Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Physics and Chemistry of Solids 67 (2006) 1063–1066
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

NMR property of arrayed K clusters in zeolite LTA with Si/Al = 1.5

M. Igarashi [a,*], T. Kodaira [b,c], T. Shimizu [d], A. Goto [d], K. Hashi [d]

[a] Department of Applied Physics, Gunma National College of Technology, Toribamachi 580, Maebashi 371-8530, Japan
[b] National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1, Tsukuba 305-8565, Japan
[c] PRESTO, Japan Science and Technology Agency (JST), Honcho 4-1-8, Kawaguchi 332-0012, Japan
[d] National Institute for Materials Science (NIMS), Sengen 1-2-1, Tsukuba 305-0047, Japan

Abstract

NMR property of ^{27}Al in K-loaded LTA-type zeolite with Si/Al = 1.5 is reported. The higher frequency side of the monotonous spectrum of not loaded sample is changed as expanded, only at the higher frequency side, to higher frequency direction by loading of external K. Some NMR parameters, T_2 and T_2^*, of the expanded components are different from those of the original one. Since the potential for external atoms is shallower for the case of Si/Al = 1.5 than for that of Si/Al = 1.0, the origin of the shift may be attributed to Knight shift by Fermi contact interaction between nuclei and electron from adsorbed K.

Keywords: A. Magnetic materials; A. Metals; A. Microporous materials; D. Magnetic properties; D. Nuclear magnetic resonance (NMR)

1. Introduction

LTA type zeolite [1] is a system with tightly bound network of Si and Al through O, where atomic number ratio Si/Al = 1.0 for usual case. Two kinds of free spaces among the network, which are called α and β cages, line with cubic symmetry and act as potential well for the external atoms. The source of the attracting force is the charge compensation ions for the framework existing in the cages. Since the cages are not well separated but windows with relatively small radius connect cages each other, electrons of adsorbed atoms can interact not only within one cage but also through the windows. The interaction may cause some cooperation effect among electrons. In fact for the case of potassium loading, cationic clusters are formed in α cage and ferromagnetic property appears [2]. Electron spins are stabilized in the potential well and interact each other antiferromagnetically [3]. The local field, which is a reflection of the spin configuration in the cages, from localized electron spins has been observed by ^{27}Al NMR [4] and by ^{29}Si NMR [5]. Profile of local field is varied obviously by changing the kind of loaded atoms [4] and by changing loading level of atoms [5]. NMR technique would be a valuable tool to investigate local environment in metal-loaded zeolite system.

The property of the interaction is determined not only by the kind of the cations but also by the degree of deepness of the potential well. If the attracting force from charge compensation ions can be controlled, the interaction among cationic clusters would be changed and new kind of property is expected. Recently it has been shown that in ZK-4 type zeolite, which has similar structure with usual LTA but has higher value for Si/Al than usual LTA, cationic clusters were formed too [6]. This system is expected to have shallower potential for the cationic clusters than usual LTA because of its lower concentration of the charge compensation ions. For such a system the wave function of the electrons in cationic clusters would more be spread to wider area. Increment of a chance for electrons to move among neighboring cages makes us expect electronic conduction property. Moreover the framework atoms would have possibility to interact with the electrons of the clusters.

In this paper we report ^{27}Al NMR property of potassium-loaded K-form ZK-4.

2. Experimental

We name K-form ZK-4 sample of this time, whose chemical composition is $K_{9.1}H_{0.4}Al_{9.5}Si_{14.5}O_{48}$, as K-LTA(1.5), where 1.5 corresponds Si-to-Al atomic ratio of the framework. We denote the ratio as Si/Al. It is powdered one and is the same lot one as synthesized before [6]. After dehydration the obtained powder was packed in quartz glass tube with distilled

* Corresponding author. Tel.: +81 27 254 9126; fax: +81 27 254 9022.
E-mail address: igarashi@nat.gunma-ct.ac.jp (M. Igarashi).

0022-3697/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.jpcs.2006.01.082

potassium metal and heated in a furnace after sealing. The adsorption of potassium was done by this treatment and the resulting sample without residual K metal was transferred into quartz glass ampoule without exposure to the air. We call the resulting sample K_x/K-LTA(1.5), where x denotes the average number of adsorbed K atoms per one α cage. We prepared samples with $x=0$, 2.0, 4.0, 5.6, where 5.6 corresponds to saturated condition. For a purpose of reference, $K_{5.2}$/K-LTA(1.0), where 5.2 and 1.0 correspond to 5.2 atoms per α cage and to Si/Al, respectively, as for ZK-4, was also prepared by the same method as before [2]. This reference sample shows a ferromagnetic transition at 8 K.

^{27}Al NMR had been observed by a pulse type spectrometer (Thamway PROT-8000) in the field of 11.7 T, which corresponds approximately to 130.32 MHz for a zero shift reference or aqueous solution of $AlCl_3$. For most of measurements, a spin echo signal was observed using doubled pulse sequence, p_1–τ–p_2, where τ is a pulse separation. p_1 and p_2 correspond to high power rf pulses with the duration of $\pi/2$ and π, respectively. The ratio of the duration of p_1 and p_2, as usual way for tuning of the experimental condition, has been kept as $t_{p_1} : t_{p_2} = 1 : 2$ and the power of the rf pulses was tuned to give maximal echo intensity.

3. Results and discussion

^{27}Al NMR spectra of K_x/K-LTA(1.5) at 300 K are shown in Fig. 1. Each spectrum is normalized by integrated intensity. The transverse axis is taken in the frequency scale as relative shift from ^{27}Al in $AlCl_3$ aqueous solution. Scale in ppm unit is shown on the upper transverse axis. Much higher gain of the receiver and number of averaging can make a signal from the satellite transitions be observed for several 100 kHz area in both sides of the peak as discussed before [7] but we do not show them. We are interested in the central transition and in an influence or widening by introduced clusters. The $x=2.0$ case is an exceptional one but we postpone the discussion for that to later. Moreover there is a possibility that the width of the centered spectrum is given by multiple component which requires magic angle spinning (MAS) NMR other than static NMR for being distinguished [8]. Since, however, we do not have such facility, we here do not discuss the included components among the statically narrow NMR spectrum.

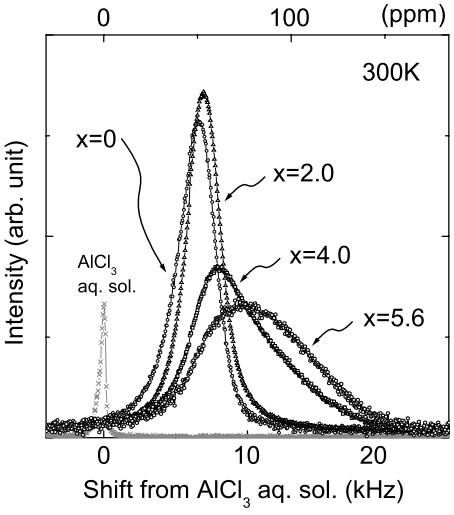

Fig. 1. Loading level variation of ^{27}Al NMR spectra at 300 K in K_x/K-LTA(1.5).

The peak shifts to higher frequency direction also as increasing loading level. The shift of the sample of $x=0$ from aqueous solution of $AlCl_3$, 55 ppm, may correspond to pure chemical shift. No existence of adsorbed electron hardly causes shift other than chemical one. The value itself gradually decreases as decreasing temperature as in the case of Rb_x/Rb-LTA(1.0)[4], where 1.0 corresponds Si/Al. This temperature dependence may originate in the nature of ^{27}Al in zeolite LTA system. The peak of every sample shows similar temperature dependence, which here we do not show. The plots of the shifts versus temperature behave parallelly with holding constant difference among each other. Therefore all the components of the spectrum may basically have chemical shift with common temperature dependence. But the values 60 ppm ($x=4.0$) and 75 ppm ($x=5.6$) may be seen as containing an additional shift other than simple chemical one. Moreover the shapes of these cases are seen as synthesized with multiple component because of their asymmetry.

We now concentrate our attention to the case of $x=5.6$. The temperature variation of ^{27}Al NMR spectra is shown in Fig. 2 with referring that of $K_{5.2}$/K-LTA(1.0). Each spectrum is normalized by peak intensity. The transverse axis is taken as same as Fig. 1. As clearly seen, full width at half maximum (FWHM) of LTA(1.5) case is wider than LTA(1.0) case at every temperature. In addition, the higher frequency side is expanded to higher frequency direction. Mass center of the spectrum clearly shifts to higher frequency side. This deformation of the spectrum makes one imagine an appearance of a component with relatively positive shift. Since there remain some problems to give a clear separation of that from other component, we here check the signal in the aspects of the experimental conditions.

At first let us vary τ, which is the pulse separation time between $\pi/2$ and π pulses. The result at 300 K is shown in the lower part of Fig. 3. The gain of the longitudinal axis is kept constant all through the observation. Difference among the shapes of the spectra for each τ is not so clear but, as shown in the middle part of Fig. 3, where longitudinal axis is normalized by the peak intensity, we see relatively rapid decrease around higher frequency side of the peak. This means that the component at higher frequency side has smaller T_2 value than the remained component. Feature of this situation is more clearly displayed by another way of data processing. A processed shape of the spectrum with $\tau=50$ μs, which is the one obtained by subtracting that with $\tau=500$ μs, appears as shifted for higher frequency side as shown in the upper part of Fig. 3 with an arrow. This also corresponds to smaller T_2 of the higher frequency component. Lower frequency side component has longer T_2 value and suppressed by this treatment.