The Influence of the Exchangeable Monovalent Cations on Vibrations of Y Zeolite Framework

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The influence of the exchangeable monovalent cations on the vibrations of the framework of Y zeolite has been studied. A regular shift of the frequencies of some absorption bands is observed and described as a function of interaction between the exchangeable cation and the oxygen from the zeolite framework. The linear dependence of the frequencies of some absorption bands and the reciprocal of the sum of ionic radii of the cation and the framework oxygen suggests that the exchanged cations: Na+, Ag+, K+ and Tl+ are occupying similar positions in the zeolite lattice. Li+ and Cs+ ions do not obey this regularity. The present IR studies agree with the results of chemical analysis of the studied zeolites.

Introduction

The fundamental vibrations of $\text{TO}_4$ ($T = \text{Al}, \text{Si}$) tetrahedra appear in the mid-infrared region from 200–1200 cm$^{-1}$, which therefore provide informations on the structure of zeolite frameworks. Mid-infrared spectroscopy has been used so far in the study of zeolite where the vibration frequencies were correlated either to the Si/Al ratio or to the cation which characterizes the lattice. The latter approach attracted our interest in the present work.

Zhdanov et al. [1] have shown that the IR vibrations of the dehydrated X zeolite framework depend very much on the exchanged cation in it. Flanigen et al. [2] observed no considerable changes of the characteristic spectra after cation exchange in a limited number of fully hydrated exchanged forms of A, X and Y zeolites and only slight spectral changes after dehydration. Kanter [3], however, has found some regularity of the frequency shift of some framework vibrations in a series of hydrated monovalent forms of A zeolite in the IR and Raman spectra. Extending the work of Kanter, Maxwell and Baks [4] have shown that in the shifts of IR framework vibrations the similar relation exists for the series of monovalent hydrated forms of A and X zeolites.

In the present work we have attempted to extend the study to the Y zeolite by using mid-infrared spectroscopy as a source of information on the monovalent cation locations in the framework. Such a study was of particular interest since one can find only scarce data on the cation positions in Y zeolites in the literature.

Experimental

Preparation of the exchanged forms of zeolite

The exchange of Na+ ion from the basic form of NaY zeolite (Linde SK-40) by the monovalent metallic ions (Li+, K+, Cs+, Ag+ and Tl+) were performed by equilibrating by shaking at ambient temperature [5, 6]. The solutions for exchange (0.1 mol dm$^{-3}$) were prepared from the chlorides of the corresponding cations (except for Ag+ and Tl+ where nitrates were used). Preparation of TiY zeolite with a high extent of exchange was done at elevated temperatures (80 °C) and the equilibration procedure extended to about two weeks. The exchanged forms were first dried at 110 °C and then hydrated by equilibrating them over the saturated NH$_4$Cl solution.

Chemical analysis: The chemical composition of the exchanged zeolites and their extent of exchange were determined by direct analysis of solid samples as follows: SiO$_2$ gravimetrically, aluminium by EDTA titration, Na, Li and K by the flame photometry, Ag potentiometrically, Tl by polarography and water by the weight loss at 800 °C.

The compositions of the unit cells were determined from experimentally measured weight fractions of all elements, and by using the experimentally determined Si/Al ratio as well as the fact that the sum of Si and Al atoms has to amount to 192.

IR studies: IR spectra of the hydrated zeolites were taken at ambient temperature by using a Perkin-Elmer model 457 spectrometer in the range 200–1200 cm$^{-1}$. The samples were pressed discs containing approximately 1 mg of zeolite in 150 mg...
KBr or CsI. The influence of traces of moisture was compensated with a reference KBr or CsI sample.

**Results and Discussion**

IR spectra of Li\(^+\), Na\(^+\), K\(^+\), Ag\(^+\), Tl\(^+\) and Cs\(^+\) exchanged Y zeolites in the region 200–850 cm\(^{-1}\) are compared in Fig. 1. This spectral range was chosen because any influence of the cations on the framework vibrations appears only within these limits. The interpretation of IR spectra was based on the data of Flanigen et al. [2]. The absorption bands in this region are due to asymmetric and symmetric bending vibrations of different units of the zeolite skeleton. The general form of the spectra of the exchanged zeolites is almost identical to the spectrum of the basic NaY form. Therefore, it could be concluded that in this frequency range the nature of the exchanged cations has no significant influence on the IR spectra of monovalent hydrated forms of Y zeolite.

In the lowermost frequency spectral range of the MY (M - metal ion) zeolite a symmetric band of medium intensity was observed at 380 cm\(^{-1}\), slight shifts of this band being due to the vibrations of the opening of the large cage formed of 12-membered oxygen rings. Similar small changes are observed in the position and character of the bands which have been assigned to the symmetric stretch vibrations \(\text{O} \rightarrow \text{T} \rightarrow \text{O}\) at 650–820 cm\(^{-1}\). They are actually classified as internal tetrahedral stretches in the

### Table I. Infrared frequencies for monovalent cation exchanged Y zeolite*

<table>
<thead>
<tr>
<th>Exchanged cation</th>
<th>Exchange [%]</th>
<th>(1/(r_{\text{cat}}^+ + r_{\text{cat}^+})) [nm(^{-1})]</th>
<th>Pore opening</th>
<th>Si(Al)–O bend</th>
<th>Double 6-rings</th>
<th>Si(Al)–O sym stretch</th>
<th>External linkage sym stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>55.2</td>
<td>0.0500</td>
<td>380 (m)</td>
<td>455 (ms)</td>
<td>575 (m)</td>
<td>710 (m)</td>
<td>785 (m)</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>100.0</td>
<td>0.0426</td>
<td>380 (m)</td>
<td>460 (ms)</td>
<td>580 (m)</td>
<td>710 (m)</td>
<td>780 (m)</td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>98.2</td>
<td>0.0376</td>
<td>375 (m)</td>
<td>453 (s)</td>
<td>570 (ms)</td>
<td>715 (m)</td>
<td>785 (ms)</td>
</tr>
<tr>
<td>K(^+)</td>
<td>99.1</td>
<td>0.0366</td>
<td>380 (ms)</td>
<td>450 (s)</td>
<td>570 (ms)</td>
<td>715 (ms)</td>
<td>785 (ms)</td>
</tr>
<tr>
<td>Tl(^+)</td>
<td>99.6</td>
<td>0.0357</td>
<td>375 (ms)</td>
<td>450 (s)</td>
<td>568 (ms)</td>
<td>715 (ms)</td>
<td>778 (ms)</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>69.9</td>
<td>0.0324</td>
<td>380 (ms)</td>
<td>455 (s)</td>
<td>575 (ms)</td>
<td>710 (ms)</td>
<td>785 (ms)</td>
</tr>
</tbody>
</table>

* s = strong, ms = medium strong, m = medium, sh = shoulder.
The influence of the exchangeable monovalent cations.

Fig. 2. Plots of IR frequency $\nu$ against the reciprocal of the sum of the cation and oxygen ionic radii, $1/(r_{\text{cat}} + r_{\text{o}})^2$ for various monovalent cation exchanged forms of Y zeolite: (a) 560 to 580 cm$^{-1}$ IR band, (b) 440–460 cm$^{-1}$ IR band.

The rather limited exchange of Li$^+$ and Cs$^+$ ions is due to steric effects only, i.e. to the difference of the ionic radii and the extent of hydration. For the distribution of cations, their occupation of definite sites in the zeolite skeleton, the geometry factor is essential. The presence of two independent three-dimensional frameworks of cavities with the cations situated in both of them, gives rise to the effects of double “sieving” through the defined sizes of the openings through which the ions diffuse. One of these frameworks is closely packed and contains small amount of water (sodalite cages and hexagonal prisms), whereas the other one is more opened and highly hydrated. The two frameworks show different ion exchange properties as could be seen from the unit cell compositions given above.
The 32 Li\(^+\) ions, as determined by chemical analysis, are considered to be situated in the sodalite cages (S\(_1\) and S\(_{11}\)) and also in the supercages (S\(_{11}\) and S\(_{11}^*\))\([7]\). These cages, in which the Li\(^+\) ions are rather loosely bound to the zeolite skeleton, are in the most hydrated zone of the zeolite structure which is probably energetically most favorable for these ions. Due to their large hydrated ionic radius (\(r_h = 0.382\) nm) Li\(^+\) ions cannot pass through the 6-membered oxygen rings (\(0.25 < d \text{ nm} < 0.26\)) to the S\(_{1}\) sites in the hexagonal prisms.

A study of the ion exchange equilibria in synthetic zeolites of the faujasite type X and Y has shown that alkali cations with a large crystal radius, as Rb\(^+\) and Cs\(^+\), cannot replace all Na\(^+\) ions in the NaX and NaY zeolite\([8]\). It is also known from the work of Barrer\[9]\) that 16 Na\(^+\) ions per unit cell cannot be replaced by Cs\(^+\) ions. Therefore it can be assumed that Cs\(^+\) ions (40 as found by chemical analysis) are also located in sites of supercages and of the sodalite framework. The 16 S\(_{1}\) sites in the centre of hexagonal prisms are not occupied by the Cs\(^+\) ions.

There are different explanations of why the Tl\(^+\) ion cannot completely replace the Na\(^+\) ions in NaY zeolite at the ambient temperature. According to Sherry\([8]\) this is due to a very slow exchange of Tl\(^+\) ions in the Y zeolite due to the contraction of Y framework as compared with the X zeolite in which the Tl\(^+\) ions can enter the sodalite cages. Barrer \textit{et al.}\[9]\ have shown by the ion exchange isotherms that in an ion exchange process the advantage which a more polarizable ion has is lower if the charge of the framework is lower. The extent of exchange of Tl\(^+\) is therefore higher in the higher charged X framework than in the Y zeolite. In a later work of Sherry\([10]\), however, the inability of Tl\(^+\) ions to enter the sodalite cages, if it is due to a low diffusion rate and not to a thermodynamic origin, could be overcome at the higher temperature; by equilibrating TINO\(_3\) and NaY the total exchange of Na\(^+\) by Tl\(^+\) ion should occur. In order to achieve a higher extent of exchange with Tl\(^+\) ions a higher temperatures (80 °C) was applied during the equilibration process.

The high extent of exchange of K\(^+\) and Ag\(^+\) ions points out that all three types of cation sites are occupied (supercages, sodalite cages and hexagonal prisms) in the Y zeolite. It is probably due to the appropriate size of ionic radius and to their weak electrostatic interaction with the water molecules to which they are linked. In the S\(_{1}\) sites (hexagonal prisms) their electrostatic interaction with oxygen atoms from the skeleton is strong which has been proven by the IR spectroscopy.