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Short communication

Simple one-step preparation of cerium trifluoride nanoparticles

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ABSTRACT

Cerium trifluoride have great potential in material applications for luminescent materials, composite materials or ionic conductors especially in the form of nanoparticles and nanoobjects. In this work, nanoparticles of CeF_3 were prepared by simple one pot reaction of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) with CeO_2 and by reaction of CeO_2 with KPF_6 in ionic liquid 1-butyl-3-methylimidazolium chloride (bmimCl). Prepared nanoparticles were analyzed by XRD and SEM analysis. Average diameter of prepared nanoparticles resulting from Sherrer formula is 12 nm. Nanoparticles did not form ordered agglomerates and could be used in the form of separate nanoparticles which are desired in some applications.

1. Introduction

Cerium is the most abundant of the lanthanides. Two common oxidation states Ce^{3+} and Ce^{4+} exhibit great differences: Ce^{4+} is stable under alkaline conditions and strong oxidant under acidic conditions, Ce^{3+} is strong base, strong reductant and could be easily oxidized by atmospheric oxygen under alkaline conditions. Importance of optically active Ce^{3+} ions is increasing due to possibility of creating luminescent materials in UV and VUV regions [1–4]. CeF_3 could be used as ionic conductor [5], nanocomposite scintillators for gamma-ray detection [6], as additives to lubricating oils [7] and for drug release [8]. CeF_3 has been previously prepared by several methods including reaction of CeO_2 with fluorine gas at elevated temperature [9], using high-intensity ultrasound [10], rapid microwave method [11] and many other reactions and processes have been described in literature [12–19].

Ionic liquids are low melting salts composed of organic cations and mostly inorganic anions. Their low melting temperatures (near to room temperature) are due to the delocalization of a charge on voluminous ions. The first ionic liquid was prepared one hundred years ago [20], however ionic liquids have experienced boom in last two decades. It has been found that such liquids can be useful solvents for organic reactions. Their advantages in comparison to common organic solvents are thermal stability, negligible vapor pressure, non-flammability, liquid-state at wide range of temperature, easy purification by crystallization, tunable solubility for both organic and inorganic molecules, and large synthetic flexibility. Use of ionic liquids in solvent extraction, organic synthesis and catalysis has been extensively studied, but their use in inorganic synthesis has just begun. They can act as templates and precursors to inorganic materials, as well as solvents [21,22].

1-Butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) (Fig. 1) is one of the most widely studied commercially available ionic liquids. $BmimPF_6$ is a colorless, viscous, hygroscopic, and hydrophobic liquid exhibiting low aqueous solubility caused mainly by hydrophobicity of hexafluorophosphate anion [23]. Ionic liquids are commonly described as environmentally friendly "green solvents" due to their negligible vapor pressure but they can suffer from environmentally unfriendly degradations. Especially, hexafluorophosphate anion is known to very slowly decompose in the presence of water forming hydrofluoric acid [24,25].

Ionic liquids containing anions like tetrafluoroborate or hexafluorophosphate could be used both as thermally stable solvent and source of fluoride ions. 1-Butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) have been previously used for preparation of rare-earths fluorides including CeF_3 by reaction with rare-earths nitrides [26,27]. In this work is shown different, simpler and cheaper method of preparing CeF_3 nanoparticles by reaction of CeO_2 nanoparticles with 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) for significantly shorter time than for example in [26]. It has been found that size of CeF_3 nanoparticles is independent on the particle size of CeO_2.

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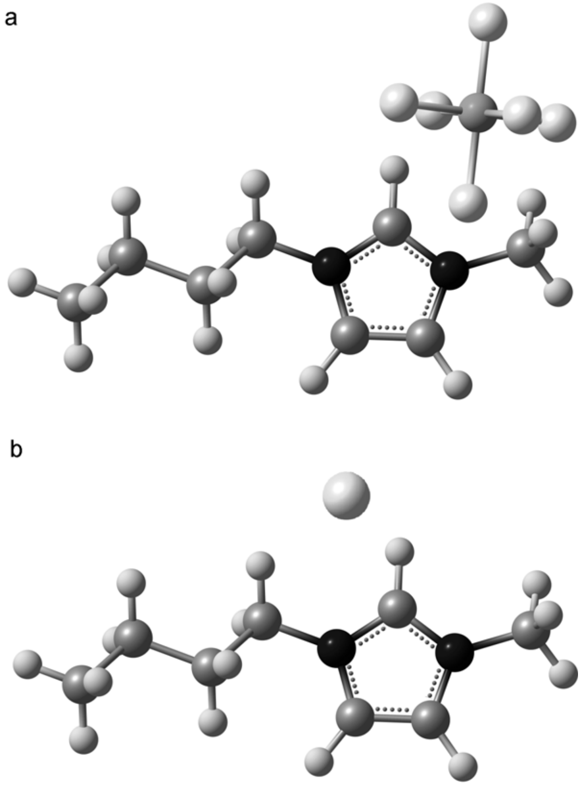

Fig. 1. Ionic liquids: (a) 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) and (b) 1-butyl-3-methylimidazolium chloride (bmimCl).

2. Results and discussion

Cerium trifluoride has been obtained by a reaction of CeO_2 of various sizes with ionic liquid $bmimPF_6$ or KPF_6 in bmimCl as pale yellow powder (described in the Section 3). Direct preparations of CeF_3 nanoparticles from $Ce(NO_3)_3$ have been described elsewhere [26,27] however both ways ($Ce(NO_3)_3$ vs. CeO_2) differ in sizes of nanoparticles, formation of agglomerates and also mechanism (red-ox). Preparation of CeO_2 nanoparticles of various sizes (necessary for size-dependence study) form $Ce(NO_3)_3$ is shortly described in Section 3. All samples were analyzed by XRD to identify sample composition and sizes of nanoparticles. All peaks on XRD pattern of reaction products were identified as belonging to CeF_3 and no other phase was found. Peak broadening clearly indicates that CeF_3 is in form of nanoparticles (Fig. 2). Using Scherrer formula, average diameter of nanoparticles was calculated as 12 nm (for calculation details see Section 3). XRD patterns of samples prepared from CeO_2 with average diameters about 2 nm, 5 nm and 8 nm and even estimated few micrometers were practically the same. FT-IR spectra of CeF_3 nanoparticles in KBr pellets (spectra shown in online Supplementary content) correspond with those known from literature [19]. Signal originating from CeF_3 nanoparticles is broad band at the edge of spectra with maxima out of spectra (below 400 cm^{-1}). In spectra are significant peaks of crystalline water (sharper peaks than those form liquid state due to limited hydrogen bonding) at 1630 and 3425 cm^{-1}, that partially originate from crystalline water of nanoparticles ($CeF_3{\cdot}nH_2O$, $n \sim 0.5$) and partially from KBr. There are also signals of impurities from KBr (the same peaks have been observed in pure KBr pellets) and signals around 2400 cm^{-1} originating from carbon dioxide (air). Observation does not contradict expectation; however for substance identification is XRD more adequate technique and FT-IR gives only supporting data.

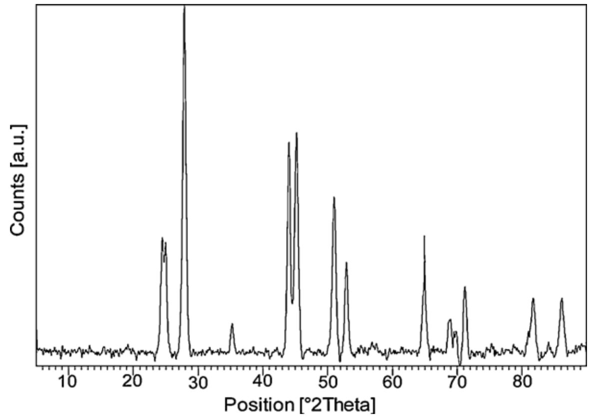

Fig. 2. XRD pattern of nanoparticles CeF_3 created by reaction of $bmimPF_6$ with CeO_2. All peaks belong to CeF_3.

From behavior of this reaction the mechanism of reaction could be expected. Independence of CeF_3 nanoparticles sizes indicates that CeO_2 is dissolved in ionic liquid and CeO_2 crystals do not act as nucleation centers. CeF_3 is formed by reaction of CeO_2 with HF from hydrated hexafluorophosphate anion and forms nanoparticles of average size about 12 nm.

During preliminary experiments performed in glass vessels corrosion of glass occurred and product of corrosion was seen in XRD patterns. From this resulting, HF probably unbends from $bmimPF_6$ and subsequently reacts with CeO_2 in the solution. Corrosive effect of HF was removed by placing reaction into Teflon tubes into silica gel.

Reaction of CeO_2 with bmimCl and KPF_6 yielded the same results as CeO_2 with $bmimPF_6$, thus presence of chloride anion and potassium cation do not influence the reaction. $BmimPF_6$ could be easily prepared from bmimCl and KPF_6 by ionic exchange (partitioning between water and dichloromethane) but the observation indicates that this step could be skipped.

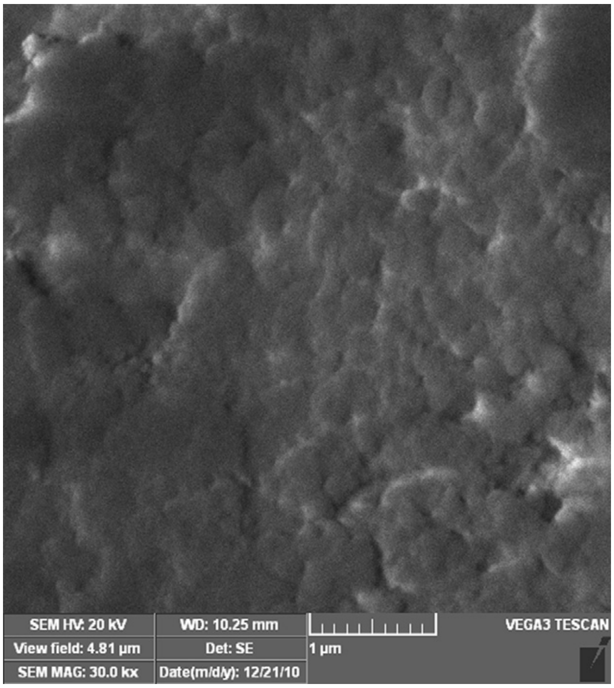

Fig. 3. SEM image of surface of CeF_3. No oriented structures visible.

In the case of reaction with bmimCl and KPF_6 the reaction conditions are the same as in reaction $bmimPF_6$ with only two differences. The bmimCl is solid at ambient temperature and must be melted firstly and final product has to be washed by distilled water to remove residual KPF_6.

Presence of possible aggregate structures of CeF_3 nanoparticles in final product was examined by SEM. On SEM picture (Fig. 3) any structure formed by aggregated nanoparticles has not been found. SEM does not show any evidence of nanoparticles due to their small sizes; however presence of nanoparticles is proved by XRD. SEM image is shown as evidence that in contrast with other works [26] there are not any ordered agglomerates. Therefore it could be expected monotonic distribution of tiny nanoparticles, separable and usable as needed. It should be noted that only part of ionic liquids were spend in reaction and other part served as solvent and could be regenerated for another use. It was also found that products of hydrolysis of PF_6^- anion (HF, POF_3, etc. [26]) are well soluble in water and thus they could be easily replaced by new PF_6^- anions from KPF_6 by partitioning between water and dichloromethane. This leads to possibility to regenerate ionic liquid and thus significantly decrease reaction costs.

3. Experimental

Ionic liquids 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) and KPF_6 were purchased from Sigma–Aldrich Co. CeO_2 was prepared by reaction of $Ce(NO_3)_3$ with aqueous ammonia. Prepared nanoparticles were treated in various solvents for given times and temperatures and so various sizes of CeO_2 were created [28]. Also greater crystals of CeO_2, prepared by calcination of $Ce(NO_3)_3$ on air at 850 °C were used.

Experiments were performed in the sealed-off Teflon tubes, 4 mm internal diameter and about 5 cm long. Tubes were penetrated and placed to the silica gel. In the first set of experiments, 0.10 g of CeO_2 was weighed and volume of ionic liquid ($bmimPF_6$) was 10 ml. Therefore ionic liquid was significantly redundant. In the second set of experiments amount of CeO_2 and bmimCl ionic liquid was used instead of $bmimPF_6$. In addition, KPF_6 was added as a source of fluorine. Amount of KPF_6 was also redundant to CeO_2. All samples were placed to the furnace and treated at 200 °C for 90 min. Subsequently, samples were cooled, taken of Teflon tubes and washed with methanol and distilled water. After multiple washing, powder was dried on air and analyzed by XRD and SEM.

X-ray powder diffraction data were collected at room temperature with X'Pert PRO θ-θ powder diffractometer with parafocusing Bragg–Brentano geometry using Cu K_α radiation (λ = 1.5418 Å, U = 40 kV, I = 30 mA). Samples were characterized by XRD measurements and nanoparticles sizes were identified from the width in half high of peak 27.95° 2θ. This peak was used due to its single position in XRD pattern of CeF_3 and due to its high intensity. X́Pert HighScore Plus program was used for processing data from XRD and calculating of nanoparticles sizes were made using Scherrer formula. SEM pictures were made using electron microscope Tescan Vega 3 with EDS analyzer Oxford Instruments INCA 350.

The conventional potassium bromide (KBr) disk method was employed to measure the infrared spectra. The infrared spectra of samples were recorded by FT-IR spectrometer Avatar 320 (Nicolet, USA) in spectral range from 4000 cm^{-1} to 400 cm^{-1} at room temperature. For all samples 128 scans were collected at a resolution of 1 cm^{-1} and analyzed using OMNIC software. The amounts of samples were approximately 1 mg in 200 mg of KBr. A sample homogenization process was performed in a mortar and then the mixture was pressed to the pellet form. All spectra have been baseline corrected (automatic baseline correction as implemented in OMNIC software).

Size of nanoparticles have been calculated from Scherrer equation $\tau = K\lambda/(\beta\cos\theta)$, where $K = 0.9$, $\lambda = 0.15418$ nm, β = 0.0122 rad, $\theta = 13.9^\circ$ (values for XRD diffractogram shown in Fig. 2). Calculated size of nanoparticles is 11.72 nm. This value is in agreement with value obtained from Scherrer Calculator which is part of X'Pert HighScore software. Scherrer formula has its limits but works well for fine nanoparticles. XRD reflections have not been indexed because all of them belong to CeF_3.

4. Conclusion

Small separable nanoparticles with average diameter 12 nm were prepared by one pot simple reaction of ionic liquid $bmimPF_6$ and CeO_2 in the Teflon tube. Nanoparticles did not form ordered agglomerates and could be easily separated. Subsequently the same result was achieved using bmimCl with KPF_6 instead of $bmimPF_6$. Ionic liquid could be regenerated by new KPF_6 after reaction. This dramatically decreases cost of preparation. Nanoparticles of CeF_3 have great potential on various fields of materials applications including luminescent materials in UV and VUV regions, ionic conductors, nanocomposites and other.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.02.009.

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