Fast Synthesis of CeO$_2$ Nanoparticles in a Continuous Microreactor Using Deep Eutectic Reline As Solvent

Antonio Jose Exposito, Patrick J. Barrie, and Laura Torrente-Murciano

**ABSTRACT:** Hydrothermal methods have conventionally enabled the synthesis of a wide range of nanomaterials. However, these simple, single-step syntheses lack scalability due to the need of high temperatures and autogenous pressures to enable the dissolution of reagents and crystallization of the product. In this work, we demonstrate for the first time fast continuous synthesis of ceria nanoparticles at moderate conditions through the combination of the deep eutectic solvent reline (an eutectic mixture of choline chloride and urea) as reaction medium and the high heat and mass transfer rate offered by microreactors. Almost 100% yields are obtained within 100 s of residence time at 160 °C, with some conversion achieved even at temperatures as low as 120 °C. Such rapid synthesis takes place thanks to the molecular structure of the solvent which facilitates the fast nucleation of cerium oxycarbonate as an intermediate product. As expected in a kinetically controlled system, pressure and initial cerium concentration have negligible effects on the yield obtained. The rapid reaction, the cheap, benign, and environmentally friendly solvent, and the lack of additional additives in this work open the door to sustainable large-scale continuous synthesis of ceria nanoparticles as well as other nanostructured materials.

**KEYWORDS:** Ceria, nanoparticles, microreactors, deep eutectic solvents, reline

**INTRODUCTION**

Ceria (CeO$_2$) has a wide variety of applications, in particular as a catalyst and catalyst support material because of its capacity to store and exchange oxygen under different conditions.$^{1,2}$ The performance of CeO$_2$ critically depends on its nanostructure.$^{3-7}$ First, the different crystal planes present on nanostructures such as nanorods, nanoplates, and nanocubes have intrinsically different chemical reactivities.$^{7-10}$ Second, the nanostructure affects the number and nature of oxygen vacancy sites associated with defects.$^{11-13}$ There is therefore significant interest in the preparation of nanostructured CeO$_2$ in a controlled and sustainable way.

There are a variety of methods for synthesizing nanoparticles.$^{14,15}$ The most common method to prepare nanostructured metal oxides such as CeO$_2$ is by hydrothermal synthesis (if the solvent is water) or solvothermal synthesis (if the solvent is not water).$^{15-17}$ In these methods, the syntheses take place above the boiling point of the solvent so there is a high autogenous pressure within the reaction vessel which leads to dissolution of reagents and crystallization of products. Under appropriate conditions of temperature, pressure, and pH, nucleation is normally rapid while crystal growth is slow, and it is possible to obtain nanoparticles with a fairly narrow size distribution.$^{17,18}$ Templating agents such as ethylene glycol or polyvinylpyrrolidone (PVP) are often added to provide morphological control.$^{19}$ However, a main disadvantage of the hydro/solvothermal methods is that the reaction time is generally long: a recent review found that reaction times for the synthesis of CeO$_2$ were typically 12 h or longer when temperatures below 200 °C are used.$^{19}$

As well as long reaction times when CeO$_2$ hydrothermal synthesis is performed in batch vessels, it can be hard to control the temperature and concentration, particularly if on a large scale. In this context, microreactors offer an opportunity for the large-scale synthesis of nanostructured materials due to the high rate of heat and mass transport enabled by the small diameter of the reactor channels. To date, previous reports of continuous hydrothermal synthesis of CeO$_2$ nanoparticles in microreactors have either used NaOH, with or without additional structure-directing agents,$^{20,21}$ or have used supercritical conditions.$^{22-24}$ Such continuous synthesis methods tend to have shorter reaction times compared to batch vessels.
but present environmental issues such as the use of corrosive NaOH and/or require significant energy input.

There has been recent interest in using deep eutectic solvents as the medium for synthesis of materials including nanoparticles. These have melting points far lower than the individual components from which they are made and so have the advantage of low vapor pressures even at high temperature. Our group has recently reported the use of the deep eutectic solvent reline for the solvothermal synthesis of nanostructured ceria in a batch system in the absence of solubilizing base or a structure directing agent. Instead, the supramolecular structure of the solvent acted as a template found from neutron scattering experiments that the molecular viscosity more than 1000 times that of water at 20 °C. However, the physical properties of reline such as viscosity can be modified by addition of water. Interestingly, it has been found from neutron scattering experiments that the molecular structure of reline is largely retained even after addition of significant amounts of water (up to 50 wt %).

In this work, we present for the first time the continuous synthesis of CeO2 nanoparticles in a continuous microreactor using reline-water as a benign solvent. It is shown that the reaction is rapid even at relatively mild conditions, with reaction on the time scale of minutes (rather than hours) at moderate temperatures such as 140 °C. Because of the chemical interactions within the solvent, there is no need for additional chemicals such as NaOH, ethylene glycol, or other structure directing agents. Further there is no need for the high pressures required for continuous synthesis in conventional solvents. This opens the door to sustainable large-scale continuous synthesis of CeO2 nanoparticles.

### EXPERIMENTAL METHODS

The deep eutectic solvent reline was prepared with a 1:2 molar ratio of choline chloride:urea. It was stirred at 250 rpm for 4 h at 80 °C. After 4 h, a viscous transparent liquid was obtained. For most experiments, water was then added so that the molar ratio of water:choline chloride was 10:1. At 293 K, this amount of water reduces the viscosity from 1370 mPa s to 3.4 mPa s. Interestingly, it has been found from neutron scattering experiments that the molecular structure of reline is largely retained even after addition of significant amounts of water (up to 50 wt %).

In this work, we present for the first time the continuous synthesis of CeO2 nanoparticles in a continuous microreactor using reline-water as a benign solvent. It is shown that the reaction is rapid even at relatively mild conditions, with reaction on the time scale of minutes (rather than hours) at moderate temperatures such as 140 °C. Because of the chemical interactions within the solvent, there is no need for additional chemicals such as NaOH, ethylene glycol, or other structure directing agents. Further there is no need for the high pressures required for continuous synthesis in conventional solvents. This opens the door to sustainable large-scale continuous synthesis of CeO2 nanoparticles.

**Figure 1.** Experimental setup of the pressurized continuous microreactor.
Effect on the residence time. The yields of the ceria product obtained at different temperatures and pressures are reported in Table 1. The yield does not depend on pressure at a given temperature, nor on the initial concentration of cerium precursor as similar yields of 48%, 40%, and 45% are obtained when using initial concentrations of cerium nitrate of 14.4, 28.8, and 43.2 mM, respectively. The results demonstrate that CeO$_2$ nanoparticles form very quickly under the conditions employed, with full conversion achieved on a time scale of minutes (96 s) at a moderate temperature of 160 °C. This is far faster than other preparation methods of CeO$_2$ nanoparticles at this temperature due to the rapid mass and heat transfer enabled by the microfluidic system.

The effect of the mean residence time on the yield was studied by varying the flow rate at the given temperature of 140 °C (Figure 4a). Similarly, the effect of reaction temperature on the yield at a residence time of 96 s is shown in Figure 4b.

Conventional hydrothermal synthesis of ceria nanoparticles is believed to start with formation of cerium hydroxides, followed by conversion to CeO$_2$ at high temperature and pressures, with shape changes due to some combination of Ostwald ripening and oriented attachment mechanisms. There is some recent evidence that the presence of urea influences the reaction, for instance by accelerating the oriented attachment mechanism. There is also evidence that hydrothermal synthesis in the presence of urea can form carbonate species such as Ce(OH)CO$_3$ and Ce$_2$O(CO$_3$)$_3$ as primary products, which then form CeO$_2$ on calcination. Figure 5 shows the carbonate bands for asymmetric stretch vibration at 1400–1600 cm$^{-1}$ and the peak for carbonate bond out-of-plane bend vibration at 843 cm$^{-1}$ in the sample obtained before calcination demonstrating the formation of these intermediate carbonate species. After calcination, the peaks associated with carbonate bands disappear while the broad peak at low wavelengths confirm the Ce–O bond in both samples. There is no evidence of N–H or C–H vibrations which might have arisen from residual urea or choline species on the surface of the nanoparticles. The carbonate species must form from cerium ions reacting with the products of urea hydrolysis at elevated temperature.

Table 1. Effect of Pressure and Temperature on the Yield of Ceria Synthesized in Reline/Water Mixtures

| temperature (°C) | residence time (s) | pressure | 2.8 bar | 5.2 bar | 6.7 bar | 8.0 bar |
|-----------------|-------------------|----------|---------|---------|---------|---------|
| 100             | 96                | 0        | 0       | 0       | 0       | 0       |
| 120             | 96                | 3%       | 3%      | 4%      | 7%      |         |
| 140             | 96                | 45%      | 39%     | 45%     |         |         |
| 160             | 96                | 94%      | 99%     |         |         |         |

*aConditions: 1:10 molar mixture of reline:water. Initial concentration of cerium nitrate: 43.2 mM.*

Figure 3. Powder XRD pattern of nanoparticles synthesized in a microreactor with a space time of 96 s at 140 °C using a 1:10 molar mixture of reline:water. The initial concentration of cerium nitrate was 43.2 mM. The pressure was 5.2 bar, and the calcination temperature was 500 °C.

Figure 4. Effect of (a) mean residence time at 140 °C and (b) synthesis temperature at a residence time of 96 s on the yield of ceria nanoparticles synthesized in a microreactor using a 1:10 molar mixture of reline:water. Initial concentration of ceria nitrate: 43.2 mM. The dashed lines are those predicted for an isothermal plug flow reactor assuming pseudo-first-order kinetics.

Figure 5. FTIR analysis of the powder obtained in a microreactor with a space time of 96 s at 140 °C using a 1:10 molar mixture of reline:water before and after calcination. The initial concentration of cerium nitrate was 43.2 mM. The pressure was 5.2 bar, and the calcination temperature was 500 °C.
the absence of cerium ions, the main urea hydrolysis reactions are
\[ \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_2\text{COO}^- + \text{NH}_3^+ \quad (1) \]
\[ \text{NH}_2\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{NH}_3 \quad (2) \]
\[ \text{NH}_3^+ + \text{OH}^- \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O} \quad (3) \]
\[ \text{HCO}_3^- \rightleftharpoons \text{OH}^- + \text{CO}_2 \quad (4) \]
The sum of these reactions shows that the eventual products will be CO₂ and NH₃. Urea hydrolysis is known to occur at 100 °C but is slow. At 140 °C, a first-order rate constant of 0.008 min⁻¹ has been reported based on formation of product gases, so the time constant for the hydrolysis reaction is about 2 h at this temperature; our results suggest that the first step in the reaction mechanism takes place faster than this. The extent of hydrolysis is limited by the position of thermodynamic equilibrium. The eventual composition depends on pH; for instance, carbonate ions will form in highly alkaline conditions. When cerium ions are present, one reaction that has been proposed is eq 5:28
\[ [(\text{Ce})^{3+} (\text{L})^n (\text{H}_2\text{O})_x]^y + 3\text{CO}_3^{2-} \]
\[ \rightarrow \text{Ce}_2\text{O} (\text{CO}_3)_2 \cdot \text{H}_2\text{O} + \text{CO}_2 + (\text{L})_x + (y - 1)\text{H}_2\text{O} \quad (5) \]
where L denotes a ligand (such as chloride ions). Reaction schemes can also be written in which carbamate ions or hydrogen carbonate ions are the reacting species.

The synthesis of particulate ceria in reline-water in a batch process is believed to involve Ce(OH)CO₃ formation as the primary product.28 Urea molecules in reline have been found to bind to cerium ions present. This means that any hydrolysis of urea will give reactive carbonate species in close proximity to cerium ions, so the supramolecular structure of the solvent facilitates nucleation of cerium-containing particles.28

Our results demonstrate that ceria particles are formed in continuous microreactors in less than 2 min at 120 °C when using reline/water as a solvent. This implies that nucleation is rapid, and this presumably takes place by the carbonate route mechanism as in the batch process.28 The reaction is faster than the batch process because of the rapid heat and mass transfer in microfluidic reactors. No significant change in morphology is observed after calcination (Figure S1). Subsequent particle morphology changes to form nanorods take place far slower (on a time scale of hours) by dissolution and recrystallization or by the oriented attachment mechanism as shown by SEM images of the ceria product prepared at a range of flow rates, including those at which the residence times were very long (time scale of hours). Figure 6 shows the evolution in particle morphology with residence time in the reactor. After 96 s, when the yield is 45%, more than one morphology is present. After 1 h, clusters of nanoparticles are present. There is then a gradual evolution to give bundles of nanorods.

The synthesis at 140 °C with a residence time of 96 s was also attempted at different water concentrations. No product was obtained with pure water or with a 1:2:2 molar ratio of choline chloride:urea:water. Ceria product was obtained with a 1:2:4 molar ratio of choline chloride:urea:water but with a yield about half that for the solvent with a molar composition 1:2:10 reported in Table 1. Such difference could potentially be a result of viscosity being reduced when more water is present. However, a similar yield was found when nitrogen bubbles were introduced into the reactant flow through the reactor. Taylor flow promotes recirculation patterns across the longitudinal axis of the liquid slug and so is expected to enhance mixing under laminar flow. The fact that Taylor flow did not affect yield suggests that the kinetics are unaffected by mass transport limitations.

The kinetics of crystallization in flow reactors are hard to model because nucleation, growth, and redissolution mean that the population balance is complicated, even when mass transport limitations are negligible. While the kinetic contributions of each individual step in the crystallization mechanism is outside the scope of this study, our results offer some insight into the overall kinetic behavior assuming that the formation of the ceria product obeys overall pseudo-first-order kinetics. This assumption is supported by the fact that the experimental yield does not depend on the original concentration of the cerium precursor as mentioned above.

Pseudo-first-order kinetic calculations are straightforward if the reactor is treated as isothermal. Microfluidic reactors are hard to model because nucleation, growth, and redissolution mean that the population balance is complicated, even when mass transport limitations are negligible. While the kinetic contributions of each individual step in the crystallization mechanism is outside the scope of this study, our results offer some insight into the overall kinetic behavior assuming that the formation of the ceria product obeys overall pseudo-first-order kinetics. This assumption is supported by the fact that the experimental yield does not depend on the original concentration of the cerium precursor as mentioned above.

Pseudo-first-order kinetic calculations are straightforward if the reactor is treated as isothermal. Microfluidic reactors are known to have fast heat transfer so this may be a reasonable approximation. However, the reactor is not truly isothermal because the feed stream is at room temperature (about 20 °C), far lower than the temperature of the oil bath used to control the temperature of the reactor. The temperature of the reagents will vary along the reactor, at least in the early stages. This will principally affect the rate constant but will also alter the physical properties such as density slightly. The time constant for reagents to reach the temperature of the oil bath is estimated to be 2 s for the reactor used (see the Supporting Information); this is a short time compared to the residence times used, so an isothermal treatment is reasonable.

If the reactor is treated as an isothermal plug flow reactor, then the fractional conversion X will be given by eq 6:
\[ X = 1 - \exp(-kt) \quad (6) \]
where k is an overall rate constant and t is the residence time. The Arrhenius equation with an overall activation energy E can be used to describe the temperature dependence of k. A simultaneous fit of the data in Table 1 using nonlinear regression was performed; the results are shown in Figure 4. This gave an overall activation energy of 158 kJ/mol, though with a high standard error (69 kJ/mol). The uncertainty is
large because there are few data points at different temperatures.

More sophisticated kinetic models were also implemented. The flow in the microreactor is laminar; the highest Reynolds number for the experiments was 370. If the reactor is treated as an isothermal laminar flow reactor, then the fractional conversion will be given by eq 7:

\[
X = 1 - \int_{\tau/2}^{\infty} \exp(-kt) \frac{t^2}{2t^2} \, dt
\]

(7)

Nonisothermal models were also considered. For instance a plug flow reactor with a temperature profile will have fractional conversion (assuming density is roughly constant) given by eq 8

\[
X = 1 - \exp \left[ \frac{A}{Q} \int_0^L k \, dl \right]
\]

(8)

where \( A \) is the area of the tube, \( L \) is the length of the tube, \( Q \) is the volumetric flow rate, and \( k \) now depends on distance along the reactor as temperature is not constant.

Nonlinear regression using the more sophisticated models did not change the conclusion that the overall activation energy is about 150 kJ/mol (with a standard error of about 50 kJ/mol). While the uncertainty is large, it is apparent that the overall activation energy is high and reflective of a chemical reaction rather than, say, a viscosity change. This confirms that mass transport limitations are negligible in the microreactor, which is one of the reasons for the rapid formation of ceria nanoparticles by this method.

**CONCLUSIONS**

The continuous synthesis of ceria nanoparticles is demonstrated using reline-water as a reaction medium in microreactors. This low cost, readily biodegradable, and low toxicity solvent provides a supramolecular interaction with the cerium reactor as temperature is not constant.

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**ACKNOWLEDGMENTS**

The authors greatly acknowledge the financial support from UK Engineering and Physical Science and Research Council (grant EP/S021019/1).

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