. The use of CeO$_2$ nanoparticle building blocks, monodispersed in size (5 nm diameter) offers the advantage to perfectly control the composite structure of the surface down to the nanometer scale.

In this paper, a variety of techniques was used to determine the surface structure down to the nanometer scale of our high surface area materials prepared using the co-self-assembling route. We will show that the resulting ordered arrays of CeO$_2$ nanoparticles, embedded in thin layers of SiO$_2$ binder, display an oxygen storage interfering from those of a pure CeO$_2$ material. This opens up some modification of surface acid/property of the functional nanoparticles.

Methods, Materials, and Experimental Procedures

Synthesis and Characteristics of Nanostructured Materials. SiO$_2$–CeO$_2$ nanostructured materials with different molar fractions of CeO$_2$, $C_{CeO_2} = 0.2$ and $C_{CeO_2} = 0.5$ (denoted Si$_{0.8}$Ce$_{0.2}$ and Si$_{0.5}$Ce$_{0.5}$, respectively), were prepared using 5 nm diameter CeO$_2$ nanoparticle building blocks through a co-self-assembly process on a liquid crystal phase template based on an amphiphilic copolymer HO(CH$_2$CH$_2$O)$_{20}$(CH$_3$CH$_2$O)$_{70}$-(CH$_2$O)$_{100}$OH (designated EO$_{20}$PO$_{70}$EO$_{20}$ Pluronics P123, BASF). In a typical synthesis (sample Si$_{0.5}$Ce$_{0.5}$), 10 g of Pluronics P123 was dissolved in 330 cm$^3$ of water and 37.6 cm$^3$ of 2 M HCl, and 25.0 cm$^3$ of 2 M CeO$_2$ colloidal dispersion was poured into this solution. Then 10.4 g of tetraethyl orthosilicate (TEOS) was added in one hour at room temperature into the dispersion. The resulting dispersion was first aged at 118 K for 16 h and then aged overnight at 353 K. The solid product was washed and dried, and the copolymer template was removed by calcination at 773 K. As a reference sample, pure SiO$_2$ nanostructured material was prepared using the same recipe, but without the incorporation of CeO$_2$ nanoparticles, following a classical procedure.$^{18}$ Pure CeO$_2$ nanostructured material was also synthesized using identical spherical CeO$_2$ nanoparticles building blocks, through a self-assembly process on a liquid crystal phase using a method described elsewhere.$^{20}$ The pure SiO$_2$ and pure CeO$_2$ nanostructured materials were calcined at 773 K. A physical mixture composed of pure CeO$_2$ and pure SiO$_2$ nanostructured materials was also prepared at a CeO$_2$ molar ratio of 0.26 (sample denoted Si$_{0.74}$Ce$_{0.26}$).

SAXS and Nitrogen Adsorption–Desorption Characterization. The textural characteristics of the nanostructured materials were obtained from nitrogen adsorption–desorption isotherms and from small-angle X-ray scattering SAXS experiments). The nitrogen adsorption and desorption isotherms were determined at 77 K using a Micromeritics ASAP 2000 system with previous overnight drying of samples under vacuum at 20 °C. The pore size distribution was obtained from the BJH (Barret–Joyner–Halenda) analysis of the desorption branch of the isotherms. SAXS data were collected using the 2 m pinhole instrument fitted with a two-dimensional gas-filled detector operating at a wavelength of 1.54 Å (Cu Kα radiation) at the Centre d’Etudes de Saclay, France. This instrument is fully described in ref 21.

Electron Microscopy. (A) Electron Microscopy. The high-resolution transmission electron microscopy (HRTEM) investigation was performed with a Tecnai F20/FEG/STEM, a 200 kV microscope equipped with a field emission electron gun (FEG), and a super twin objective lens of low spherical and chromatic aberrations ($C$s = Ce = 1.3 nm). Point-to-point resolution is 0.17 nm in high-resolution scanning transmission electron microscopy (HRSTEM) and 0.24 nm in HRTEM, although the high coherency of the beam currently allows imaging distances down to 0.15 nm.

(B) Analytical Equipment. Analytical investigations of the distribution of chemical elements were carried out using an energy Si–Li energy-dispersive X-ray emission spectrometer (EDS) with energy resolution about 1.35 eV. The detector is equipped with a Super Thin Window (SUTW), therefore, light elements down to boron can be detected and quantified. The spatial resolution at which EDS analyses can be carried out is essentially related to the probe size: optimum EDS operating conditions for the present analyses were obtained with a probe size of about 1 nm. The EDS investigations have been coupled to STEM–high-angular annular dark field (HAADF) imaging in order to get a better insight into the repartition of the CeO$_2$ nanoparticles embedded in SiO$_2$ thin layers. Note that the HAADF image contrast is approximately the reverse of a conventional TEM bright field micrograph, with pores displayed in black color, low Z atoms in gray, and high Z atoms in white.

(C) Sample Preparation. TEM samples were prepared in cross section after impregnation of the powder in an organic resin. Ultrathin films of 10–30 nm were prepared using an ultramicrotome.

Surface Characteristics Determined by Inverse Gas Chromatography (IGC). IGC is currently applied for the characterization of powders and allows evaluation of surface properties in terms of surface interaction potential and surface nanomorphology.$^{22,23}$ In an IGC experiment, chosen probes are injected in a column containing the powder of interest. When determining the time the chosen probe spends in the column (retention time), compared to the corresponding time of a noninteractive or poorly interactive probe, it becomes possible to appreciate the affinity of the support for the probe. When selecting for example alkane probes that are only capable of London or dispersive types of interactions, one may evaluate the dispersive interaction potential or dispersive component of the surface energy of the solid possessing probes only or possessing the same interaction potential (London), and will lead to information on the solid surface accessibility or on its surface nanomorphology. By injecting very small quantities of probes, one may consider that the adsorbed probe molecules are sufficiently separated so as to become unable to exchange lateral interaction between them: hence their retention time reflects only the probe–solid surface interaction capacity. This type of IGC is called IGC at infinite dilution conditions (IGC-ID).

(A) Preparation of IGC Columns and IGC Measurements. IGC measurements were performed, using commercial equipment (FISONs HRGC Mega 2 series), fitted with a flame ionization detector. The length of the IGC column was 20 cm and the internal diameter about 2 mm. Before analysis, the oxide surfaces, placed inside the GC columns, were outgassed by heating at 473 K, under helium flow. Helium flow rate was 20 cm$^3$ min$^{-1}$. The IGC-ID analysis temperature was adapted to each of them. Chromatograms were recorded at 383 K on SiO$_2$ and SiO$_2$–CeO$_2$ composites and at 413 K on pure CeO$_2$ material and sample prepared from the physical mixture (Si$_{0.74}$Ce$_{0.26}$ sample). The carrier gas (He) flow rate was 20 cm$^3$ min$^{-1}$.

(B) Dispersive or Nonspecific Component of the Surface Energy. Dispersive component of the surface energy is commonly determined using the Dorris and Gray approach,$^{24}$ i.e., by injecting small amounts of n-alkane probes (capable of sole dispersive interactions) in the column filled with the solid

of interest. The variation of free energy of adsorption of the probe $\Delta G$ is easily determined since it is directly related to the retention time or retention volume (volume of carrier gas required to push the probe through the column).

The dispersive component of the surface energy ($\gamma^d$) may be calculated according to the Dorris and Gray relation

$$\gamma^d = \frac{(\Delta G_{\text{CH}_2})^2}{4N^2 \gamma_{\text{CH}_2}} \quad (1)$$

where $N$ is Avogadro’s number, $a_{\text{CH}_2}$ is the area covered by one adsorbed methylene group (0.06 nm$^2$), $\gamma_{\text{CH}_2}$ is the surface energy of a solid entirely made of methylene groups (i.e., polyethylene). $\Delta G^{\text{CH}_2}$ is the variation of adsorption free energy of a methylene group. It is given by the slope of the straight line relating the free adsorption energies to the number of carbon atoms of the injected $n$-alkanes as shown on Figure 1.

The units on the abscissa axis are either the number of C atoms ($n_C$) of the injected alkane or the topology index ($\tau$) that happens to equal to $n_C$ for alkane probes.

(C) IGC-ID Measurements of the Nanomorphology Index. The intensity of interaction of a solid with a solute is governed not only by the theoretical interaction potential but also by the accessibility of the two partners at the molecular layer. IGC-ID is capable of detecting such surface roughness at the molecular level. This is achieved by comparing the behaviors of bulky, branched (or cyclic) hydrocarbons with the ones of flexible $n$-alkanes. When bulkiness hinders branched or cyclic isomers from entering the structure in which linear alkanes readily adsorb, much lower retention times are observed. Now, when comparing adsorption behaviors of linear and nonlinear alkanes, it is necessary to consider the fact that the molecular structure introduces also a nonnegligible variation of the molecular polarizability that cannot be ignored. Brentlde and Papirer$^{2,23}$ defined an adequate $\tau$ topology index, derived from Wiener’s molecular topology indexes, in order to take into account both parameters, bulkiness and polarizability, of the molecular probe. Experimentally, size exclusion effects lead to a decrease of retention volumes (or the free energy of adsorption).

The morphology index (IM) is given by the ratio of the retention volume of a branched alkane molecule $V_M(M)$ and $V(C)$ the retention volume of a virtual $n$-alkane having the same topology index. This method is well documented in the literature$^{25}$

$$\text{IM}_{\text{branched probes}} = \frac{V_M(M)}{V(C)} \quad (2)$$

One may also start from the free adsorption energy

$$\text{IM}_{\text{branched probes}} = \exp \frac{\Delta G(M)}{\Delta G(C)} \quad (3)$$

A value of 1 or close to 1 indicates that both branched and $n$-alkanes have equivalent accessibility to the surface. In other terms, we may conclude that the surface is flat at the molecular level. If IM is below 1, the solid’s surface exhibits rugosity.

**Chemical Determination of the Number of Accessible Surface Groups.** The evaluation of the number of accessible surface groups on the different nanostructured materials was made using two reactive organic acids differing by their bulkiness: propionic acid and pivalic acid. Those acids were selected regarding their strong complexing ability towards the Ce$^{4+}$ cation. Moreover, propionic acid scarcely chemisorbs on pyrogenic silica. Its irreversible fixation on the present composite materials may therefore be mainly attributed to the existence of Ce surface groups. The percentage ($\gamma$) of irreversibly adsorbed acid was determined by elemental analysis of C, using a LECO CS 444 equipped with a IR detection of CO$_2$ evolved from the complete oxidation of C. From the percentage of fixed carbon, the graft density ($n$), expressed as graft/nm$^2$, was computed according to

$$n = \frac{6023r}{12n_C S_m} \quad (4)$$

where $n_C$ is the number of carbon atoms contained in the acid molecule and $S_m$ is the specific surface area determined from nitrogen adsorption isotherms, expressed in m$^2$ g$^{-1}$.

In practice, the carboxylic acid grafting was made either in the chromatographic column with propionic acid (in situ technique) or in a desiccator with pivalic acid. Successive injections of 10 $\mu$L of pure propionic acid (Aldrich 40,290-7, 99.5+%) were introduced at a temperature of 383 K and under a carrier gas flow of 20 cm$^3$ min$^{-1}$ until reproducible chromatograms were obtained. Water vapor was then injected in order to hydrolyze the nonstable derivative possibly formed between propionic acid and the surface silanol groups of the silica component of the composite material. Finally, the surface cleaning was followed by a thermal treatment at 473 K for 2 h.

Pivalic acid (Acros Organics 75-98-9 99%) treatment was performed by placing the composite material in a glass closed reactor containing solid pivalic acid. Thereafter, the reactor was heated, in an oven, at 383 K during 24 h. Finally, the treated material was submitted to a solvent extraction (ethyl ether) in order to eliminate from the surface all reversibly or physisorbed acid. Additional heating at 333 K allowed removal of the residual solvent.

**Determination of the Oxygen Storage Capacity and Acid–Base Properties Using FTIR.** Before FTIR examination, the powders were pressed into self-supported wafers of about 10 mg cm$^{-2}$ and introduced in a quartz cell, placed in the IR beam. The wafer was then heated under vacuum (1.3 $\times$ 10$^{-4}$ Pa) up to 773 K. Then, oxygen was introduced in the quartz cell until a pressure of 13 kPa after 1 h of contact was reached. The cell was thereafter outgassed, at the same temperature, for one additional hour. FTIR spectra were recorded with a Nicolet Magna 550 FT-IR spectrometer (resolution 4 cm$^{-1}$) after quenching the samples to room temperature. Probe molecules were introduced at room temperature on the activated samples, and the cell was again outgassed. The FTIR spectra were treated using the Nicolet OMNIC software.

For the FTIR studies involving a chemical reduction step, samples were exposed to 13 kPa of H$_2$ at room temperature, then heated for 0.5 h at the reduction temperature, and evacuated at the same reduction temperature under 1.3 $\times$ 10$^{-4}$ Pa for 15 mn. This procedure was repeated twice.

Modification of acid–base surface properties of CeO$_2$ nanodomains resulting from the nanostructuration were investigated by FTIR using different probes. CO$_2$ adsorption on CeO$_2$ surfaces was usually used to investigate their basic properties through the various carbonate adsorbed species. These adsorbed species could be identified by determining the splitting of the bands arising from the degenerated $\nu_1$ vibration centered at around 1415 cm$^{-1}$: the presence of polyydentate or monodentate carbon-

![Figure 1. Example of determination of $\Delta G_{\text{CH}_2}$ on CeO$_2$ sample, at 413 K.](image-url)
observed for Ce and Si in the thin layers for all the concentration profiles we carried out gives evidence of the intimate and homogeneous distribution of the CeO$_2$ nanoparticles in the silica thin layers.

From all these observations it can be inferred that the CeO$_2$ nanoparticles are individualized and homogeneously distributed in the silica thin layers resulting in an ordered array of CeO$_2$ nanoparticles embedded in thin layers of SiO$_2$ arranged in a hexagonal symmetry.

Textural characteristics of studied samples are presented in Table 1.

The SAXS and TEM investigations have shown the formation of an ordered array of CeO$_2$ nanoparticles embedded in silica thin layers possessing a thickness slightly larger than the CeO$_2$ nanoparticle size. However, at this stage, we do not have any evidence of the surface nanostructure by the CeO$_2$ nanoparticles. To get a better insight in the surface nanostructure, Si$_{0.8}$Ce$_{0.2}$ and Si$_{0.5}$Ce$_{0.5}$ materials were investigated by IGC and FTIR techniques.

2. Surface Nanorugosity of the Nanostructured Composites. Adsorption behavior of linear (n-alkanes) and nonlinear alkanes (cyclohexane and 2,2-dimethylbutane) on Si$_{0.5}$Ce$_{0.5}$ materials are reported in Figure 5. The representative points of the latter probes are clearly below the alkane line demonstrating thus the existence of nanoroughness on the given composite oxide samples.

The morphology index (IM) values of the studied oxides are reported in Table 2. Mesostructured silica displays a morphological index value of 0.96 when determined with dimethylhexane and 0.98 for cyclooctane. Those values, close to 1, point to the existence of a rather flat surface whatever the branched or cyclic alkane probe used to test the surface morphology. A morphological index value lower than 1, indicating nanoroughness, was determined for the pure CeO$_2$ materials, consistent with the preparation route of this material involving self-assembly of CeO$_2$ nanoparticles. Significantly lower IM values are observed for composite ordered arrays of nanoparticles. This surface nanoroughness observed on these materials prepared using nanoparticles building blocks suggests that the CeO$_2$ nanoparticles building blocks significantly affected the surface morphology.

3. Assessment of the Surface Heterogeneity with Surface Accessibility of the CeO$_2$ Nanodomains of the SiO$_2$–CeO$_2$ Composites. To show a composite aspect of the surface, that is, a surface nanostructure consisting of CeO$_2$ patch domains resulting from embedded CeO$_2$ nanoparticle bumps, a description of the chemical nature of the surfaces was performed using, first, a macroscopic surface energy term, the dispersive component of the surface interaction potential, $\gamma_{sd}$, and, second, measuring the acid chemisorption capacity of CeO$_2$ specific probes.

Surface Interaction Potential. $\Delta G_{CH}$ and $\gamma_{sf}^d$ values, determined from IGC-ID experiments on the different studied materials, are reported in Table 3. The dispersive component of the surface energy, $\gamma_{sd}^d$, of the SiO$_2$ mesostructured material is equal to $40 \pm 2 \text{ mJ m}^{-2}$. A higher value is observed with nanostructured CeO$_2$ for which $\gamma_{sf}^d = 230 \pm 9 \text{ mJ m}^{-2}$. Intermediate values measured on the nanostructured composite materials suggest that the composite materials display CeO$_2$ and SiO$_2$ surfaces.

Table 3 relates the surface energy values determined on the sample made of a physical mixture of mesostructured SiO$_2$ and nanostructured CeO$_2$ materials. A value of $200 \pm 7 \text{ mJ m}^{-2}$ was obtained for this sample (sample Si$_{0.74}$Ce$_{0.26}$). Although $\gamma_{sd}^d$ applies to the sole energetic homogeneous materials, those observations show never-
theless completely different behavior for nanostructured SiO2-CeO2 composite materials, compared to a physical mixture composed of mesostructured SiO2 and nanostructured CeO2 materials.

**Determination of the Number of Accessible Ce Surface Sites.** As indicated above, the chemical fixation of organic acid constitutes a direct way for the evaluation of the Ce surface reactive groups. Table 4 displays the results in terms of C content of the oxides after reaction and subsequent purification as well as the number of grafts per unit surface area (determined by

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**Table 1. Structural and Morphological Characteristics of Studied Samples**

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>dSAXS (nm)</th>
<th>Vp (cm³ g⁻¹)</th>
<th>Dp (nm)</th>
<th>Sb (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>hexagonal</td>
<td>10.2</td>
<td>0.81</td>
<td>6</td>
<td>906</td>
</tr>
<tr>
<td>Si₀.₈₋Ce₀.₂</td>
<td>hexagonal</td>
<td>11.5</td>
<td>0.80</td>
<td>4</td>
<td>663</td>
</tr>
<tr>
<td>Si₀.₅₋Ce₀.₅</td>
<td>hexagonal</td>
<td>9.8</td>
<td>0.3</td>
<td>4</td>
<td>310</td>
</tr>
<tr>
<td>CeO₂</td>
<td>hexagonal</td>
<td>10.2</td>
<td>0.3</td>
<td>5</td>
<td>165</td>
</tr>
</tbody>
</table>

a These materials exhibit micropores (Dp < 2 nm). Surface area and porous volume corresponding to the micropores are evaluated to be 440 m² g⁻¹ and 0.19 cm³ g⁻¹ (SiO₂) and to be 270 m² g⁻¹ and 0.12 cm³ g⁻¹ (Si₀.₈₋Ce₀.₂), respectively. Wall thickness was determined from dSAXS and pore diameter assuming a hexagonal structure with a cell parameter a = 2dSAXS/3¹/₂. b e and S represent the wall thickness and the surface area, respectively.

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The SiO₂—CeO₂ composite materials consisted of 5 nm CeO₂ nanoparticles homogeneously distributed in the SiO₂ thin textured framework. EDS/TEM investigations suggested that the CeO₂ nanoparticles could emerge from the SiO₂ thin layer and be accessible through the pore or, on the contrary, be totally embedded by the silica thin layers. These CeO₂ nanoparticles, located near the surfaces, produced a surface nanorugosity as evidenced by IGC-ID experiments. The surfaces of these CeO₂ nanoparticles partially embedded in the thin layers of silica are accessible through the porous volume as shown by chemisorption of propionic acid. The surface coverage ratio by the CeO₂ nanodomains was determined to be 30% for
particles emerges from the SiO2 thin layers resulting in not observed\(^{31}\), this dissociative adsorption of methanol determined a value of 270 \(\mu\)mol of O\(_2\) per gram of catalyst for the OSC of our pure nanostructured CeO\(_2\) reduced at 673 K. This method does not hold for the SiO\(_2\)–CeO\(_2\) composite material since silica skeletal vibrations hide spectral features below 1300 cm\(^{-1}\). This difficulty was overcome by considering the \(\nu(CH)\) vibration modes: the symmetrical elongation of the C–H bond is also sensitive to the oxidation state of the cerium cation,\(^{24}\) with a shift in the frequency vibration from 2807 to 2782 cm\(^{-1}\) accompanying the Ce\(^{4+}\) → Ce\(^{3+}\) reduction reaction for the CeO\(_2\) sample. Moreover, the apparition of an intense Fermi resonance (due to a shift of the \(\delta(CH_3)\) vibration mode from 1447 to 1462 cm\(^{-1}\)) between the \(\nu(CH_3)\) mode and the \(2\nu(CH_3)\) overtone generates two intense bands located at 2919 and 2836 cm\(^{-1}\). On analysis of the evolution of the \(\nu(CH_3)\) vibration band at 2921 cm\(^{-1}\) (for the composite material) or the shift of the \(\nu(CH_2)\) stretch (Figure 6), an OSC value between 270 and 280 \(\mu\)mol g\(^{-1}\), similar to that determined above, was recorded for the pure CeO\(_2\) nanostructured material. The method having therefore been validated, an OSC value of 170 \(\mu\)mol g\(^{-1}\) was obtained for the SiO\(_2\)–CeO\(_2\) composite material using the same procedure, yielding a corresponding normalized value of 212 \(\mu\)mol g\(^{-1}\) of CeO\(_2\). This value is slightly lower than the previous one determined for the pure CeO\(_2\) nanostructured materials. Hence, the composite nanostructuration of the surface does not affect significantly the OSC of the CeO\(_2\) nanodomains, a characteristic property of the CeO\(_2\) material.

While maintaining an intrinsic property such as the oxygen storage capacity of CeO\(_2\), we previously observed that the composite structure of the surface down to the nanoscale modifies some surface properties of the CeO\(_2\) nanodomains. First, different values of the dispersive component of the surface energy were determined for the composite materials compared to the physical mixture of the pure materials. Second, the modification of surface energy by the nanostructuration was corroborated by similar observations made during the chemisorption experiments. After chemisorption with a propionic acid probe, an outgassing temperature of 413 K was required for the pure CeO\(_2\) nanostructured material. A reference SiO\(_2\)–CeO\(_2\) sample, prepared from a physical mixture of pure nanostructured CeO\(_2\) material and pure SiO\(_2\) nanostruc-

| Table 2. Morphology Index (IM) Determined Using Various Probes |
|-----------------------------|-----------------------------|-----------------------------|
| morphology index            | SiO\(_2\)                  | Si\(_{0.8}\)–CeO\(_{0.2}\)   |
| 2,2-dimethylhexane          | 0.96 ± 0.04                | 0.67 ± 0.03                 |
| 2,2-dimethylbutane          |                            | 0.77 ± 0.02                 |
| cyclohexane                 |                            | 0.42 ± 0.03                 |
| cycloheptane                |                            | 0.46 ± 0.01                 |
| cyclooctane                 |                            | 0.50 ± 0.02                 |

| Table 3. Comparison of “Apparent” Dispersive Components of Surface Energy Measured on Mixtures of Silica and Cerium Oxide and on the Composite Oxide Materials |
|---------------------------------------------|-----------------------------|-----------------------------|
| \(\gamma_s^d\) (mJ/m\(^2\)) | \(\Delta G^\ddagger\) (kJ/mole) |
| SiO\(_2\)                  | 39 ± 2                      | 2.5 ± 0.1                   |
| Si\(_{0.8}\)–CeO\(_{0.2}\) | 108 ± 4                     | 4.1 ± 0.1                   |
| Si\(_{0.5}\)–CeO\(_{0.5}\) | 120 ± 5                     | 4.4 ± 0.4                   |
| Si\(_{0.74}\) + Ce\(_{0.26}\) | 200 ± 7                     | 5.5 ± 0.2                   |
| CeO\(_2\)                  | 230 ± 9                     | 5.9 ± 0.1                   |

\(\gamma_s^d\) is the dispersive component of the surface energy. It is determined by the van der Waals forces and is expressed by the following equation:

\[
\gamma_s^d = \frac{3}{8} \pi R T \rho^2 \left( \frac{N_a}{V_r} \right) \left( \frac{R T}{V_r} \right) \frac{1}{\rho^2}
\]

where \(\rho\) is the density of the solid, \(V_r\) is the molar volume of the gas, and \(N_a\) is the Avogadro number.

tured material, required the same outgassing temperature of 413 K. In contrast, a lower outgassing temperature of 383 K was needed for the SiO2–CeO2 composite materials. These observations indicated some modification of the strength of the interactions between the propionic acid and the surfaces of CeO2 domains partially embedded in the thin layers of silica.

Monitoring acid–base properties of pure CeO2 surfaces represents a challenge for some catalytic applications such as the production of hydrogen involving the water gas shift reaction, i.e., $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$. CeO2 based material is reported as a good candidate for catalyzing29,30 this reaction requiring oxygen storage capacity. To improve its long-term catalytic activity, industrial development of CeO2 based materials for this application requires the inhibition of formation of carbonate species at the CeO2 surfaces due to the presence of CO2 formed from the water gas shift reaction. We will thus explore the acid–base properties of the CeO2 arrays displaying high thermal stability and high surface area using FTIR spectroscopy.

Basic molecules, such as CO or pyridine, did not show modifications in the weak Lewis acid behavior of cerium oxide due to silica matrix embedding. CO2 is a more appropriate probe since, after adsorption of CO2 at room temperature, typical bands attributed to hydrogen–carbonates, monodentate, bidentate, and polydentate carbonates29,30 were observed on our pure CeO2 nanostructured material (Figure 7a). After evacuation at 373 K we observed the decomposition of hydrogen–carbonates (Figure 7b). Bidentate carbonates are stable until 573 K (Figure 7c). These observations are consistent with the basic character of CeO2 surfaces usually reported in the literature.

Spectra recorded on SiO2–CeO2 composite materials (Figure 8) showed a completely different spectrum with hydrogen–carbonate bands (1594 and 1415 cm$^{-1}$), linearly adsorbed CO2 (1377 cm$^{-1}$), and small amounts of monodentate carbonates (1510 cm$^{-1}$). These species are fully eliminated after evacuation at 373 K. Note that CO2 adsorption on a pure mesostructured SiO2 material indicates only physisorbed species developing low interactions with the OH of the silanol groups. We can therefore argue from these FTIR investigations that the CeO2 nanodomains of the SiO2–CeO2 composite materials have displayed a lower basic character. The presence of hydrogen–carbonate species indicates the existence of OH basic sites in a higher proportion compared to oxygen basic sites, showing that the dispersion of CeO2 nanodomains in the silica thin layer generates a high density of interfaces between silica and CeO2 nanoparticles, resulting in a modification of the CeO2 basic character. This illustrated that the composite nanostructuration approach can be exploited to tailor the acid–base properties of the CeO2 surface for catalytic applications.

Conclusions

Ordered arrays of 5 nm CeO2 nanoparticles, embedded in a thin layer of SiO2, were investigated using SAXS, TEM, inverse chromatography, chemisorption, and FTIR techniques. A homogeneous distribution of the CeO2 nanoparticles within ordered silica thin layers was found by TEM studies. From inverse chromatography at infinite dilution (IGC-ID), we showed that this preparation route produces materials displaying surface nanrugosity. Assessment of the accessibility to the CeO2 surfaces through the porous volume was performed through an organic acid chemisorption study along a quantitative determination of the CeO2 surface coverage ratio. From all these observations, we can conclude that the SiO2–CeO2 materials displayed a structured composite surface down to the nanometer scale produced by the emergence of 5 nm individualized CeO2 nanoparticles from the SiO2 thin layers. The ability to tune some of the surface properties such as its acid base character while preserving a fundamental property of CeO2 such as the oxygen storage capacity, should offer new opportunities for these ordered arrays of CeO2 nanoparticles. Preparation of a variety of nanoparticle arrays displaying high surface area and high thermal stability involving this approach will allow a wide range of applications to be explored such as catalysis, sensors, etc.

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