Bull. Chem. Soc. Jpn., *61*, *1797—1799 (1988)*

Dielectric Losses of Dehydrated Na_{11}-ZK4 and K_3Na_8-ZK4 Zeolites

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(Received October 28, 1987)

Synopsis. Dielectric properties of completely dehydrated Na_{11}-ZK4 and K_3Na_8-ZK4 zeolites were studied. A relaxation loss peak and a loss in the lower frequency region were observed in both zeolites. The relaxation losses were assigned to the jump of a cation from the 8-ring site to the 4-ring site. The losses in the lower frequency region were attributed to a cation movement beyond the unit cell dimension.

Zeolite ZK4 is isostructural with zeolite A and contains fewer cations than zeolite A,[1] and thus the cation distribution in zeolite ZK4 becomes simpler than that in zeolite A. This simplicity facilitates the determination as to which cation movement an observed dielectric loss is to be assigned. In a previous work,[2] the dielectric properties of the completely dehydrated Rb_3Na_8-ZK4 zeolite were studied, and a relaxation loss peak observed was tentatively assigned to a jump of a Rb^+ ion on the site of an 8-membered oxygen ring (abbreviated as the 8-ring site) to the 4-ring site. The purpose of this study is to confirm this assignment.

Experimental

The apparatus and procedures for dielectric measurements were the same as in the previous paper.[2] The starting material, $Na_{11.0}(AlO_2)_{11.0}(SiO_2)_{13.0}$ ($(AlO_2)_{11.0}(SiO_2)_{13.0}$ is abbreviated as -ZK4), was ion-exchanged with a 0.2 mol dm^{-3} solution of CH_3COOK and the composition of the resultant zeolite was shown by atomic absorption spectrometry to be $K_{3.0}Na_{8.0}$-ZK4 (K_3Na_8-ZK4). Complex dielectric constants ($\varepsilon^*=\varepsilon'-i\varepsilon''$) of Na_{11}-ZK4 and K_3Na_8-ZK4 zeolites were measured as functions of frequency f (10—2×10^6 Hz) and temperature T (room temperature—680 K), and were not corrected for the packing density. A sample placed in a vacuum system was gently heated under pumping and finally baked out at 670 K. The degree of dehydration of the sample was shown to be complete in the same manner as in the previous paper.[2]

Results

Representative spectra of loss tangent and the Cole–Cole plots are shown in Figs. 1 and 2. The figures show the presence of two kinds of dielectric losses, a relaxation loss peak and a loss in the lower frequency region. The frequency of the applied field giving the peak of loss tangent, $f_{\tan}$, is determined on the spectrum of loss tangent and an activation energy of the cation jump, $E_{\tan}$, is determined from Arrhenius plots of $\ln f_{\tan}$ vs. $1/T$ to be 89 ± 2 kJ mol^{-1} for Na_{11}-ZK4 and 94 ± 3 kJ mol^{-1} for K_3Na_8-ZK4. By the method described in the previous paper,[2] the contribution of the conduction loss, ε_c'', and the apparent specific d.c. conductivity, σ, are estimated and the activation energy of the conduction process is obtained from plots of $\ln \sigma$ vs. $1/T$ to be 86 ± 4 kJ mol^{-1} for Na_{11}-ZK4 and 88 ± 5 kJ mol^{-1} for K_3Na_8-ZK4. A relaxation loss part, ε_r'', is separated from the observed dielectric loss, ε_{obs}'', by the relation of $\varepsilon_r''=\varepsilon_{obs}''-\varepsilon_c''$, as illustrated in Figs. 1(b) and 2(b). Let $f_{\varepsilon''}$ be the frequency at the maximum value of ε_r'', then the activation energy of the cation jump, $E_{\varepsilon''}$, and the frequency factor, ω_0, are determined from Arrhenius plots of $\ln f_{\varepsilon''}$ vs. $1/T$, where ω_0 and $E_{\varepsilon''}$ are defined as $\ln f_{\varepsilon''}=\ln \omega_0/2\pi-E_{\varepsilon''}/RT$. The values of $\log \omega_0$ for Na_{11}-ZK4 and K_3Na_8-ZK4 are 12.1 ± 0.4 and 11.6 ± 0.3, respectively, and $E_{\varepsilon''}$ is 91 ± 3 kJ mol^{-1} for Na_{11}-ZK4 and 94 ± 4 kJ mol^{-1} for K_3Na_8-ZK4. Plots of $E_{\tan}$ vs. r and $\log \omega_0$ vs. $\log M$ are shown in Figs. 3 and 4, respectively, where r denotes a radius of cation and M a mass of the cation. For comparison, data for Rb_3Na_8-ZK4 zeolite[2] are shown in Figs. 3 and 4.

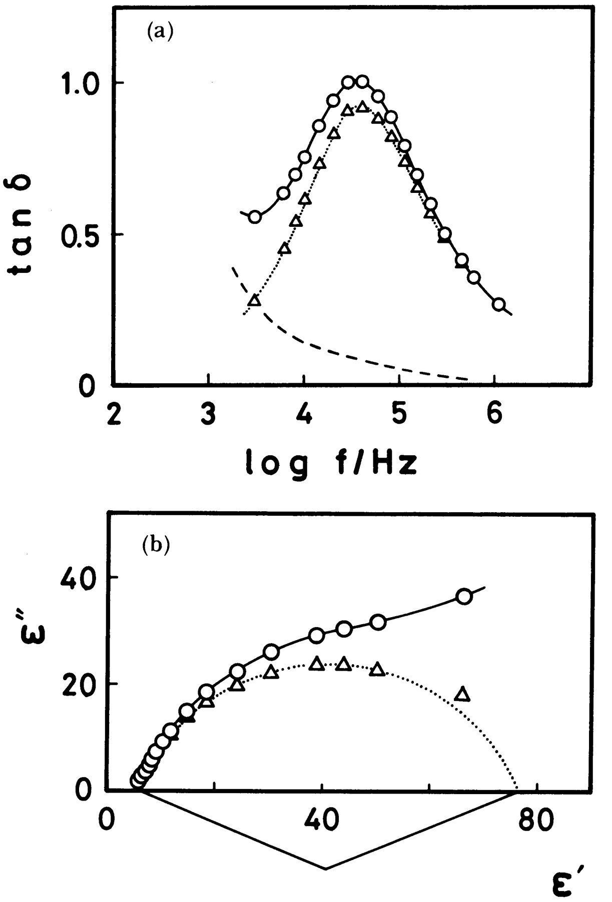

Fig. 1. Dielectric properties of Na_{11}-ZK4 zeolite. (a) Spectrum of loss tangent at 649.0 K. ○: observed ($\tan \delta_{obs}$), △: loss tangent of relaxation ($\tan \delta_r=\tan \delta_{obs}-\tan \delta_c$), broken line: loss tangent of conduction ($\tan \delta_c=\varepsilon_c''/\varepsilon_{obs}'$). Subscript obs denotes observed value. ε_c'' is conduction loss obtained by the method described in Ref. 2. (b) Cole–Cole plots at 649.0 K. ○: ε_{obs}'' vs. ε_{obs}', △: ε_r'' vs. ε_{obs}', ($\varepsilon_r''=\varepsilon_{obs}''-\varepsilon_c''$).

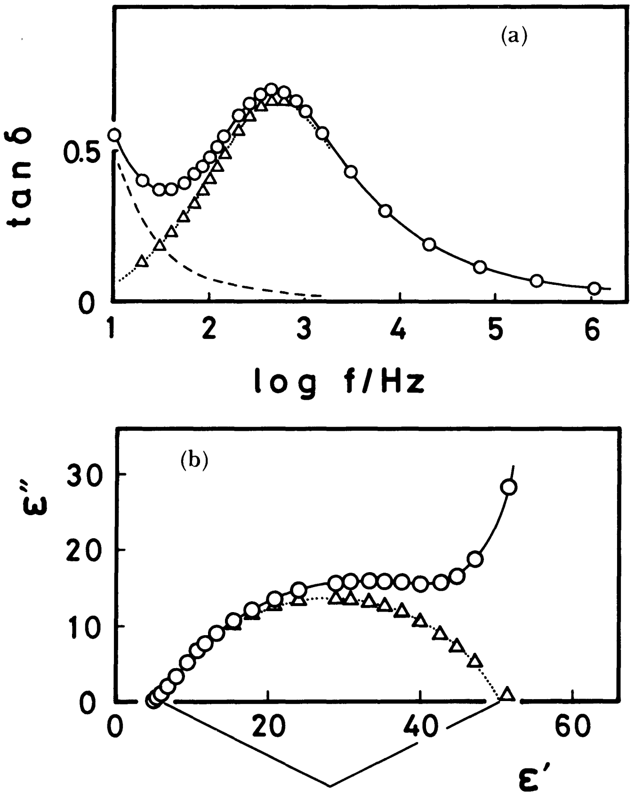

Fig. 2. Dielectric properties of K_3Na_8-ZK4 zeolite. (a) Spectrum of loss tangent at 566.7 K. O: tan δ_{obs}, Δ: tan δ_r, broken line: loss tangent of conduction. (b) Cole-Cole plots at 566.7 K. O: ε''_{obs} vs. ε'_{obs}, Δ: ε''_r vs. ε'_{obs}, ($\varepsilon''_r=\varepsilon''_{obs}-\varepsilon''_c$).

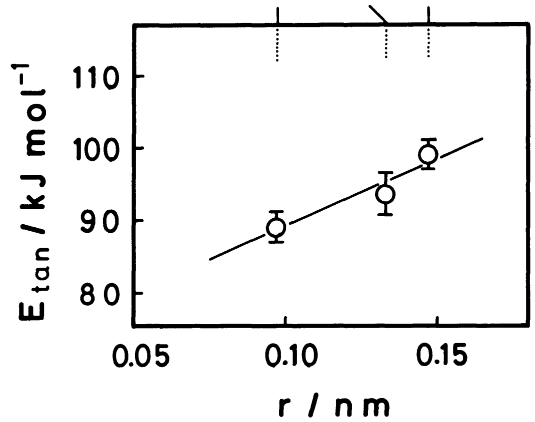

Fig. 3. Plots of activation energy of cation jump against radius of cation. Value concerned with Rb^+ ion is from Ref. 2.

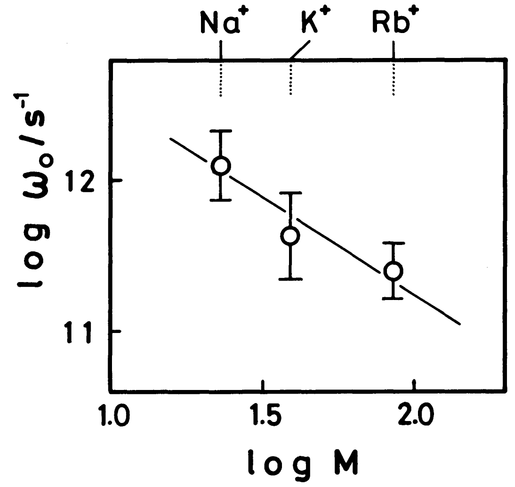

Fig. 4. Plots of frequency factor of jumping cation against mass of cation. Value concerned with Rb^+ ion is from Ref. 2.

Discussion

Let us consider which cation, the 8-ring cation or the 6-ring cation, causes the relaxation loss. As yet the cation distribution of K_3Na_8-ZK4 zeolite has not been studied. The cation distribution in zeolite A containing Na^+ and/or K^+ ion has been studied in detail,[3–6] and it was shown that the K^+ ion prefers the 8-ring site to the 6-ring site and the Na^+ ion has a reverse site-selectivity. It is presumed that the site-selectivities of K^+ and Na^+ ions do not change in both zeolites A and ZK4 and thus K^+ and Na^+ ions occupy the 8-ring site and the 6-ring site in K_3Na_8-ZK4 zeolite, respectively. In three zeolites, Na_{11}-, K_3Na_8-, and Rb_3Na_8-ZK4,[2] all 6-rings are fully occupied by Na^+ ions. Hence, if the relaxation loss is brought about by the movement of Na^+ ion on the 6-ring site, the activation energy and the frequency factor in the relaxation process must respectively have almost the same values for all three zeolites. These expectations are in contradiction to the observations as shown in Figs. 3 and 4. Thus it is concluded that the relaxation loss is due to the jump of the 8-ring cation.

In the next place, let us discuss the mechanism of the cation jump. Only two jumps are allowed for the 8-ring cation in the present zeolites, since a cation cannot jump to the sites occupied by the other cations. The 8-ring has four equivalent sites in its plane and can accomodate only one cation. Thus the 8-ring cation can jump to the neighbouring site in the plane. Another possible jump is the jump between the 8-ring site and the 4-ring site (the 4-ring site is vacant in the zeolite ZK4[7]). In these two jumps, the jump in the 8-ring plane is not likely to be the cause of the relaxation loss observed. The jump distance, l, between the sites in the 8-ring plane decreases with the increasing radius of the 8-ring cation and finally converges to zero when Rb^+ ion occupies the 8-ring (l=0.18 nm for Na^+, 0.063 nm for K^+ and 0 nm for Rb^+).[8–10]† Then the jump in the 8-ring plane

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[†] The jump distances were calculated from data of X-ray structural analyses of zeolite A at room temperature. Thus the values may not be valid for zeolite ZK4 at such higher temperatures as the present experimental temperatures. However, it is considered that the dependence of the jump distance upon the ionic radius is valid for the present zeolites.

becomes impossible for the Rb_3Na_8-ZK4 zeolite. Figures 3 and 4 strongly suggest that the same mechanism operates in all three zeolites and the jump in the 8-ring plane is not the cause of the relaxation loss. Therefore, the possible mechanism as the cause of the relaxation loss observed is only the cation jump from the 8-ring site to the 4-ring site. This assignment is supported by the following. In completely dehydrated M_3Na_8-ZK4 zeolite with M= Na, K, or Rb, the allowed conduction mechanism is only the movement of the 8-ring cation through the route of 8-ring→4-ring→another 8-ring.[2] If the mechanisms of the conduction process and the relaxation process are the same, the equation, $E_{\varepsilon''}-E_c=RT$, is valid.[2,11,12] In the present systems, the above relation is satisfied within the experimental error. From the above considerations, it is concluded that the relaxation losses observed in K_3Na_8-ZK4 with M=Na, K, or Rb are caused by the cation jump from the 8-ring site to the 4-ring site.

The present authors sincerely thank Prof. Tetsuo Takaishi of Toyohashi University of Technology, for useful discussions.

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