Ionic Liquid-Assisted Sonochemical Preparation of CeO2 Nanoparticles for CO Oxidation

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Abstract
CeO$_2$ nanoparticles were synthesized via a one-step ultrasound synthesis in different kinds of ionic liquids based on bis(trifluoromethanesulfonylamide, [Tf$_2$N]$^-$, in combination with various cations including 1-butyl-3-methylimidazolium ([C$_4$mim]$^+$), 1-ethyl-2,3-dimethylimidazolium ([Edimim]$^+$), butyl-pyridinium([Py$_4^+$]), 1-butyl-1-methyl-pyrrolidinium ([Pyrr$_{14}^+$]), and 2-hydroxyethyl-trimethylammonium ([N$_{1112}$OH]$^+$). Depending on synthetic parameters, such as ionic liquid, Ce(IV) precursor, heating method, and precipitator, formed ceria exhibits different morphologies, varying from nanospheres, nanorods, nanoribbons, and nanoflowers. The morphology, crystallinity, and chemical composition of the obtained materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy, and N$_2$ adsorption. The structural and electronic properties of the as-prepared CeO$_2$ samples were probed by CO adsorption using IR spectroscopy under ultrahigh vacuum conditions. The catalytic activities of CeO$_2$ nanoparticles were investigated in the oxidation of CO. CeO$_2$ nanospheres obtained sonochemically in [C$_4$mim][Tf$_2$N] exhibit the best performance for low-temperature CO oxidation. The superior catalytic performance of this material can be related to its mesoporous structure, small particle size, large surface area, and high number of surface oxygen vacancy sites.

Keywords
catalysis, ceria, CO oxidation, ionic liquids, nanomaterials, critcial materials institute, Amer Laboratory

Disciplines
Ceramic Materials | Complex Fluids | Nanoscience and Nanotechnology | Other Materials Science and Engineering

Comments

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Ionic Liquid-Assisted Sonochemical Preparation of CeO₂ Nanoparticles for CO Oxidation

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ABSTRACT: CeO₂ nanoparticles were synthesized via a one-step ultrasound synthesis in different kinds of ionic liquids based on bis(trifluoromethanesulfonylamide, [Tf₂N]⁻, in combination with various cations including 1-butyl-3-methylimidazolium ([C₄mim]⁺), 1-ethyl-2,3-dimethylimidazolium ([Edimim]⁺), butyl-pyridinium ([Py 4]⁺), 1-butyl-1-methyl-pyrrolidinium ([Pyrr 14]⁺), and 2-hydroxyethyl-trimethylammonium ([N1112OH]⁺). Depending on synthetic parameters, such as ionic liquid, Ce(IV) precursor, heating method, and precipitator, formed ceria exhibits different morphologies, varying from nanospheres, nanorods, nanoribbons, and nanoflowers. The morphology, crystallinity, and chemical composition of the obtained materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy, and N₂ adsorption. The structural and electronic properties of the as-prepared CeO₂ samples were probed by CO adsorption using IR spectroscopy under ultrahigh vacuum conditions. The catalytic activities of CeO₂ nanoparticles were investigated in the oxidation of CO. CeO₂ nanospheres obtained sonochemically in [C₄mim][Tf₂N] exhibit the best performance for low-temperature CO oxidation. The superior catalytic performance of this material can be related to its mesoporous structure, small particle size, large surface area, and high number of surface oxygen vacancy sites.

KEYWORDS: Catalysis, Ceria, CO oxidation, Ionic liquids, Nanomaterials

INTRODUCTION

Rare earth metal oxides, especially cerium oxide, have been a topic of interest to researchers in different fields owing to applications in solid oxide fuel cell anodes, as a catalyst in the three-way automobile exhaust system, as an oxygen storage capacitor, UV blockers and filters, efficient polishing agent for glasses, hybrid solar cells, high refractive index materials, coatings for corrosion protection of metals and alloys, cosmetics, ceramics, and in phosphors, where cerium is one of the most important constituent in several of the new generation of phosphors in tricolor lamps. Cerium(IV) oxide as a wide band gap semiconducting material (≈3.2 eV) can absorb light in the near UV region and slightly in the visible region and has therefore been regarded as a promising material for photocatalysis, especially when brought to the nanoscale. However, it is well known that important physical and chemical properties such as the band gap of CeO₂ nanoparticles can be quite different from the bulk. Their properties rely mainly on the morphology, size, and dimensions. Hence, considerable effort has been dedicated to prepare CeO₂ nanoparticles with controlled shape such as nanoplates, nanotubes, shuttle-shaped, nanorods, nanowires, and flower-like using different methods such as hydrothermal synthesis, solvothermal, thermal decomposition, microwave-assisted hydrothermal, sol-gel process, mechanochemical processing, and gas condensation. These methods all have certain drawbacks as they either use high pressure or high temperatures and expensive raw materials such as surface capping agents or organic solvents. Therefore, improving and exploring a new technique to prepare the size and shape-controlled ceria, which relies on a simple approach to reduce the cost of production using environmentally benign reagents and mild preparation conditions, is desirable. In that context, the exploration of ionic liquids for synthesis appears to be beneficial. Ionic liquids are salts...
composed of only ions that are liquid at relatively low temperatures (below 100 °C). Ionic liquids (ILs) have received substantial attention for materials synthesis in recent years because of their special properties. The possibility to vary the cation and anion as well as the ion combination makes it possible to engineer a solvent with unique properties such as high ion mobility, low melting point, negligible vapor pressure, good thermal stability, low toxicity, large electrochemical window, nonflammability, and the ability to dissolve a variety of chemicals in a highly polar yet weakly coordinating solvent.\textsuperscript{17,18} Recently, we were able to show that the combination of ionic liquids with ultrasound is a powerful method when it comes to the synthesis of nanooxides.\textsuperscript{19–22}

Sonochemistry, albeit mostly in conventional and volatile solvents, has attracted increasing interest of many researchers over the past decade for the synthesis of inorganic nanostructured materials. The chemical effects of ultrasound originate from acoustic cavitation,\textsuperscript{23} which occurs in several stages involving the steps of nucleation, growth, and collapse of bubbles in the liquid. The collapse of the bubbles provokes extreme conditions; high temperatures up to 5000 °C and high pressures of about 500 atm can be reached.\textsuperscript{24} Yet sonochemical synthesis has the advantage that it is experimentally comparatively simple.

We have employed sonochemistry for the synthesis of nano-CeO\textsubscript{2} in ionic liquids. Here, the ionic liquid can act not only as the solvent but also as the structure directing agent. Aside from a variation of the ionic liquid, the influences of the synthesis conditions such as conversion method, precipitator, irradiation time, and Ce precursor on the morphology, size, and the catalytic activity toward CO oxidation were investigated in detail.

\section*{EXPERIMENTAL SECTION}

\subsection*{Materials.}
All reagents employed were commercially available and directly used without further purification. All the ILs used in this study were synthesized according to the literature.\textsuperscript{15,24} Lithium bis(trifluoromethansulfonyl)amide (99%), butylpyridiniumbis(trifluoromethansulfonyl)amide (99%), and 1-butyl-1-methylpyrroldinium chloride (99%) were purchased from Iolitec; 1-ethyl-2,3-dimethylimidazolium chloride (99%) was from Acros; cerium(III) nitrate hydrate (99%) and cerium(III) chloride hydrate (99%) were from ABCR. Sodium hydroxide (98%) and ammonium hydroxide (33%) were from Sigma-Aldrich. Choline chloride (99%) was from Acros; cerium(III) acetate hydrate (99%) and cerium(III) nitrate hydrate (99%) were from Alfa-Aesar. The nano-CeO\textsubscript{2} materials were compared with a microcrystalline CeO\textsubscript{2}, which was purchased from Sigma-Aldrich and is labeled M-CeO\textsubscript{2}.

\subsection*{Experimental Procedures.}
In a typical synthesis, 0.2 g of cerium(III) acetate monohydrate was added to 0.1 g of sodium hydroxide and 2 mL of the respective bis(trifluoromethane)-sulfonylamide IL with either 1-ethyl-2,3-dimethylimidazolium ([Emim]\textsuperscript{+}), butyl-pyridinium ([Pyrr\textsubscript{14}]\textsuperscript{+}), 1-butyl-1-methylpyrroldinium ([Pyrr\textsubscript{14}]\textsuperscript{+}), or 2-hydroxyethyl-trimethylammonium ([N\textsubscript{1112}OH]\textsuperscript{+}) as the cation. The reaction mixture was then stirred for 30 min.

For the sonochemical synthesis, a commercial ultrasound bath (USC200T, VWR International, 45 kHz and 60 W) was used. The reaction mixtures were placed in glass tubes with a screw top and then irradiated in an ultrasound bath for 12 h under ambient conditions. The product was separated by centrifugation for 5 min at 2000 rpm, washed thoroughly with ethanol and distilled water, and dried overnight in the air at 80 °C (yield: 85%).

To explore the effect of the precipitating agent on the product, we used an aqueous solution of NH\textsubscript{4}OH under otherwise similar conditions. The samples were also prepared by using different Ce sources such as cerium(III) nitrate hydrate and cerium(III) chloride hydrate.

For the microwave synthesis, the reaction mixture was placed in 10 mL glass vessels equipped with a Teflon septum and irradiated for 10 min at 80 °C using a single-mode microwave operating at 2455 MHz (CEM Discover, Kamp Lintfort, D). The reaction time, temperature, and irradiation power were computer controlled. The sample was then allowed to cool to room temperature, and the product was separated by centrifugation for 5 min at 2000 rpm, washed thoroughly with ethanol and distilled water, and dried overnight in the air at 80 °C (yield: 79%). Finally, the dried solid was calcined in air at 425 °C for 4 h.

Ionothermal experiments were performed in 50 mL Teflon cups enclosed in stainless steel autoclaves (Parr Instrument, U.S.A.). The reaction mixture was transferred to a Teflon cup and sealed in the autoclave, which was placed into a laboratory furnace where it was held at 170 °C for 20 h. The autoclave was then cooled in air. The resulting powders were separated by centrifugation for 5 min at 2000 rpm, washed with ethanol and deionized water several times, and dried overnight at 80 °C (yield: 92%). Finally, the dried solid was calcined in air at 425 °C for 4 h.

Characterization. Powder Diffraction. Powder X-ray diffraction measurements were carried out on a G670 diffractometer with an image plate detector (Huber, Rimsting, D) operating with Mo K\textalpha\textsubscript{r} radiation (\(\lambda = 0.70737\) nm).

Spectroscopy. Attenuated total reflection (ATR) spectroscopy was carried out on an Alpha ATR spectrometer equipped with a diamond crystal (Bruker, Karlsruhe, D). Solid samples were pressed on the crystal.

Scanning Electron Microscopy (SEM). Scanning electron microscopy measurements were performed with a high resolution SEM (Zeiss, LEO 1530 Gemini) with a thermally aided field emission gun (FEG) at an acceleration voltage of \(U_{\text{acc}}\) = 0.2–30 kV. For the SEM measurements, the CeO\textsubscript{2} nanopowders were placed on a carbon film, dried under vacuum for 20 min, and covered with gold to allow for a better electric conductivity.

Surface Area by \(N_{2}\) Physisorption. Nitrogen physisorption experiments were carried out in a modified Autosorb 1C setup (Quantachrome). The sample was thermally pretreated at 200 °C in He for 2 h. The physisorption measurement was performed at the boiling point of liquid N\textsubscript{2} (78 K). The surface area was calculated according to the BET (Brunauer–Emmett–Teller) equation. The pore size distribution was obtained through the BJH (Barrett–Joyner–Halenda) method.

\(U\textsuperscript{−}V\textsuperscript{−}I\textsuperscript{−}S\textsuperscript{−}Vis\textsuperscript{−}Vis\) Spectra were measured at room temperature on a Cary 5000 spectrometer (Varian, Palo Alto, U.S.A.) in reflection mode.

High-Resolution X-ray Photoelectron Spectroscopy (XPS). XPS measurements were carried out in an ultrahigh vacuum (UHV) setup equipped with a high-resolution Gammasdata-Sciencia SES 2002 analyzer. Monochromatized Al K\textalpha\textsubscript{r} X-rays (1486.6 eV; anode operating at 14 kV and 55 mA) were used as incident radiation. The base pressure in the measurement chamber was around 2 × 10\textsuperscript{−10} mbar. XP spectra were recorded in the fixed transmission mode. The analyzer slit width was set to 0.3 mm, and pass energy of 200 eV was chosen, resulting in an overall energy resolution better than 0.5 eV. Charging effects were compensated by applying a flood gun. The binding energies were referenced to adventitious carbon (C 1s set to 284.8 eV). The CASA XPS program was employed to analyze the spectra. For determination of signal areas, a Shirley background was used. The O 1s signals were fitted with line shapes mixed from Gaussian and Lorentzian contributions.

Ultrahigh Vacuum Fourier Transform Infrared Spectroscopy (UHV-FTIRS). The UHV-FTIRS experiments on different ceria powder samples were performed in an UHV apparatus, which combines a state-of-the-art vacuum IR spectrometer (Bruker, VERTEX 80v) with a novel UHV system (PREVAC) (for details, see ref 27, 28). The base pressure in the measurement chamber was 2 × 10\textsuperscript{−10} mbar. The optical path inside the IR spectrometer and the space between the spectrometer and UHV chamber were evacuated to avoid adsorption of atmospheric moisture, resulting in superior sensitivity and stability.

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of the system. The polycrystalline ceria powders were first pressed onto a gold-plated stainless steel grid (0.5 cm × 0.5 cm) and then mounted on a sample holder, making it possible to record FTIR data in transmission geometry.

The grid and the attached powder particles were cleaned in the UHV chamber by heating to 750 K in order to remove all contaminations, such as water and hydroxyl groups. Prior to each exposure to CO, a spectrum of the clean powder was recorded as a background reference. We carried out the exposure of the sample to CO by backfilling the measurement chamber through a leak valve. The gas purity was 99.99 vol % for CO. All UHV-FTIR spectra were collected with 1024 scans at a resolution of 2 cm⁻¹.

**RESULTS AND DISCUSSIONS**

To evaluate the benefit of the sonochemical synthesis (sample identifier: S1), it was compared with microwave synthesis (sample identifier: S2), which is another nonconventional synthesis method allowing for quick heating rates, and classical ionothermal synthesis (sample identifier: S3). In a typical synthesis, the desired amount of cerium(III) acetate monohydrate was reacted with the necessary amount of NaOH in the ionic liquid under the conditions of the respective conversion method (see Experimental Section for details). To determine the phase purity and crystallinity of the obtained material, the XRD patterns for all samples were measured. As shown in Figure 1a, the sonochemical method results in pure CeO₂; all recorded diffraction peaks can be attributed to CeO₂ crystallizing in the CaF₂ structure type (PDF 34-394). No other crystalline phases are observable. The XRD patterns of the materials obtained by microwave reaction (Figure 1b) and ionothermal synthesis (Figure 1c) show in addition peaks characteristic for Ce₂O₃ and Ce(OH)₃, albeit in different intensities. It is possible to convert the latter two samples to pure CeO₂ by calcination at 425 °C in air for 4 h (Figure S1, Supporting Information, shows the XRD patterns of the samples after calcination). The average crystallite sizes have been estimated applying the Scherrer equation to the most intense diffraction peak of CeO₂, which corresponds to d_{(111)}. This yielded crystallite sizes of approximately 4, 6.5, and 8.8 nm for samples prepared using the ultrasound (S1), microwave (S2), and ionothermal methods (S3), respectively. The data are summarized in Table 1, where the labels used for these materials (in the states after post-treatment if applied) are introduced as well. There is a shift in the (111) diffraction peak position, with the material from the ionothermal route exhibiting the highest, and the material from sonochemical synthesis exhibiting the lowest angle, which is associated with an increase in the lattice constant as shown in Table 1 (Supporting Information). Moreover, from Table 1, we find that the lattice parameters of the prepared CeO₂ increase with decreasing crystallite sizes, a frequently observed phenomenon for oxide nanoparticles, which is due to increased lattice strain.²⁹,³⁰ For CeO₂, the presence of Ce³⁺ and/or oxygen vacancies also could lead to a lattice expansion.³¹

The morphology of the samples was investigated using SEM. It is shown in Figure 2 (left) that S1 is composed of aggregated spherical particles with a size of about 20 nm. When microwave

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**Table 1. Estimated Crystal Sizes, Lattice Parameters, and Cell Volumes of CeO₂ Samples Prepared in [C₄mim][Tf₂N] Using Different Preparation Methods**

<table>
<thead>
<tr>
<th>sample</th>
<th>grain size (nm)</th>
<th>lattice parameter (Å)</th>
<th>cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (sonochemical, as-obtained)</td>
<td>4.0</td>
<td>5.409(6)</td>
<td>158.2(3)</td>
</tr>
<tr>
<td>S2 (microwave, calcined at 425 °C)</td>
<td>6.5</td>
<td>5.381(5)</td>
<td>155.8(3)</td>
</tr>
<tr>
<td>S3 (ionothermal, calcined at 425 °C)</td>
<td>8.8</td>
<td>5.363(8)</td>
<td>154.2(4)</td>
</tr>
</tbody>
</table>

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Figure 1. XRD patterns of as-prepared samples in [C₄mim][Tf₂N] synthesized by the ultrasound (a), microwave (b), and ionothermal routes (c), S1 through S3, respectively.

Figure 2. SEM images of CeO₂ prepared in [C₄mim][Tf₂N] using ultrasound (S1-as-prepared, left), microwave (S2-calcined, right), and the ionothermal route (S3-calcined, bottom).
irradiation was used, CeO2 nanorods (S2-calcined, Figure 2, right) were obtained with widths of about 50 nm and lengths of about 300 nm. The ionothermal synthesis methods leads to flower-like shaped nanostructures of CeO2 (S3-calcined, Figure 2, bottom).

Structure and purity of the S1, S2, and S3 CeO2 materials were also analyzed by Raman spectroscopy (Figure 3).

Characteristic for fluorite-type CeO2 is a band at about 464 cm$^{-1}$, which arises from the symmetrical stretching (F$_{2g}$) mode of the {CeO$_8$} unit. As shown in Figure 3, a strong and broad band can be found at about 461 cm$^{-1}$ for S1 and at about 464 cm$^{-1}$ for S2 and S3, which can be assigned to the F$_{2g}$ mode. This mode appears at lower frequencies for S1 than for S2 and S3. The values for S2 and S3 are similar to that reported for bulk CeO2 in the literature (464 cm$^{-1}$). The red-shift for S1 is in agreement with the observation of a larger lattice constant. A broadening of the line can be an effect of defects in the oxygen sublattice resulting from thermal or grain size-provoked nonstoichiometry, phonon confinement, and variations in phonon relaxation as a function of particle size strain. The existence of a weak and less prominent broad band in sample S1 at about 600 cm$^{-1}$ can be assigned to a nondegenerate longitudinal optical (LO) mode of ceria. This occurs by the relaxation of symmetry rules, which in turn is associated with oxygen vacancies in the lattice. Furthermore, the presence of one more weak and broad band at 300 cm$^{-1}$ in S1 can be attributed to dislocation of oxygen atoms from their ideal fluorite lattice positions.

It is also possible to estimate the particle size from the Raman line broadening by using the following equation

$$\Gamma(cm^{-1}) = 10 + 124.7/D_{R}$$  \hspace{1cm} (1)

where $\Gamma(cm^{-1})$ is the full width at half-maximum of the Raman active mode band, and $D_{R}$ is the particle size of CeO2 sample. The particle size ($D_{R}$) of the CeO2 aggregates is 5.6 nm (S1), 14.7 nm (S2), and 14.4 nm (S3), respectively. The trend for the particles sizes estimated by this method is similar to the one from PXRD.

IR spectroscopy also allows insight into the chemical composition and the purity of the samples. Figure 4 shows the IR spectra recorded of samples S1–S3. Overall, the spectra are quite similar to the one of M-CeO2 (Figure 4d). For all samples, an absorption band at about 455 cm$^{-1}$ can be observed, which originates from Ce–O stretching vibrations. The absorption bands at about 1125 and 1326 cm$^{-1}$ correspond to the characteristic vibrations of the Ce=O–Ce moiety. Moreover, the existence of absorbed water molecules on the surface of S1 is evident from the bands at 3324.7 and 1628 cm$^{-1}$, which are due to $\nu$(O–H) and $\delta$(O–H) vibrations. Comparing the IR spectra of S1–S3 with the IR spectra of Ce$_{3}$(mim)$_{2}$[Tf$_2$N] and cerium(III) acetate monohydrate shows that these compounds are no longer present in the samples prepared using different preparation methods. They contain no starting materials, and the ionic liquid is removed completely by the cleaning step. The IR data of the sonochemically prepared sample are confirmed by TG analysis as shown in Figure S3 of the Supporting Information.

To check the constituents of the CeO2 prepared by different preparation methods, EDX analysis was carried out during the SEM measurement (Figure S4, Supporting Information). As shown in Figure S4 of the Supporting Information, the EDX spectra show peaks corresponding to cerium and oxygen. The presence of carbon peak comes from the carbon film of the sample holder. No signals corresponding to elements from the ionic liquid from which the samples were obtained could be observed. This confirms the sample purity.

To get more detailed information about the oxidation states as well as the surface composition of the samples prepared via different synthesis methods, XPS measurements were carried out. Figure 5 shows the Ce 3d spectra obtained for the three as-prepared CeO2 samples. The spin–orbit doublet with unprimed labels, v and u, corresponds to the primary Ce
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3d_{5/2} and Ce 3d_{3/2} states, while the bands labeled v_{0p}, v', v'', v‴ and u_{0p}, u', u'', u‴ represent satellite features arising from the Ce 3d_{5/2} and Ce 3d_{3/2} ionization, respectively. Furthermore, the correct (cf. ref 40), but the method will relate the Ce⁴⁺ content surface of well-crystalline CeO₂ exposes exclusively Ce⁴⁺ the Ce⁴⁺ contents in the near-surface region of samples made via reference, here taken from ref 40. From the spectra in Figure 5, in the surface regions of experimental samples to that of a surface region all other CeO₂ materials including M-CeO₂ routes S1, S2, and S3 and of M-CeO₂ were estimated to be 86%, 93%, 67%, and 86%, respectively, of that in well-crystalline CeO₂. The exact analysis of the Ce³⁺ content from such spectra is, in principle, possible by fitting the signal shape with the corresponding component lines, but it is highly prone to errors. We used instead a simplified method, which takes advantage of the fact that intensity in the binding energy region of u‴ arises from Ce⁶⁺ alone.⁴¹ The method assumes that the surface of well-crystalline CeO₂ exposes exclusively Ce⁴⁺ (reduction degree: 0%, 100% Ce⁴⁺). This is not necessarily correct (cf. ref 40), but the method will relate the Ce⁴⁺ content in the surface regions of experimental samples to that of a reference, here taken from ref 40. From the spectra in Figure S5, the Ce⁵⁺ contents in the near-surface region of samples made via routes S₁, S₂, and S₃ and of M-CeO₂ were estimated to be 86%, 93%, 67%, and 86%, respectively, of that in well-crystalline CeO₂.⁴¹

The corresponding O 1s spectra are dominated by a major signal centered at 529.6 eV (Figure S5, Supporting Information), which originates from the bonding of oxygen anions to cerium centers. ⁴²,⁴³ A second O 1s peak at about 532.2 eV is ascribed primarily to the existence of hydroxyl species formed at surfaces of the as-prepared CeO₂ samples. The surface area exposed by the different samples was elucidated by nitrogen adsorption−desorption isotherm measurements. Figure 6 reveals some differences in the shape of the N2 adsorption−desorption isotherms of the samples. The shape of the hysteresis loops of the samples corresponds to a type IV isotherm according to the IUPAC classification, indicating a mesoporous structure of the samples. For S₁, the hysteresis loop is a composite of the H2 and H3 types, indicating that the sample has channel-like or ink-bottle pores. The hysteresis loops for S₂ and S₃ are a composite of H1 and H3, suggesting they may have slit-shape pores or plate-like particles. The values of the BET surface area calculated from the linear part of the nitrogen adsorption isotherm plot at 77 K are 162 m²/g for the sonochemically prepared CeO₂ nanoparticles (S₁), 81 m²/g for CeO₂ nanorods obtained via microwave synthesis (S₂), and 22 m²/g for ionothermally synthesized CeO₂ flower-like particles (S₃). All values are considerably higher compared to the reported value for M-CeO₂ (3.1 m²/g). ⁴⁴ The most frequent pore diameter derived from the nitrogen adsorption isotherm by the BJH method (Figure S6, Supporting Information) was 1.83 nm for sonochemically prepared CeO₂ (S₁), with a narrow pore size distribution, while the pore size distributions were broad around 4 and 8 nm for the samples prepared via the microwave (S₂) and ionothermal (S₃) routes, respectively. The BET measurement can also be used to approximate the particle diameter. For spherical particles, the specific surface area (SSA) of a particle can be calculated according to

\[ \text{SA} = \frac{6}{\rho D} \]  

(2)

here \( \rho \) is the density of the material, and \( D \) is the particle diameter. The density of bulk ceria is 7 g/cm³. However, because the particles obtained via the ionothermal (S₃) and microwave (S₂) routes are not spherical, eq 2 can only be used for the sonochemically prepared nanospherical CeO₂. The result is 5.2 nm, which matches well with the particle size determined from PXRD and eq 1.

Optical Properties of CeO₂. The optical properties of the samples were determined by recording the absorption spectra in the range of 325–700 nm (Figure 7, top). An absorption edge at about 345 nm could be evidenced for the CeO₂ nanoparticles and flower-like morphologies (routes S₂ and S₃) and at about 360 nm for the sonochemically prepared CeO₂ nanoparticles (S₁). The charge−transfer transition between the O^{2−} (2p) and Ce⁴⁺ (4f) bands is responsible for this UV absorption. ⁴⁵ The optical band gap (E_g) can be calculated on the basis of the optical absorption spectrum by the following equation

\[ (Ahv)^n = B(hv - E_g) \]  

(3)

where \( h \) is Planck’s constant, \( ν \) is the frequency of light, \( A \) is the absorbance, \( B \) is a materials constant, and \( n \) is either 2 for an indirect allowed transition or 1/2 for a direct allowed transition. Figure S7 of the Supporting Information shows the \((Ahv)^2\) versus \( hv \) curve for the sample for the direct transitions. The band gaps of the CeO₂ nanoparticles (S₁), nanorods (S₂), and nanoflowers (S₃) are determined to be about 2.56, 2.45, and

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Compared to that of bulk CeO$_2$ (3.15 eV)\textsuperscript{46} can arise from the existence of Ce$^{3+}$ and related O$_2$\textsuperscript{2-} vacancies.\textsuperscript{47} This initiates intermediate energy levels causing a decrease in the band gap.

2.41 eV, respectively, estimated from the intersection of the extrapolated linear portions with the abscissa. It is well known that the red shift for the band gap in the CeO$_2$ samples compared to that of bulk CeO$_2$ (3.15 eV)\textsuperscript{46} can arise from defects in the fluorite structure of CeO$_2$, namely, due to the existence of Ce$^{3+}$ and related O$_2$\textsuperscript{2-} vacancies. This initiates intermediate energy levels causing a decrease in the band gap. From these band gaps, $E_r$, the average crystallite sizes can be estimated by eq 4\textsuperscript{48}

$$E = E_0 + \frac{\hbar^2}{8\mu R^2}$$

where $E_0$ is the energy gap for bulk materials, and $\hbar$ is Planck’s constant. $R$ denotes the particle radius of the studied material, and $\mu$ is the reduced mass of exciton, which can be calculated from

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

$m_e$ and $m_h$ are the electron and hole effective masses, respectively. From our data, the particle sizes are approximately 5.6, 5.1, and 5 nm for CeO$_2$ prepared using the ultrasound (S1), ionothermal (S2), microwave methods (S3), respectively. In contrast to the grain size obtained from the BET surface area (eq 2) for S1, which is in good agreement with the value obtained using the Scherrer formula and eq 1, the values for S2 and S3 are less than that determined using Scherrer formula and eq 1.

The room temperature photoluminescence (PL) spectra of the as-obtained CeO$_2$ nanoparticles (S1) and CeO$_2$ nanorods (S2) from the microwave route and ionothermally prepared flower-like CeO$_2$ (S3) were recorded (Figure 7, bottom) using a 295 nm filter with an excitation wavelength of 250 nm. Strong UV emissions at ~393 nm was observed in the nanoparticles (S1), nanorods (S2), and flower-like particles (S3), which comes from defects including oxygen vacancies in the crystal with electronic energy levels below the 4f band. These defects act as radiative recombination centers for electrons initially excited from the valence band to the 4f band of the oxide.\textsuperscript{48,49}

**CO Adsorption Studies.** The structural and electronic properties of all as-prepared CeO$_2$ samples using the ultrasound (S1-as-prepared), microwave (S2-calcined), and ionothermal routes (S3-calcined) were further probed by CO adsorption using vibrational spectroscopy. For comparison, the adsorption of CO on the commercial M-CeO$_2$ was first investigated. Figure S8 of the Supporting Information displays the UHV-FTIR spectra recorded after exposing the clean M-CeO$_2$ sample to CO at 90 K and subsequently heating to the indicated temperatures. After CO adsorption at 90 K, two C–O stretching bands are resolved at 2174 and 2160 cm$^{-1}$, which originate from CO molecules adsorbed at coordinatively unsaturated (CUS) surface Ce$^{4+}$ and Ce$^{3+}$ sites, respectively.\textsuperscript{50} The existence of two Ce cation species is further confirmed by the temperature-dependent IR data (Figure S8b, Supporting Information). Upon heating under vacuum, the CO band at 2160 cm$^{-1}$ shows a rapid decrease in intensity and vanishes completely around 130 K, while the intense IR band at 2174 cm$^{-1}$ diminishes gently and shifts slightly to higher frequency at 2179 cm$^{-1}$ before it disappears at 160 K.

The corresponding binding energies are estimated to amount to about 42 kJ/mol for CO on Ce$^{3+}$ and 34 kJ/mol for CO on Ce$^{4+}$, revealing that CO is more strongly bound to Ce$^{4+}$ sites. The enhanced interaction between CO and Ce$^{4+}$ can be explained by the higher Lewis acidity of Ce$^{4+}$ than Ce$^{3+}$ cations. As a consequence, one would expect the 5r donation from CO to Ce$^{4+}$ to be increased, thus causing enhancement of the CO binding energy and a blue shift of the C–O stretch band, as observed for CO adsorption on CO$_2$-pretreated ZnO surfaces.\textsuperscript{51,52}

As shown in Figure 8a, CO adsorption on the sonochemically prepared CeO$_2$ sample (S1) at 90 K leads to the appearance of one dominating IR band at 2165 cm$^{-1}$ with a shoulder centered at 2174 cm$^{-1}$. Upon heating to 120 K (Figure 8b), the 2165 cm$^{-1}$ band shrinks substantially, while the band at 2174 cm$^{-1}$ remains stable in intensity and shifts to 2185 cm$^{-1}$. Its complete desorption takes place at about 160 K. On the basis of the frequency and thermal stability data, the bands at 2165 and 2174 cm$^{-1}$ are assigned to CO molecules bound to surface Ce$^{3+}$ and Ce$^{4+}$ CUS sites, respectively. The shift of the Ce$^{4+}$-related CO band from 2174 to 2185 cm$^{-1}$ could be attributed to the slight modification of the electron density at the Ce cations induced by the decrease of CO coverage.

Figure 9 shows the IR data obtained after CO adsorption on the ionothermally prepared CeO$_2$ sample (S3) at 90 K and then heating to different temperatures. Only one C–O stretch band is observed at 2177 cm$^{-1}$, which shifts to 2185 cm$^{-1}$ at higher temperatures and disappears nearly completely at about 160 K. This band is characteristic for the CO species adsorbed on
surface Ce⁴⁺ CUS sites, in accordance with the results for the M-CeO₂ and S₁ samples. However, the IR spectra for the S₃ sample do not show any peaks originating from CO bound to Ce³⁺ sites.

In summary, the present IR spectra demonstrate the coexistence of Ce⁴⁺ and Ce³⁺ cations on the surface of the S₁ sample where Ce³⁺-related CO was detected as major species. For the S₃ sample, only the surface Ce⁴⁺ site was identified by CO adsorption experiments. However, the XPS data (Figure 5) confirm the presence of both Ce⁴⁺ and Ce³⁺ cations, with the former being predominant for all three as-prepared CeO₂ samples. This discrepancy between the IR and XPS results can be explained by the fact that the IR data of CO adsorption provide only information on Ce cation sites at the top surface layer. However, in XPS, chemical information from a depth of several nanometers is averaged. The IR data (Figure 8) reveal that for the sonochemically prepared CeO₂ sample (S₁) the surface concentration of Ce³⁺ is very significant and clearly higher than in the ionothermally prepared sample (S₃). The reduction of Ce⁴⁺ to Ce³⁺ is accompanied by the formation of surface oxygen vacancy sites, which have been considered to play a crucial role in the catalytic activity of oxides. Indeed, the catalysis experiments (see below) prove that the S₁ sample exhibits the highest activity for CO oxidation, whereas the catalytic activity of the ionothermally prepared CeO₂ sample (S₃) is much lower. This corresponds to the fact that no surface Ce³⁺ species were identified for the S₃ sample.

In addition, it should be noted that the electronic structure of the metal sites could be modified with different synthesis methods, thus resulting in a change in the Lewis acidity of surface Ce cations. One would expect that a lower Lewis acidity of a Ce cation decreases the binding strength of CO with this site. The lack of the Ce³⁺-related CO band for the S₃ sample (Figure 9) may also be related to a less stable Ce³⁺—CO binding that cannot be detected at 90 K.

The catalytic activities of CeO₂ obtained by different methods were evaluated in CO oxidation as shown in Figure 10, and significantly different activities were observed. The CO oxidation begins at a temperature of 175 °C in the case of sonochemically prepared CeO₂ (S₁), and the conversion rapidly increased to 100%. In the case of ionothermally (S₃)
chlore hydrate was used as a precursor, CeO₂ nanosheets were obtained. These results are in accordance with previous results reported by Elidrissi et al., 53 who observed the formation of CeO₂ nanosheets from an aqueous solution of cerium(III) chloride hydrate. In all cases, phase pure CeO₂ was obtained, but the morphology of the product varied from nanospheres to nanosheets. This shows that the cerium precursor plays a key role in determining the cerium morphology. The effect of different precursors on the morphology of the final product can be due to different reaction kinetics, namely, the hydrolysis rate, but also the ionic strength of the solvent can affect the nucleation process. Furthermore, after ionolysis, the counterions can act as ligands and can influence the morphology by preferential coordination to the growth facets. 54,11

Sonication Time and Drying Temperature. To check the influence of irradiation time on the particle morphology, a series of experiments were carried out with reaction times varying between 1 and 12 h. A total of 0.2 g of cerium(III) acetate monohydrate was used together with 0.1 g of sodium hydroxide in 2 mL of [C₄mim][Tf₂N]. The XRD patterns (Figure S9, Supporting Information) indicate that the crystallinity and particle size of the as-prepared CeO₂ are dependent on the irradiation time, where the as-obtained samples were characterized by XRD. As shown in Figure S9 (top) of the Supporting Information, the diffraction peaks of as-prepared CeO₂ at 9 h are much sharper than those of as-prepared CeO₂ at 1 h. It is found that the particle size of CeO₂ increases with increasing the irradiation time from 1 to 12 h, which is 4 nm at 9 h, but further increasing of the irradiation time beyond 9 h does not alter the particle size any more. Figure S11 of the Supporting Information shows XRD patterns of the sonochemically prepared CeO₂ after drying at different drying temperatures from 30 to 90 ºC. The patterns in Figure S11 of the Supporting Information show that the increase in the drying temperature causes no remarkable change in the crystallinity. These results verify that the sonication process yield nanocrystalline CeO₂ directly without going noticeably through an intermediate phase such as hydroxides, thus there is no need for sample calcination.

Effect of Precipitator. To evaluate the effect of the precipitator on the morphology, crystallinity, and particle size, NaOH (pKₐ = −0.8) was replaced with an aqueous solution of NH₄OH (pKₐ = 4.75) (equal molar ratio) under otherwise identical conditions. Although PXRD shows that the sample consists of fluorite-type ceria (Figure S12, Supporting Information), the crystallinity is noticeably less compared to the samples that are prepared with NaOH. As shown in Figure 12, the as-prepared sample is composed of nanosporphical CeO₂ with a particle size in the range 50−100 nm. Figure S13 of the Supporting Information shows the nitrogen−adsorption−desorption isotherm of CeO₂ prepared using NH₄OH as the precipitator. The BET surface area of CeO₂ obtained using NH₄OH (133 m² g⁻¹) is significantly less than that of CeO₂ prepared using NaOH (162 m² g⁻¹). These observations are in agreement with previous reports about the effect of the precipitator on the crystallinity and morphology of nanometal oxides. It was demonstrated that the precipitator has a remarkable influence on the morphology of ZnO nanocrystals, where substituting NaOH with NH₄OH led to formation of ZnO nanoparticles with an average size less than 10 nm instead of belt-like ZnO nanowires. 55,56 Mai found that the mesoporous CeO₂ prepared using NaOH by the precipitation method with cetyltrimethylammonium bromide as the templating agent at 400 ºC shows larger surface area (205 m² g⁻¹) than that of the mesoporous CeO₂ prepared using NH₄OH (166 m² g⁻¹) and that in the case of Na₂CO₃ no mesoporous structures could be detected. 56
Variation of the Ionic Liquid. There are studies that provide evidence that ILs can act as templates and influence the structure and surface properties of nanoparticles. The formation of small particles can be attributed to the higher nucleation rates of nanomaterials in ionic liquids. To check the influence of the structure of ionic liquids on the morphologies and the crystallization of sonochemically prepared CeO$_2$, four different ionic liquids, all with the same anion, were tested (Scheme 1). The bis(trifluorosulfonyl)amide anion is weakly coordinating, and previous studies have shown that the anions in fact have little direct impact on particle formation and growth compared to the cation.\textsuperscript{57,58}

On the basis of the nature of the IL, the interaction energies can be variable as well as the organization of IL.\textsuperscript{59} Furthermore, depending on the fact that the CeO$_2$ crystals are polarly composed of positively charged Ce layers and negatively charged O layers and the different cationic structures of the ionic liquid, different mechanisms including electrostatic attraction, hydrogen bonds, $\pi-\pi$ stacking interaction, and self-assembly mechanism can be expected to occur between ionic liquids and the unit growth of CeO$_2$, leading to control of the growth rate in a certain direction.\textsuperscript{60}

The cations were chosen for the following reasons. Imidazolium-based ionic liquids are among the most commonly used species because of their unusual physical and chemical properties. The $[\text{C}_4\text{mim}]^+$ cation contains an aromatic core, which can participate in $\pi$-interactions. It offers a highly electron accepting region and is likely to be responsible for the electrostatic attraction with polar moieties on the surface of particles.\textsuperscript{60} An acidic proton is attached to the aromatic ring structure, which could act as a bridging species through hydrogen bonding. It is believed that both electrostatic and coordination effects of imidazolium cations contribute to nanoparticle stabilization in the ionic liquid.\textsuperscript{61} The presence of the alkyl chain is thought to control the size distribution and agglomeration of the nanoparticles in dispersion.\textsuperscript{62} $[\text{Edimim}]^+$ also contains an imidazolium core like $[\text{C}_4\text{mim}]^+$, but it does not possess any acidic protons. $[\text{C}_4\text{Py}]^+$ is a pyridinium-based cation. It does not possess any acidic protons like the imidazolium-based cations, but the aromatic group is still present. The pyrrolidinium $[\text{Pyr}_{14}]^+$ cation is a quaternary ammonium, which does not possess either an acidic proton or aromatic ring system. $[\text{N}_{1112}\text{OH}]$ is a saturated quaternary ammonium cation with $-\text{OH}$ functionality in the side chain.

We found with this series that the structure of ionic liquids has an important influence on the morphology, crystallinity, and particle size of the products. Figure 13a shows the morphology of the product derived from using $[\text{Edimim}][\text{TF}_2\text{N}]$, which is composed of nanorods with 20 nm diameter and 100–150 nm length. When $[\text{Pyr}_{14}][\text{TF}_2\text{N}]$ is used, the as-prepared sample is composed of ribbon-like shaped particles (Figure 13b). Nanospherical CeO$_2$ with a crystal size of 10 nm formed when $[\text{C}_4\text{Py}][\text{TF}_2\text{N}]$ and $[\text{N}_{1112}\text{OH}][\text{TF}_2\text{N}]$ are used as shown in Figure 13c and d.

The PXRD data (Figure 14) confirm that in all ionic liquids phase pure CeO$_2$ could be directly obtained. No diffraction peaks of the starting material, cerium(III) acetate, or other cerium oxides and hydroxides can be evidenced. The crystal domain sizes ($d_{hk0}$) have been estimated from the most intense peaks of the starting material, cerium(III) acetate, or other cerium oxides and hydroxides can be evidenced. The crystal domain sizes ($d_{hk0}$) have been estimated from the most intense
The diffraction peak (111) using the Scherrer equation. The crystallite sizes vary from 3.2 to 5.7 nm (Table 2). The sample prepared in [Edimim][Tf2N] showed better crystallinity and a larger crystal particle size of 5.7 nm, and the sample prepared in [C4Py][Tf2N] showed the smallest crystallite size of 3.2 nm.

The nitrogen adsorption–desorption isotherms and corresponding pore size distributions of the synthesized samples are shown in Figure 15 and Figure S14 of the Supporting Information, respectively; the texture properties are listed in Table 2. The isotherms of the synthesized samples are of type IV with a hysteresis loop of the H2 type, characteristic of mesoporous materials, according to the IUPAC classification. The specific surface area values range from 78 m² g⁻¹ for the material prepared in [Edimim][Tf2N] to 163 m² g⁻¹ for the sample prepared in [Cdimim][Tf2N]. The pore size distribution for the as-prepared samples was determined by the BHJ method from the adsorption branch. One rather narrow peak with a maximum at 1.8 nm was observed on a broad background extending to 6 nm (Figure S14, Supporting Information). The porosity arising from the interparticle space of the CeO₂ samples can be attributed to the organized agglomeration of monodisperse CeO₂ particles obtained by ionolysis under ultrasound irradiation.

The hysteresis loops for the nitrogen adsorption–desorption experiments on the CeO₂ samples prepared in [Cdimim][Tf₂N], [C₄Py][Tf₂N], and [Pyr₁₄][Tf₂N] show a triangular shape and a steep desorption branch, which can be ascribed to the pore connectivity effect resulting from formation of pores with narrow mouths (ink-bottle pores).

Moreover, all samples show very high surface areas (Table 2), which are substantially larger than that reported for M-CeO₂ (3.1 m² g⁻¹) as well as those of previously reported for double-shelled CeO₂ synthesized by a solvothermal method using a solvent mix of PEG-400 (poly(ethylene glycol)) and H₂O (47 m² g⁻¹)⁶³ or mesoporous CeO₂ prepared via heating Ce(NO₃)₃ in 1-allyl-3-methylimidazolium chloride containing cellulose (62 m² g⁻¹).⁶⁴ However, the surface areas of the CeO₂ samples prepared in different types of ionic liquids are lower than those of spherical aggregates of CeO₂ particles prepared solvothermally using 1-hexadecyl-3-methylimidazolium bromide [C₁₆mim][Br] and ethanol (227 m² g⁻¹).⁶⁵

The CO conversions as a function of temperature by the as-prepared CeO₂ in different ionic liquids and of bulk ceria are shown in Figure 16. Obviously, the materials prepared in the different types of ionic liquids cannot compete with the one made in [Cdimim][Tf₂N] with respect to CO oxidation activity. While the former achieved full conversion already below 400 °C, the CeO₂ made in [Pyr₁₄][Tf₂N] achieved 70%, that prepared in [Edimim][Tf₂N] achieved 57%, CeO₂ obtained in [N₁₁₁₂OH][Tf₂N] achieved 16%, and that prepared in [C₄Py][Tf₂N] converted only 8%.

![Figure 14](image_url) XRD patterns of CeO₂ prepared in different ionic liquids (uncalcined); database pattern of ceria given for comparison.

![Figure 15](image_url) N₂ adsorption–desorption isotherms of the synthesized CeO₂ samples in different ionic liquids.

![Figure 16](image_url) Catalytic activity for CO oxidation of CeO₂ prepared in different ionic liquids in comparison with bulk ceria (M-CeO₂).
As mentioned above, the differences cannot be rationalized in terms of surface area, although the sample prepared in \([\text{C4mim}][\text{Tf2N}]\) with the highest surface area (162 m\(^2\) g\(^{-1}\)) exhibits the highest activity; CeO\(_2\) prepared in \([\text{N1112OH}]^{-}\) has a surface area of the same order (128 m\(^2\) g\(^{-1}\)) but is a much poorer catalyst. It is, however, well known that nanocrystalline metal oxide catalysts with high surface area exhibit a large number of active sites such as crystal facets, oxygen vacancies, edges, and corners for the adsorption of reactants that can result in better catalytic performance. Indeed, apart from the surface area the high catalytic activity of CeO\(_2\) can be explained by the oxygen vacancy formation and migration, where the oxygen vacancy formation provides freedom for the movement of lattice oxygen, thus increasing the mobility of oxygen on ceria and improving the catalytic performance. This is further supported by our UHV-FTIRS results (Figures 8 and 9) that provide direct spectroscopic evidence that the high catalytic activity of the CeO\(_2\) samples is related to the high concentration of surface oxygen vacancy sites (whereby the Ce\(^{3+}\) ions are formed).

**CONCLUSIONS**

In summary, various nanostructured CeO\(_2\) materials were successfully synthesized by one-step ultrasound synthesis with different kinds of ionic liquids directly without subsequent thermal treatment. This method is simple, one-step, and reproducible, and there is no need to use templates or surfactant because the ionic liquid acts as solvent and template. Control of the reaction conditions such as the heating method, chemical nature of the ionic liquid, Ce precursor, and nature of the precipitator allows preparation of CeO\(_2\) with different morphologies. The heating method exerts a crucial impact on the final structure and morphologies of ceria, where nanorods and flower-like shapes were obtained in \([\text{C4mim}][\text{Tf2N}]\) using microwave and ionothermal synthesis methods, whereas nanospheres were obtained using ultrasound. The dependence of the morphology of ceria on the structure of the ionic liquid was studied. Varying the cation of the ionic liquid resulted in a change in the morphology of ceria from nanospheres \(([\text{C}4\text{mim}])^+, [\text{C}4\text{Py}]^+, \text{and}[\text{N}1112\text{OH}]^+\), average crystal sizes of 5–10 nm) to nanorods with 20 nm diameter and 100–150 nm length \(([\text{Edimim}])^+\) and ribbon-like shapes \(([\text{Pyrr14}])^+\). Moreover, using different Ce sources (chloride or nitrate instead of acetate) resulted in the formation CeO\(_2\) nanosheets. The precipitator also exhibited an important influence on the morphology, crystallinity, and particle size of the products. The samples prepared using different ionic liquids showed different catalytic activities for CO oxidation. The highest catalytic activity was obtained for the material prepared from cerium acetate via the sonochemical route with NaOH in \([\text{C}4\text{mim}][\text{Tf2N}]\), which is related to the high concentration of surface oxygen vacancies created by the reduction of Ce\(^{4+}\) to Ce\(^{3+}\) as evidenced by the UHV-FTIRS data. This material exhibited full CO conversion under conditions where conventional CeO\(_2\) achieved no conversion at all. This shows how tremendously important the selection of reaction parameters is and that it is important to study unconventional yet green preparation methods for catalysts.

**REFERENCES**


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