A Second-derivative IR Study of Zeolite Y in the Asymmetric Stretching Region of Framework Vibration

Xinsheng Liu, Zhihong Zhang, Yuhua Xu, and Ruren Xu

Synthetic and Catalytic Chemistry Institute of Jilin University, Changchun, The People's Republic of China

Deconvolution of the framework asymmetric stretching vibration band of NaY zeolite using a second-derivative technique shows that the band envelope is made up of seven major components, and dealumination using ethylenediaminetetra-acetic acid (EDTA) and realumination using an aqueous solution of $NaAlO_2$ demonstrate that the component at ~980 cm^{-1} is the most sensitive band for the removal and reinsertion of aluminium in the framework.

The fine tuning of Si and Al siting in zeolite frameworks is of great fundamental and practical importance. Dealumination and realumination processes fulfil this requirement. Various methods such as extraction of Al with ethylenediaminetetra-acetic acid (EDTA), acid-leaching, water vapour steaming, treatment with reagents such as $SiCl_4$, $(NH_4)_2SiF_6$, and phosgene,[1—5] have been used to dealuminate zeolite Y and increase its framework Si/Al ratio. The reverse process, for decreasing the Si/Al ratio, has also been performed by treating the dealuminated zeolite Y with a solution of either KOH[6] or $NaAlO_2$.[7]

Framework asymmetric stretching vibration bands in the region of 1300—900 cm^{-1}[8] are quite sensitive to the Si/Al ratio. Dealumination of zeolite Y leads to a shift of the bands towards higher frequency; the reverse is true for the realumination.

Here we report deconvolution of the asymmetric stretching vibration bands using a second-derivative technique for a series of NaY zeolites having different Si/Al ratios which were obtained *via* direct hydrothermal synthesis, dealumination, and realumination. It is demonstrated that the asymmetric stretching band is made up of a number of components. The relative intensities (not exactly in the second-derivative sense) of the components for the direct hydrothermally synthesized NaY zeolites with different Si/Al ratios are shown to be sensitive to the framework Si/Al ratio. Framework dealumination using EDTA leads to a decrease in the relative intensity of the band at about 980 cm^{-1} and a shift of all other components towards higher frequency. Realumination of the dealuminated NaY zeolite *via* $NaAlO_2$ solution is shown to lead to recovery of the intensity of the band.

NaY zeolites with different Si/Al ratios were prepared according to Breck[9] with modification of the Si/Al ratios in the starting gel. Dealumination with EDTA followed Kerr's method[1] and realumination of the dealuminated NaY zeolite with $NaAlO_2$ was as described in the literature.[7] The IR spectra were recorded on a Nicolet 5DX Fourier transform instrument. Deconvolution was performed following the literature guidelines.[10,11]† The Si/Al ratio of the samples studied is given in Table 1. All the samples were in the Na^+ form.

---

† The software was written by one of the authors, Yuhua Xu.

Table 1. Si/Al ratios of the samples used in this study, and wavenumbers of the components of the asymmetric stretching vibration band of the zeolites Y.

Sample	Si/Al	Wavenumber $\bar{\nu}$/cm^{-1}						
NaY-I	1.72	1142		1075		1017	1000(sh)	977
NaY-II	2.50	1148		1090		1030	1001(sh)	982
Dealuminated Y (DY)	3.06	1149		1074		1044		
Realuminated DY (RY)	2.62	1152	1118	1093	1040	1025	1006	984

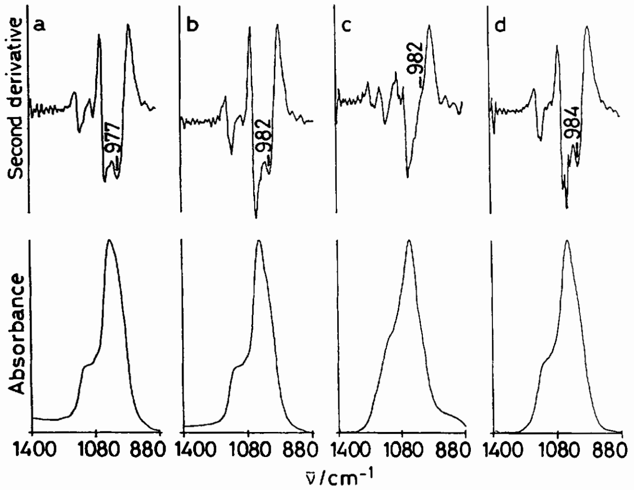

Figure 1. FTIR absorption spectra and second-derivative FTIR spectra of zeolites Y: (a) NaY-I, (b) NaY-II, (c) DY, (d) RY.

Figure 1 shows the deconvoluted asymmetric stretching band and the absorption band for the samples in Table 1. The increased resolution of the deconvoluted spectrum of the NaY zeolite clearly indicates that the asymmetric stretching vibration band is composed of at least five subcomponents for the NaY zeolite of Si/Al = 2.40 (Figure 1b), with values of 1148, 1090, 1030, 1001sh, and 982 cm^{-1}, respectively. The deconvoluted spectrum of the NaY zeolite of Si/Al = 1.72 shows similar spectral features but with an increase in the relative intensity of the 982 cm^{-1} band and a slight shift of the frequencies of all the components towards lower frequency (Figure 1a). This indicates the effects of the framework aluminium content on the framework vibrations. The increase in the relative intensity of the component at 982 cm^{-1} on decreasing the Si/Al ratio from 2.40 to 1.72 suggests that this component can be assigned to O–Al–O linkages. The other components which show frequency shifts on decreasing the Si/Al ratio are assigned to O–Si–O linkages.

Dealumination (Figure 1c) leads to a significant decrease in the relative intensity of the component at ~980 cm^{-1} and shifts in other components towards higher frequencies. Realumination of the dealuminated sample (Figure 1d) leads to nearly complete recovery of the components and gives better spectral resolution. The spectrum in Figure 1d shows seven major components at 1152, 1118, 1093, 1040, 1025, 1006, and 984 cm^{-1}, respectively. Table 1 summarises the frequencies of the components of all the samples. The results obtained from both dealumination and realumination prove that the assignment of the components for the isolated O–T–O (T = Si, Al) linkages are correct. The present study therefore sheds new light on the understanding of the shifts of the asymmetric stretching vibration upon dealumination. The shifts of the asymmetric stretching bands upon dealumination are caused by the decrease in the relative intensity of the band for the O–Al–O linkage and the shifts of the frequencies of the bands for the O–Si–O linkages.

In conclusion, the IR band of framework stretching vibration is shown to be made up of seven components. The component at 980 cm^{-1} is assigned to be due to the O–Al–O linkages and the other components are assigned to be due to the O–Si–O linkages. Dealumination using EDTA and realumination of the dealuminated sample *via* $NaAlO_2$ reversibly change the relative intensity of the component at about 980 cm^{-1} and the positions of the other components. The shift of the asymmetric stretching vibration bands observed previously is caused by the decrease in the relative intensity of the band for the O–Al–O linkage and the shift of the frequencies of the bands for the O–Si–O linkages.

We thank National Natural Science Foundation of China for financial support.

Received, 9th August 1989; Com. 9/03399H

References

1 G. T. Kerr, *J. Phys. Chem.*, 1968, **72**, 2594.
2 C. V. McDaniel and P. K. Maher, in 'Molecular Sieves,' ed. R. M. Barrer, Soc. Chem. Ind., London, 1968, p. 186.
3 H. K. Beyer and I. M. Belenykaja, in 'Catalysis by Zeolites,' eds. B. Imelik, C. Naccache, Y. Ben Taarit, J. C. Vedrine, G. Coudurier, and H. Praliaud, Elsevier, Amsterdam, 1980, p. 203.
4 G. W. Skeel and D. W. Breck, in 'Proc. 5th Intl. Conf. Zeolites,' ed. L. V. C. Rees, Heyden, London, 1980, p. 87.
5 Pal Fejes, I. Hannus, and I. Kiricsi, *Zeolites*, 1984, **4**, 73.
6 X. Liu, J. Klinowski, and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1986, 582.
7 X. Liu, Ph.D. Thesis, University of Cambridge, England, 1986.
8 E. M. Flanigen, in 'Zeolite Chemistry and Catalysis,' ed. J. A. Rabo, ACS Monograph 171, ACS Washington, DC, 1976.
9 D. W. Breck, in 'Zeolite Molecular Sieves: Structure, Chemistry and Use,' Wiley, New York, 1974.
10 Y. Xu and R. Xu, *Acta Petrolei Sinica* (*Petroleum Processing Section*), 1985, **2**, 49.
11 J. K. Kauppinen, D. J. Moffatt, H. H. Mantsch, and D. G. Cameron, *Anal. Chem.*, 1981, **53**, 1454.