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CeO₂ Nanocrystals from Supercritical Alcohols: New Opportunities for Versatile Functionalizations?

Cedric Slostowski,^{†,‡} Samuel Marre,^{†,‡} Odile Babot,[§] Thierry Toupance,[§] and Cyril Aymonier^{*,†,‡}

[†]CNRS, ICMCB, UPR9048, F-33600 Pessac, France

[‡]Université de Bordeaux, ICMCB, UPR9048, F-33600 Pessac, France

[§]Institut des Sciences Moléculaires, Université de Bordeaux, UMR 5255 CNRS, C2M Team, 351 cours de la Libération, 33405 Talence, France

ABSTRACT: The fast and controlled synthesis of surface-modified cerium oxide nanoparticles was carried out in supercritical {ethanol + alcohol derivative} mixtures. The newly found ability of supercritical alcohols to graft onto cerium oxide nanocrystals (CeO₂ NCs) during their synthesis was exploited to control their surface chemistry via the addition of three aminoalcohols: ethanolamine, 3-amino-1-propanol and 6-amino-1-hexanol. Although the ethanol to aminoalcohol ratio was consistent (285:1), the successful grafting of these alcohol derivatives onto CeO₂ NCs was identified based on Fourier transform infrared (FTIR) and thermogravimetric analysis–mass spectrometry (TGA-MS) measurements. Smaller crystallite size of CeO₂ NCs synthesized in the presence of aminoalcohols, compared to those synthesized in supercritical ethanol alone, were also noticed and attributed to a possible intervention of amine groups helping the grafting of the alcohols, allowing one to stop the growth of the CeO₂ NCs faster. The use of supercritical alcohol mixture—ethanol with hexanol, dodecanol, or octadecanol, with a 285:1 ratio—was also investigated. Such mixtures allow accessing a finer control in CeO₂ NCs crystallite size compared to pure alcohols, according to calculation made from X-ray diffraction measurements. Finally, fluorescent molecules (fluorescein isothiocyanate) were grafted onto amine-modified CeO₂ NCs. The powders displayed a fluorescent behavior under UV light, confirming the suitability and interest of CeO₂ NCs surface modification by such technique.



■ INTRODUCTION

Cerium oxide is a widely studied material used in many application fields such as catalysis, oxygen storage, polishing, optics or medicine.^{1–7} The synthesis of this oxide at supercritical conditions has been demonstrated to be particularly efficient and easy to process, for the control of cerium oxide properties (size, morphology, surface properties, oxygen capacity, etc.), which are of key importance for these applications. Among the process operating parameters, the choice of solvents, cerium precursors, temperature or residence time allows accessing various morphologies (nanoparticles, cubes, polyhedrons, etc.) and particles sizes.^{8–15} Additionally, the use of surface modification agents turns out to be an interesting way to control cerium oxide nanocrystals characteristics.^{16–19} Indeed, a controlled surface modification allows adding new functionalities to cerium oxide nanoparticles, which can be used, for instance, to improve dispersion or to create chemical anchor points for further complex surface chemistries.²⁰

Carboxylic acids are known for their high affinity with metal oxide surfaces and appear to be particularly efficient for the surface modification of cerium oxide nanoparticles (NPs).^{21–24} This property has been extensively used by Adschiri et al., in

supercritical water batch processes, in order to modify the surface of CeO₂ structures with several molecules, such as decanoic, dodecanoic, oleic, polyacrylic or adipic acids.^{25–27} The batch process was used because of the limited solubility of such fat acids. Indeed, due to their large carbon chain length, such acids are insoluble in water at normal temperature–pressure conditions, creating issues for their homogeneous injection in continuous processes.

To address this issue, two strategies have been proposed for the continuous design of cerium oxide NPs with specific surface properties. First, the use of relatively short carbon chain length as hexanedioic acid, being water-soluble at room pressure and temperature (important for the injection), has been deeply considered by Takami et al.¹⁶ Then, the use of methanol solvent was considered by Veriansyah et al. to have the opportunity to inject surface modifiers (fatty acids: decanoic and oleic acids or oligomers: PEG-350 and PEG-600) in the supercritical process.^{17,20,28,29}

Table 1. Initial Feed Mixture Composition, Crystallite Sizes (d_{cr}) and Particles Sizes (d_{TEM}) of CeO₂ NCs Synthesized from Ammonium Cerium Nitrate at 300 °C and 24.5 MPa, with a Residence Time of 55 s

| sample name | solvent | surface modification agent ^a | crystallite size d_{cr} (nm) ^b | particles size d_{TEM} (nm) ^c |
|--------------------------|------------|---|---|--|
| Aminoalcohols | | | | |
| C2-NH2 | ethanol | ethanolamine | 3.7 | 4.0 ± 0.5 |
| C3-NH2 | ethanol | 3-amino-1-propanol | 3.5 | 3.7 ± 0.4 |
| C6-NH2 | ethanol | 6-amino-1-hexanol | 3.1 | 3.3 ± 0.4 |
| Reference Samples | | | | |
| ref-1 | ethanol | - | 4.1 | 4.3 ± 0.6 |
| ref-2 | 1-propanol | - | 4.6 | 5.1 ± 0.7 |
| ref-3 | 1-hexanol | - | 6.1 | 6.4 ± 0.8 |
| ref-4 | ethanol | hexanoic acid | 8.0 | 8.6 ± 1.0 |
| Alcohol Mixtures | | | | |
| C6 | ethanol | 1-hexanol | 4.6 | 5.0 ± 0.7 |
| C12 | ethanol | 1-dodecanol | 4.4 | 4.7 ± 0.7 |
| C18 | ethanol | 1-octadecanol | 4.2 | 4.4 ± 0.5 |

^aCerium precursor to surface modification agent ratio = 1:6. ^bCrystallite sizes (d_{cr}) are calculated from the X-ray patterns using the Scherrer equation (higher intensity diffraction peak (111)). ^cParticles sizes (d_{TEM}) have been analyzed using the ImageJ software by counting over 100 particles.

Both approaches led to the recovery of CeO₂ nanocrystals (NCs) with small crystallite sizes, between 2 and 7 nm, depending mainly on the surface modification agent nature, its concentration, and the reaction time. We recently proposed a third strategy by demonstrating that near- and supercritical alcohols are not only playing the role of solvent but also of surface modification agents.¹⁴ Six primary (from methanol to hexanol) and one secondary (isopropanol) alcohols were initially used as solvent for the synthesis of CeO₂ NCs in near- and supercritical conditions. This work demonstrated that such solvent acts as a CeO₂ NCs surface modification agent, through its adsorption onto the CeO₂ NCs surface followed by dehydrogenation(s) of the resulting alkoxide, in order to create a stable carboxylate interaction. This results in a control of CeO₂ crystallite sizes depending on the alcohol nature and chain length. Such results open the question of functionalization of NCs surface with specific properties in a system where the solvent also acts as a surface modification agent.

The present work reports the study of CeO₂ NCs formation in supercritical alcohols in the presence of specific surface modification agents to answer to the aforementioned question. Aminoalcohol derivatives are used as CeO₂ surface modification agents during the synthesis from ammonium cerium nitrate in supercritical ethanol (300 °C and 24.5 MPa). Mixtures of ethanol with other long carbon chain alcohols are also used to access a precise control of CeO₂ NCs crystallite sizes.

■ EXPERIMENTAL SECTION

Materials. Ethanol (EtOH, purity ≥99.8%), 1-propanol (purity ≥99%), 1-hexanol (purity: 98%), 1-dodecanol (purity ≥98%), 1-octadecanol (purity ≥99%), ethanolamine (purity ≥99%), 3-amino-1-propanol (purity ≥99%), 6-amino-1-hexanol (purity: 97%), ammonium cerium(IV) nitrate (CAN, purity ≥98.5%), and fluorescein isothiocyanate (FITC, purity ≥97.5%) were purchased from Sigma-Aldrich and used as received.

Apparatus and Procedure. The surface-modified cerium oxide NCs were synthesized using a simple custom-built, continuous-flow reactor with a single injection line.^{14,15} Only one feed-tank was used: a 500 mL Pyrex beaker containing the CAN, the ethanol, and the surface modification agent under fast magnetic agitation. The reactor was made of 1/8" 316 L stainless steel coiled tubing with an internal diameter of 1.57 mm, for a total volume of 8 cm³. The heater was a homemade coiled ceramic resistance controlling the temperature up to 500 ± 1 °C. The high-pressure pump (P) was a controlled JASCO flow pump (PU2080), delivering flow rates up to 10 ± 0.001 mL

min⁻¹. A back pressure regulator (BPR - JASCO BP 2080), placed downstream from the reactor, allows controlling the pressure in the reactor up to 40 ± 0.1 MPa.

The feed solution is flown through the reactor at supercritical conditions, where the nucleation/growth of cerium oxide NCs occurs. The reaction is quenched thermally downstream with an ice bath, and the NCs can be recovered in solution upon depressurization through the BPR. The solution is then filtered and the surface modified CeO₂ NCs are washed on a Büchner filter system. The dry powders can then be analyzed as produced, without any annealing post-treatment.

The temperature was fixed at 300 °C in the reactor and the pressure at 24.5 MPa, meaning supercritical conditions for all experiments conducted in ethanol ($T_c = 240.8$ °C and $p_c = 6.1$ MPa). The residence time was fixed at 55 s in each experiment. The appropriate flow rate, for this residence time, has been calculated assuming that the presence of the cerium precursor and a surface modification agent do not affect the density of the mixture (i.e., reactants solution density equivalent to ethanol density: 805.2 kg·m⁻³ at 25 °C and 24.5 MPa, and 464.0 kg·m⁻³ at 300 °C and 24.5 MPa). The CAN and the surface modification agent concentration in the feed solution were set at 10 mM and 60 mM, respectively. Such concentrations lead to a cerium precursor-to-surface modification agent molar ratio of 1:6 (conventional for functionalization in supercritical fluids²⁸) and to a surface modification agent-to-ethanol molar ratio of 1:285.

The influence of alcohol derivatives, as potential surface modification agents, has been studied via the use of three aminoalcohols: ethanolamine, 3-amino-1-propanol, and 6-amino-1-hexanol. All experiments were performed in ethanol.

Four reference experiments were conducted in order to compare and conclude. Three CeO₂ NCs syntheses were performed in pure alcohols (ethanol, propanol, and hexanol) in the same experimental conditions, as already reported in our previous work.¹⁴ Another experiment was performed in ethanol with hexanoic acid as the reference surface modification agent (cerium precursor-to-hexanoic acid ratio 1:6) for cerium oxide. Regarding the obtain results, alcohol mixtures—ethanol with hexanol, dodecanol, or octadecanol (molar ratio: 285:1)—were also investigated.

Table 1 summarizes the experiments performed in the frame of this study.

Each synthesis has been reproduced at least three times and submitted to the same analyses. For a same synthesis type, NCs morphologies, sizes, and surface chemistry were the same, meaning a great reproducibility in the NCs characteristics.

Characterization. X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert MPD powder diffractometer (θ - θ Bragg-Brentano geometry using Cu K _{α} 1,2 ($\lambda_1 = 1.54060$ Å, $\lambda_2 = 1.54441$ Å) radiation, equipped with a secondary monochromator and a X'Celerator detector, in the range of 8–120°, in a continuous scan

mode at $3.5 \times 10^{-3} \text{ s}^{-1}$. The powder was ground and sieved at $50 \mu\text{m}$ before being subjected to XRD.

Transmission electron microscopy (TEM) images were obtained using a Hitachi H7650 transmission electron microscope operating at 90 kV. Samples were prepared by drop-coating diluted CeO_2 NPs suspension onto carbon supported copper grids. The average sizes of the primary nanoparticles have been determined using the ImageJ software. TEM images have been analyzed using this software to realize a counting over more than 100 particles.

Fourier transform infrared (FTIR) measurements were carried out using a Bruker Equinox 55 spectrophotometer. The spectra were recorded over 32 scans in the range of $400\text{--}4000 \text{ cm}^{-1}$, with a resolution of 4 cm^{-1} , using KBr powder technique. Thermogravimetric analysis–mass spectrometry (TGA-MS) measurements were performed with a NETZSCH STA 409 apparatus coupled with a ThermoStar Balzers Instruments quadrupole spectrometer. Thermogravimetry (TG) analyses were recorded in the $30\text{--}1000 \text{ }^\circ\text{C}$ temperature range with a heating rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under argon.

RESULTS

CeO_2 NCs Characterization. Representative XRD patterns of the as-synthesized powders (without the annealing step) are given in Figure 1. All experiments led to CeO_2 crystallized in a face-centered cubic (fcc) system.

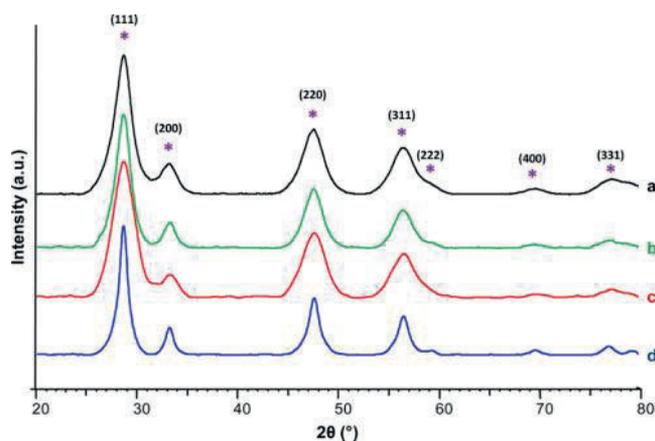


Figure 1. XRD patterns of CeO_2 nanopowder synthesized from ammonium cerium nitrate (CAN) at $300 \text{ }^\circ\text{C}$ and 24.5 MPa ($t_s = 55 \text{ s}$) in (a) pure ethanol, (b) ethanol and hexanol mixture (285:1 ratio), (c) ethanol and 6-amino-1-hexanol mixture (285:1 ratio), and (d) ethanol and hexanoic acid (285:1 ratio). When mixtures were used, the CAN-to-surface modifier ratio was 1:6.

From these patterns, CeO_2 crystallite sizes have been determined using the Scherrer equation, and results are reported in Table 1. It has to be noticed that this technique induces an incertitude for the determination of CeO_2 crystallite sizes ($\pm 10\%$), which corresponds to an average value for the total population in the samples. However, since the samples have all been prepared the same way, the values given in this study (Table 1) can be compared with each other, and the influence of aminoalcohols and alcohol mixtures can be discussed from these results.

First, CeO_2 NCs synthesized in ethanol with aminoalcohols as surface modification agent display lower crystallite sizes (3.7, 3.5, and 3.1 nm with ethanolamine, 3-amino-1-propanol and 6-amino-1-hexanol, respectively) than those obtained in pure ethanol (4.1 nm). Furthermore, an increasing aminoalcohol carbon chain length leads to a decreasing size.

Then, the CeO_2 NCs synthesized in ethanol in the presence of longer carbon chain alcohols (ratio 285:1) display higher crystallite sizes (4.6, 4.4, and 4.2 nm with hexanol, dodecanol and octadecanol, respectively) than those synthesized in pure ethanol (4.1 nm). In that case, the longer the alcohol carbon chain length of the additive, the smaller the NCs size. It has to be noticed that these sizes are intermediate between those obtained in pure ethanol and in pure propanol (4.6 nm). Moreover, crystallite sizes tend to approach the size of CeO_2 crystallites synthesized in pure propanol (4.6 nm) when the alcohol used as the surface modification agent has a low carbon chain length (hexanol, 4.6 nm), while they tend to approach the size of those obtained in pure ethanol (4.1 nm) when the surface modification agent has a higher carbon chain length (octadecanol, 4.2 nm).

Finally, CeO_2 NCs synthesized in ethanol with hexanoic acid as the surface modification agent display the highest crystallite size in this study (8.0 nm). This size is even higher than the one of the particles synthesized in pure hexanol (6.1 nm), and tends to approach the crystallite size of CeO_2 NCs synthesized from ammonium cerium nitrate in scH_2O .¹⁴

The CeO_2 powders synthesized in ethanol using amino-alcohol, alcohol mixtures, and hexanoic acid have been further observed by TEM. Representative micrographs are shown in Figure 2.

All CeO_2 nanopowders present the same morphology regarding TEM images. Primary NCs (3–8 nm depending on the surface modification agent) were organized in larger round-shape like structures (20–100 nm in diameter), although these morphologies are less evident when hexanoic acid is used (Figure 2e). Such morphology has already been observed for CeO_2 nanopowders synthesized in near- or supercritical alcohols from ammonium cerium nitrate or cerium nitrate.^{14,15,28} Thus, we can deduce that the addition of alcohol derivatives or alcohols does not affect the morphology of CeO_2 nanopowders synthesized in supercritical ethanol but affect CeO_2 NCs size. Finally, the average sizes of primary NCs, analyzed using TEM images, match well with the crystallite sizes determined from XRD for each experiment (Table 1).

The CeO_2 NCs surface was characterized using FTIR spectroscopy in order to confirm the interaction between CeO_2 NCs and the alcohol or alcohol derivatives. Knowing that the CH_2/CH_3 groups' vibrations are not easily observable, our interest was focused on the $1900\text{--}900 \text{ cm}^{-1}$ region of the spectra in order to characterize the interaction method between CeO_2 and the surface modification agents (Figure 3).³⁰

These spectra evidence the presence of the stretching vibration band of the --C--O group, around 1050 cm^{-1} , for all samples. Additionally, the absence of stretching vibration band of the C=O group (1780 cm^{-1}) indicates the absence of free carboxylic acid functions (formation of carboxylate functions).^{18,31} These two observations allow confirming the grafting of organic molecules onto the surface of CeO_2 NCs.

The presence of (symmetric and asymmetric) stretching vibration bands of the --COO group is also detected for all powders. Yet, a noticeable difference is visible for samples synthesized in the presence of aminoalcohols.

Indeed, in the case of CeO_2 NCs, which surface was modified with hexanoic acid (ref-4) and alcohol mixtures (C6, C12 and C18), these two bands are attributed around 1540 cm^{-1} ($\nu_{\text{as}}(\text{--COO})$) and 1450 cm^{-1} ($\nu_{\text{s}}(\text{--COO})$), as it can be observed with pure ethanol (ref-1) or pure alcohols.¹⁴ However, the attribution of these two bands, for the --COO

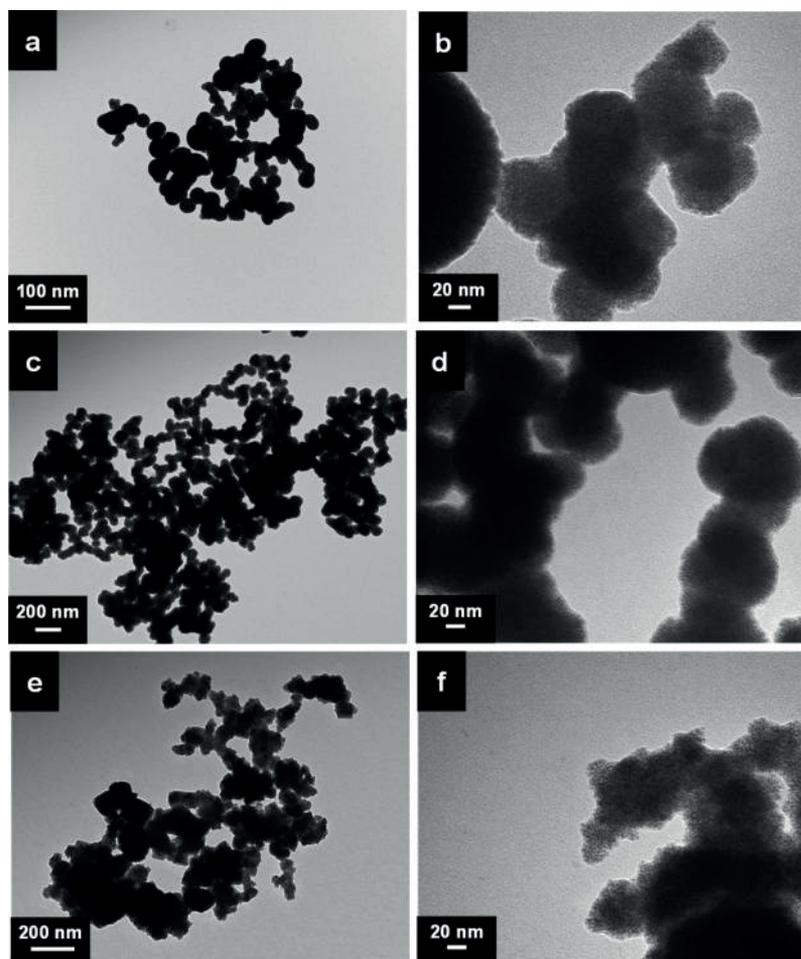


Figure 2. TEM images of CeO₂ powders prepared from ammonium cerium nitrate in ethanol with different surface modifiers: (a and b) 6-amino-1-hexanol, (c and d) hexanol, and (e and f) hexanoic acid. The cerium precursor-to-surface modification agent ratio was 1:6 for all syntheses.

group stretching vibration band, is shifted for the amino-alcohols (C2-NH₂, C3-NH₂, and C6-NH₂).

Interestingly, these attributions are characteristic of the [carboxylate function - oxide surface] type of interaction,^{25,32} as shown in Figure 3. The difference (Δ) between the wavenumbers attributed to $\nu_{as}(-\text{COO})$ and $\nu_s(-\text{COO})$ allows differentiating each type. In powders synthesized with pure alcohols (ref-1, ref-2, and ref-3), alcohols mixtures (C6, C12, and C18) and hexanoic acid (ref-4), Δ is around 90 cm⁻¹, typical of a “chelating bidentate” interaction type between the surface modifier and cerium oxide NCs. In contrast, Δ ranges from 140 to 168 cm⁻¹ (Table 2) for powders synthesized with aminoalcohols (C2-NH₂, C3-NH₂, and C6-NH₂), which is typical of a “bridging” type interaction.

FTIR spectroscopy confirms the presence of organic molecules on the surface of cerium oxide NCs synthesized with alcohol mixtures, aminoalcohols, and hexanoic acid, with a significant influence of the surface modifier on the type of interaction between the organic molecule and the CeO₂ NCs.

In order to characterize the nature of the organic compounds grafted onto the CeO₂ surface, TGA-MS analyses were performed. Our interest was first focused on CeO₂ formed in the presence of surface modification agents with the same carbon chain length, i.e., samples C6 (hexanol), C6-NH₂ (6-amino-1-hexanol), and ref-4 (hexanoic acid). The evolution of heavy fragments has been followed through $m/z = 55$ (C₄H₇⁺, alkene fragment), $m/z = 58$ (C₂H₅CHNH₂⁺, amine

fragment) and $m/z = 67$ (C₅H₇⁺, alkyne fragment). Figure 4 presents mass spectra of the three samples.

These mass spectra reveal the presence of the considered surface modification agents onto the surface of the CeO₂ NCs. Indeed, alkene and/or alkyne fragments ($m/z = 55$ and/or 67) are detected for the three samples. Furthermore, heavy amine fragment ($m/z = 58$) is detected only for the sample C6-NH₂ (6-amino-1-hexanol; Figure 4b), while it is missing in the other samples (Figure 4a,c). This confirms that the organic molecules used are present in the CeO₂ powder samples, and their structural integrity seems to be conserved during the syntheses as amine terminal function are detected ($m/z = 58$) in the sample C6-NH₂.

The release of these heavy fragments resulting from the decomposition of chemisorbed organics occurs between 300 and 470 °C. Results obtained from FTIR and TGA-SM analyses therefore confirm the surface modification of CeO₂ NCs by hexanol, 6-amino-1-hexanol, and hexanoic acid in EtOH at 300 °C and 24.5 MPa ($t_s = 55$ s).

Concerning samples C12 (dodecanol) and C18 (octadecanol), no heavy fragment could be observed ($m/z > 46$). Either these heavy alcohols did not graft onto the CeO₂ NCs surface, or their amount is too small to be properly detected.

Similarly, aminoalcohols with shorter carbon chains (ethanol-amine and 3-amino-1-propanol) are hardly detectable via TGA-MS technique. Indeed, the release of species such as CO₂ or ethanol gives signals at the same masses than these two

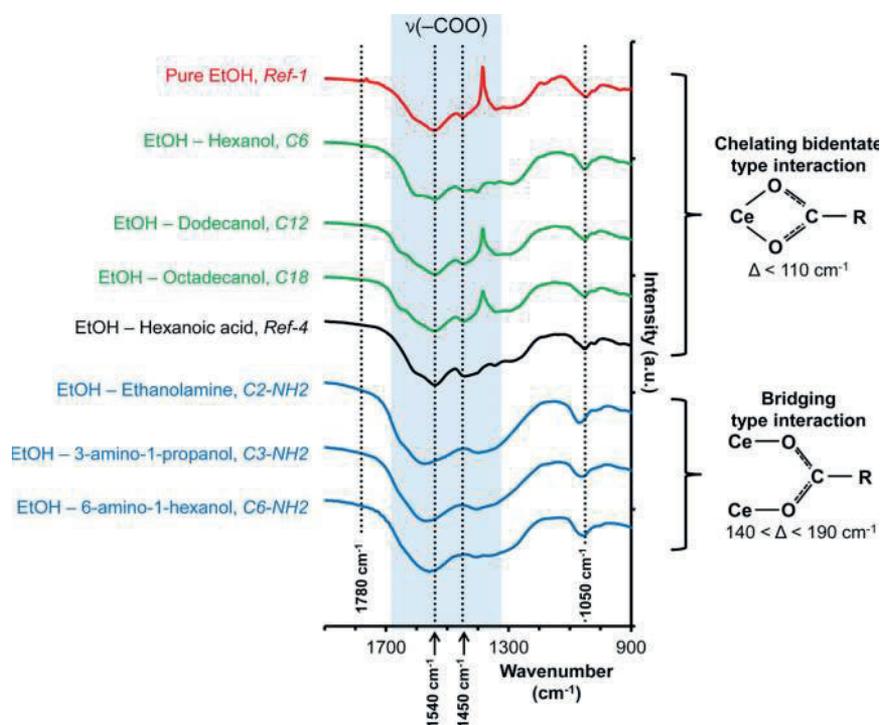


Figure 3. IR spectra of the surface modified CeO_2 powders obtained during the synthesis in ethanol at 300°C and 24.5 MPa ($t_s = 55\text{ s}$) with different surface modifiers.

Table 2. Stretching Vibration Bands (ν_{as} and ν_s) of the $-\text{COO}$ Group for Samples C2-NH2, C3-NH2, and C6-NH2

| surface modification agent | $\nu_{as}(-\text{COO})$ | $\nu_s(-\text{COO})$ | Δ |
|----------------------------|-------------------------|-----------------------|----------------------|
| ethanolamine | 1585 cm^{-1} | 1417 cm^{-1} | 168 cm^{-1} |
| 3-amino-1-propanol | 1579 cm^{-1} | 1417 cm^{-1} | 162 cm^{-1} |
| 6-amino-1-hexanol | 1567 cm^{-1} | 1417 cm^{-1} | 140 cm^{-1} |

aminoalcohols (e.g., $m/z = 15$ and 44 , for CH_3^+ and $\text{C}_2\text{H}_6\text{N}^+$ / CO_2^+ , respectively) and so, makes the identification of the released species not possible. However, the detection of these fragments also occurs between 340 and 500°C , as previously observed (Figure 4). Yet, those considerations, coupled with FTIR analyses, are in favor of the presence of amine organic

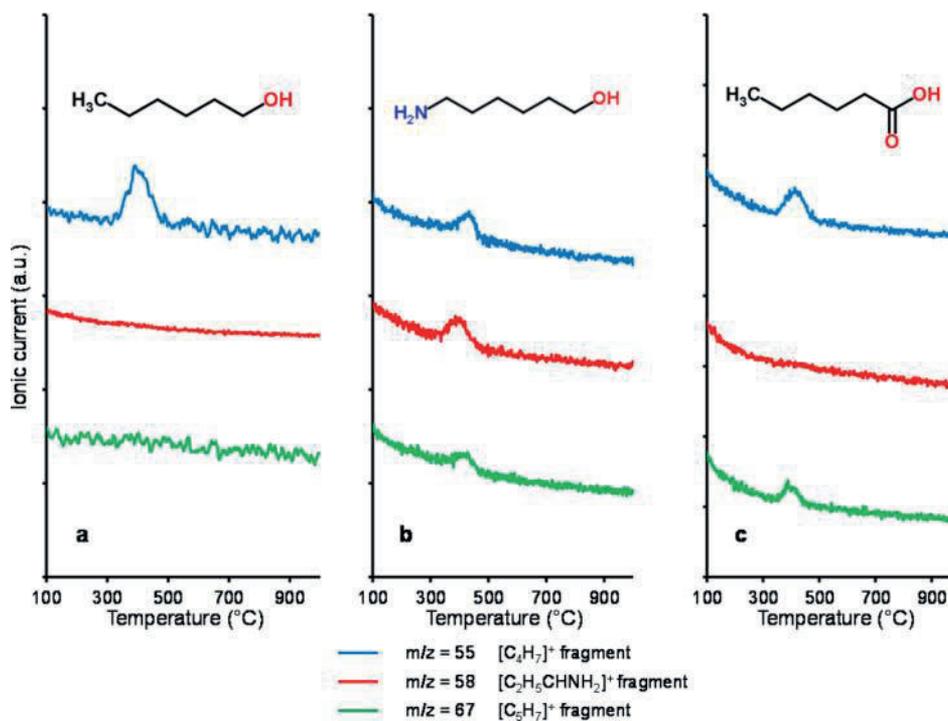


Figure 4. Mass spectra of CeO_2 powders formed at 300°C and 24.5 MPa from ammonium cerium nitrate in ethanol in the presence of (a) hexanol, (b) aminohexanol, and (c) hexanoic acid.

grafts onto the surface of CeO₂ NCs prepared with ethanol-amine and 3-amino-1-propanol.

■ DISCUSSION

Precise Control of CeO₂ NCs Sizes with Alcohol Mixtures. Our previous work showed that the crystallite sizes of CeO₂ NCs synthesized from ammonium cerium nitrate in near- and supercritical alcohol (from methanol to hexanol; 300 °C, 24.5 MPa and 55 s) could be controlled by choosing the alcohol solvent (nature and carbon chain length). The above results show that this size control could still be more precisely controlled using alcohol mixtures.

Furthermore, we can notice that the crystallite sizes of the CeO₂ NCs obtained in alcohol mixtures (i) are higher than those obtained in pure ethanol (Table 1), (ii) decrease with the carbon chain length of the alcohol additive (4.6, 4.4, and 4.2 nm with hexanol, dodecanol, and octadecanol, respectively) and, (iii) tend to approach the sizes observed in pure ethanol (4.1 nm) when long carbon chain length alcohols are used. Obviously, this phenomenon is driven by a competition between the surface modification of CeO₂ NCs by both alcohols. Indeed, surface modification by the alcohols is evidenced by FTIR analyses via the formation of carboxylate interaction (Figure 3). Considering alcohol mixtures, especially in the case of ethanol and hexanol, the synthesis leads to CeO₂ NCs sizes (4.6 nm) intermediate between those observed in pure ethanol and pure hexanol (4.1 and 6.0 nm, respectively). A significant amount of hexanol can intervene in the surface modification of CeO₂ NCs, in competition with ethanol. However, the smallest steric hindrance of ethanol may give it an advantage for the surface modification, explaining that the crystallite sizes (4.6 nm) tend to approach more those obtained in pure ethanol (4.1 nm) than in pure hexanol (6.0 nm – Table 1). In the case of dodecanol and octadecanol mixtures, steric hindrance differences with ethanol are higher and surface modification may mostly be performed by ethanol. Thus, heavy fragments become hardly detectable by TGA-MS, due to low presence of such high carbon chain length alcohols and crystallite sizes tend to decrease toward those obtained in pure ethanol; ethanol grafting becomes predominant when high carbon chain length alcohols are used. Based on such conclusions, it could be hypothesized that CeO₂ NCs properties (crystallite sizes, specific surface area, thermal behavior, etc.) can be controlled precisely by playing with alcohol mixture composition (alcohol carbon chain lengths, nature, and/or molar ratio).

It has also to be noticed that CeO₂ NCs with smaller sizes are obtained when an alcohol is used as surface modifier compared to its carboxylic acid equivalent ($d_{cr} = 4.6$ and 8.0 nm, with hexanol and hexanoic acid, respectively). This is attributed to a weaker steric hindrance in the case of alcohol grafting, allowing a higher grafting rate and so, a faster quenching of CeO₂ crystal growth.

CeO₂ Surface Modification by Alcohol Derivatives: Amine Groups Role. The characterization results obtained for CeO₂ powders modified in scEtOH by aminoalcohols and hexanol allow identifying the influence of amine groups in such synthesis conditions. Indeed, (i) CeO₂ NCs sizes tend to decrease with increasing aminoalcohol carbon chain length ($d_{cr} = 3.7, 3.5,$ and 3.1 nm for C2-NH₂, C3-NH₂, and C6-NH₂ samples, respectively) and (ii) CeO₂ crystallite sizes are smaller when an aminoalcohol is used in comparison with its

nonaminated equivalent ($d_{cr} = 3.1$ and 4.6 for 6-amino-1-hexanol and hexanol, respectively).

It was proposed in our previous work that alcohol adsorption on CeO₂ surface was followed by two dehydrogenation steps of the formed alkoxide in order to create a carboxylate interaction type.¹⁴ Yet, such carboxylate-based interaction is more stable than alcohol adsorption (room temperature reversible alkoxide bound) and so, more able to stop particles growth.

The amine group displaying a free doublet is particularly apt to capture H⁺ protons. From then on, it appears possible that amine groups from aminoalcohols intervene during these dehydrogenation steps of the alcohols, favoring the carboxylate functions formation. This dehydrogenation could be more efficient than the dehydrogenation occurring via the CeO₂ surface (Ce–O–Ce + R–O–H → Ce–O–R + Ce–O–H, etc.), allowing a faster formation of carboxylate functions than without amine groups. Therefore, this would favor the stabilization of amino-alcohols and alcohols, over the CeO₂ surface, inhibiting particle growth.

Such hypothesis tends to be validated by FTIR results (Figure 3). Indeed, aminoalcohol-mediated surface modification results in the formation of bridged carboxylate interaction type, involving 2 surface Ce atoms, while surface modification occurring without aminated molecules results in the formation of chelating bidentate carboxylate interaction type, involving only one surface Ce atom (Figure 3). It appears obvious that dehydrogenation, via CeO₂ surface, induces a steric hindrance due to the formation of nearby surface hydroxide groups inhibiting the formation of bridged carboxylates (requiring available surface oxygen atoms). Oppositely, H⁺ proton capture by the amine group, during the dehydrogenation, limits the formation of surface hydroxides allowing the formation of bridged carboxylates. Thus, amine groups, from aminoalcohols, could intervene as “metal free catalysts” during the surface modification of CeO₂ NCs by alcohols or alcohol derivatives.

Finally, the interest of such surface modification was evidenced with a last experiment consisting in grafting fluorescent molecules over modified CeO₂ NCs. As previously mentioned, controlling surface chemistry of CeO₂ NCs via the grafting of alcohol derivatives offers chemical anchor points for potential further functionality addition. As an illustration, we chose to graft FITC molecules on dry powders of CeO₂ NCs previously modified with 6-amino-1-hexanol (C6-NH₂). Ten milligrams of C6-NH₂ sample were dispersed in 30 mL of ethanol with 50 mg of FITC (molar excess). The solution was heated at 50 °C overnight under stirring. Then, the recovered particles were washed three times in ethanol by centrifugation (6000 rpm, 10 min) and elimination of the supernatant. Finally, the FITC-grafted CeO₂ NCs were redispersed in a large amount of ethanol. As a reference, dry powders of CeO₂ NCs synthesized in pure ethanol (ref-1) were submitted to the same treatment. The two solutions were then submitted to an UV light (365 nm). Photographs of the solutions under visible and UV light (365 nm) are presented in Figure 5.

The pictures show that no fluorescence is detected under $\lambda = 365$ nm illumination when particles were synthesized in pure ethanol, then treated with FITC (Figure 5b, Solution 1), indicating that FITC did not graft onto the CeO₂ powders. On the contrary, a fluorescent behavior appears for the CeO₂ NCs synthesized in the presence of 6-amino-1-hexanol, then treated with FITC (Figure 5b, Solution 2), indicating that those powders were modified by FITC. This clearly shows that CeO₂ NCs modified with alcohol derivatives offer “anchoring points”

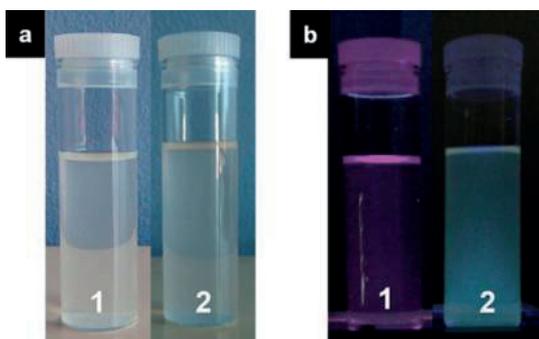


Figure 5. Photographs of CeO₂ powders dispersed in ethanol under (a) visible light and (b) UV-light at 365 nm. Powder for Solution 1 was prepared from ammonium cerium nitrate in ethanol at 300 °C and 24.5 MPa ($t_s = 55$ s; ref-1), then treated with FITC. Powder for Solution 2 was prepared from ammonium cerium nitrate in ethanol at 300 °C and 24.5 MPa ($t_s = 55$ s) in the presence of 6-amino-1-hexanol, then modified with FITC. (Note: The purple color in the photograph b, Solution 1, is due to U.V. light detection by the CCD captor of the camera.)

for further surface chemistry, with organic moieties and/or inorganic functionalities. Furthermore, with FTIC molecules reacting with amine groups, this experiment once more confirms that the integrity of the alcohol derivative molecule is conserved during the synthesis at 300 °C and 24.5 MPa ($t_s = 55$ s).

CONCLUSION

The synthesis of CeO₂ NCs in supercritical ethanol-based alcohol mixtures allows demonstrating the intervention of the alcohol as a surface modification agent of the oxide during the synthesis. These observations opened a basic question at the origin of this study on the possibility to add other functionalities on the surface of CeO₂ NCs using this synthetic approach.

The present work demonstrates the feasibility of the surface modification of cerium oxide by other functionalities during the synthesis in supercritical ethanol at 300 °C and 24.5 MPa ($t_s = 55$ s) from ammonium cerium nitrate. Thus, this method offers an alternative route to the classical surface modification method, generally involving carboxylic acid molecules.

Beyond bringing functionality, the amine group participates in the formation of bridged carboxylate interaction type during the adsorption of alcohols. Such bound alcohols (more stable) can therefore stop particles growth faster. Indeed, smaller sizes are obtained when aminoalcohols are used in comparison with its nonaminated alcohol equivalent ($d_{cr} = 3.1$ and 4.6 nm, with 6-amino-1-hexanol and hexanol, respectively). Furthermore, the aminoalcohols carbon chain length could intervene during the dehydrogenation process of the surface alkoxides, a longer chain allowing an easier access to the nearby alkoxide groups and then a faster quench of the growth (d_{cr} increases when carbon chain length decreases).

CeO₂ particles modified with amino-alcohols offer chemical “anchoring points” over their surface (–NH₂ amine groups) offering possibilities for later organic and/or inorganic modification, as demonstrated with FITC grafting.

Then we showed that characteristics of the reaction media can be optimized by the use of alcohol mixtures. This study showed that it is possible to finely control CeO₂ powders properties, while playing with the alcohol mixture composition

(alcohols choice and proportions), which is not accessible with a unique alcohol.

Thus, this study not only proposes a solution to finely select the characteristics of CeO₂ NCs via the use of alcohol mixtures, but also opens a new route for their surface modification via the use of other alcohol derivatives (chloroalcohols, phosphoalcohols, etc.) in a reaction media also playing the role of surface modification agent.

AUTHOR INFORMATION

Corresponding Author

*E-mail: aymonier@icmcb-bordeaux.cnrs.fr.

Notes

The authors declare no competing financial interest.

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