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Changes upon heating of the distribution of Al, P and Si atoms in the SAPO-37 molecular sieve

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A drastic change in the environment of Si atoms in SAPO-37 after heating at 1173 K is seen in the ^{29}Si MAS NMR spectrum. This suggests a modification of the location of Si, Al and P atoms. Three main phases would coexist in large amounts in the faujasite structure, the SAPO-37 originating phase, pure SiO_4 islands and an aluminosilicate phase comparable to Si–Al faujasite.

Keywords: ^{29}Si NMR; SAPO-37; molecular sieve; framework atom distribution

1. Introduction

The synthesis of SAPO-37, an isotype of faujasite, gives rise to a framework of a majority of Si atoms surrounded by four Al atoms referred to as Si(4Al). This is the so-called isolated Si in an AlPO framework [1–6]. It was early shown that, in as-synthesized SAPOs, silicon-rich islands exist in the framework [4,7,8]. In the particular case of SAPO-37, these domains were described as consisting of either an aluminosilicate phase where Al atoms are present inside the Si-rich region [2–4] or as islands formed only of SiO_4 tetrahedra [4–6] referred to as Si islands. In both cases the border between, on the one side, the aluminosilicate phase or the Si islands and, on the other side, the SAPO-37 phase (i.e. that containing the isolated Si) generates specific environments [2–5]. The first neighbours for a Si atom may be Al or Si, referred to as Si(nAl) with $n \leqslant 3$. The second neighbours are Si or P, which can be written Si(nAl)(ySi, zP) with $y + z = 9$ in the faujasite crystalline structure. A detailed topological study of the possible distribution of Al, P and Si atoms at the border between the Si islands and the SAPO-37 phase shows, in agreement with ^{29}Si MAS NMR results, that the order of occurrence of the various Si environments is Si(3Al) > Si(0Al) >

Si(2Al) > Si(1Al). Each species has a specific ^{29}Si chemical shift, which differs from that in the Si–Al faujasite zeolite with the same number of Al atoms in the first tetrahedral ion coordination shell, the difference increasing as the number of Al increases [5]. Catalytic studies showed that the acidic [9,10] and cracking properties of SAPO-37 [10,11] increase as the pretreatment of the materials is carried out at higher temperatures, up to 1173 K. They decrease after heating at 1223 K. It is of interest to check if these pretreatments involve modifications of the distribution of the framework atoms.

2. Experimental

A SAPO-37 sample synthesized as in ref. [1] using tetramethylammonium (TMA) and tetrapropylammonium (TPA) hydroxides as templates has the framework formula $(Si_{0.14}Al_{0.48}P_{0.38})O_2$. The accuracy is ± 0.01 on atomic fractions. For the NMR experiments the samples are heated in flowing dry air at 873, 1073 or 1173 K for 8 h and then evacuated at the same temperature for 20 h. They are kept in sealed tubes and transferred to the NMR rotor under a flow of dry nitrogen.

^{29}Si MAS NMR was recorded at 79.5 MHz with a Bruker MSL 400 multinuclear high power pulsed spectrometer. The standard Bruker double bearing probe and a 7 mm external diameter ZrO_2 rotor were used. The ^{29}Si chemical shift is reported in ppm from external tetramethylsilane. The sign convention of high-frequency (low-field, paramagnetic, deshielded) shifts being positive is used. The acquisition parameters were: a $\pi/4$ pulse length of 2 μs was applied with a 5 s recycle delay and a rotor spinning rate of 4 kHz. 20000–30000 scans were acquired to obtain adequate signal to noise ratio. The spectrum was deconvoluted with the program GLINFIT.3004 using Gaussian line shapes.

3. Results and discussion

The sample has a composition very close to that of an ideal homogeneous SAPO-37 [1] where all the Si atoms are of the Si(4Al)(9P) type and which has the theoretical formula $(SiO_{0.125}Al_{0.50}P_{0.375}O_2)$. The difference in formula between the actual and the theoretical samples is explained on the basis of incorporation of Si in a hypothetical AlPO structure. If Si replace only P atoms (mechanism 2), the Al content is 0.5. In mechanism 3, the Al level decreases due to the replacement of Al by some Si atoms. This generates Si islands. The present results show that the material studied contains a small number of Si atoms incorporated according to mechanism 3. As a consequence, there should be a small amount of Si–Si pairs or Si islands. This is confirmed by the ^{29}Si MAS NMR spectra of the as-synthesized material. Curve a of fig. 1 shows,

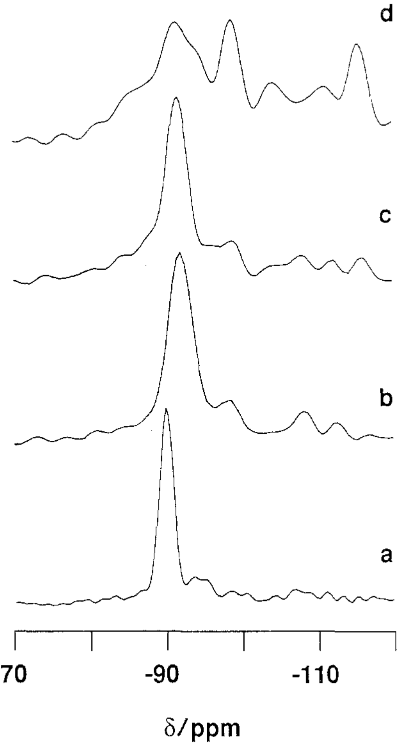

Fig. 1. ^{29}Si MAS NMR spectra of (a) as-synthesized SAPO-37, after heating at 873 K (b), 1073 K (c), 1173 K (d).

besides the narrow Si(4Al)(9P) peak at -89 ppm, very small peaks of Si(3Al) and Si(0Al) as previously observed in this composition range [5]. Like for other samples prepared in the same way, no peak at -84.9 ppm characteristic of Si(4Al) in an aluminosilicate faujasite phase [2–4] is observed. Table 1 lists the chemical shifts observed for the as-synthesized SAPO-37 material as taken from the present results and from ref. [5]. Curves b, c, d in fig. 1 give the spectra after heating at 873, 1073 and 1173 K respectively and table 1 reports the chemical shifts observed. The full removal of the template at 873 K (curve b) moves the peaks to more negative chemical shifts. Heating at 1073 K (curve c) allows for the detection of the Si(2Al) and Si(1Al) peaks attributed to the SAPO-37 phase. In addition, a shoulder near -84.7 ppm is observed. It may be assigned to the presence of an aluminosilicate phase as it can be seen from the chemical shifts usually observed for Si–Al faujasites [12] and reported in table 2. A deconvolution of the spectrum c of fig. 1 shows a peak at -89.2 ppm, which may be assigned to the Si(3Al) species in Si–Al faujasites. A comparison of the curves b and c of fig. 1 shows that the contribution of the peak Si(4Al)(9P) decreases from around 85–90% in the as-synthesized and 873 K samples to $\approx 40\%$ after the 1073 K pretreatment. The large Si(0Al) peak suggests that the size of the Si

Table 1
Chemical shifts (ppm) for SAPO-37 as-synthesized and after heating at T (K)

SAPO-37	Si(4Al)	Si(3Al)	Si(2Al)
as-synthesized	−89.1	−92.1 to −94.4	−98.0 to −98.4
873 K	−91.5	−97.8 to −98	nd [a]
1073 K	−91.2 to −91.7	−95.8 and −98.9	−102.7 to −103.6
1173 K	−91.3	(−95.5) [b] −98.6	(−104.1) [b]
	Si(1Al)	Si(0Al)	
as-synthesized	−101.8 to −103.0	−106.2 to −106.7	
873 K	nd	−107.6 to −108	
1073 K	−106.0	−107.0 to −108.2	
1173 K	nd	−107.7	

[a] Not detected.

[b] Alternatively partly assigned to Si–Al faujasite phase.

islands is increasing. It was shown [5] that the ratio of the occurrence of the species Si(3Al)/Si(0Al) increases as the size of the Si islands goes up. This is in line with the relative intensities of the corresponding peaks after the 873 and 1073 K pretreatments compared to the as-synthesized material.

A drastic modification of the ^{29}Si spectrum occurs after the heating at 1173 K (fig. 1, curve d). A large number of broad peaks is formed. A first attempt to deconvolute these peaks is presented in fig. 2. Peaks of Si(4Al) at −84.3 and Si(3Al) at −87.2 ppm characteristic of an aluminosilicate phase (table 2) are clearly shown. The Si(4Al)(9P) peak of the SAPO-37 phase at −91.2 ppm is greatly decreased. Peaks of Si(nAl) with $n \leqslant 3$ are located at different positions in SAPO-37 and in the aluminosilicate phase. The broadness of all the peaks in the range from −91 ppm to −108 ppm shows an overlapping of these ten possible peaks, which makes the deconvolution and the assignment difficult. The peaks originating from the deconvolution of the spectrum (fig. 2c) are tentatively assigned in tables 1 and 2 to a SAPO-37 or a Si–Al faujasite phase. Some uncertainties exist for the peaks at −95.5 and −104.1 ppm. Despite the low accuracy in the range from −92 to −104 ppm due to the large overlapping of

Table 2
Chemical shifts (ppm) of Si–Al faujasite from ref. [12] and after heating SAPO-37 at T (K)

Si–Al faujasite	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
ref. [12]	−84.7	−89.1	−94.0 to −95.7	−98.8 to −101.6	−103.0 to −107.8
873 K	nd [a]	nd	nd	nd	nd
1073 K	−84.7	−89.2	nd	nd	nd
1173 K	−84.3	−87.2	−93.9 (−95.5) [b]	nd	(−104.1) [b]

[a] Not detected.

[b] Alternatively partly assigned to the SAPO-37 phase (Si islands).

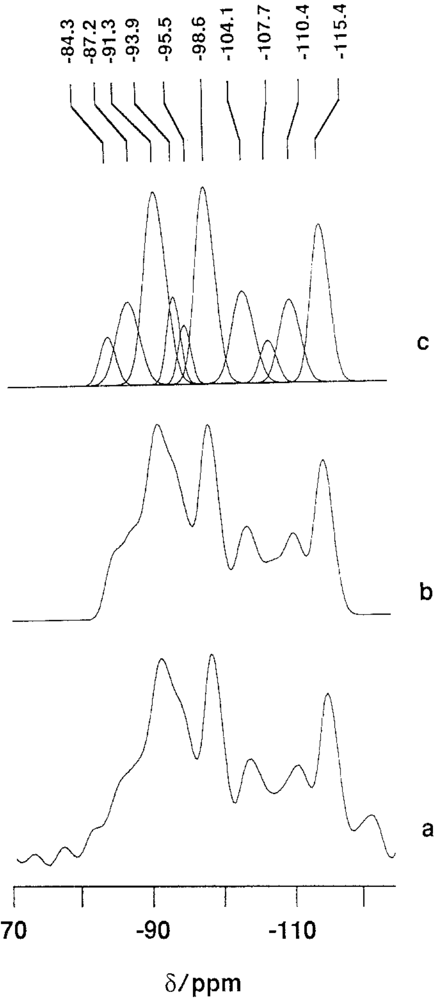

Fig. 2. ^{29}Si MAS NMR spectra of SAPO-37 after heating at 1173 K (a), simulated (b), deconvoluted (c).

peaks, the attempt to rationalize the ^{29}Si MAS NMR spectra of fig. 2 shows that very likely a Si–Al faujasite phase is formed at the expense of the isolated Si(4Al)(9P) species of the SAPO-37 phase. The peak at -115.4 ppm may be assigned to a silica polymorph structure [13] like, for instance, the tridymite one which is detected by XRD after heating at 1223 K [14]. The formation of this dense phase at this temperature explains the simultaneous drop of the catalytic activity and of the ammonia adsorption capacity [11]. Research in this field is in progress.

It was checked that no amorphisation of the material could be detected by XRD after the 1173 K pretreatment [15]. The ^{29}Si MAS NMR spectrum shows that a very large change in the distribution of Si and consequently of Al and P atoms occurs in this faujasite structure. The isolated Si atoms, Si(4Al)(9P), would move during a solid state transformation, involving a relocation of the Al and P atoms. This gives rise to an aluminosilicate phase coexisting with the SAPO-37 phase (isolated Si atom) and pure SiO_4 islands. The resulting materials consisting of intergrowing phases appear very stable since their XRD crystallinity is comparable to that of the as-synthesized sample [15]. It was shown that the crystallinity is lost after heating at 1223 K. Only the phase with a tridymite structure is seen [14].

In conclusion, the SAPO-37 materials are very stable thermally. Nevertheless at 1173 K a high mobility of framework atoms leads to their large redistribution. This may be important for the observed rise in cracking properties at this temperature [10,11].

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