

On the Efficiency of Insertion of Aluminium into the Framework of Y-type Zeolite by the Hydrothermal Process of Liu, Klinowski, and Thomas

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Liu *et al.*'s procedure¹ for completely reversing the ultrastabilization of Y-type zeolite was applied to a sample of high quality, commercially prepared ultrastable Y-zeolite (USY); a combination of characterization techniques showed that significant framework realumination occurred, but that the product was only 80% crystalline.

Liu, Klinowski, and Thomas recently described a simple hydrothermal method by which '... the process of ultrastabilization of Y-type zeolite can be *completely* reversed.'¹ We have attempted to reproduce such results and have found that the method does yield a Y-type zeolite with a greatly increased unit cell size. However, our solid product was only 80% crystalline, so we conclude that the method does *not* completely reverse ultrastabilization. We attribute the discrepancy in apparent extent of reversal to differences in analytical approaches: Liu's structural characterizations were applied only to the crystalline component of his sample, whereas we specifically sought both qualitative indications of framework realumination and quantitative data on the actual zeolite content of the product.

Our ultrastable Y-zeolite (USY) starting material was Linde Molecular Sieves LZ-Y72 (Lot 9664790001, Union

Table 1. Mass balance summary: KOH treatment of LZ-Y72.

	M(Na)/g	M(K)/g	M(Si)/g	M(Al)/g
<i>Taken</i>				
40.0 g LZ-Y72 (anhyd. basis)	0.86	—	13.6	5.1
2000 ml KOH (0.250 M)	—	19.6	—	—
Totals taken	0.86	19.6	13.6	5.1
<i>Found</i>				
44.0 g Solid Product (anhyd. basis)	0.46	5.6	12.7	4.9
1875 g filtrate	0.40	12.9	0.7	0.11
Totals found	0.86	18.5	13.4	5.0
Recovery/%	100	94	99	98

Table 2. Chemical and physical properties of Y-type zeolites.

Material	Na-Y (LZ-Y52)	K-Y	USY (LZ-Y72)	K-USY	KOH-treated USY
Composition					
Na ₂ O, Wt % (anhyd. basis)	13.5	0.9	2.9	0.1	1.4
K ₂ O	—	16.4	—	6.2	15.2
SiO ₂	64.3	60.9	71.6	72.0	61.2
Al ₂ O ₃	22.1	19.8	23.6	21.4	20.9
SiO ₂ /Al ₂ O ₃ , mol/mol	4.91	5.21	5.14	5.71	4.97
M ₂ O/Al ₂ O ₃	1.00	0.97	0.20	0.32	0.90
Physical properties					
Micropore volume, ml g ⁻¹	0.34	0.31	0.26	0.27	0.25
Unit cell size, Å	24.69	24.69	24.53	24.57	24.69
<i>X</i> -ray crystallinity					
Observed	100	60	73	62	52
Potassium-corrected	100	100	73	73	82

Carbide Corporation). A 40 g portion was digested in 2 l KOH (0.25 M) for 24 h at 78–82 °C. The solid and filtrate were collected quantitatively, after which the solid was washed thoroughly and dried at 120 °C.

Reference materials were prepared by exhaustive potassium exchange of Na-Y† (Linde LZ-Y52, Lot 96808461002) and the USY with aqueous KCl (3 one-hour reflux exchanges with 30 ml fresh KCl (2 M) per g of zeolite). These products were washed chloride-free with KOH (pH 8) and dried at 120 °C.

Analyses were carried out by Chevron Research Company's Analytical Research and Services Division. Zeolite compositions were determined by dissolving samples in a lithium borate flux, then analysing solutions of the products by an inductively coupled plasma method. Micropore volumes were determined by nitrogen adsorption at -196 °C, $p/p_0 = 0.100$, a relative pressure found to be within the saturation region for all of the materials.

X-ray diffraction measurements of crystallinity and unit cell size were done in accord with ASTM procedures D 3906-80 and D 3942-80, with Na-Y assigned an *X*-ray crystallinity of 100%. Replicate determinations showed the precisions to be 3% and 0.01 Å, respectively.

Crystallinities were subsequently corrected for signal attenuation by potassium. The correction used two assumptions: first, that signal attenuation was first-order in potassium content, and second, that no structure loss occurred during the ion exchanges with KCl. The correction coefficient was then calculated from the chemical compositions and ASTM crystallinities of the Na-Y and K-Y.

We established three criteria to determine if Liu's hydrothermal method would cause the LZ-Y72 to revert completely to a nonstabilized form of Y-type zeolite. The first was that the process should not dissolve the starting material. A mass balance summary for the experiment (Table 1) shows that overall recoveries were good and that <5% of the zeolite dissolved. We consider our first criteria to have been satisfied.

The second was that the product should be phase-pure. The *X*-ray diffraction pattern of the KOH-treated LZ-Y72 contained only reflections attributable to Y-type zeolite (estimated limit of detection ~2%), thus we also consider our second criteria to have been satisfied.

Our third criteria was the most important: the solid product should be a fully crystalline, nonstabilized form of Y-type zeolite. The chemical compositions and physical properties of the various zeolites are summarized in Table 2. We note first that the KOH treatment did produce a large increase in unit cell size, 0.16 to 24.69 Å. ²⁹Si n.m.r. spectral data showed the lattice expansion to result from framework realumination. Together, these observations show that the KOH treatment did yield a nonstabilized Y-type zeolite. However, from the KOH-treated product's *X*-ray crystallinity, 82% (corrected), and the ratio of its micropore volume to that of the K-Y, 0.80, we conclude that ultrastabilization reversal was substantially incomplete.

In summary, we have shown that Liu's hydrothermal method is not universally capable of completely reversing the ultrastabilization of Y-type zeolite. We admit the possibility that Liu *et al.* might have completely reversed the ultrastabilization of their USY. However, their primary analytical techniques, *X*-ray diffractometry and n.m.r. and i.r. spectroscopies, were used in a manner such that they characterized only the crystalline component of the product, rather than assaying overall zeolite content. We also note that comparing bulk chemical composition with n.m.r.-determined framework composition may not disclose significant amounts of intimately mixed amorphous by-product. Were Liu's product 80 rather than 100% crystalline, their reported (Si/Al) bulk 2.60, with (Si/Al) framework 2.56, would imply an amorphous impurity with (Si/Al) bulk of only 2.73.

The most likely reason that the KOH treatment yields an only partially crystalline product is that even carefully prepared ultrastable Y's may contain substantial (10–25%) amounts of amorphous material. Product purity, hence suitability for catalytic or sorptive applications, will thus be very sensitive to starting material quality.

We gratefully acknowledge the assistance of Dr. R. C. Medrud in acquiring and interpreting the *X*-ray diffraction data and Mr. F. M. Banks in performing the experimental work. Dr. S. A. Bezman suggested several valuable additions to our initial studies.

Received, 5th May 1987; Com. 606

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† The LZ-Y52 had an average crystal size of 1 micron, and was >97 wt% Na-Y. The latter was computed from overall composition via chemical analysis, and framework composition via unit cell size.²