Occlusion of the LiCl-KCl Eutectic Salt by Zeolite 4A by Simultaneous Differential Scanning Calorimetry/X-ray Diffraction

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Introduction

A glass-zeolite ceramic waste form is being developed at Argonne National Laboratory for the disposal of radioactive waste salts. A typical waste salt is LiCl-KCl eutectic salt with variable amounts of fission product and actinide chlorides (e.g., CsCl, $SrCl_2$, UCl_3, $NpCl_3$, and $PuCl_3$). A key step in the production of the waste form is the occlusion of the waste salt by zeolite 4A at 823K. The properties of the waste form depend critically on the detailed mechanism of the occlusion process. Hence, as a first step in understanding the occlusion of the waste salt by zeolite 4A, an investigation by simultaneous differential scanning calorimetry (DSC)/synchrotron powder x-ray diffraction (XRD) of the occlusion of the LiCl-KCl eutectic salt by zeolite 4A was undertaken. (Reactive occlusion of the UCl_3-LiCl-KCl salt by zeolite 4A has been studied previously [1].)

Methods and Materials

Zeolite 4A (hereinafter referred to as "zeolite") and the LiCl-KCl eutectic salt (hereinafter called "salt") were stored and manipulated inside a He atmosphere glove box (<1 ppm of O_2, <1 ppm of H_2O). Zeolite 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. The salt was obtained from AAPL (Urbana, IL). A mixture (salt plus zeolite) with a composition of 30 wt% salt was prepared by combining appropriate amounts of the component powders. Samples were transferred into weighed graphite pans and lightly compacted. The pans were weighed and placed inside a DSC/XRD enclosure, as described in detail in Refs. 1 and 2. The sealed enclosure was removed from the glove box and transferred to the Materials Research Collaborative Access Team (MR-CAT) insertion device (undulator A) beamline at sector 10 of the APS. Experiments consisted of two heating runs, each starting with a 1-min isotherm at 300K, followed by a temperature increase from 300 to 800K at 10K/min and a 1-min isotherm at 800K. The DSC signal obtained in the second run was subtracted from that obtained in the first run to yield the net DSC signal, which includes the reaction contribution but does not include the heat capacity contribution. The x-ray energy, selected by using a cryogenically cooled double-crystal Si(111) monochromator, was set to 11.000 keV (λ = 1.1273 Å). The DSC/XRD 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. The sample angle (θ) was fixed at 3-5°. 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 and avoid exciting the Pt (sample cup) L-edge fluorescence x-rays, which would not be resolvable with a scintillation detector. Analyzer slits were used instead of a crystal to maximize flux and simplify setup, at the expense of decreased resolution and increased background. The 2θ scan speeds were 1.0° s^{-1}. The angular resolution (2θ) was measured to be 0.04-0.12° for the various configurations (incident and analyzer slit sizes). XRD patterns obtained in the experiments were subject to Rietveld refinement by using the GSAS software package [4].

Results

A color-contour map of a typical temperature-resolved XRD pattern is shown in Fig. 1. Three sets of diffraction peaks are visible. A set of peaks that shift to lower 2θ values with increasing temperature and then abruptly disappear at about 650K belongs to the LiCl-KCl eutectic salt. The shift is a result of thermal expansion, and the disappearance is a sign of melting. The set of peaks that is seemingly unchanged with increasing temperature belongs to zeolite. The last set of peaks that emerges at about 650K at the high-2θ side of every zeolite peak also belongs to zeolite, but zeolite with a significantly smaller lattice parameter.

A DSC trace acquired simultaneously with the XRD pattern (Fig. 1) is shown in Fig. 2. The endothermic peak around 400K is due to zeolite dehydration. The sharp exotherm at about 625K is a manifestation of the molten salt occlusion. (The salt melting endotherm is not resolved, because it is immediately accompanied by the more exothermic occlusion.) Note the high degree of agreement between the temperature at which both the salt XRD peaks disappear and the peaks of the new zeolite phase appear on the one hand and the temperature at which the occlusion exotherm is observed on the other. Hence, these processes must be intimately related.

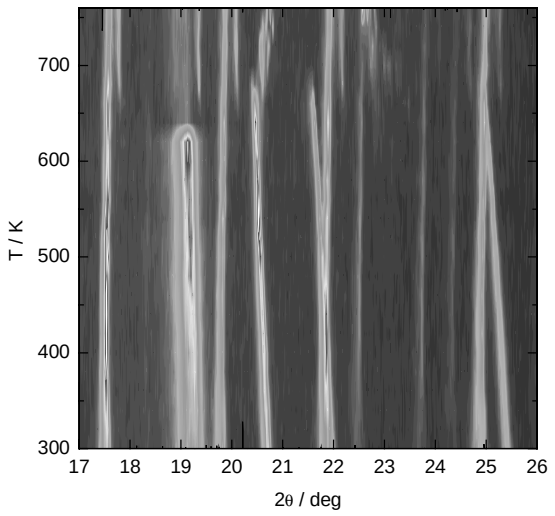

FIG. 1. Contour map of a temperature-resolved XRD pattern.

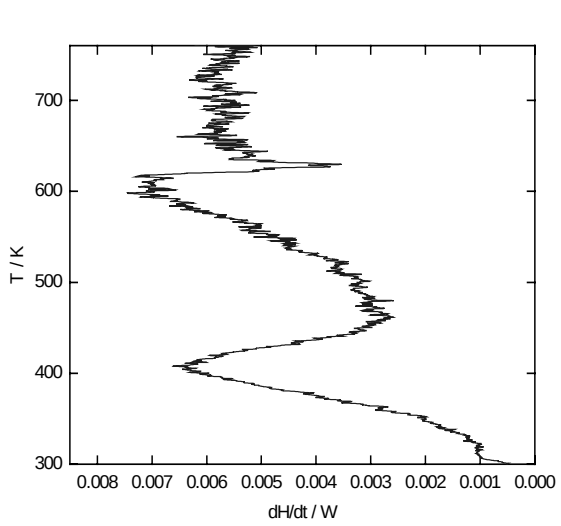

FIG. 2. DSC trace at 10 K/min.

A detail of a temperature-resolved XRD pattern is presented in Fig. 3. It shows that the appearance and growth of the new zeolite peaks beyond about 650K is accompanied by a decrease in the intensity of the original zeolite peaks. The amount of the new zeolite thus increases at the expense of the original zeolite. A color contour map of the same XRD pattern is presented in Fig. 4. It reveals that the original zeolite peaks undergo a 2θ movement of their own. Between 300 and about 450K, the peaks shift to lower 2θ values — a sign of thermal expansion. However, between about 450 and 800K, this trend is reversed, implying a zeolite lattice contraction.

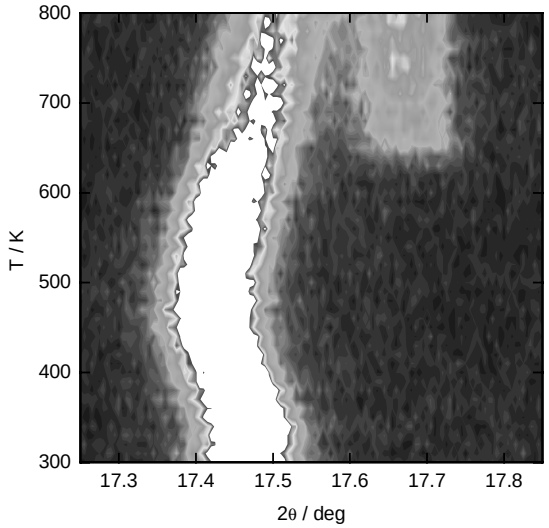

FIG. 3. A detail of a temperature-resolved XRD pattern.

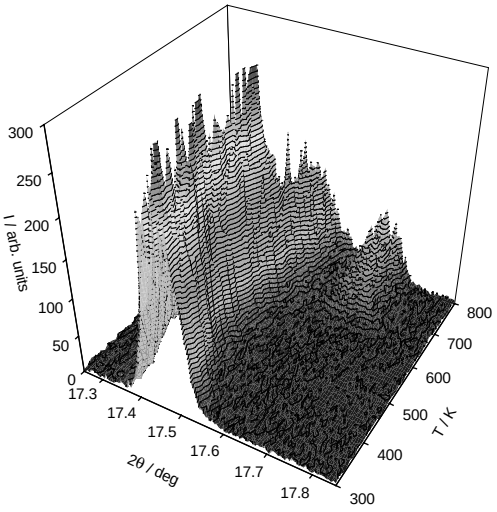

FIG. 4. Contour map of a detail of a temperature-resolved XRD pattern.

Discussion

The occlusion of the LiCl-KCl eutectic salt by zeolite 4A is a complex process. Between 300 and about 450K, only physical changes are observed, including thermal expansion of salt and zeolite and the endothermic dehydration of zeolite. Between about 450 and about 625K, occlusion of the salt by zeolite proceeds by solid-state diffusion and/or vapor-phase transport. The occlusion is accompanied by a zeolite lattice contraction. At about 625K, essentially identical with the salt melting point of 628K, abrupt molten salt occlusion occurs. This

process is exothermic (even including the endothermic salt melting). It gives rise to a new zeolite phase with a significantly smaller lattice parameter. The new zeolite phase grows at the expense of the original zeolite. The lattice parameter of the original zeolite continues to decrease but never reaches the lattice parameter of the new zeolite phase. We speculate that the first phase of occlusion, between about 450 and about 625K, produces partially salt-loaded zeolite particles, with the salt spatially occlusion, between about 625 and 800K, results in salt-loaded zeolite particles with a highly occluded crust and a partially occluded core (a remnant of the first phase of occlusion).

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Work performed at MR-CAT is supported, in part, by funding from DOE under Grant No. DEFG0200ER45811.

References

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