Penta-co-ordinated Aluminium in Zeolites and Aluminosilicates

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Solid state ^{27}Al n.m.r. spectroscopy of various aluminosilicates (zeolites, clays, amorphous SiO_2–Al_2O_3) shows that upon thermal or hydrothermal treatment a line appears at ~30 p.p.m.; the position of this line suggests that penta-co-ordinated Al is present in all these aluminosilicates.

Since the introduction of magic angle spinning (m.a.s.) n.m.r. spectroscopy at high field (up to 14.0 T), much work has been done on the characterization of the state of Al in various aluminosilicates.[1] Most of this work has been devoted to the study of zeolites where during steam calcination, hydrolysis of framework (tetrahedral) Al leads to the formation of extra-framework (octahedral) Al.[2] ^{27}Al N.m.r. spectroscopy has proved to be a unique tool in the description of this 'stabilization' process.

Recently, ^{27}Al n.m.r. spectra of aluminates,[3] 'dehydrated' clays, and dense aluminosilicates[4] have shown that penta-co-ordinated Al gives rise to a resonance at approximately 35 p.p.m. In this communication we show that penta-co-ordinated Al can be generated in crystalline and amorphous aluminosilicates after a hydrothermal treatment (steaming).

We used a Brucker AM-400 n.m.r. spectrometer (^{27}Al frequency, 104.25 MHz). The samples, equilibrated with a 50% relative humidity atmosphere for 16 h, were spun at the magic angle at a frequency of 4.5 kHz. About 10 000 scans were accumulated before Fourier transformation. A line broadening of 50 Hz was used to eliminate the high frequency noise without affecting the peak widths. A 2 μs pulse (10 degree) was used with a repetition time of 0.1 s between pulses. Commercially available kaolin and laboratory prepared samples of co-gelled silica alumina, dealuminated faujasite, and ZSM-5 were used in this study.

Kaolin clays are known to undergo the transformation[5] shown in equation (1) upon calcination. The ^{27}Al n.m.r. spectra of kaolin (Natka from the Davison division of W. R. Grace & Co.) and metakaolin (product of calcination of the Natka kaolin at 700 °C for 3 h) show that, as expected, kaolin contains only octahedral Al (1.8 p.p.m.) while the *X*-ray amorphous metakaolin contains both octahedral (−0.3 p.p.m.) and tetrahedral (67.3 p.p.m.) Al as well as a third peak. The third peak appears at 31.2 p.p.m., very close to the position of the pentaco-ordinated Al reported for andalusite.[4] Moreover, the position of this 31.2 p.p.m. did not change with any increase (up to 6 khz) or decrease (down to 3 khz) of the m.a.s. frequency, ruling out the possibility of this peak being a spinning side band of the tetrahedral or octahedral Al peaks. Upon further heating of the metakaolin, this 31.2 p.p.m. resonance disappears when a spinel phase ($Si_3Al_4O_{12}$) and SiO_2 form at about 950 °C.

Table 1. ^{27}Al N.m.r. spectroscopy of steamed amorphous SiO_2–Al_2O_3.

Sample[a]	Steaming[b]	Relative intensities of Al peaks		
		T	P	O
A	None	~100	0	~0
B	4 h, 427 °C	52.6	9.3	38.1
C	4 h, 538 °C	50.5	17.3	32.2
D	4 h, 649 °C	54.0	18.5	27.5
E	1 h, 760 °C	49.9	19.7	30.4
F	4 h, 760 °C	53.7	26.9	19.4

[a] Starting amorphous SiO_2–Al_2O_3 has Si/Al 2.15, from chemical analysis. [b] 100% steam, total pressure 1 atm.

$$\underset{\text{Kaolin}}{Al_2Si_2O_5(OH)_4} \xrightarrow{550\text{—}600\,°C} \underset{\text{Metakaolin}}{Al_2Si_2O_7} + 2\,H_2O \qquad (1)$$

A peak around 30 p.p.m. also appears in the spectra of an amorphous SiO_2–Al_2O_3 gel, after steaming (Figure 1). This

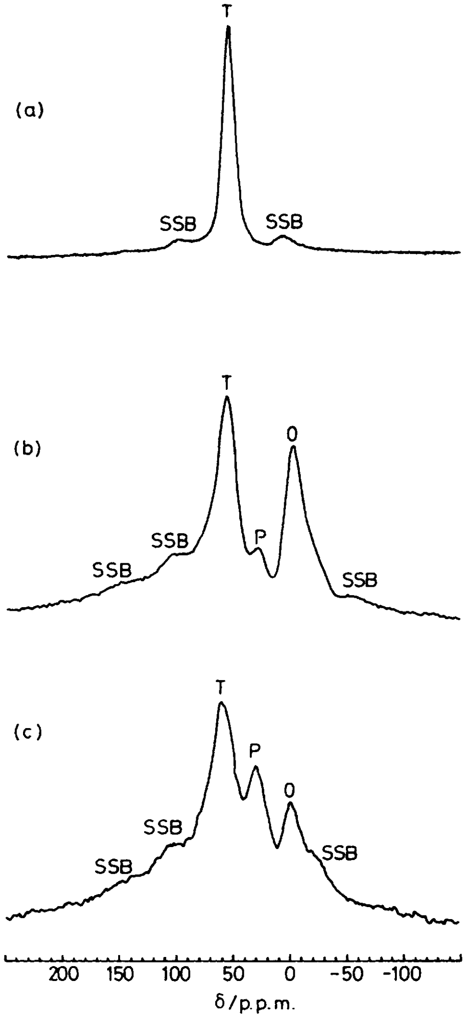

Figure 1. ^{27}Al N.m.r. spectra of steamed amorphous SiO_2–Al_2O_3. (a) Sample A [T (tetrahedral) 56.2, O (octahedral) + SSB (spinning side band) 8.5 p.p.m.]. (b) Sample B [T 57.9, P (penta-co-ordinated) 28.8, O −0.8 p.p.m.]. (c) Sample F(T 59.6, P 29.1, O −1.3 p.p.m.).

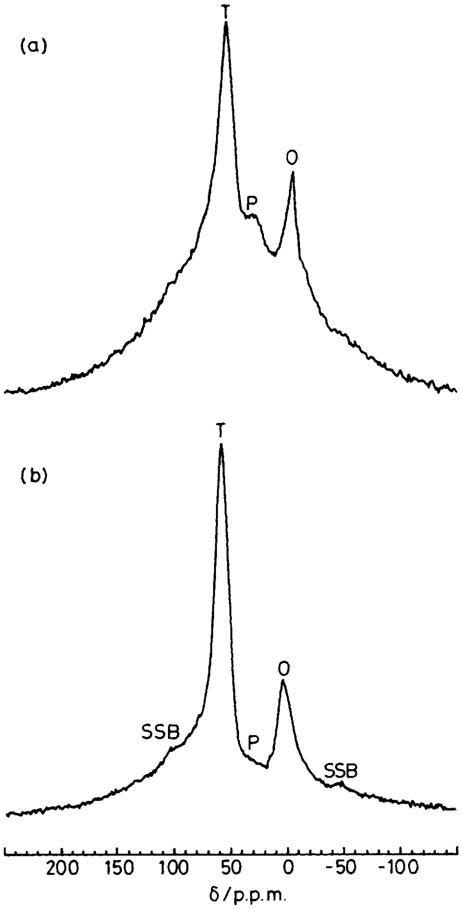

Figure 2. ^{27}Al N.m.r. spectra of hydrothermally dealuminated faujasite. (a) Faujasite with 8 Al per unit cell (T 61.0, P 33.9, O −0.4 p.p.m.). (b) Sample (a) washed with NaOH.

peak is apparently created at the expense of octahedral Al and its intensity is a function of the steaming severity (Table 1). The relative intensities reported in Table 1 are meant to indicate a qualitative trend however, in view of the problems outlined by Lippmaa *et al.*[4] when quantitative measurements are performed. The parent (unsteamed) sample did not show the 30 p.p.m. resonance. Again, the position of the line does not move upon changing the spinning frequency.

Highly dealuminated faujasite (8 Al per unit cell), produced by repeated steam calcinations (760 °C for 3 h with 100% steam) and NH_4^+ exchanges also shows a resonance at ~30 p.p.m. in addition to the well known tetrahedrally and octahedrally co-ordinated Al. This peak can be selectively removed by washing the zeolite with a 0.1 M NaOH solution at 25 °C as illustrated in Figure 2. The dealuminated zeolite sample studied in this communication is typical of the zeolites found in steam deactivated commercial FCC catalysts producing high octane gasoline. This 30 p.p.m. resonance is also present on other steamed zeolites, including such high Si/Al materials as ZSM-5. No such resonance appeared, however, on the various Al_2O_3 materials we studied.

Further work is being done to characterize better this new resonance and the exact conditions of its appearance and to correlate the presence of this penta-co-ordinated Al with the catalytic properties of the various aluminosilicates described in this report. Preliminary results indicate for instance that in the case of faujasite, the presence of penta-co-ordinated Al may reduce the extent of coke formation during hydrocarbon cracking reactions.

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