The interaction between UCl_3 and zeolite 4A by *in situ* temperature-resolved powder x-ray diffraction

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Introduction

Glass-zeolite ceramic waste forms are being developed at Argonne National Laboratory for the disposal of radioactive waste salts. The process salt contains up to 2 mol% actinide chlorides (e.g., UCl_3, $NpCl_3$, and $PuCl_3$). Because of the stability of uranium dioxide, UO_2, the potential exists for reaction between UCl_3 and both the zeolite 4A framework and the water contained therein. Thermodynamic calculations indicate that both reactions are possible. Damage to the zeolite 4A framework could compromise its capability to retain the fission products. Hence, an investigation by *in situ* temperature-resolved synchrotron powder x-ray diffraction (XRD) was undertaken to better understand the nature and the extent of the interaction between UCl_3 and zeolite 4A.

Methods and Materials

All chemicals were stored and manipulated inside a He atmosphere glove box (< 1 ppm O_2, < 1 ppm H_2O). The UCl_3-LiCl-KCl eutectic salt was produced by oxidizing U metal with $CdCl_2$ in a LiCl-KCl salt. Zeolite 4A is an alumino-silicate with the overall formula $Na_{12}(AlSiO_4)_{12}$. The powder was obtained from UOP (Des Plaines, IL). It was dehydrated to less than 0.2 wt% H_2O. A mixture (salt + zeolite) with composition of 30.14 wt% salt was prepared by combining appropriate amounts of the component powders. XRD samples were transferred into weighed graphite pans and lightly compacted. The pans were weighed and placed inside a Beryl/2 XRD enclosure, which is described in detail elsewhere [1]. The sealed enclosure was removed from the glove box and transported to the Materials Research Collaborative Access Team (MR-CAT) insertion device (undulator A) beamline at sector 10 at the Advanced Photon Source at Argonne National Laboratory. Experiments consisted of a single heating run starting with a one minute isotherm at 300 K, followed by a temperature increase from 300 K to 800 K at 10 K·min^{-1}, and a 10 minute isotherm at 800 K. The x-ray energy, selected using a cryogenically cooled double-crystal Si(111) monochromator, was set to 11.000 keV (λ = 1.1273 Å). The Beryl/2 enclosure was mounted on an x-y motion stage and aligned to the center of an eight-circle Huber goniometer. After final alignment, only the detector circle (2θ) was moved during the experiment, except for one experiment which employed $\theta - 2\theta$ scanning. For the other scans the sample angle was fixed at 3° or 5°. The photon flux, measured by an ionization chamber behind the beam-defining slit, was found to be ~10^{11} s^{-1}. The x-ray wavelength was chosen to reduce the scan range, as well as to avoid exciting Pt (sample cup) and U L-edge fluorescence x-rays, which would not be resolvable with a scintillation detector. Analyzer slits were used, rather than a crystal, in order to maximize flux and simplify setup, at the expense of decreased resolution and increased background. The 2θ scan speeds were 1.0° or 2.5° s^{-1}. The angular resolution (2θ) was measured to be between 0.04° and 0.12° for the various configurations (incident and analyzer slit sizes). The data acquisition system consisted of reading the ratemeter output with an analog-digital converter board installed in a PC. Small-angle skewing resulted from this method of data collection due to the 0.01 second time constant on the ratemeter. XRD patterns obtained in the experiments were subject to Rietveld refinement using the GSAS [2] software package.

Results

In every set of XRD patterns, diffraction peaks of uranium dioxide, UO_2, first observed at 600 K and increasing in intensity with increasing temperature, were the most prominent feature. The evolution of the (111) diffraction peak of UO_2 is shown in Fig. 1.

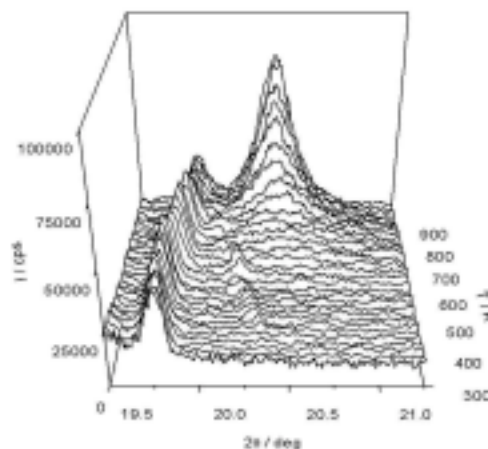Figure 1: Evolution of the (111) diffraction peak of UO_2.

For two of the experiments, the Rietveld refinement yielded values of a = 5.496 ± 0.016 Å and a = 5.481 ± 0.054 Å, respectively, for the UO_2 cubic cell parameter. These numbers agree rather well with the literature value of a = 5.467 Å at room temperature. The mean UO_2 crystallite size as a function of temperature is plotted in Fig. 2.
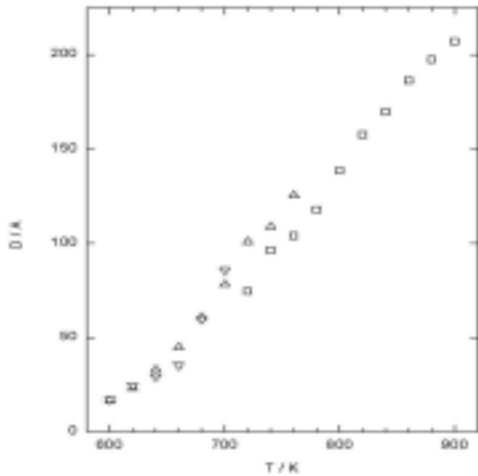
Figure 2: Mean UO_2 crystallite size plotted as a function of temperature.

It is seen that UO_2 formation starts in the vicinity of 600 K. The UO_2 crystallite size, increasing from 20 Å at 600 K to 200 Å at 900 K, strongly suggests that the observed UO_2 crystallites are located outside the zeolite lattice. (The diameter of the α- and β-cage of zeolite is 11.4 Å and 6.6 Å, respectively) [3]. The results of the zeolite lattice parameter evaluation are given in Fig. 3.
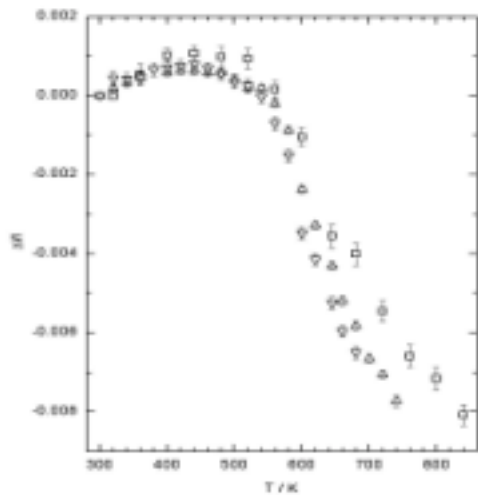

Figure 3: Results of the zeolite lattice parameter evaluation.

It is seen that, at temperatures below 450 K, the zeolite lattice expands with increasing temperature. Above 450 K, however, the zeolite lattice contraction becomes apparent. An example of the small changes in the position of the zeolite peaks can be seen in Fig. 1 at $2\theta = 19.5^{\circ}$. It has been observed previously that the zeolite lattice contracts upon molten salt occlusion. Since the UCl_3-LiCl-KCl eutectic salt does not melt until 685 K, some form of solid-state transport of the salt into the zeolite lattice is implicated below that temperature. No XRD evidence of zeolite 4A decomposition products, such as Si , SiO_2, Al_2O_3, and

NaCl, was found. A transformation of the uranium-rich $K_3U_5Cl_{18}$ salt, present in the starting (salt + zeolite) mixture, into the uranium-poor K_2UCl_5 salt has been observed at at 600 K. Accordingly, equation (1) might be written:

$$2\ K_3U_5Cl_{18} \rightarrow 3\ K_2UCl_5 + 7\ UCl_3 \qquad (1)$$
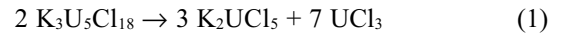
The UCl_3 formed in this reaction, thus, becomes available for a subsequent reaction.

Discussion

The following sequence of events taking place in the (UCl_3-LiCl-KCl eutectic salt + zeolite 4A) mixture upon heating from room temperature can be proposed. Between 300 K and 450 K, no chemical changes occur. At 450 K, the LiCl and/or the KCl start diffusing into the zeolite 4A lattice forming an occlusion compound. This process results in a significant zeolite 4A lattice contraction. At 600 K, continuing LiCl and/or KCl occlusion leads to the expulsion of the zeolitic H_2O (< 0.2 wt%) from the zeolite 4A lattice. There, it reacts with the UCl_3-LiCl-KCl eutectic salt via equation (2):

$$8/7\ K_3U_5Cl_{18} + 8\ H_2O \rightarrow$$
$$12/7\ K_2UCl_5 + 4\ UO_2 + 12\ HCl\ (g) + 2\ H_2\ (g) \qquad (2)$$
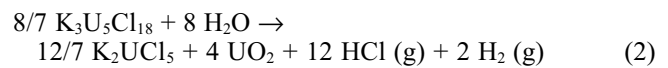
The UO_2 crystallites being formed increase in size from 20 Å at 600 K to 200 Å at 900 K. At 685 K, the UCl_3-LiCl-KCl eutectic salt melts and is occluded by the zeolite 4A. The UCl_3 in the UCl_3-LiCl-KCl eutectic salt does not appear to react with the zeolite 4A.

Acknowledgments

References

[1]   D. Lexa, *Rev. Sci. Instruments* **70(5)**, 2242 – 2245 (1999).
[2]   A. C. Larson and R. B. Von Dreele, GSAS, *LANL Report LA-UR-86-748*, (1987).
[3]   D. W. Breck, *Zeolite Molecular Sieves* (John Wiley and Sons, Inc., New York, 1974) p. 84.