Investigations of Solid-state Ion Exchange in Zeolites by Far Infrared Spectroscopy

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Far infrared spectroscopy is a new powerful tool for monitoring solid-state ion exchange in zeolites.

Owing to their commercial importance, the ion exchange properties of zeolites have been studied extensively.[1] However, most of these studies refer to the conventional ion exchange carried out in aqueous solution. On the other hand, as is known since 1972, ion exchange in zeolites may also be achieved by thermal treatment of solid zeolite–salt mixtures.[2] Systematic studies of this kind of ion exchange have been reviewed.[3,4] In contrast to the previous IR studies, which were confined to the mid-IR region, the aim of our studies was to shed light on the elementary processes of solid-state ion exchange by far-IR studies, a promising method, which provides more detailed information than previous techniques.

We now show that this method allows the direct observation of the incorporation of cations into the zeolite simultaneously monitoring the consumption of the salt. Furthermore, it is possible to distinguish cations on their individual positions in the zeolite and, thereby, to obtain information about the distribution of the cations over these sites, especially in comparison with spectra of conventionally exchanged samples.

Zeolites have a transmission window in the far-IR region as shown in Fig. 1 (NH_4Y) and Fig. 2 (bottom, NaY). In this region, low-energy framework deformation bands occur as well as those which are assigned to stretching vibrations of cations against the zeolite lattice. The frequencies of these cation motions depend on the mass, charge, size and surroundings of the cations. Owing to the different local symmetries and force constants of the cation–lattice interaction at different cation positions a discrimination of cations on these sites is possible.[5] The spectrum of NaY zeolite (see Fig. 2, bottom) exhibits four intense cation bands which can be assigned to sodium ions on S II (188 cm^{-1}, E mode), S I (160 cm^{-1}, T_{1u} mode), S I′ (106 cm^{-1}, E mode) and S III positions (90 cm^{-1}, E mode).[6]

Also the solid metal chlorides used for solid-state ion exchange have strong bands in the far-IR region as shown in Fig. 1 for sodium chloride. Therefore the consumption of the salt may be observed by the decrease in intensity of these so-called reststrahlen bands.[7]

Solid-state ion exchange was carried out by heating self-supporting wafers pressed from mixtures of vacuum-dried HY or NH_4Y zeolite with different amounts of pulverised chlorides of alkaline metals, alkaline earth metals, zinc or lanthanum in a stream of dry nitrogen at temperatures up to 600 K for 2–20 h. A nitrogen-flushed far-IR cell with integrated oven was used, which allowed the alternate heating and recording of spectra of five samples at room temperature without opening the cell or the sample chamber of the spectrometer and thereby ensuring that spectra were free from interfering rotational lines of water vapour. Spectra were obtained with a Digilab FTS 15E spectrometer equipped with an ordinary ceramic source, a 6.25 μm Mylar beamsplitter and a liquid helium-cooled silicon bolometer (Infrared Laboratories) as detector. Reference spectra of the salts were run with polyethylene dilutions of the pulverised compounds.

$$NH_4Y + NaCl \rightarrow NaY + HCl + NH_3 \qquad (1)$$

In Fig. 1 the far-IR spectra of the starting materials NH_4Y zeolite and NaCl show two cation bands of the former and the well known reststrahlen band of sodium chloride. Fig. 2 illustrates by means of three spectra recorded at selected times the course of the solid-state reaction (1). At the beginning of the reaction (top) the spectrum is dominated by the intense reststrahlen band of sodium chloride together with those of the original NH_4Y zeolite. After two hours (middle) the band of the salt has diminished and the cation bands of Na^+ ions on S II, S I and S III positions emerge, indicating the incorporation of cations into the zeolite at the expense of sodium chloride conversion. After another two hours (bottom) a spectrum is obtained, which is nearly identical with that of

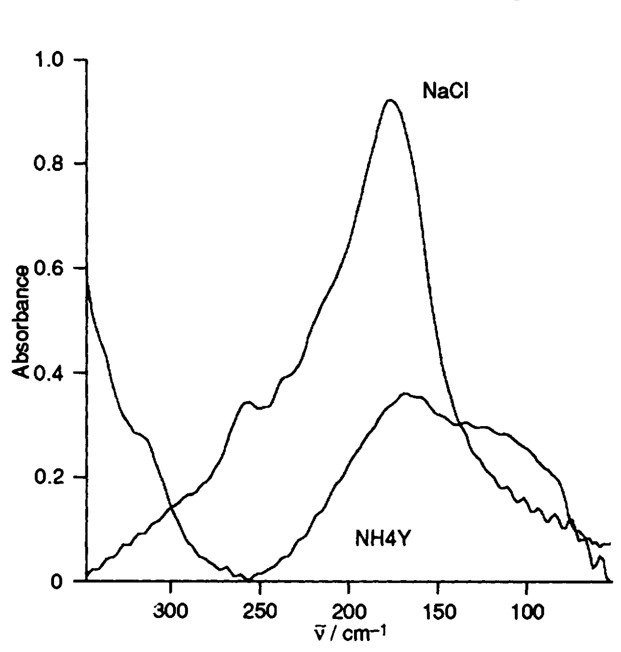

Fig. 1 Far-IR spectra of the starting compounds

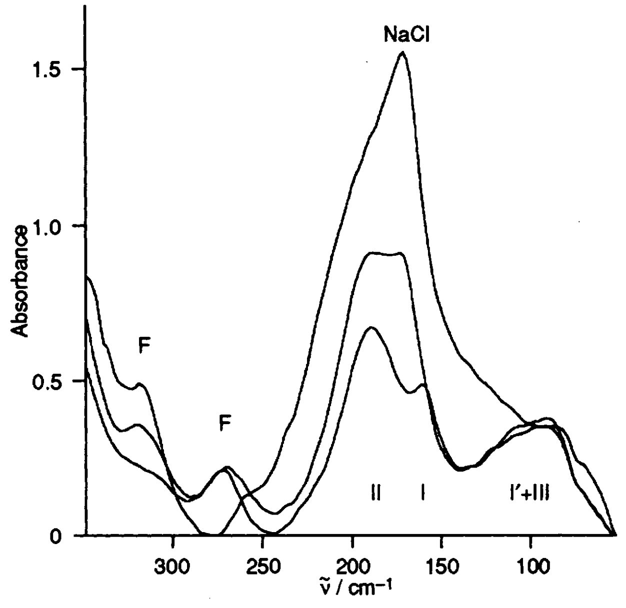

Fig. 2 Solid-state reaction of NH_4Y with NaCl: t = 0 (top), t = 2 h (middle), t = 4 h (bottom). F = framework deformation band; I, I′, II, III = cation bands assigned to cations on positions S I, S I′, S II, S III.

commercially available NaY zeolite. The NaCl reststrahlen band has disappeared owing to the complete consumption of the salt.

This example shows the potential of far-IR spectroscopy for the investigation of solid-state ion exchange. It provides direct evidence of the incorporation of cations into the zeolite and their distribution over different cation positions paralleled by the observation of the consumption of the salt component. More detailed results on this topic will be published in the near future, including a comparison between the cation distribution in solid-state and conventionally exchanged samples and a discussion about the preferable use of ammonium or hydrogen forms of zeolites.

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