Dealumination of zeolite L with $SiCl_4$: influence of ion exchange

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The dealumination of zeolite L with $SiCl_4$ is made feasible through its exchange into the sodium form; a higher degree of framework dealumination than previously reported, for any dealumination method, is achieved.

L is a synthetic zeolite with typical composition $K_6Na_3Al_9Si_{27}O_{72}{\cdot}21\ H_2O$ and is synthesized under conditions similar to those of zeolite Y, but requiring the presence of large amounts of potassium cations. Its framework delineates twelve-membered oxygen rings, building the parallel unidimensional channels with diameter of 7.1 Å characteristic of this zeolite.[1] As a support of platinum clusters it has proven to be an outstanding catalyst for the aromatization of alkanes and the photochemical production of hydrogen from water.[2]

The SiO_2/Al_2O_3 molar ratio strongly affects a zeolite's physico-chemical and catalytic properties; therefore dealumination methods have been developed, especially for zeolite Y and mordenite. Dealuminated USY zeolites form the basis of most fluid cracking catalysts.[3] By contrast, zeolite L has not been satisfactorily dealuminated through the usual methods; L is unstable in the acid form as is its ammonium form when calcined. While a patent has been claimed for the dealumination of L through steaming, no sufficient evidence was given that the zeolite retained its crystallinity.[4] Treatment with $(NH_4)_2SiF_6$ is effective only to a limited extent.[5]

Dealumination of zeolites through contact with $SiCl_4$ vapour at high temperatures was first reported by Beyer *et al.* and has been intensively studied, especially for obtaining highly microporous dealuminated Y zeolites, and it has also been applied for mordenite and zeolite beta. But, according to these workers, zeolite L could not be dealuminated with $SiCl_4$, and apparently no further reports have been published.[6]

We report here that zeolite L can actually be dealuminated with $SiCl_4$, provided it has been previously ion exchanged into the sodium form. Under the same conditions the potassium form can be dealuminated only slightly.

KL zeolite samples were provided by Bayer AG (KL-B) and the Tosoh Corporation (KL-T). Their sodium forms, NaL-B and NaL-T respectively, were obtained through ion exchange three times with a 2 mol dm^{-3} NaCl solution, overnight at 373 K. X-Ray fluorescence showed that 36% of the original potassium cations were exchanged by sodium; this corresponds to the percentage of cations located on the channel walls, or D positions, that can be easily exchanged;[1b] most of the remaining potassium cations are surrounded by framework atoms, and can be removed only with great difficulty which may lead to structural damage.[1] For the dealumination the samples were dried for 2 h at 623 K under a nitrogen flow; the system was then cooled to 423 K and the nitrogen stream was saturated with $SiCl_4$ at room temperature. The reactor was then heated at 10 K min^{-1} to the preset reaction temperature. After the desired reaction time, the flow was switched back to pure nitrogen, and after 30 min the reactor was allowed to cool.

Runs with samples KL-B and NaL-B were carried out to compare the dealumination degree of the two cation forms under several conditions (Table 1). The dealumination of the zeolite framework is demonstrated by a shifting of the IR lattice bands to higher wavenumbers, especially that of the external symmetric stretch. The strong intensity of the double-ring vibration band provides evidence for retention of crystallinity.[4a,5a]

It can be seen that ion exchange alone had no effect on the IR spectra. For both cation forms the symmetric stretch and the double-ring vibration were shifted to higher wavenumbers with increasing reaction time and/or temperature, but the NaL-B sample could be dealuminated to a higher degree than KL-B under the same conditions. In the potassium form, to attain a symmetric stretch wavenumber of 780 cm^{-1} required a temperature of 873 K, which also resulted in damage of the structure, as shown by the weak intensity of the double-ring vibration (sample 4). By contrast, in the sodium form the zeolite could be dealuminated to a larger extent at 823 K, as can be seen from the symmetric stretching band at 786 cm^{-1}, without a pronounced loss in crystallinity (sample 7). This temperature was selected for runs carried out with the samples KL-T and NaL-T, which displayed a slightly higher starting SiO_2/Al_2O_3 ratio and X-ray crystallinity than the Bayer samples. Again the sodium form is clearly easier to dealuminate than the potassium form. This is probably due to the sodium cations being smaller, leaving a wider free pore channel within which the $SiCl_4$ molecules can diffuse more easily.[1a]

After exposure to $SiCl_4$ vapour at 823 K for 14 h a shift of the symmetric stretch to 799 cm^{-1} was observed (sample 13). The lattice vibration region of the IR spectrum of this sample is shown in Fig. 1. X-Ray powder diffractometry (Fig. 2) provided further evidence that the sample remained essentially crystalline. ^{29}Si MAS NMR spectroscopy (Fig. 3) confirms that sample 13 has a higher framework SiO_2/Al_2O_3 ratio than the original zeolite. Through the $SiCl_4$ treatment the peak at δ −107 [Si(0Al)] increased drastically while the peak at δ −97 [Si(2Al)] was reduced to be present as only a shoulder of the

Table 1 IR spectroscopy analysis of dealuminated zeolite L samples

Sample	Parent sample	Dealumination conditions		Lattice-band wavenumbers/cm^{-1}	
		t/h	T/K	s.s.[a]	d.r.[b]
KL-B	—	—	—	767	608s
1	KL-B	2	723	771	609s
2	KL-B	2	773	776	610s
3	KL-B	3	823	779	610s
4	KL-B	2	873	*ca.* 780	*ca.* 613w
NaL-B	KL-B	—	—	767	608s
5	NaL-B	2	723	775	610s
6	NaL-B	2	773	781	612s
7	NaL-B	3	823	786	613s
KL-T	—	—	—	771	610s
8	KL-T	3	823	777	611s
NaL-T	KL-T	—	—	771	610s
9	NaL-T	1.5	823	777	611s
10	NaL-T	3	823	785	613s
11	NaL-T	5	823	794	613s
12	NaL-T	7	823	795	615s
13	NaL-T	14	823	799	616s

[a] s.s. = External symmetric stretch. [b] d.r. = Double ring vibration; s = strong, w = weak.

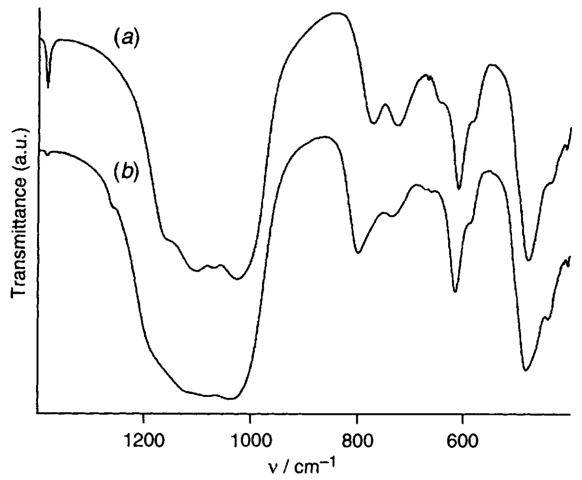

Fig. 1 IR spectra of samples KL-T (*a*) and 13 (*b*)

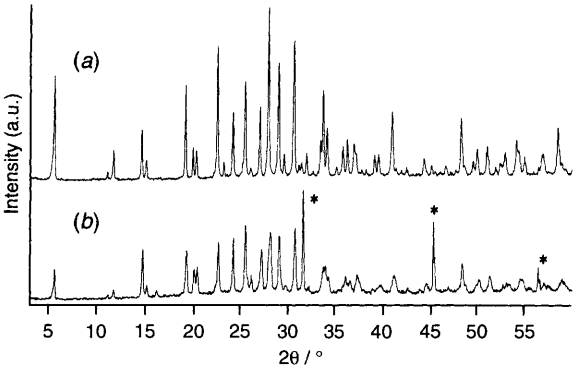

Fig. 2 X-Ray powder patterns of samples KL-T (*a*) and 13 (*b*); * indicates the presence of NaCl

signal at δ −102 [Si(1Al)].[7] Although the effect of dealumination is clear, a quantitative evaluation, which requires an exact measurement of the NMR peak areas,[8] is not possible due to the presence of amorphous SiO_2, as can also be seen from a broad signal centred at 2θ *ca.* 24° in the X-ray powder pattern in Fig. 2(*b*). However, the value of 782 cm^{-1} is the highest wavenumber for the symmetric stretch which has been reported for dealuminated zeolite L.[5a] This was achieved through treatment with $(NH_4)_2SiF_6$ and was claimed to corrrespond to a SiO_2/Al_2O_3 ratio of *ca.* 12. Therefore we assume that samples 7 and 10–13 have framework ratios higher than this value.

In conclusion, we have demonstrated the feasibility of dealuminating zeolite L with $SiCl_4$ after exchanging the original potassium form into the sodium form. Higher degrees of dealumination than previously reported, using this or other methods, can be achieved, and the dealuminated L zeolites remain essentially crystalline.

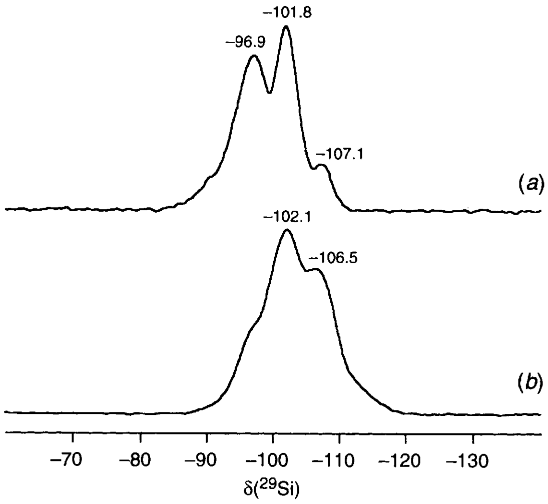

Fig. 3 ^{29}Si MAS NMR spectra of samples KL-T (*a*) and 13 (*b*)

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