JOURNAL OF CATALYSIS 91, 352–355 (1985)

NOTES

Determination of Structural Boron in Borosilicate Molecular Sieves via X-Ray Diffraction

Substitution of silicon in crystalline molecular sieve structures by various heteroatoms has been a topic of interest for several decades. Attempts to substitute boron for silicon were reported to be unsuccessful (*1*) until Klotz (*2*) synthesized the crystalline borosilicate molecular sieve AMS-1B in 1976. This was the first of a new class of compounds that are interesting because they offer the combination of shape selectivity along with acid–base properties different from those exhibited by (aluminosilicate) zeolites and other known molecular sieves. These materials could, therefore, exhibit useful and unique activity, selectivity, and stability properties.

Based on studies of alloys (*3*), substitution of a heteroatom into a tetrahedral site of a crystalline silica structure might occur if the Si–O and heteroatom–oxygen bond distances differ by ≲10%. Since a Si–O bond distance is 1.61 Å (*4, 5*), substitution by both Al and B atoms should be permissible [bond distances of 1.74 Å (*5, 6*) and 1.47 Å (*5, 7, 8*), respectively]. Incorporation of Al would result in lattice expansion, whereas substitution by boron would result in a contraction of the lattice.

Precise determination of unit cell dimensions by X-ray diffraction is an accepted technique for characterizing molecular sieves having similar framework topology but varying composition (*9, 10*). Studies on faujasites are the classic examples of this technique. The cubic unit cell parameter decreases from 25.02 to 24.19 Å as the Al content is successively reduced in zeolite X, zeolite Y, and ultrastable Y.

X-Ray diffraction data indicate that silicalite, AMS-1B, and ZSM-5 are members of the pentasil family of molecular sieves. The heteroatom content of these materials is low enough that application of conventional techniques of elemental analysis is time consuming. More importantly, careful application of the X-ray diffraction technique provides an accurate, precise, and convenient method for determining the framework heteroatom content of crystalline pentasil molecular sieves.

EXPERIMENTAL

Crystalline aluminosilicate molecular sieves with aluminum contents of 1.26–4.47 wt% were prepared according to Ref. (*11*). Crystalline borosilicate molecular sieves with boron contents of ~0–1 wt% were prepared according to Ref. (*2*). Boron and aluminum contents were determined by wet chemical and atomic absorption methods. All samples were exchanged with ammonium acetate, and then calcined to yield the H form. In Naperville, each sample was allowed to equilibrate for at least 16 hr in an ambient atmosphere of 60% RH (controlled laboratory air). Equilibration at 35% RH (saturated $CaCl_2$ solution) led to equivalent results. The reproducibility of the diffraction results is much higher when hydrated samples are used. An internal standard of α-Al_2O_3 was used. X-Ray diffraction measurements were made using a Philips Electronics diffractometer. A curved graphite crystal monochromator was used with a high-intensity fine-focus copper X-ray source. Scans of $45° < 2\theta < 53°$ were made at 0.25°/min with a time constant of 10 sec. The empirical parameter Σ_T, the sum of the *d* spacings of the four reflections 1000/491,

0021-9517/85 $3.00

TABLE 1

Chemical and Crystallographic Data for Molecular Sieve Samples

Sample	B (wt%)	B/unit cell	Al (wt%)	Al/unit cell	a (Å)	b (Å)	c (Å)	$V(\sigma)$ (Å^3)	Σ_T (Å)
125	0.64	3.4	—[a]	—	ND[b]	ND	ND	ND	7.8197
127	0.61	3.2	—	—	19.968	19.785	13.324	5264(14)	7.8217
126	0.55	2.9	—	—	19.982	19.796	13.321	5269(11)	7.8259
116	0.54	2.9	—	—	19.982	19.792	13.325	5270(13)	7.8284
66	0.49	2.6	—	—	19.974	19.811	13.330	5275(19)	7.8297
128	0.46	2.5	—	—	20.004	19.825	13.333	5287(15)	7.8364
27	0.32	1.7	—	—	20.038	19.845	13.350	5309(16)	7.8392
117	0.32	1.7	—	—	20.038	19.846	13.338	5304(16)	7.8416
11	0.01	0.1	—	—	20.034	19.917	13.396	5345(15)	7.8606
40	ND	—	1.26	2.7	20.095	19.902	13.415	5365(12)	7.8649
81	ND	—	1.88	4.0	20.108	19.913	13.410	5369(13)	7.8696
82	ND	—	2.47	5.3	20.110	19.907	13.420	5373(18)	7.8742
83	ND	—	3.65	7.8	20.121	19.934	13.456	5397(14)	7.8770
84	ND	—	4.47	9.4	ND	ND	ND	ND	7.8796

[a] The aluminum contents of the borosilicate samples vary from 10 to 380 ppmw, values negligible for the purposes of this work.

[b] Not determined.

0100/184, 436, and 933, was defined and calculated for each sample.

In Leuven, the H forms were reexchanged with ammonium acetate and allowed to equilibrate for at least 16 hr in an ambient atmosphere of 70% RH (saturated NH_4Cl solution). An internal standard of KCl was used. The NH_4 forms are preferable if KCl is used as the internal standard, to avoid the effects of solid-state ion exchange on the unit cell dimensions. X-ray measurements were performed on a computer-controlled Seifert–Scintag diffractometer, equipped with a position-sensitive proportional detector (*12*). The X-ray pattern was recorded between 5 and 55° 2θ.

The patterns were indexed by comparison to a simulated powder pattern, generated by the POWD program (*13*), using the single-crystal data of Olson *et al.* (*14*). For each sample, the orthorhombic unit cell parameters were determined by a least squares procedure. Two groups of intense peaks, $20° < 2\theta < 35°$ and $45° < 2\theta < 50°$, were used for the calculations of unit cell parameters. Calculations were made using all the peaks. In a second calculation, only the low-angle set was used. The average standard deviation of the unit cell volume calculated using the full set was 15 Å^3, while that calculated using the low-angle peaks was 19 Å^3. The low-angle peaks yield results nearly as precise as those obtained using the whole set of peaks.

DISCUSSION

The heteroatom content, unit cell parameters, and Σ_T for the borosilicate, aluminosilicate, and silica molecular sieves are presented in Table 1. A formula weight of 5768 ($Si_{96}O_{192}$) cell was used in the calculation of heteroatom contents. Variations of the unit cell volume (UCV) and the individual cell parameters as a function of the boron content of the NH_4AMS-1B samples are illustrated in Fig. 1. As the boron content increases, the unit cell volume decreases, and the contraction is approximately isotropic (*15*). We believe that the deviation of the a and c parameters of sample 11 from the trend lines indicates a lowering of the crystal symmetry to monoclinic at low boron concentrations. An isotropic expansion is observed in the aluminosilicate samples.

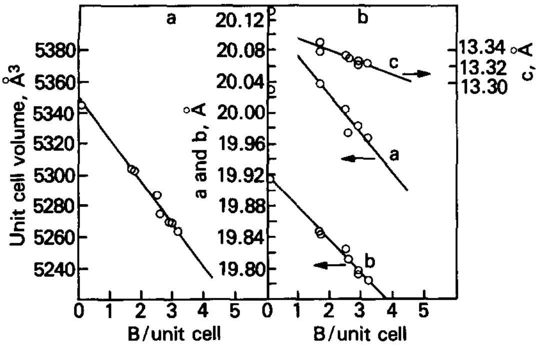

FIG. 1. Variation of (a) unit cell volume (UCV) and (b) individual cell parameters as a function of the boron content of NH_4AMS-1B samples.

With the use of linear regression, the following equation relating UCV to structural boron content is obtained:

$$\mathrm{UCV}(\text{Å}^3) = 5350 - 27.11\ \mathrm{B/unit\ cell}$$

The correlation coefficient from this relationship is 0.998 when both groups of peaks are used. Using only the low-angle peaks, we obtained a correlation coefficient of 0.992.

Figure 2 illustrates the correlation between UCV and Σ_T. The unit-weighted least-squares equation describing this relation is

$$\mathrm{UCV}(\text{Å}^3) = 2340\Sigma_T(\text{Å}) - 13{,}045$$

The correlation coefficient is 0.992. Since the magnitude of a general reciprocal lattice vector should be highly correlated to UCV, this is not surprising. The relative standard deviation of the UCV is approximately 0.3%. Since the standard deviation of the measurement of a single d spacing in the region 45–50° 2θ is approximately 0.001 Å, the relative standard deviation of the sum of four d spacings is approximately 0.1%. We have found that this empirical parameter is more convenient for routine analytical work.

The least-squares equation relating boron content to Σ_T for AMS-1B samples is

$$\Sigma_B(\text{Å}) = 7.862 - 0.0121\ \mathrm{B/unit\ cell}.$$

The correlation coefficient for the relationship is 0.983. The least-squares line relating structural aluminum content to Σ_T for the ZSM-5 samples is

$$\Sigma_{Al}(\text{Å}) = 7.861 + 0.0021\ \mathrm{Al/unit\ cell}.$$

The correlation coefficient is 0.955. The reproducibility of an individual determination of boron content by this method is 0.01 wt%. As little as 0.04% B can be determined at the 99% confidence level. The precision of an individual determination of aluminum content is somewhat lower, but 0.5% Al is detectable easily.

Figure 3 illustrates the variation of Σ_T as a function of heteroatom content for both AMS-1B and ZSM-5. The pentasil silicalite structure seems to be more sensitive to the presence of boron than to the presence of aluminum. The observed changes are close to those calculated using a simple weighting

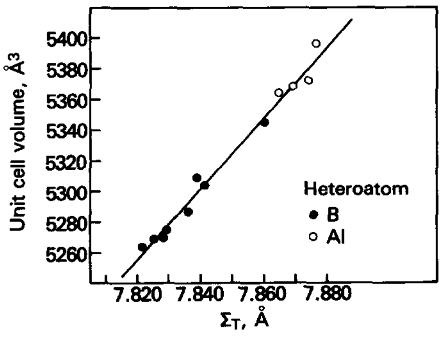

FIG. 2. Correlation between UCV and Σ_T.

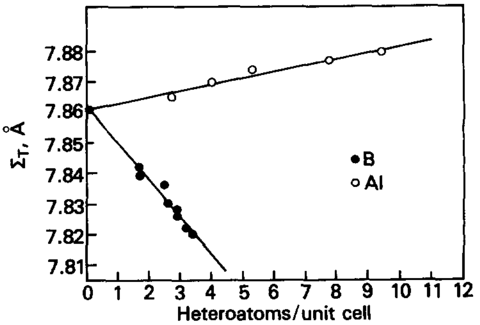

FIG. 3 Variation of Σ_T as a function of heteroatom content for both AMS-1B and ZSM-5.

of bond distances. Since heteroatom substitution may alter not only bond distances but also bond angles and the orientation of secondary building units, the significance of such a simple calculation is uncertain.

In all of these studies a broadening of the X-ray diffraction peak profiles was noted as heteroatom content increased. We believe that this reflects the shifts of the individual components of the complex lines, as well as concentration gradients within individual crystallites, in addition to actual variations in the crystallite size.

CONCLUSIONS

Careful X-ray diffraction monitoring is a useful procedure for determining the framework Al or B content of molecular sieves. Either the unit cell volume or an empirical sum of four *d* spacings of high-angle reflections can be used. Framework heteroatom content is an important quantity not obtained with confidence by typical chemical analysis. As little as 0.04 wt% B can be determined at the 99% confidence level. The method is less sensitive to Al incorporation, but 0.5 wt% Al is quantifiable easily. Incorporation of B into the silicalite structure results in a contraction of the unit cell, while Al incorporation expands the structure. Substitution of other metals such as Fe or Cr can also be followed by the procedure of this paper, but the peak shifts are smaller, and more care is required to make precise measurements.

ACKNOWLEDGMENTS

We thank Thanh Nguyen and Sophia Konecny for dedicated assistance in the experimental portion of this work.

REFERENCES

1. Breck, D. W., "Zeolite Molecular Sieves," pp. 321–322. Wiley, New York, 1974.
2. Klotz, M. R., U.S. Patent 4,269,813 (1981).
3. Cullity, B. D., "Elements of X-Ray Diffraction," p. 352, Addison–Wesley, Reading, Mass., 1967.
4. Smith, J. V., *Acta Crystallogr.* **7,** 479 (1954).
5. Appleman, D. E., and Clark, J. R., *Amer. Mineral.* **59,** 1827 (1965).
6. Barrer, R. M., "Hydrothermal Chemistry of Zeolites," p. 293, Academic Press, New York, 1982.
7. Krogh-Moe, J., *Acta Crystallogr. B* **28,** 169 (1972).
8. Mesline, S., and Santoni, F., *Acta Crystallogr. B* **28,** 3559 (1972).
9. Breck, D. W., and Flanigen, E. M., "Molecular Sieves," p. 47. Soc. of Chem. Ind., London, 1968.
10. Bibby, D. M., Aldrige, L. P. and Milestone, N. B., *J. Catal.* **72,** 373 (1981).
11. Argauer, R. G., and Landolt, G. R., U.S. Patent 3,702,886 (1972).
12. Application Note Nos. 267 and 271, Siemens Atkiengesellschaft.
13. Smith, D. K., Program POWD, *Norelco Rep.* **15,** 57 (1968).
14. Olson, D. H ., Kokotailo, G. T., Lawton, L. S., and Meier, W. M., *J. Phys. Chem.* **25,** 2238 (1981).
15. Taramasso, M., Perego, J., and Notari, B., *in* "Proceedings of the Fifth International Conference on Zeolites" (L. V. Rees, Ed.), p. 40ff. Heyden & Son Ltd., London, 1980.

BERNARD L. MEYERS
STEPHEN R. ELY
NANCY A. KUTZ
JAMES A. KADUK

Amoco Research Center
P.O. Box 400
Naperville, Illinois 60566

E. VAN DEN BOSSCHE

Katholieke Universiteit Leuven
Laboratorium voor Oppervlaktescheikunde
Kardinaal Mercierlaan 92
B-3030 Heverlee, Belgium

Received December 22, 1983; revised August 10, 1984