

MICROOPTICAL SPECTROSCOPY OF POTASSIUM ADSORBED IN CHANNEL-TYPE ZEOLITE

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The polarized absorption and the reflection spectra are reported for K-incorporated single crystals of zeolite AFI and MOR, both of which have one dimensional channels. K does not come in through the AFI channel, but is adsorbed in the wall of the channel. The reflection spectra of K-incorporated AFI don't show large polarization dependence. In the case of MOR, however, the absorption spectra show clear polarization dependence. The existence of cation is found to play a very important role in the adsorption of K.

1. INTRODUCTION

Much attempts have been made to generate clusters, molecules or chains incorporated into nano-space of cages or channels, such as carbon nanotubes[1], zeolites[2] etc. Their properties have attracted much interests, for example, ferromagnetic properties of potassium clusters adsorbed into zeolite LTA[3]. In order to investigate their properties, it is important to study how materials are incorporated into cages or channels.

Zeolites are crystalline materials having nanoscale cages or channels. In the present paper, channel type zeolites MOR and AFI are used for K adsorption into channel. No other study have been done about the alkali metal adsorption into channel type of zeolites. The adsorption process of K into AFI and MOR is observed by optical microscope. Polarized absorption and reflection spectra are measured by using a microoptical spectroscopy. According to experimental results, the position of K cations as well as the framework potential is found to be an important parameter in the adsorption process.

2. EXPERIMENTAL PROCEDURE

We used single crystals of AFI and MOR. AFI single crystals with the chemical composition of $\text{Si}_x\text{Al}_{12-x/2}\text{P}_{12-x/2}\text{O}_{48}$ ($x=1\sim 2$), so called SAPO-5, was synthesized. The crystal size was about 150 μm along the *c*-axis, and 50 μm across the *c*-axis. AFI has one dimensional channels along *c*-axis with an effective diameter of 7.3 \AA . AFI framework is electrically neutral, and has no cation in the space of framework. K-form MOR with the Si to Al ratio of 6.5 was used. The crystal size was almost same as that of the AFI single crystal. MOR has also one dimensional channels along the *c*-axis and their effective size are 6.5 \times 7.0 \AA . The MOR framework has negative charge, and includes K cations in the space of framework. A special technique was needed to synthesize large crystals with smooth surface. In the case of the MOR, two silica sources, a sodium silicate aqueous solution and an aerosil, were used in order to feed Si to the zeolite crystal at a suitable speed during the growing process

of the crystal. The synthetic process of AFI was referred to the method of Finger's method[4] with some modifications.

Each zeolite crystals were dehydrated in vacuum at 550 °C for 15 hours, and then sealed in a quartz glass tube together with distilled K source. K were incorporated into the zeolites by the adsorption through vapor phase at the temperature between 100 and 150 °C.

In order to measure the optical spectra of zeolite single crystal, a hand-made microoptical spectroscopy system was constructed by using Cassegrain objective lenses. The typical spot size on the sample was less than 50 μm . A Gran-Taylor prism was used for the measurement of the polarized absorption and reflection spectra.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 K adsorbed in AFI

Figure 1 shows a photograph of the first step of the K-adsorption into AFI crystal. The crystal shape of AFI is the hexagonal prism. Crystals (a) and (b) are for the side and top views of the channel direction, respectively. From the side view (a), the crystal color is brown. The color is darkened with increasing the K concentration. From the top view (b), the hexagonal shape can be seen obviously, but only the edge has the brown color. The inside of the hexagonal prism is completely transparent. It means

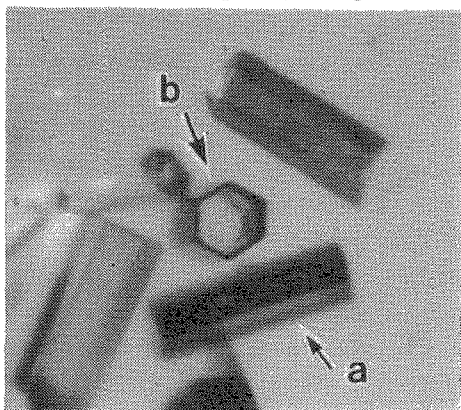


Fig. 1 The photograph of the first step of the K-adsorption into the AFI crystal. (a) and (b) are the side and top of the AFI crystal with the shape of hexagonal prism.

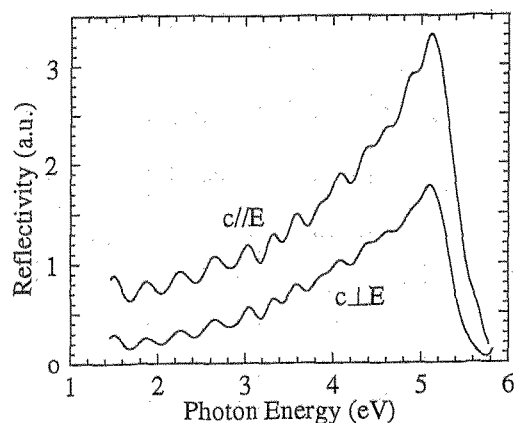


Fig. 2 Polarized reflection spectra are shown for K incorporated in the single crystal of zeolite AFI.

that the adsorption starts not from the top (the bottom) but from the side of AFI crystal. This result indicates that K cannot come in through the channel but is absorbed by the wall. The effective diameter of the channel is about 7.3 Å, and the wall of the channel consists of 6-membered rings with a diameter of 3.4 Å. By using same AFI crystals, BiI_3 molecules can be incorporated into the channels[5]. Hence, the channel size is large enough for K atom. It is surprising that K does not enter through the channels.

In order to investigate the electronic state of adsorbed K atoms and their electronic anisotropy in AFI, the polarized reflection spectra was measured by using microoptical spectroscopy. Figure 2 shows the polarized reflection spectra measured from the side of the AFI crystal at room temperature. In both polarization, the peak is observed at 5.1 eV. The reflection spectra are due to K adsorbed in the AFI, because the spectral shape is quite different from those of bulk K metal. The spectral shape does not depend on the successive K adsorption. In the spectrum, the interference pattern overlaps with the reflection, but those can be seen in original AFI crystal without any K adsorption. The AFI crystal is supposed to be covered with transparent material. Therefore, we do not pay attention to the interference pattern in this paper. The polarization dependence is not so obvious. Much lower energy spectrum is needed to clarify whether the K in the AFI is metallic or insulating. If the guest K atoms form

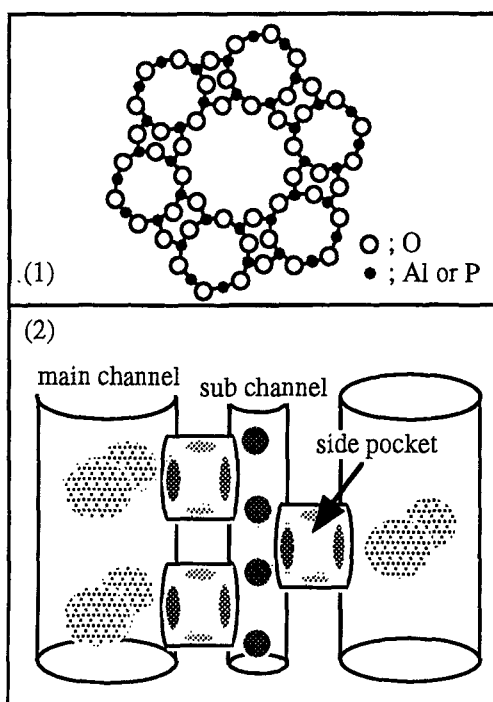


Fig. 3 (1) Schematic illustration of the channel of AFI are shown. (2) Schematic illustration of channel of MOR are shown. The slash area show the distribution of K^+ ions. The slash is darkened with increasing the distribution.

the one-dimensional metallic quantum wire, the reflection spectrum may shows a strong metallic reflection along the channel direction of the polarization at lower energy region. In the spectrum, however, no indication of such quantum wire is seen. The strong spectral peak in the UV region is assigned to s -electrons of K atoms. These electronic state is thought to be well localized, because of a high energy resonance peak. This localized state is assigned to the transition of K incorporated not in the channel but in the small cage in the wall of channel.

This adsorption process is quite different from the simple expectation that the guest K atoms come in through the channel. The main origin of the strange adsorption process may be ascribed to the framework potential. Figure 3(1) shows the schematic illustration of the AFI channel. The channel is constructed by 12-membered ring which

consists of 6Al, 6P and 12O atoms. The wall is constructed of the network of the 6-membered rings facing to the channel. O atoms are located little bit inside of the channel than Al or P. Inside the channel, the Coulomb potential is repulsive for electron, because O atoms are charged negatively. Hence, outer 4s-electron of K atom may be repulsive against the channel space, and they prefer to be in the wall. K cation may be near the 4s electron, then finally K atoms are in the small space (cage) in the wall of channel. However, above assignment is speculative, and we need much information about the adsorption process of K atoms.

In *p*-nitroaniline, molecules are expected to be entered to the AFI channel with the head-to-tail connection, and this orientation is thought to enhance the second harmonic generation of incident laser light [2]. The *p*-nitroaniline molecule can not rotate inside the channel. Hence, the head-to-tail orientation occurs when the molecule comes into the channel. However, the mechanism is not known yet. According to above discussion, the following speculation may be possible. If the channel is repulsive for the negative charge, the NH_2 group of *p*-nitroaniline molecule comes into the channel first, and NO_2 group follows it. The successive process leads to the head-to-tail connection of molecular chain.

The above results indicate that the charge balance of the zeolite framework plays a very important role in adsorption of K. In order to compare the adsorption process, another channel type zeolite MOR was used in the next section.

3.2 K adsorption in K-form MOR

When K adsorbed into K-form MOR, crystal was uniformly colored. The color was blue, when K concentration was low. The color depends on the polarization direction. The adsorption process of K into MOR crystals was quite different from that of AFI. Figure 4 shows the polarized absorption spectra of K adsorbed into the K-form MOR single crystal. The apparent polarization dependence is observed in the spectra. When the polarization direction is perpendicular to the c -axis, two absorption bands are observed at 1.60 and 2.00 eV. However, the polarization is parallel to the c -axis,

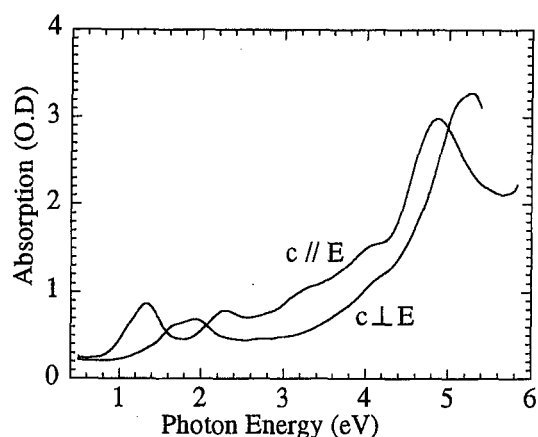


Fig. 4 Paralyzed absorption spectra are shown for K incorporated in the single crystal of zeolite MOR.

absorption bands are observed at 1.32 and 2.28 eV. This polarization dependence suggests that the electronic state of generated K cluster is quite anisotropic. The anisotropy itself is easily expected from the anisotropic framework. In the higher energy region, the absorption spectra have other bands. The dependence on the K-concentration is different from lower energy bands. Hence, the origin of higher energy bands are different from that of lower energy bands. In this paper, only the lower energy bands are discussed.

LTA and FAU have large cages with effective diameter of 11 and 13 Å. When K cluster is incorporated into zeolite LTA and FAU[3], the 4s electrons of the K atom carry the electronic properties of cationic K clusters incorporated into zeolites. Those electrons feel repulsion for the negatively charged framework and are attracted by the K^+ cations.

In the case of MOR also, the framework has negatively charged and includes K^+ cations in the space of the framework. The electrons are supposed to be distributed around K^+ ions. Figure 3(2) shows the distribution site of K^+ cations in the MOR framework. MOR crystal has two channels; one consists of 12-membered ring, and called the main channel, and the other consists of 8-membered ring, called the sub-channel. These two channels are connected with double 8-membered rings, called 'side pocket'. The most of cation are located at the side

pocket (a), the sub-channel (b) and the main channel (c). Cations are distributed mainly at the site (a), partly at the site (b), and a few at the site (c). When sites (a) and (b) are connected, the zigzag chain can be realized. From the integrated absorption intensity, the concentration of adsorbed K is estimated to be very low. The electrons of adsorbed K are supposed to be localized around the zigzag chain, because of the following reasons. A large number of K^+ cations are distributed around the site (a), and the distance between sites (a) and (b) is near. According to the absorption spectra, the resonance energy around 1.6 - 2.3 eV indicates that the electron wave function has the size with the order of 1 nm. The spectrum shows a clear anisotropy. Hence, it is quite reasonable to assign that K clusters are generated around the sub-channel with zigzag chain or side pocket, because of their size and anisotropic structure of the space. In order to investigate K in MOR in detail, the experiment in highly K-loaded MOR crystal is in progress by means of the wide range microoptical spectroscopy.

4. SUMMARY

K are incorporated into the channel type of zeolite AFI and MOR. In the case of AFI, K atoms are adsorbed not in the channels but in the wall. This results is attributed to no cation in the space of the AFI framework. In the case of K-form MOR, the absorption show the polarization dependence on the channel. The difference is assigned to the distribution of cations. The importance of the cation distribution is pointed out in the adsorption process of K.

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