

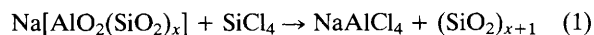
## Dealumination of Zeolite Y with SiCl<sub>4</sub>: a Two-Step Reaction

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Evidence is presented that the dealumination of zeolite Y with SiCl<sub>4</sub> occurs in two distinguishable reaction steps; in the first step, lattice-attached 'SiCl<sub>3</sub>' species and the chloride salt of the charge compensating cation are formed, followed secondly by the isomorphous substitution of Al for Si and the subsequent formation of chloro-aluminium complexes.

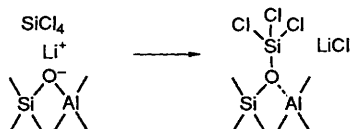
Dealumination of zeolite Y with SiCl<sub>4</sub> was first reported by Beyer and Belenykaja.<sup>1</sup> Zeolite Y samples with a wide variety of Si/Al ratios have been obtained using the SiCl<sub>4</sub> method.<sup>1-7</sup> The stoichiometry of the dealumination reaction of NaY zeolite with SiCl<sub>4</sub> corresponds to eqn. 1.<sup>1</sup>



It is highly improbable that this reaction occurs in one step, given the multiplicity of chemical bonds to be broken and formed. A temporary exothermicity is observed during the first contact of the zeolite with SiCl<sub>4</sub> at moderate reaction temperatures (e.g. 520 K).<sup>1,3,7</sup> Deeply dealuminated materials with high crystallinity are obtained when the reaction temperature is further increased once the initial exothermicity of the process has disappeared.<sup>1,3,7</sup> Evidence from <sup>29</sup>Si MAS NMR is now provided showing that the exothermicity is due to a first reaction step, in which framework-bound 'SiCl<sub>3</sub>' species and the chloride salt of the charge compensating cations are formed.

NaY zeolite with a Si/Al ratio of 2.4 was ion exchanged for 68% with Li<sup>+</sup>. The zeolite powder was compressed and crushed into 0.3–0.5 mm particles. A tubular reactor containing a bed of 30 × 15 mm of these particles was heated at 623 K in a stream of dry nitrogen for 16 h to dehydrate the zeolite completely. At 423 K, this bed was connected with a flow of nitrogen gas containing 250 hPa of SiCl<sub>4</sub> vapour. The WHSV of SiCl<sub>4</sub> was 1.7 h<sup>-1</sup>. The temperature rise in the zeolite bed was approximately 20 K due to the exothermicity of the reaction. After a reaction time of 35 min the temperature rise was over. The zeolite was flushed with nitrogen and a <sup>29</sup>Si MAS NMR spectrum recorded (Fig. 1a); chemical shifts ranging from -80 to -110 ppm and at ca. -45 ppm were observed. The first signal represents the silicon of the zeolite framework. The different Si(*n*Al) lines are not resolved due to the dehydrated state of the sample. The -45 ppm signal cannot result from adsorbed SiCl<sub>4</sub>, since it was verified that the chemical shift of <sup>29</sup>Si in liquid SiCl<sub>4</sub> is -20 ppm. The chemical shift of -45 ppm suggests the formation of a SiCl<sub>x</sub>O<sub>4-x</sub> species. Therefore, the first step in the dealumination process most probably corresponds to the rupture of one Si-Cl bond in SiCl<sub>4</sub> and formation of a Si-O bond and a chloride salt of the charge compensating cation (Scheme 1).

This hypothesis is supported by the <sup>27</sup>Al MAS NMR spectra shown in Fig. 2. A single <sup>27</sup>Al resonance is observed at 55 ppm indicating that all the aluminium remains in the zeolite lattice.



Scheme 1

The sample was then hydrated in order for the Si/Al ratio to be determined with <sup>29</sup>Si MAS NMR (Fig. 1b); the Si/Al ratio calculated from the intensity of the individual Si(*n*Al) signals is 3.0. The low degree of dealumination with respect to the starting material (Si/Al ratio of 2.4) can be merely due to the strong acidity generated during the hydrolysis of the SiCl<sub>3</sub> species. It confirms that the isomorphous substitution of Si for Al does not take place at the low reaction temperature applied.

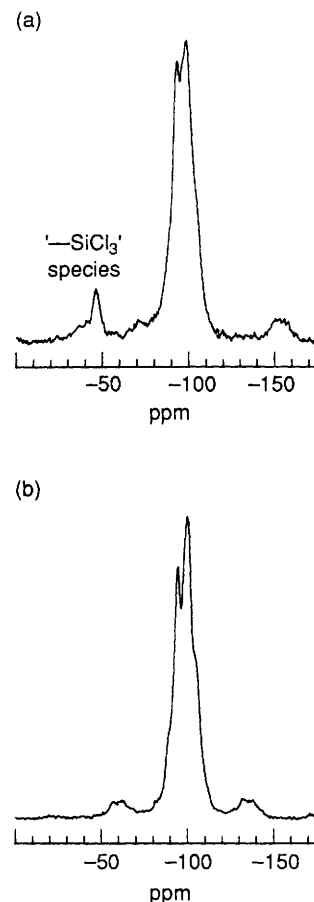


Fig. 1 <sup>29</sup>Si MAS NMR spectra of LiY, contacted with SiCl<sub>4</sub> at a temperature of 423 K before hydration (a) and after hydration in the open atmosphere (b)†

† <sup>29</sup>Si MAS NMR spectra were run at 79.5 MHz, using a pulse angle of 45°, a pulse length of 4 μs, a pulse interval of 5 s, a spinning rate of 4 kHz, and 8000 scans. The chemical shift is relative to tetramethylsilane.

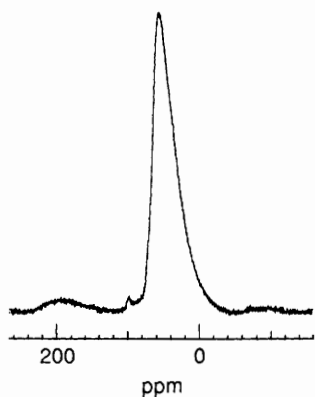


Fig. 2  $^{27}\text{Al}$  MAS NMR spectrum of LiY, contacted with  $\text{SiCl}_4$  at a temperature of 423 K before hydration $\ddagger$

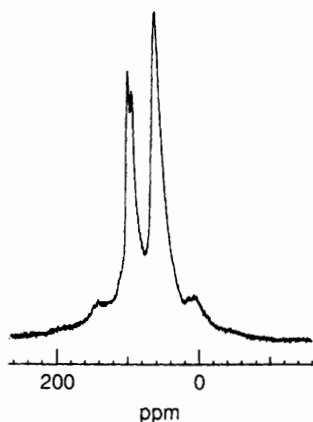
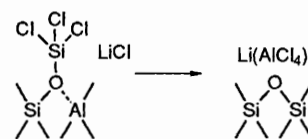


Fig. 3  $^{27}\text{Al}$  MAS NMR spectrum of LiY, contacted with  $\text{SiCl}_4$  at 523 K, and calcined in nitrogen at 623 K (the spinning rate was 5 kHz)

$\ddagger$   $^{27}\text{Al}$  MAS NMR experiments were run at 104.2 MHz, using a pulse angle of  $20^\circ$ , a pulse length of 0.6  $\mu\text{s}$ , a pulse interval of 0.1 s, a spinning rate of 15 kHz, and 3000 scans. The chemical shift is relative to a 1 M  $\text{AlCl}_3$  solution.



Scheme 2

Chloro-aluminium complexes with a characteristic  $^{27}\text{Al}$  MAS NMR signal at ca. 100 ppm $^4$  appear when, after the contact with  $\text{SiCl}_4$ , the sample is calcined in flowing nitrogen at a temperature of 623 K (Fig. 3). At high temperatures the aluminium-silicon exchange takes place with concomitant formation of chloro-aluminium complexes (Scheme 2). The Si/Al ratio of the calcined sample, determined with  $^{29}\text{Si}$  MAS NMR was now 6.0.

A similar two-step reaction was also observed for NaY, treated in the same way. The two-step dealumination of zeolite Y with  $\text{SiCl}_4$  opens perspectives to a better control on the generation of mesopores and of extra-framework aluminium species.

J. A. M. and P. J. G. acknowledge the Flemish National Fund for Scientific Research for fellowships as a Research Associate and Senior Research Associate, respectively. This work has been sponsored by the Belgian Government in the context of a concerted action on catalysis.

Received, 26th June 1990; Com. 0/02885A

## References

- 1 H. K. Beyer and I. M. Belenykaja, in *Catalysis by Zeolites*, ed. B. Imelik, C. Naccache, Y. Ben Taarit, J. Vadrine, G. Coudurier and H. Prialiaud, *Stud. Surf. Sci. Catal.*, 1980, **5**, 203.
- 2 J. Klinowski, J. M. Thomas, C. A. Fyfe, G. C. Gobbi and J. S. Hartman, *Inorg. Chem.*, 1983, **22**, 63.
- 3 H. K. Beyer, I. M. Belenykaja, F. Hange, M. Tielen, P. J. Grobet and P. A. Jacobs, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2889.
- 4 M. W. Anderson and J. Klinowski, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 1449.
- 5 J. R. Sohn, S. J. DeCanio, P. O. Fritz and J. Lunsford, *J. Phys. Chem.*, 1986, **90**, 4847.
- 6 B. Sulikowski, G. Borbely, H. K. Beyer, H. G. Karge and I. W. Mishin, *J. Phys. Chem.*, 1989, **93**, 3240.
- 7 B. Sulikowski and J. Klinowski, *J. Chem. Soc., Faraday Trans. 1*, 1990, **86**, 199.