Thermal and Hydrothermal Stability of SAPO-5 and SAPO-37 Molecular Sieves

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The stability of the crystalline structure of SAPO-5 and SAPO-37 has been studied in a heating chamber from room temperature to 1 400 K. After template decomposition a lowering in crystal symmetry was observed for SAPO-37 but not for SAPO-5. The stability of the two SAPOs is very similar up to about 1 300 K in a dry or a water vapour-containing atmosphere. Below about 345 K in the presence of water, only SAPO-37 progressively loses its crystallinity simultaneously with a decrease in unit-cell parameter.

It has been reported that the stability of SAPOs (porous silico-alumino phosphates) upon heating is similar to that of zeolites,[1] or that upon calcination SAPO-37 is moisture sensitive[2] and that the instability of the structure results from exposure of the activated SAPO-37 to moisture at room temperature.[3] It is thus of practical interest to study the conditions under which structure collapse is avoided and to compare the stability of this material to that of other SAPOs.

Experimental

Materials.—SAPO-5 was synthesized as previously described.[4a] Its chemical composition is $(Si_{0.07}Al_{0.46}P_{0.47})O_2$. Two batches of SAPO-37 were obtained, one (prepared as in ref. 3) gives SAPO-37A of formula $(Si_{0.22}Al_{0.45}P_{0.33})O_2$. The second, SAPO-37B, was prepared as given in ref. 4*b* and contains less silicon, $(Si_{0.13}Al_{0.49}P_{0.37})O_2$.

Crystallinity Study.—First a check of crystallinity was made using i.r. spectrometry in the TO (T = Al, Si, or P) vibration range. A more detailed and precise study was conducted using *X*-ray diffraction in a Guinier–Lenné camera equipped with a heating chamber, which allows *X*-ray studies to be performed under a controlled atmosphere between room temperature and 1 400 K. Heating to high temperature, or cooling to room temperature, was carried out over 40 h under a flow of dry oxygen, or of oxygen saturated with water at room temperature. Some experiments were carried out with a Siemens diffractometer D 500 under ambient conditions.

Results and Discussion

The samples, prepared as given above, appear to be pure and well crystallized.

Infrared studies confirmed that the crystallinity of SAPO-37 was lost after exposure to an ambient atmosphere; the calcined material was free of template. A detailed *X*-ray study was carried out to follow the changes in structural characteristics.

Unit-cell Changes.—The unit-cell parameters of the samples were determined under ASTM conditions for the three materials. Table 1 gives the values obtained at room temperature in the presence of the templates (tetramethylammonium and tetrapropylammonium hydroxides for SAPO-37 and tetrapropylammonium hydroxide for SAPO-5). The values were obtained using a Siemens diffractometer, which gives an accuracy of ± 0.01 Å, or the Guinier–Lenné camera for which the accuracy is only ± 0.02 Å. The reproducibility of the measurements was checked and found to be good.

Table 1. Unit-cell parameters (Å)

	SAPO-37A	SAPO-37B	SAPO-5
a^a	24.69 ± 0.01	24.73 ± 0.01	13.77 ± 0.01
c^a			8.43 ± 0.01
a^b	24.65 ± 0.02		13.71 ± 0.01
c^b			8.40 ± 0.01
a^c	24.05 ± 0.02		

[a] In the presence of the template. [b] After template decomposition. [c] After contact of the sample (after template decomposition) with water vapour at room temperature.

Values in Table 1 show that the *a* and *c* parameters of SAPO-5 decrease after heating in an oven at 1 025 K, *i.e.* above the template decomposition temperature. In $AlPO_4$-5 a lowering of symmetry was observed with an expansion of *a* and contraction of *c* after removing the template.[5] In the present case no change in the compact hexagonal symmetry is observed. For SAPO-37 in the presence of the template the value of *a* is in fact a_0 ($a_0 = a = b = c$). A higher a_0 value is obtained for SAPO-37B which contains less silicon. Heating SAPO-37A in the Guinier–Lenné camera allows the unit-cell parameters to be determined *in situ* after template decomposition and without contact with water. A significant decrease in unit-cell parameter was observed and a lowering in symmetry noted, *a* being slightly higher and *c* slightly lower than the mean $\bar{a}$ (*i.e.*, a_0) value given in Table 1. Precise determination of *a* and *c* is not possible in this type of experiment. Such changes in *a* and *c* have previously been observed, as for $AlPO_4$-5 mentioned above. They resemble modifications of symmetry evidenced in the zeolite, ZSM-5, changing from orthorhombic to monoclinic under various experimental conditions (temperature, presence of adsorbate).[6,7] The SAPO-37A sample, free of template, was contacted with water vapour, as will be described further. When cooled close to room temperature its crystallinity was partly damaged and a drop in unit-cell parameter observed as seen in Table 1. The lowering of symmetry was maintained under those conditions.

In order to study precisely the changes in crystallinity upon heating, the two SAPO-37 samples and SAPO-5 were studied *in situ* in the Guinier–Lenné camera.

Heating of SAPO-37 *and* SAPO-5.—The maximum temperature for structure stability was determined *in situ* during heating of the SAPOs. Table 2 gives the results when the gas

Table 2. Temperature (K) for loss of crystallinity

Material	Flushing gas	
	Dry O_2	$O_2 + H_2O$*
SAPO-5	1 380 ± 30	1 330 ± 30
SAPO-37A	1 320 ± 30	1 275 ± 30
SAPO-37B	1 270 ± 30	1 240 ± 30

* Oxygen saturated with water at room temperature.

flushing the chamber is dry oxygen or oxygen plus water. The temperature at which crystallinity is lost is determined by calibrating the chamber with the temperature of quartz transformation (846 K).

The results show, in each case, very good stability to high temperature. The templates are decomposed at 875 K which is lower than the temperatures of Table 2. The stability cannot be related to the presence of the template and it is higher than that of faujasites which have the same structure as that of SAPO-37. A second point is that heating in the presence of water vapour, at least under the present experimental conditions, does not significantly change the stability of the structure at high temperatures. Ultrastabilization by steaming does not seem to operate. Thirdly, SAPO-5 is only slightly more stable than the two SAPO-37 samples at high temperatures.

Cooling of SAPO-37 *and* SAPO-5.—The good stability of the samples to high temperatures prompted us to follow any structure change as the temperature was decreased to room temperature. At first a sample of SAPO-37A was heated, as previously, up to 1 220 K under a flow of dry oxygen. The structure was maintained. The temperature was decreased, over 40 h, to room temperature in a flow of dry oxygen. The structure remained identical. After exposure of the sample at 300 K to the air a unit-cell contraction was observed as soon as the air containing the water vapour made contact with the sample, and the crystallinity decreased significantly. In order to determine at what temperature water vapour modifies the SAPO-37 structure, another sample of SAPO-37A was heated at 1 230 K under a flow of dry oxygen. At this temperature the flushing gas was replaced by oxygen saturated at room temperature with water and the temperature was decreased, as previously, over 40 h, to room temperature. The crystallinity remained very good down to 340 ± 15 K, where a large unit-cell contraction occurs abruptly, as reported in Table 1. A loss of about 50% crystallinity was observed and maintained as room temperature was reached. In a last experiment the SAPO-37A sample was heated to 1 100 K and cooled to 345 ± 15 K in a flow of dry oxygen. The temperature was maintained at the same value for 10 h and at this point oxygen saturated at room temperature with water was introduced for a period of 8 h at the same temperature. The crystallinity was maintained and the unit cell parameter decreases smoothly and very slightly.

These experiments indicate that SAPO-37, free of template, is stable in the presence of water vapour at temperatures above *ca.* 345 K. At this point the unit-cell parameter decreases which may suggest a modification of bond angles and lengths associated with framework hydrolysis. Either aluminium or phosphorus could be extracted as in the dealumination process. The crystallinity in the presence of water vapour decreases only if the contact with water occurs at temperatures below 345 ± 15 K, which suggests that liquid water may be more efficient than vapour in modifying the framework. The extent of loss of crystallinity is the highest when the temperature at which contact with water occurs is lowest.

Under similar experimental conditions SAPO-5 is stable at any temperature in the presence of dry oxygen or of oxygen saturated with water vapour.

Comparison between SAPO-37 *and* SAPO-5.—Both SAPO-37 and SAPO-5 have a high thermal and hydrothermal stability at elevated temperatures, but SAPO-37 loses its stability upon water adsorption at temperatures below about 345 ± 15 K, where adsorbed water would behave as liquid water in the pores. Looking at the differences between SAPO-5 and SAPO-37 in resisting the action of water on TO bonds several hypotheses may be proposed. At first this may result from a different distribution of Si, Al, and P atoms in the framework. From the formulae the introduction of Si into SAPO-5 should result in a replacement of Si for (Al + P) or P alone[8] while in SAPO-37 only P should be replaced by Si.[2,8] The arrangement of PO_4 tetrahedra with regard to SiO_4 and AlO_4 is then very different. The existence of P–O–P bonds in SAPO-37 could explain low stability of the solid in the presence of water close to room temperature due to easy hydrolysis of phosphates.[9] Nevertheless, this seems unlikely due to the relative amount of Si, Al, and P in the framework[8] and to the fact that ^{31}P m.a.s. (m.a.s. = magic-angle spinning) n.m.r. spectroscopy shows only one environment for P atoms in our samples or, as reported previously, in other SAPO-37 samples.[2] Alternatively, a second hypothesis considers the TO bond lengths and angles which are different in the two SAPO structures. They are also different in SAPO-37 compared with faujasites with no phosphorus. Some constraints may occur in the SAPO-37 framework at room temperature in the presence of a high water level. First, this may induce, upon mild hydration, small changes in the framework characteristics, giving only a small decrease in unit-cell parameter. Secondly, at high water content and temperatures close to ambient the large decrease in unit cell parameters would be followed by breaking of TO bonds in the building units unable to sustain such strains.

Conclusions

The loss of hydrothermal stability of SAPO-37 at temperatures below 345 K as opposed to its high stability at elevated temperatures is quite unusual in the molecular sieve field. It is in contrast to the low thermal stability of low silica zeolites at increasing temperatures and to the ultrastabilization phenomenon upon steaming. A better understanding of SAPO-37 behaviour requires more information on the changes in framework bond lengths and bond angles upon water adsorption as well as a more detailed description of the topology of Si, Al, and P atom distribution.

References

1 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.*, 1984, **106**, 6092.
2 L. S. de Saldarriaga, C. Saldarriaga, and M. E. Davis, *J. Am. Chem. Soc.*, 1987, **109**, 2686.
3 G. C. Edwards, J. P. Gilson, and V. McDaniel, U.S.P. 4 681 864/1987.
4 (*a*) B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan, and E. M. Flanigen, U.S.P. 4 440 871/1984, p. 14, example 9; (*b*) *ibid.*, p. 49, example 43.
5 J. W. Richardson, jun., J. J. Pluth, and J. V. Smith, *Acta Crystallogr., Sect. C*, 1987, **43**, 1469.
6 C. A. Fyfe, G. J. Kennedy, C. T. Deschutter, and G. T. Kokotailo, *J. Chem. Soc., Chem. Commun.*, 1984, 541.
7 G. T. Kokotailo, C. A. Fyfe, G. C. Gobbi, G. J. Kennedy, C. T. Deschutter, R. S. Ozubko, and W. J. Murphy, *Stud. Surf. Sci. Catal.*, 1985, **24**, 219.
8 E. M. Flanigen, R. L. Patton, and S. T. Wilson, *Stud. Surf. Sci. Catal.*, 1988, **37**, 13.
9 R. K. Osterheld, *Top. Phosphorus Chem.*, 1972, 103.

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