Citric acid adsorption on cerium oxide nanoparticles in aqueous suspensions at acidic and circumneutral pH

Abstract

Citric acid is a naturally abundant organic acid, which can play an important role in determining the environmental fate of nanomaterials. This study focuses on citric acid adsorption onto cerium oxide nanoparticles with a particle diameter of ca. 4 nm and ca. 9 nm. Speciation of adsorbed citric acid on CeO$_2$ nanoparticles as a function of pH, has probed using ATR-FTIR measurements, whereas the zeta potential measurements and X-Ray photoelectron spectroscopy have been used as the supplementary experiments. The results show that the surface speciation of citric acid differs from that of bulk solution in all pHs studied. In addition, the fully deprotonated form of adsorbed citric acid is prominent in all pHs: 2.0, 4.0, 5.5 and 7.5, which is a distinct difference from the speciation of citric acid on other metal oxide nanoparticles reported up to date. ATR-FTIR spectroscopy showed some distinct adsorption bands present for citric acid adsorbed on ca. 4 nm particles compared to 9 nm particles. These bands can be attributed to the adsorption of citric acid onto specific adsorption sites which are widely available on very small nanoparticles. These trends in surface adsorption of citric acid on ceria are of interest in determining the environmental and biological fate of nanoceria, as it can have a direct impact on the distribution of both nanoceria and citric acid in various environments. Thus the studies describe here provide an insight in to the behavior of some smallest CeO$_2$ particles and their surface chemistry with citric acid.
Introduction

Cerium oxide (ceria, CeO$_2$) is an important rare-earth metal oxide with important applications. In its most stable phase, CeO$_2$ adopts a fluorite-type crystal structure, thereby having eight oxygen atoms surrounding each cerium metal cation in the lattice.$^{1,2}$ Nanoceria is being a main concern for a wide variety of applications due to its distinct properties derived from smaller size, large specific surface area and greater reactivity. Many of these interesting applications employ the low redox potential of the Ce$^{IV}$/Ce$^{III}$ couple, high oxygen storage ability and the UV absorbing capacity. Currently, CeO$_2$ is being used in solid oxide fuel cells as an electrolyte material, as supporting material in three-way catalysts, in optical coatings, in high storage capacitor devices, as components of semiconductors and superconductors.$^{1,3}$ Thus the production of cerium oxide nanomaterials has been increased during past few years.$^4$

The increased production of CeO$_2$ nanoparticles has raised the need of investigating the environmental fate for these important nanoparticles. The environmental and toxicological definitions of nanoceria are still remain controversial.$^{4,5}$ Several studies have been recently reported about their solubility and retention in soils,$^4$ aggregation,$^6$ dispersion,$^7$ protein adsorption$^8$ as well as their toxicological significance.$^{9,10}$ However, relatively few studies have probed the effect of surface properties of ceria on its environmental fate. Adsorption of organic acids such as formic, citric, oxalic, adipic, malonic and succinic, have been reported recently for metal oxide nanoparticles.$^{11-17}$ Because these adsorbed organic acids can alter the surface chemistry of the nanoparticles, organic acid adsorption studies on nanoparticles are of high interest to understand the environmental fate of them as well as their toxicological effects.
Citric acid is an important biologically and environmentally relevant ligand. It is a tricarboxylic acid with $pK_{a1} = 3.13$, $pK_{a2} = 4.76$, $pK_{a3} = 6.40$. In addition to its natural abundance, citrate is a common agent used in nanomaterial synthesis in controlling the size and morphology of nanoparticles.\textsuperscript{11} The use of citric acid in synthesizing CeO$_2$ nanoparticles is very common.\textsuperscript{27-31} Further, the role of citric acid as a coating material on CeO$_2$ for its biomedical applications has been reported recently.\textsuperscript{18,19} In addition, Cornelis \textit{et.al} reports the effect of citric acid on zeta potential and the hydrodynamic diameter of CeO$_2$ nanoparticles.\textsuperscript{4} However, the citric acid adsorption on ceria in aqueous phase has not been reported up to date.

The study described herein focuses on the surface adsorption of citric acid on cerium oxide at circumneutral and acidic pHs. In particular, the adsorption of citric acid has been studied here with emphasis on particle size effects using ATR-FTIR spectroscopy to probe surface speciation. The thermodynamic considerations predict higher organic acid adsorption on smaller particles.\textsuperscript{12} However, the variation of the mode of adsorption of organic acid on particle size will also be important and which is another main concern in this study.

**Experimental section**

**Characterization**

Powder X-ray diffraction (XRD) was used to determine the bulk crystalline phase of CeO$_2$ particles. Diffraction patterns were collected using a Rigaku Miniflex II diffractometer with a Co source. The specific surface area of the particles was determined from seven-point N$_2$-BET adsorption isotherm measurements using a Quantachrome 4200e surface area analyzer. Samples were degassed at 120 °C overnight (~16 h) prior to the analysis. In addition to the experimentally
measured BET specific surface areas, the geometric surface area of each particle size was estimated using CeO$_2$ density of 7.21 g/cm$^3$ and by assuming a spherical particle shape. Transmission electronic microscopic images of the samples were collected using JEM JEOL-1230 microscope, operated at 120 kV. The samples were suspended in methanol and one or two drops were dried on a copper grid with holey amorphous carbon film, at room temperature. The size of the ceria particles was then determined by analyzing TEM images in the software package Image J. Particles size distributions were determined from the analysis of approximately 400 and 550 particles form 4 nm and 9 nm samples respectively. A custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy system was used to investigate the surface oxidation states CeO$_2$ samples. High resolution spectra were acquired in the regions of interest using 20 to 40 eV energy window; pass energy of 20 eV; step size of 0.1 eV and dwell time of 1000 ms.

**ATR-FTIR Spectroscopy**

Surface adsorption and speciation of citric acid were studied at pH 2.0, 4.0, 5.5 and 7.5. Solutions at pH 2.0 and 4.0 consisted of 0.01 and 0.0001 N HCl solutions, while solutions at pH 6.0 and 7.5 consisted of 25 mM of MES and HEPES, respectively. A NaOH solution (8 M) was used to adjust pHs of higher pH solutions. As a result of the ionic strength of pH 2.0 solution, all the solutions were prepared to have an ionic strength of 0.03 M NaCl. The adsorption experiments were conducted as follow.

Solution phase attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy measurements were recorded of 100 mM citric acid solutions prepared at pH values: 2.0, 4.0, 5.5 and 7.5 using a Thermo-Nicolet FTIR spectrometer equipped with a MCT/A detector. After
that, citric acid adsorption on to CeO$_2$ surface was also probed with ATR-FTIR spectroscopy. For surface adsorption studies, a thin, evenly coated CeO$_2$ film was deposited on to an AMTIR crystal element in a horizontal ATR cell (Pike Technologies, Inc.). The film was prepared by placing a suspension of CeO$_2$ (~10 mg in 1 mL of optima water) on to the crystal and drying overnight. After recording the CeO$_2$ surface spectra, the 1.0 mM citric acid solution at selected pH (2.0, 4.0, 5.5 and 7.5) was placed on the thin film of CeO$_2$ and spectra were recorded for 1h in 10 min intervals, for the spectral range extending from 500 to 4000 cm$^{-1}$ using 150 scans at an instrument resolution of 4 cm$^{-1}$. The spectra obtained were referenced to the CeO$_2$ surface spectrum, the dry AMTIR crystal spectrum and the water spectrum to get the spectra of the adsorbed citric acid on CeO$_2$ thin film for each experiment.

**Supplementary experiments to adsorption studies**

The surface charge of the nanoparticles was measured using the zeta potential mode of the Malvern Zetasizer Nano ZS. All suspensions were prepared to have a solid loading of 1.0 g/L and 1 mM of citric acid, and a fixed ionic strength of 0.03 M. Measurements were made at pH 2.0, 4.0, 5.5 and 7.5. The experiments were also conducted in the absence of citric acid.

Further, the Ce, C and the O regions were analyzed in the high resolution XPS spectra of citric acid adsorbed CeO$_2$, obtained by a custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy system.
Reagents

All the experiments were conducted with CeO$_2$ nanoparticles purchased from STREM chemicals (4 nm) and from Meliorum (9 nm). Solution phase studies were conducted using solutions of 2-(n-morpholino)ethanesulfonic acid (MES; Sigma Aldrich; ≥ 99%), 4-(2-hydroxyethyl)-1-piparazeneethanesulfonic acid (HEPES; Sigma Aldrich, ≥ 99.5%), or hydrochloric acid (HCl; Fisher Scientific; certified ACS plus). To adjust the pH of the solutions, sodium hydroxide (NaOH; Fisher Scientific; certified ACS plus) was used. To keep the solution ionic speciation at minimum, sodium chloride (NaCl; Fisher Scientific; certified ACS plus) was used to adjust ionic strength. The aqueous solutions of citric acid (Sigma Aldrich, 99.5% certified ACS plus) and all reactors were prepared using Optima water (Fisher Scientific).

Results and Discussion

Nanoparticle characterization

A summary of physical characterization of the three CeO$_2$ samples are summarized in Table 1. The XRD results are in agreement with the those reported previously and confirms the fluorite crystal structure of CeO$_2$ nanoparticles (Figure 1a).$^{2,19}$ As expected, the XRD peaks were broadened with decreasing particle size, which can be explained by Scherrer equation. The XPS data suggests both Ce$^{3+}$ and Ce$^{4+}$ oxidation states for all three samples (Figure 1b). The higher amount of Ce$^{3+}$ present in smaller particles can be attributed to the higher oxygen vacancies in the smaller particles.$^2$ The calculated percentages of each oxidation state are also included in Table 1. Further, the TEM characterization confirmed the particle sizes (Figure 2) reported for three samples. The measured seven-point BET surface areas were 80±7 and 62±8 m$^2$/g for 4 nm and 9 nm samples respectively, where uncertainties represent the standard deviation of four
measurements. The estimated geometric surface areas were 197 and 96 m²/g for 4 nm and 9 nm particles respectively. Differences between geometric and N₂-BET surface area values can either be due to the particle aggregation which limits the available surface area or a result of the particle geometry that deviates from a sphere.

**Citric acid adsorption on CeO₂ nanoparticles at T = 298 K**

In solution phase, citric acid shows two prominent peaks at 1570 and 1391 cm⁻¹ in pH 7.5 (Figure 3a), which can be assigned to asymmetric and symmetric stretches of carboxylate group respectively. Further, the weak band around 1280 cm⁻¹ at this pH can be assigned to the coupled stretches and bends of carboxylate group. With decreasing pH, these two bands diminish in their intensity, while two new bands corresponds to C=O stretching motion and coupled C-(OH) and C-O-H bending motions appear at 1722 cm⁻¹ and 1226 cm⁻¹ respectively. These solution phase spectra confirm the fully protonated structure of citric acid at pH 2.0 and a fully deprotonated structure at pH 7.5 and partially protonated structures at pH 4.0 and 5.5, which is consistent with the pKₐ values as well as with previous results.

Spectroscopic measurements as a f(pH) gave useful comparison of the citrate-surface adsorbed complex for 4 nm and 9 nm nanoceria samples. The ATR-FTIR spectra of the 9 nm CeO₂ particles are shown in Figure 3b. The main feature of these spectra at all four pHs is that the peak at 1722 cm⁻¹ observed at low pH solution spectra, which is corresponding to C=O stretching, is absent in the surface adsorbed citric acid complex. This implies that at citric acid has adsorbed on to the CeO₂ surface by its all three carboxylate groups irrespective of the pH, yielding the fully deprotonated form of citric acid. Further, the two peaks corresponding to asymmetric and
symmetric stretches of carboxylate groups can be observed at 1565 and 1396 cm\(^{-1}\) respectively. The shoulder around 1432 cm\(^{-1}\) is attributed to the \(v_s\text{COO}^-\) of adsorbed carboxylate.\(^{11}\) In addition, a blue shift in both of these peaks could be observed over time, which was evident with the increase of pH. This suggests the strengthening of interaction between carboxylate groups and the oxide. The weak bands at 1300 and 1263 cm\(^{-1}\) are due to bending modes of the carboxylate groups.\(^{11}\)

The ATR-FTIR spectra of 4 nm particles seem to be even more interesting (Figure 3c). Having observed no peak at 1722 cm\(^{-1}\), it can be concluded that the fully deprotonated form of citric acid exists for this very smaller nanoparticles as well. And also, having three main regions corresponding to asymmetric, symmetric and bending modes of carboxylate group, the spectra are similar to those of 9 nm particles in a very broad sense. Indeed, the spectrum of the adsorbed citric acid complex on 4 nm ceria at pH 7.5 is similar to those of 9 nm ceria nanoparticles at all four pHs. However, the resolution of peaks around 1615 and 1370 cm\(^{-1}\) are distinct at pH 2.0, 4.0 and 5.5 for 4 nm particles. In the time course experiments, both these peaks appear in the spectra collected at 5 min and thereby intensifying over time. Thus they appear to correspond to a unique adsorbed species on these very small nanoparticles. In literature, this kind of shifts in FT-IR bands of the organic acids adsorbed on very small nanoparticles have attributed to the specific binding sites available on them.\(^{12}\) Hence, the blue shift of the \(v_{as}\text{COO}^-\) band to 1615 cm\(^{-1}\) can be attributed to a carboxylate group bound to a higher energy facial site in the fluorite structure, which is populated only under high adsorption thereby not observing under low adsorption at pH 7.5. On the other hand, the red shifted \(v_s\text{COO}^-\) peak at 1370 cm\(^{-1}\) can be due to carboxylate group bound to a lower energy corner site which will be abundant for these very small CeO\(_2\)
nanoparticles. Further, the appearance of the same type of splitting in the FT-IR peaks upon adsorption of acetic acid on 4 nm CeO$_2$ particles further proves the fact that they are due to adsorbed carboxylate groups. Moreover, increased adsorption with decreasing pH suggests that the deprotonation of citric acid can be a main driving force for the citric acid adsorption on to ceria surface. In addition, the large $\Delta \nu$ value [$\nu_{\text{as}}\text{COO}^- - \nu_{\text{s}}\text{COO}^-$] of 170 cm$^{-1}$ suggests a bridging carboxylate group on the cerium atoms of both 4 and 9 nm particles.$^{13-16}$

**Zeta potential measurements of CeO$_2$ nanoparticle suspensions as a $f$(pH) with and without the presence of citric acid.**

Zeta potential measurements support the speciation of citric acid on CeO$_2$ surface as concluded from the spectroscopic data. In general, zeta potentials measure the net charge at the diffuse boundary of a particle. Table 2 summarizes the differences in the zeta potential for ca. 4nm and ca. 9 nm CeO$_2$ particles in the presence and the absence of citric acid. The negative zeta potential values in the presence of citric acid prove the deprotonated form of citric acid adsorbed on CeO$_2$ surface.

**Conclusions and Implications**

Several interesting and important conclusions come from these studies of citric acid adsorption onto CeO$_2$ nanoparticles as a function of pH. First, the adsorption of citric acid on to both types of CeO$_2$ nanoparticles is independent of pH depending speciation of citric acid. Second, although citric acid solution speciation is highly pH dependent in the range investigated here (2.0-7.5), surface speciation has restricted only to the fully deprotonated form of it. Thus, surface adsorption increases the acidity of citric acid than what is expected based on its normal pK$_a$
values. This suggests the capability of CeO$_2$ to deprotonate the citric acid irrespective of its pH dependent speciation. Further the adsorption of citric acid on CeO$_2$ nanoparticles is irreversible at T=293 K suggesting a strong coordination onto the surface which is indicative of an inner sphere complex to the surface with all three carboxylic groups. These trends in surface adsorption of citric acid on ceria are of interest in determining the environmental and biological fate of nanoceria, as it can have a direct impact on the distribution of both nanoceria and citric acid in those environments. Thus the studies describe here provide an insight in to the behavior of some smallest CeO$_2$ particles and their surface chemistry with citric acid.
Figures and Tables

Figure 1. (a) Powder XRD patterns (b) XPS spectra of 4 nm and 9 nm CeO$_2$

Figure 2. TEM images of (a) 4 nm (b) 9 nm CeO$_2$
Table 1. Summary of CeO$_2$ nanoparticle properties: size, surface area and oxidation state

<table>
<thead>
<tr>
<th></th>
<th>4 nm</th>
<th>9 nm</th>
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</thead>
<tbody>
<tr>
<td>Particle size (nm)</td>
<td>4.3±1.5</td>
<td>8.7±3.7</td>
</tr>
<tr>
<td>7-point BET surface area (m$^2$/g)</td>
<td>80±7</td>
<td>62±8</td>
</tr>
<tr>
<td>Calculated surface area (m$^2$/g)</td>
<td>197</td>
<td>96</td>
</tr>
<tr>
<td>Ce$^{3+}$ %</td>
<td>15.5</td>
<td>13.4</td>
</tr>
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</table>

Table 2. Zeta potential measurements of CeO$_2$ in the absence and the presence of citric acid

<table>
<thead>
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<th>pH</th>
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<th>9nm</th>
</tr>
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<tbody>
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<td></td>
<td>In the absence of citric acid (mV)</td>
<td>In the presence of citric acid (mV)</td>
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<tr>
<td>-----</td>
<td>--------------------------</td>
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</tr>
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<td>2.0</td>
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<td>5.5</td>
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<td>7.5</td>
<td>-17.19</td>
<td>-41.23</td>
</tr>
</tbody>
</table>

Figure 3. ATR-FTIR spectra of (a) solution phase citric acid and adsorbed citric acid on (b) 4 nm (c) 9 nm CeO$_2$ particles at different pH: 2.0, 4.0, 5.5 and 7.5
Reference

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