An Empiric Linear Formula between the Internal Tetrahedron Symmetric Stretch Frequency and the Al Content in the Framework of KL Molecular Sieves

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Abstract: KL molecular sieves with different framework compositions were secondarily synthesized by substituting Si for Al with a solution of $(NH_4)_2SiF_6$. The internal tetrahedron symmetric stretch frequency, at ~770 cm^{-1}, is linear with the molar fraction of Al (X_{Al}= Al/(Si+Al)) in the framework of KL samples: $X_{Al} = -7.309 \times 10^{-3} (\upsilon_{770}\text{-}760) + 0.3242$.

Keywords: KL molecular sieve, infrared spectroscopy, linearity, framework composition.

Since 1960's zeolite molecular sieves materials have been widely used in catalysis, adsorption, separation, host-guest chemistry and supramolecular science. During the research and application, the framework compositions of zeolite molecular sieves materials usually have to be determined, especially when the framework compositions are modified. Based on X-ray diffraction (XRD) peak positions and infrared (IR) spectroscopy frequencies, some empiric linear relationships have been reported to determine the framework compositions of zeolite molecular sieves like A, X, Y, as well as tectosilicate minerals, layer lattice silicates[1-9], and so on. However, except the framework compositions of cubic-type molecular sieves samples like A, X, Y have been widely determined according to their X-ray diffraction peak positions, the framework compositions of most zeolite molecular sieves usually have to be determined by routine chemical analysis that is time-wasting. Therefore, it is useful to find the relationship between framework composition and spectra XRD and IR of samples. Here we report an empiric linear formula between the internal tetrahedron symmetric stretch frequency at ~770 cm^{-1} and the Al content in framework of KL molecular sieves.

Typical procedure

The secondarily synthesized KL samples possess different X_{Al} (*i.e.*, Al/(Si+Al)) ratios.

Their framework molar compositions were adjusted by modifying parent KL sample (Si/Al=2.9) with $(NH_4)_2SiF_6$ solution as described previously[10-11], in which the depleted Al atoms were substituted by Si atoms, and were determined by conventional chemical analysis. X-ray powder diffraction patterns were taken with a Rigaku D/max-γA instrument. IR spectra were recorded on Nicolet 510P FT-IR instrument.

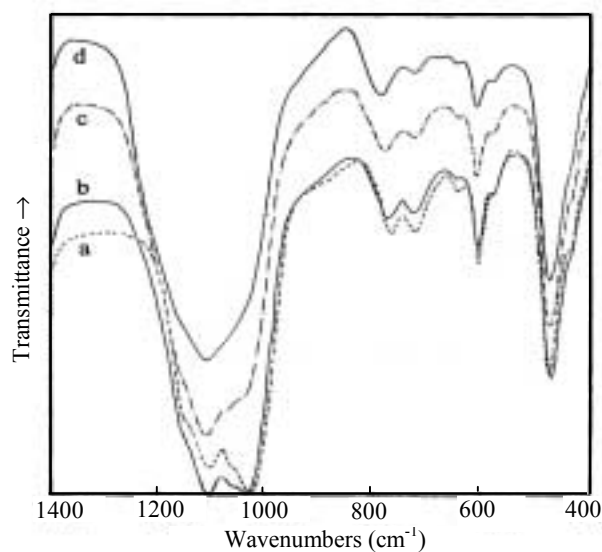## Results and Discussions

Figure 1   XRD patterns of samples.
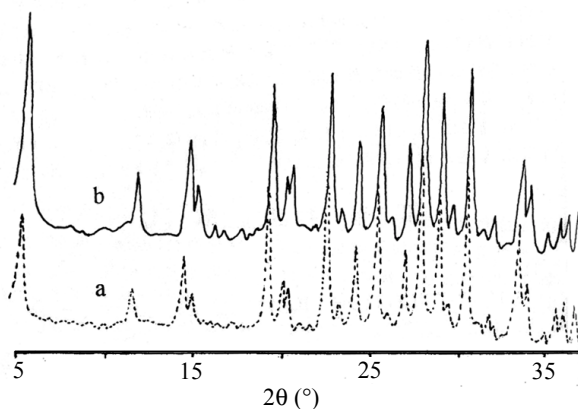
a) parent KL (Si/Al=2.90), b) modified KL sample.(Si/Al=3.94).

Figure 2   FT-IR spectra of samples.

a) parent KL, c-d) modified KL samples. Si/Al: a) 2.90, b) 3.94, c) 4.98, d) 7.37.

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Table 1 Molar compositions and frequencies of framework IR spectra for samples.

Sample	Si/Al (mole)	X_{Al} (mole)	Relative crystallinity	Frequency (cm^{-1})		
				Asymmetric	Symmetric	T-O bend
1	2.75	0.267	101	1024.33	767.77 725.33	476.48
2	2.90	0.257	100	1028.19	768.71 727.26	476.48
3	2.95	0.254	105	1027.23	769.70 726.29	478.41
4	3.41	0.227	97	1030.21	773.01 727.45	478.41
5	3.94	0.203	105	1034.46	776.45 729.67	477.44
6	4.98	0.167	99	1035.40	782.23 726.11	477.44
7	6.14	0.140	88	indiscernible	785.12 730.19	478.83
8	7.37	0.119	99	indiscernible	788.02 729.19	476.46

XRD patterns (**Figure 1**) showed that the obtained KL sample remained a good crystallinity. The good retention of the crystallinity after the modification is also demonstrated by the relative crystallinities listed in **Table 1**. A shift of the XRD peaks towards higher 2θ degree direction was ascribed the substitution of the longer Al-O bond by the shorter Si-O bond[1, 2], but no linearity between the shift and X_{Al} was gained after systematic studies.

Figure 2 shows the framework vibration FT-IR spectra for parent KL (a) and modified KL samples (c-d). According to the first class of vibrations common to all zeolites molecular sieves[2], the two most intensive band at ~1025 cm^{-1} and 420-500 cm^{-1} were assigned to the internal tetrahedron stretch vibrations. The strongest at ~1025 cm^{-1} was assigned to an asymmetric stretching vibration and the band in the region of 420-500 cm^{-1} was assigned to a T-O bending vibration mode. From the data listed in **Table 1** it was clearly found that the frequency for 420-500 cm^{-1} changed little when the Si/Al ratio was increased. On the contrary, the frequency for band at ~1025 cm^{-1} increased with the increase in Si/Al ratio. A quantitative linear relationship between the main asymmetric stretch frequency (1000-1100 cm^{-1}) and atom fraction of Al in the tetrahedral site was

Figure 3 Frequency of the internal tetrahedron symmetric band at ~770 cm^{-1} *vs.* the atom fraction of Al (X_{Al}) in the framework for KL zeolite molecular sieves samples.
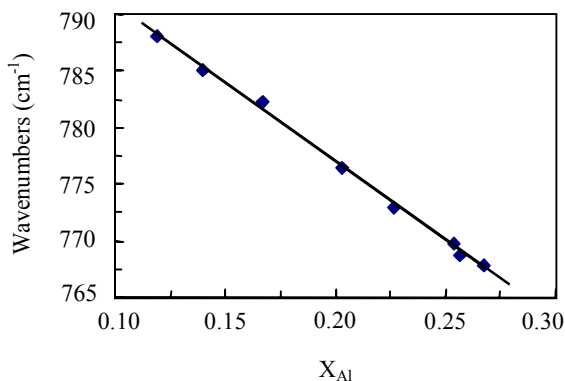
linear relationship between Si-O stretch bands and tetrahedral Al substitution in layer reported for a large number of tectosilicate minerals[3]. Stubican and Roy also reported a lattice silicates[4-6]. A linear relationship of decrease in frequency with increase in fraction of Al in the framework was found for the synthetic zeolites X and Y, both with a faujasite-type framework, and for the type A zeolite phases[3, 7-9]. The vibration frequency increases with the increase of Si concentration results not only from the shorter bond length of Si-O but also from the increased electronegativity of Si, which induces an increase in force constant[3-6]. However, for the KL samples investigated here, we can clearly observe that the definite position for band at $\sim$1025 cm^{-1} becomes more and more indiscernible, while the bands frequencies at $\sim$725 cm^{-1} (see **Figure 2** and **Table 1**) and 1100 cm^{-1} (see **Figure 2**) changed only a little, so they are not suitable to relate them to framework composition quantificationally.

Interestingly, on the contrary, the frequency for the internal tetrahedron symmetric band at $\sim$770 cm^{-1} increased significantly with the increase of Si/Al ratio and the frequency maximum position can always be determined. We plotted the frequency maximum of this band against the atom fraction of Al (X_{Al}) in the framework tetrahedral site as shown in **Figure 3**. There is a linear relationship between the frequency and X_{Al}. An empiric linear formula between the frequency and X_{Al} was drawn as (R^2=0.9982):

$$X_{Al} = -7.309 \times 10^{-3} (\upsilon_{770} - 760) + 0.3242$$

This linear relationship was verified by a series KL samples whose composition were carefully determined by conventional chemical analysis in our investigation.

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