Inorganic Chemistry
Communication

First Synthesis of Uranyl Aluminate Nanoparticles

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This paper describes, for the first time, a simple method for the synthesis of uranyl aluminate (URAL) nanoparticles. URAL was prepared by U(VI) hydrolytic precipitation with ammonia at pH = 11 in the presence of mesoporous alumina MSU-X under 20 kHz of sonication followed by annealing of the obtained solids at 800 °C. TEM, XAFS, powder XRD, and ^{27}Al MAS NMR studies revealed that the speciation of uranium in this system strongly depends on uranium concentration. The sample with 5 wt % of uranium yields air-stable nanoparticles (∼5 nm) of URAL. Presumably, UO_2^{2+} cations in this compound are coordinated with bidentate AlO_2^- groups. The increase of uranium concentration to 30 wt % causes mostly formation of U_3O_8 fine particles (∼50 nm) and small amounts of URAL.

Uranium is one of the most studied elements of the periodic table. However, a survey of recent literature revealed that no uranyl, UO_2^{2+}, complexes with aluminate anions, [Al(OH)$_4^-$], have been documented. Nevertheless, knowledge of UO_2^{2+} speciation in the presence of Al(OH)$_4^-$ anions or solid alumina, Al_2O_3, is essential for an understanding of uranium behavior in alkaline high level waste as well as its migration in the environment.[1] For a long time, it was believed that uranyl aluminate (URAL) could not be obtained from aqueous solutions due to the strong hydrolysis of UO_2^{2+} at pH ≥ 6, where Al(OH)$_4^-$ species become the dominating chemical form of Al(III). Recent studies of UO_2^{2+} hydrolysis in the presence of Al(III) suggested the formation of some oligomeric mixed forms, like [(H$_2$O)$_3$UO$_2$(μ-OH)$_2$Al(OH)(H$_2$O)$_3$]$^{2+}$ or [(H$_2$O)$_4$UO$_2$(μ-O)Al(OH)(H$_2$O)$_4$]$^{2+}$, in the pH range of 5−14.[2]

Furthermore, UO_2^{2+} cations are known to be readily adsorbed on alumina,[3] gibbsite,[4] or montmorillonite[5] from aqueous near-neutral solutions owing to the formation of inner-sphere, bidentate complexes with aluminol groups at the solid surface. These findings suggest that URAL might be synthesized under carefully selected conditions. Herein, we report for the first time the evidence for URAL formation as nanoparticles (NPs) dispersed in alumina matrix.

In the first stage, U(VI) was hydrolyzed in the presence of wormhole-like mesoporous alumina MSU-X (Aldrich, m-Al$_2$O$_3$) under ultrasound treatment (f = 20 kHz, I = 30 W·cm^{-2}, S = 1 cm^2, P_{ac} = 0.67 W·mL^{-1}, Ar, T = 37 ± 2 °C). The experimental details are presented in the Supporting Information. In a typical experiment, 300 mg of m-Al$_2$O$_3$ was mixed with 50 mL of UO$_2$Cl$_2$ solution at pH = 3. The mixture was sonicated for 30 min in pure argon. Note that U(VI) does not adsorb to alumina at this pH value.[3] Then, ammonia solution was added rapidly to raise the pH to ∼11, and the ultrasonic treatment was continued for 1 h. Finally, solids were washed until neutral pH was reached with pure water, dried at 75 °C, and annealed at 800 °C (5 °C·min^{-1}) for 5 h in the presence of air. EDS analysis (Figure S1, Supporting Information) indicates complete precipitation of uranium under these conditions.

We found that the speciation of uranium in annealed samples strongly depends on uranium concentration. The sample with 5 wt % of U in the starting mixture (5%U) yields an orange, air-stable product. The low resolution TEM image of this sample (Figure 1a) shows uranium NPs with an average size of about 5 nm dispersed in an alumina matrix. The initial wormhole-like structure of m-Al$_2$O$_3$ (Figure S2, Supporting Information) is collapsed after sonication, similar to that observed during ultrasonic treatment of m-Al$_2$O$_3$ without uranium.[6] Increasing the uranium concentration

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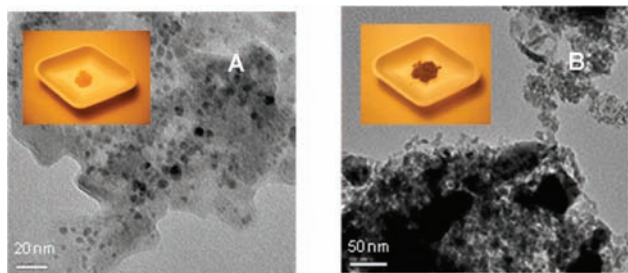
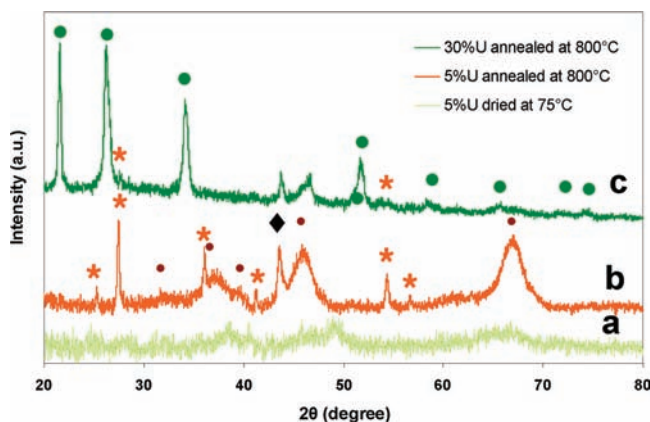**Figure 1.** Low resolution TEM images of the samples heated at 800 °C. A, 5%U; B, 30%U.

Figure 2. XRD patterns of freshly prepared and of heated samples (Cu K_α radiation). (▼) δ-Al_2O_3; (∗) URAL, (●) U_3O_8, (♦) peak originated from the stainless steel of the sample holder. Acquisition time was 2 h for 5%U (75 °C) and 30%U (800 °C) samples and 6 h for 5%U (800 °C) sample.

Figure 3. U L_{III}-edge k^3 weighted EXAFS spectra (A) and the corresponding Fourier transforms (B) uncorrected for the phase shift of unannealed and heated samples in comparison with U_3O_8 oxide.

Table 1. EXAFS Best Least-Squares Fitting Results for Nanosized URAL and UO_2^{2+} Complexes Adsorbed on Alumina

sample	shell	N^a	R (Å)^b	σ^2 (Å)
URAL 5%U 800 °C	$U-O_{ax}$	1.9	1.81	0.0022
	$U-O_{eq\ 1}$	2.5	2.36	0.0050^c
	$U-O_{eq\ 2}$	2.2	2.49	0.0050^c
	$U-Al$	1.9	3.35	0.0050^c
$[\equiv Al(O)_2UO_2]^3$	$U-O_{ax}$	2.00	1.81	0.0018
sorption complex	$U-O_{eq\ 1}$	2.64	2.32	0.0074
at γ-Al_2O_3	$U-O_{eq\ 2}$	3.13	2.47	0.0050
pH = 6.5	$U-Al^d$	1.6	3.38	0.0030^c

^{a} Errors in coordination numbers N are ±25%. ^{b} Errors in distances R are ±0.02 Å. ^{c} Value of Debye−Waller factor fixed during the fit. ^{d} UO_2^{2+} complex adsorbed at gibbsite (pH = 5.6).[4]

until 30 wt % in the starting mixture (30%U) causes the formation of bigger, cubic-shaped uranium particles after annealing (Figure 1b). Note that, in this case, the samples have a deep green-black color typical for U_3O_8 oxide.

Powder XRD patterns of solids dried at 75 °C (Figure 2a) exhibit broad peaks of m-Al_2O_3 and γ-$AlO(OH)$ with low crystallinity. The lack of peaks associated with uranium indicates the amorphous state of uranyl hydroxo-compounds precipitated at pH = 11. The sample 5%U heated at 800 °C shows XRD patterns of δ-Al_2O_3 and another crystalline phase presumably related to uranium species (Figure 2b).

A search in the JCPDF powder XRD database (Eva version 7.0) did not yield a match, suggesting the formation of a new uranium compound. In contrast to the sample 30%U, no U_3O_8 oxide was found. Note, however, that the XRD pattern of the 30%U sample contains some of the features of the 5%U sample (e.g., the peak at 27.5° 2θ; Figure 2c).

The XAFS results are in good agreement with the powder XRD data. The edge position, white line position, and the U=O multiple scattering feature in XANES spectra of the heated samples with low uranium content (Figure S3, Supporting Information) show unequivocally the presence of UO_2^{2+} groups in the 5%U sample. The U L_{III}-edge k^3 weighted EXAFS spectra and corresponding Fourier transforms (FT) are shown in Figure 3.

The FT EXAFS spectra of dried and annealed 5%U samples are dominated by the significant backscattering peak from the axial oxygen atoms of uranyl groups at about 1.8 Å, and from the equatorial oxygen atoms at about 2.2−2.5 Å. However, some differences show up at higher distances, most
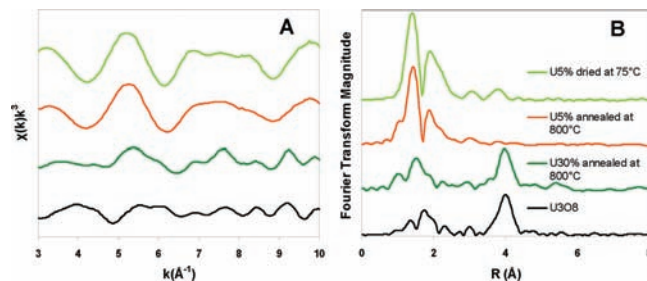
clearly visible in the EXAFS spectra at 6.5−8.5 Å^{-1}. The dried sample reveals the triplet feature typical for UO_2^{2+} tricarbonato complexes,[7] suggesting that this complex can be formed during alkaline precipitation along with UO_2^{2+} hydroxo species. The FTIR spectrum of the dried sample (not shown here) exhibits strong broad vibrational modes of adsorbed carbon dioxide centered at 1648 cm^{-1} (ν_2OCO), 1438 cm^{-1} (ν_3OCO), and 1231 cm^{-1} (δ_4COH),[8] confirming the possibility of U(VI) carbonate complex formation at the alumina surface. The FT EXAFS spectrum also indicates a U−U distance of 3.85 Å, which is typical for schoepite, $UO_2(OH)_2 \cdot H_2O$.[9] Heating this sample at 800 °C causes a strong weakening of both the tricarbonate and the hydroxide features. The absence of the U−U peak in FT EXAFS at a distance around 3.8−4.0 Å is in line with the XRD data, confirming that uranium oxide does not form under these conditions. The fit of this spectrum gives 1.9 O_{ax} at a distance of 1.81 Å, a split $O_{eq\ 1}$ shell with 2.5 O at 2.36 Å and $O_{eq\ 2}$ 2.2 O at 2.49 Å, and 0.9 Al atom at 3.35 Å. The Al backscattering peak coincides with the U−O_{ax} multiple scattering peak. Table 1 shows that the local structure of the URAL compound is very similar to inner-sphere, bidentate complexes formed by uranyl ions during adsorption at the alumina surface.[3] However, the TEM images and the diffraction patterns clearly point to the formation of an individual uranium nanocrystalline phase in our experiments. Most probably, the UO_2^{2+} cations in URAL are coordinated to AlO_2^- groups in a bidentate fashion.

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The EXAFS spectrum of the 30%U sample before annealing is similar to that of 5%U (not shown here). Heating this sample to 800 °C leads to the appearance of a strong U−U signal at 3.81 Å in the FT EXAFS spectrum, similar to that observed for U_3O_8. In the XANES spectrum, the white line peak shifts to higher energy, and the U=O multiple scattering feature disappears, suggesting a loss of the uranyl structure. Further evidence comes from the U−O peak in the FT EXAFS, which shows only one maximum intermediate in position to U−O_{ax} and U−O_{eq} shells. This observation can be explained by superposition of the dominating U−O signal from U_3O_8 oxide and a residual U=O signal from the uranyl group of URAL.

Solid state NMR provides further evidence for URAL formation. The ^{27}Al MAS NMR spectra of m-Al_2O_3 heated at 800 °C (Figure S4, Supporting Information) exhibit two major peaks assigned to an octahedral and tetrahedral local environment of aluminum, and a relatively small shoulder of pentagonal aluminum sites. In the sample 5%U, the ratio of pentagonal to tetrahedral site occupancy increases after annealing at 800 °C. In the literature, it is reported that the pentagonal coordination of aluminum is typical for the boehmite-like form of alumina, AlO(OH).[10] Therefore, the increase in aluminum pentagonal occupancy could be assigned to the coordination of UO_2^{2+} cations with AlO_2^- ligands. The lack of a noticeable ^{27}Al isotropic shift displacement in the sample 5%U 800 °C indicates that only diamagnetic UO_2^{2+} species are present, which is in line with EXAFS data.

The EXAFS spectra before and after annealing clearly show that URAL is formed during high temperature treatment rather than during uranium precipitation. Presumably, ultrasonic treatment provides the highest degree of uranium and alumina homogenization at the hydrolytic precipitation stage. Furthermore, mesoporous alumina is known to be transformed to more chemically active boehmite, AlO(OH), under the effect of a powerful ultrasound.[6] This compound does not need any significant structural modification to form metal aluminate complexes. It is noteworthy that sufficiently pure URAL cannot be prepared under mechanical stirring even at 5 wt % of uranium. The FT EXAFS spectrum of the 5%U sample obtained under silent conditions and heated at 800 °C (Figure S5, Supporting Information) exhibits a signal which could be related to uranyl U=O bonds but also shows a strong U−U peak of uranium oxide, suggesting a mixture of uranium species. Bigger particles of uranium hydrolyzed species obtained under silent conditions or at a higher uranium concentration probably promote the formation of uranium oxide during annealing.

In conclusion, we report here the synthesis of uranyl aluminate NPs dispersed in an alumina matrix. EXAFS spectra of this compound presume that UO_2^{2+} cations are coordinated to bidentate aluminate groups. However, further work is needed to establish the detailed structure of this compound as well as the mechanism of its formation. We expect this work to provide new insights into the fabrication of unusual nanosized compounds of 5f-transition metals which are still poorly studied compared to NPs of d-transition elements.

Supporting Information Available: Experimental details and additional TEM, EDS, and XAFS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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