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Unusual hydration behavior of dielectric loss in KA zeolite

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Received (in Cambridge, UK) 8th May 2002, Accepted 26th June 2002
First published as an Advance Article on the web 10th July 2002

Two relaxations measured in dehydrated KA zeolite showed different hydration behaviors; the higher frequency relaxation shifted to higher frequency with increasing hydration whereas the lower frequency relaxation shifted to lower frequency; the latter behavior being contrary to present theory.

Motions and behaviors of ions in zeolites have been studied by electric conduction and dielectric relaxation spectroscopy.[1–3] In preceding work, we accurately analyzed the dielectric spectra of NaA zeolite for the first time and studied the behavior of Na^+ ions within the zeolite.[4,5] It was found that two relaxations measured in the zeolite were caused by motions of a common Na^+ ion. Since K^+ ions in KA zeolite are distributed in the same way as Na^+ ions in NaA zeolite,[6–9] similar relaxations to NaA zeolite, except for the effect of ionic radius, are expected in KA zeolite. Hence this zeolite is best suited to investigate the effect of ionic radius on the motion and behavior of cations in A zeolite.

Freeman and Stamires investigated factors affecting the motions of ions in zeolites from the study of ionic conduction and pointed out two factors, Coulombic attraction and steric hindrance.[1] In a channel or cage with adequate size (*e.g.* Y zeolite), the steric hindrance is less important than the Coulombic attraction, and hence the activation energy of ionic conduction decreases with an increase of ionic radius.[1] In contrast, in a channel or cage with a small size (*e.g.* A zeolite), the steric hindrance is a dominant factor and the activation energy increases with an increase of ionic radius.[1] This explanation however requires examination by more accurate studies, since it is based on less reliable results.[4] The activation energy of ionic conduction is close to that of dielectric relaxation for the same ion.[4,10,11] Hence we can also examine the validity of above explanation through the study of relaxations of KA zeolite.

Commercial 4A zeolite powder (Tosoh Co.) was used as the starting material. It was repeatedly treated with a KCl solution at 353 K and changed to K type A zeolite. The chemical composition per unit cell of resultant zeolite was $K_{11.6}Na_{0.1}(AlO_2)_{11.9}(SiO_2)_{12.1}$ as determined by atomic absorption spectroscopy. This sample is denoted KA.

KA zeolite was compressed into a disk *ca.* 1 mm thick and 20 mm in diameter. Thin gold films 16 mm in diameter were sputtered on both sides of the disk, for electrical contacts, and set in a sample holder with electrodes for dielectric measurements. The holder was inserted into a clean vacuum system, the sample was gradually dehydrated by heating to 723 K and then the dielectric measurements were made as a function of frequency f at a given temperature T (415 K $\le T \le$ 502 K). The measurements were made also on the partially hydrated state at 442 K and at a water vapor pressure of $P \le 371$ Pa after reaching adsorption equilibrium.

Spectra (ε', ε'' and tanδ) measured on dehydrated KA zeolite showed two loss peaks, which shifted to the higher frequency with increasing temperature. Representative tanδ spectra are shown in Fig. 1. Cole–Cole plots of every measured data showed two circular arcs. According to Cole–Cole theory, a relaxation loss leads to a circular arc in the Cole–Cole plot,[12] and hence two loss peaks were judged as relaxation losses (for convenience, the relaxation losses on the lower and higher frequency sides are deoted I and II, respectively, in the following).

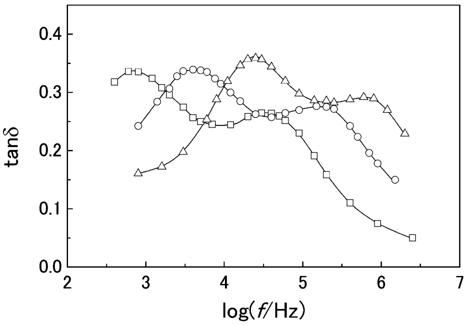

Fig. 1 Spectra of dielectric loss tangent for dehydrated KA zeolite: (□) 415 K, (○) 455 K and (△) 502 K.

In order to probe into the cause of relaxations I and II, changes of spectrum with water vapor pressure (hydration) were followed. Relaxation II shifted to higher frequency with increasing pressure (hydration) but relaxation I shifted to lower frequency as indicated in Fig. 2. Although the direction of change is opposite for relaxations I and II, both changes simultaneously began even at very low hydration. This fact indicates that both relaxations are caused by a related (or common) origin.

The separation of the two relaxations was attempted. For the separation, Cole–Cole equations were used and the optimum characteristic values were determined for each relaxation.[12] The analysis method had been already applied to the two relaxations in NaA zeolite and its usability had been confirmed.[4] The validity of the current analyses was examined by comparing the calculated spectra with the measured ones. One of the examples is illustrated in Fig. 3, where the measured loss is described as two relaxations and a conductive loss. The calculated spectrum was in good agreement with the measured one, indicating that the analyses and the determined characteristic values are valid.

The parameter f_m, which is the frequency at the maximum of ε'', was determined, in the analyses, for each relaxation at

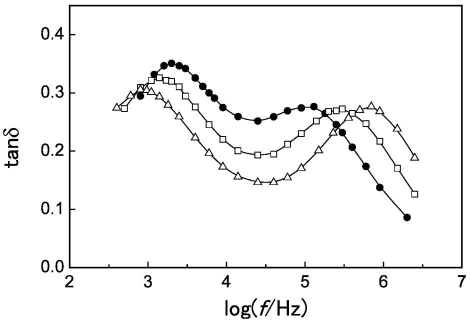

Fig. 2 Change of tanδ spectrum of KA zeolite with water vapor pressure at T = 442 K; (●) dry, (□) 38.7 Pa and (△) 371 Pa.

DOI: 10.1039/b204447c

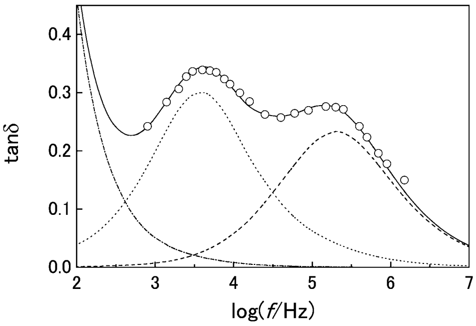

Fig. 3 Comparison between the calculated and measured tanδ spectra for dehydrated KA zeolite at T = 455 K; (○) measured value, (···) relaxation I, (---) relaxation II, (–·–) conductivity loss and (—) calculated spectrum.

various temperatures. The natural logarithm of f_m was plotted against $1/T$ (Fig. 4) and the activation energy of each relaxation was determined from the slope of the plot. The activation energies for relaxations I and II were E_I = 63 kJ mol^{-1} and E_{II} = 61 kJ mol^{-1}, respectively.

A relaxation loss is attributable to the motion of ions or molecules which causes a change of electric dipole moment. In the fully dehydrated KA zeolite, only K^+ ions can be the origin of relaxation. Hence two relaxations measured in the present study are attributable to the motions of K^+ ions, the values E_I = 63 kJ mol^{-1} and E_{II} = 61 kJ mol^{-1} reflect two different motions of a common K^+ ion. This conclusion is in accord with that for NaA zeolite.[4,5]

The ionic conduction in dehydrated KA zeolite was investigated by other workers and the activation energy for the conduction process of K^+ ion was obtained to be 59 kJ mol^{-1}.[1,13] These results show the affinity of activation energy of relaxation with that of ionic conduction.

In the fully dehydrated NaA zeolite, two relaxations, attributable to the motions of Na^+ ion, were measured and their activation energies were 60 and 49 kJ mol^{-1}.[4] The replacement of Na^+ by K^+ ion in A zeolite brought about increases of activation energy from 60, 49 kJ mol^{-1} to 63, 61 kJ mol^{-1}. Since the cation distribution of K^+ in KA zeolite is essentially the same as that of Na^+ ion in NaA zeolite, it is considered that the same type of motion were measured in both zeolites and the energy changes are due to the effect of ionic radius. It can be concluded that the dominant factor affecting the activation energies of cation motions in A zeolite is the steric hindrance (supporting the conclusion of Freeman and Stamires).

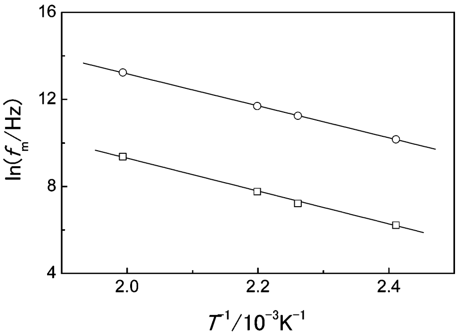

Fig. 4 Temperature dependence of ln(f_m/Hz) for dehydrated KA zeolite; (□) relaxation I and (○) relaxation II.

We expected similarities of some properties for both NaA and KA zeolites: two relaxations are measured, the activation energies are not so high and both relaxations are simultaneously shifted to higher frequency by hydration. However, the response of relaxation I to hydration was not as expected for KA. Up to now, as measured for zeolites, when a relaxation was affected by hydration, it shifted to higher frequency.[5,14–17] The shift to the higher frequency with hydration was explained as follows:[17] water molecules within zeolites preferably adsorb on cations, forming cation–H_2O complexes and reduce the Coulombic attraction between the cation and the negative charge in the framework because of a shielding effect of water. Owing to this effect, the moving species become more mobile with hydration, can follow the faster alternation of electric field and lead to relaxation loss at higher frequency. However, the hydration behavior of relaxation I does not obey this explanation. In this case, actions of water molecules on the two motions of K^+ ion are superficially contradictory, *i.e.* making the motion of relaxation II mobile but that of relaxation I less mobile. Although the hydration behaviors are complicated, at any rate the primary cause would be related to ion size.

The present work was partly supported by a Grant-in-Aid for Scientific Research (C) from the Japan Society for the Promotion of Science, contract no. 14550666.

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