Solubility of nanocrystalline cerium dioxide: Experimental data and thermodynamic modeling

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Due to its unique physical and chemical properties nanocrystalline cerium dioxide is widely used in various of modern technology. On the other hand, cerium dioxide could be considered as a simple non-radioactive model for plutonium dioxide compound, since it has the same fluorite-type crystal structure. Therefore, the study of ceria behavior in aqueous solutions is an important issue in light of environmental safety. The aim of this work is to study the behaviour of CeO_{2-x} nanoparticles in aqueous solutions and develop the thermodynamic model describing the dissolution process.

Synthesis of ceria nanoparticles was carried out by adding aqueous ammonia to cerium(III) nitrate stock solution. For solubility measurements radioactive tracers $^{141,143,144}Ce$ was added upon synthesis. The size and shape of ceria nanoparticles was studied by high-resolution transmission electron microscopy (HRTEM) and small-angle X-ray scattering (SAXS). Selected area electron diffraction (SAED) and X-ray diffraction patterns were used to confirm crystallinity of samples. The solubility was determined by measuring cerium concentration in aqueous phase using inductively coupled plasma mass spectrometry (ICP-MS) or by determining radioactive $^{141,143,144}Ce$ by γ-spectroscopy.

According to HRTEM data ultrafine CeO_{2-x} spherical nanoparticles were obtained. Influence of pH and aging time on the morphology of cerium oxide nanocrystalline samples was studied. It was indicated that spherical particles are recrystallized into nanorods under neutral and alkaline conditions. The effect of morphology changing on the CeO_{2-x} solubility was also discussed.

The solubility data show significant decrease of cerium concentration in solution from pH=2 to pH=8. In the range pH 8÷12 the solubility remained unchanged. Experimental results from this study at pH region from 2 to 8 were fitted using reductive dissolution model:

$$CeO_2 + e^- + 4H^+ \leftrightarrows Ce^{3+} + 2H_2O.$$