Dielectric Properties of Dehydrated Ca_1Na_{10}-A and Na_{12}-A Zeolites

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Synopsis. Dielectric properties of completely dehydrated Ca_1Na_{10}-A and Na_{12}-A zeolites were studied. The properties of Ca_1Na_{10}-A bore close parallels to those of Na_{11}-ZK4 having almost the same cation distribution as Ca_1Na_{10}-A. The properties of Na_{12}-A were markedly different from those of Ca_1Na_{10}-A and the unusual behavior of the zeolite were attributed to a larger mobility of Na^+ ion on the 4-ring site.

Properties of Ca_xNa_{12-2x}-A zeolites ($0 \leq x \leq 6$) have been widely investigated, e.g., heats of gas-adsorption,[1] reactivities of oxygen in zeolite framework,[2] and heat-resistivities.[3] These properties of the zeolite at composition of $x=0$ were markedly different from those at $x \geq 1$ and the differences were correlated to the Na^+ ion near a 4-membered oxygen ring (abbreviated as 4-ring Na^+ ion), since the zeolite contains the 4-ring Na^+ ion at $x=0$ but not at $x \geq 1$ (Table 1). The unusual behavior of the 4-ring Na^+ ion may be directly studied by dielectric measurements, and thus the dielectric properties of Na_{12}-A and Ca_1Na_{10}-A were measured and compared with each other. It is one objective of the present work to study the unusual properties of Na_{12}-A.

Another subject is to investigate the similarities of the dielectric properties of the Ca_1Na_{10}-A and Na_{11}-ZK4 zeolites. Zeolite A is isostructural with zeolite ZK4, and Ca_1Na_{10}-A has the same cation distribution as Na_{11}-ZK4, except for a Ca^{2+} ion being used in the place of a Na^+ ion near a 6-ring (Table 1). Thus, the dielectric properties of Ca_1Na_{10}-A are expected to be similar to those observed in Na_{11}-ZK4.[7]

Experimental

The apparatus and the procedures used in the dielectric measurements were the same as in a previous paper.[8] A commercial 4A zeolite, $Na_{11.8}(AlO_2)_{11.8}(SiO_2)_{12.2} \cdot nH_2O$ (abbreviated as Na_{12}-A), was ion-exchanged with 0.1 mol dm^{-3} solution of $(CH_3COO)_2Ca$ at 353 ± 0.5 K for 3 d, and the cation composition of zeolite after ion-exchange was determined to be $Ca_{1.05}Na_{9.7}(AlO_2)_{11.8}(SiO_2)_{12.2}$ (Ca_1Na_{10}-A), by EDTA titration of the ion exchange solution and from the material balance.

Complex dielectric constants ($\varepsilon^* = \varepsilon' - i\varepsilon''$) were measured as functions of frequency f and temperature T, in the ranges of 20—2×10^6 Hz and 273—653 K for Ca_1Na_{10}-A, and 50—2×10^6 Hz and 163—363 K for Na_{12}-A. In the present work, we did not require the absolute value of the dielectric constant and did not make the correction for the packing density of the sample disk, because we were concerned only with its dependence on the frequency and temperature.

Table 1. Cation Distribution[4-6]

Composition	8-Ring 3[a]	6-Ring 8[a]	4-Ring 12[a]
Na_{12}-A	3 Na^+	8 Na^+	1 Na^+
Ca_1Na_{10}-A	3 Na^+	1 Ca^{2+}+7 Na^+	0
Na_{11}-ZK4	3 Na^+	8 Na^+	0

a) Number of ring per pseudo unit cell. Each ring can accommodate only one cation.

Results

Spectra of the loss tangent for Ca_1Na_{10}-A are shown in Fig. 1, which contain two main losses, a loss peak in a higher frequency region and a peak-less loss in a lower region. A frequency, f_{tan}, at the peak of the loss tangent was determined and the activation energy, E_{tan}, of cation jump was found to be 87 ± 2 kJ mol^{-1} from the slope of the plots of $\ln f_{tan}$ vs. $1/T$.

Cole–Cole plots (Fig. 2) showed, in a larger ε' region, a steep rise of ε''_{obs} which is usually attributed to a conductivity loss[9-11] (subscript obs denotes observed

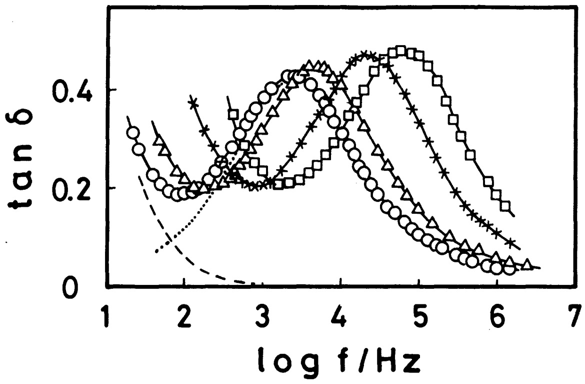

Fig. 1. Spectra of dielectric loss tangent for Ca_1Na_{10}-A zeolite. □: 657.7 K, ✕: 614.4 K, △: 566.8 K, ○: 543.8 K. Broken line for loss tangent of conduction, $\tan\delta_c = \varepsilon''_c/\varepsilon'_{obs}$, at 543.8 K ($\varepsilon''_c = \sigma/2\pi f\varepsilon_0$ with $\sigma = 2.1 \times 10^{-8}$ S m^{-1}). Dotted line for loss tangent of relaxation, $\tan\delta_r = \tan\delta_{obs} - \tan\delta_c$, at 543.8 K. Subscript obs denotes observed values.

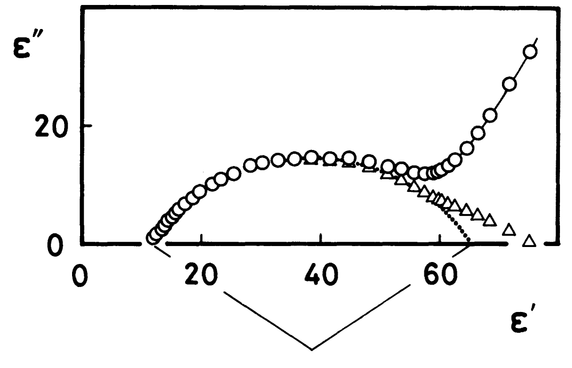

Fig. 2. Cole–Cole plots for Ca_1Na_{10}-A zeolite at 614.4 K. ○: ε''_{obs} vs. ε'_{obs}, △: ε''_r vs. ε'_{obs} ($\varepsilon''_r = \varepsilon''_{obs} - \varepsilon''_c$, $\varepsilon''_c = \sigma/2\pi f\varepsilon_0$ with $\sigma = 1.8 \times 10^{-7}$ S m^{-1}). Dotted line for Cole–Cole circular arc best fitted to ε''_r. Subscript obs denotes observed values.

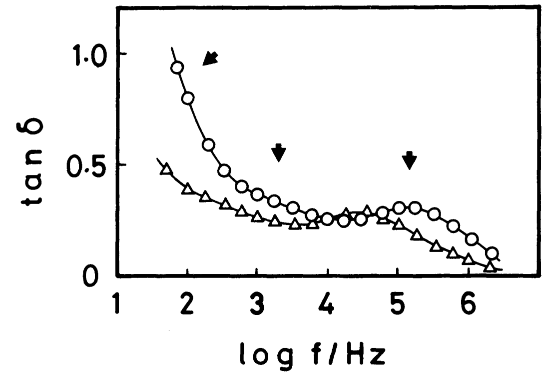

Fig. 3. Spectra of dielectric loss tangent for Na$_{12}$-A zeolite. ○: 363.2 K, △: 331.0 K. Arrows denote losses in each frequency region of spectrum at 363.2 K, losses in the lower, middle and higher frequency regions.

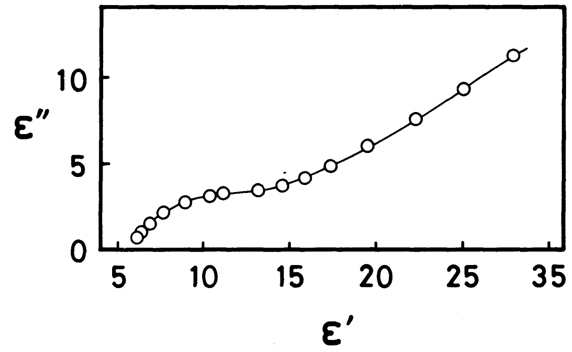

Fig. 4. Cole–Cole plots for Na$_{12}$-A zeolite at 363.2 K.

values). The loss part in the larger ε' region was described with the equation of the conductivity loss, $\varepsilon_c''=\sigma/2\pi f\varepsilon_0$, and was thereby assigned to the conductivity loss, where ε_c'' and ε_0 are the conductivity loss and the permittivity of vacuum, respectively, and σ an apparent dc conductivity. A plot of $\ln\sigma$ vs. $1/T$ gave $E_c=83\pm4$ kJ mol^{-1} for the conduction process. The observed loss was corrected for by subtracting the conductivity loss. The plots of ε_r'' $(=\varepsilon_{obs}''-\varepsilon_c'')$ vs. ε_{obs}' were well described with a single circular arc, except for the larger ε' region, as shown in Fig. 2. Hence, we concluded that the main part of ε_r'' contains only one relaxation loss. For the relaxation process, the activation energy, E_r, and the frequency factor, ω_0, were determined from plots of $\ln f_r$ vs. $1/T$, where f_r is the frequency at the maximum value of ε_r'' and ω_0 is defined as $\ln f_r=\ln\omega_0/2\pi-E_r/RT$. Their values were $E_r=87\pm3$ kJ mol^{-1} and $\log\omega_0=12.0\pm0.4$. If a relaxation process and a conduction process contain the same cation-jump, the equation of $E_r-E_c=RT$ holds true.[8] The present values of E_r and E_c satisfy this relationship, and thus it was concluded that both processes involve the same cation jump.

For Na$_{12}$-A zeolite, both ε_{obs}' and ε_{obs}'', at $T>400$ K, were too large to give useful data for analysis. The measurements were thereby limited to temperatures lower than 363 K. Representative spectra of the loss tangent and Cole–Cole plots are given in Figs. 3 and 4, respectively. The spectra of the loss tangent show that there are three kinds of losses, a loss peak in the higher frequency region, a large peak-less loss in the lower region, and a small loss in the middle region, though the last is less clear. The large loss in the larger ε' region, in Fig. 4, may be due to conduction. However, the loss part was not evaluated with the equation of conductivity loss owing to the loss in the middle region. Thus the Cole–Cole curve could not be separated into separate components. The activation energy of cation jump was thereby determined only from the spectra of loss tangent, and was $E_{tan}=48\pm4$ kJ mol^{-1}.

Discussion

Let us consider cation-jumps causing the losses observed in Ca$_1$Na$_{10}$-A. Allowed cation-jumps in Ca$_1$Na$_{10}$-A can be deduced from the cation distribution in the zeolite, since only jumps to sites unoccupied by cations are allowed. The cation distribution is essentially the same as in Na$_{11}$-ZK4 and thus the same type of cation-jumps as in Na$_{11}$-ZK4 are allowed, namely a jump from the 8- or 6-ring site to the 4-ring site, a jump from the 8-ring site to the neighboring sites in the same ring, and a jump between the 6-ring sites in the large cage side and in the soadalite cage side.[7] In the allowed jumps, the jump which can cause both relaxation and conductivity losses is only the jump of Na$^+$ ion between the 8- and 4-ring sites, since the cation can escape from the unit cell dimension only by repeating the jump of the 8-ring site → 4-ring site → another 8-ring site. Thus both relaxation and conductivity losses observed in Ca$_1$Na$_{10}$-A are assigned to the jump of Na$^+$ ion between the 8-ring and 4-ring sites.

The relaxation loss is characterized by $E_{tan}=87\pm2$ kJ mol^{-1}, $E_r=87\pm3$ kJ mol^{-1}, and $\log\omega_0=12.0\pm0.4$, and the conductivity loss by $E_c=83\pm4$ kJ mol^{-1}. These characteristics are respectively close to those for Na$_{11}$-ZK4 ($E_{tan}=89\pm2$ kJ mol^{-1}, $E_r=91\pm3$ kJ mol^{-1}, $\log\omega_0=12.1\pm0.4$ for the relaxation loss assigned to the jump between the 8- and 4-ring sites, and $E_c=86\pm4$ kJ mol^{-1} for the conductivity loss attributed to the jump of 8-ring → 4-ring → another 8-ring).[7] Hence, we can conclude that the dielectric properties of Ca$_1$Na$_{10}$-A bear close parallels to those of Na$_{11}$-ZK4.

In Na$_{12}$-A, the loss peak was observed at a lower temperature range of 273—363 K. Such a loss was not observed in Ca$_1$Na$_{10}$-A and Na$_{11}$-ZK4 zeolites lacking the 4-ring Na$^+$ ion. The loss is thereby peculiar to Na$_{12}$-A and is correlated to jumps of the 4-ring Na$^+$ ion. There are two kinds of jumps related to the 4-ring Na$^+$ ion, that is, one is the jump from the 4-ring site to the neighboring 4-ring site and another is the modification of the jump, from the 8- or 6-ring site to the 4-ring site, by the 4-ring Na$^+$ ion. If the Na$^+$ ion on the 4-ring site jumps to the nearest 4-ring site, the activation energy of the jump may be as small as $E_{tan}=48$ kJ mol^{-1}, since the cation has a weak affinity to the 4-ring site.[4,12] Thus the loss peak is most probably assigned to the jump of Na$^+$ ion between the 4-ring sites.

Conclusion

It was confirmed that the dielectric properties of Ca_1Na_{10}-A and Na_{11}-ZK4 zeolites are, in both the characteristic values and the jump mechanism, close to each other. The zeolite Na_{12}-A showed "unusual" behaviors also in dielectric properties. As can be seen from the small activation energy of jump of the 4-ring Na^+ ion, the unusual behavior has its origin in a larger mobility of the Na^+ ion on the 4-ring site.

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