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Electronic Properties and Structure of Clusters in Zeolite Crystals

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Guest materials in the nanospace of well defined zeolite cages and channels show various electronic properties and structures. When alkali metal is loaded into cages of zeolite LTA or FAU, cationic clusters are generated together with the zeolite cations. These clusters show characteristic optical spectrum and magnetism reflecting both the quantum electronic state and the intercluster interaction, such as *s*-electron ferromagnetism in potassium clusters in LTA. The photochromism and photoinduced ESR signal is observed in Na-loaded Na-LTA(1). In cation-less zeolite, the mechanism of alkali metal adsorption is quite different from that in cation-rich zeolite.

1. Introduction

The regular nanospace of zeolite crystals allows us to fabricate new type of materials by the incorporation of guest materials. The guest materials form various types of clusters (or wires) depending on the host-guest interaction as well as the guest-guest interaction. Contrary to the ordinary materials which are usually in the stable phase, the structure of above host-guest system is usually unstable, because zeolite framework is changed to amorphous phase, when the temperature rises up to more than 1000 °C. Sometimes, guest materials show chemical reaction with the framework. The essential point for the cluster fabrication is how to incorporate guest materials into zeolite space without braking the framework structure of zeolite. Therefore, the host-guest interaction is one of the key point of the material design.

Al is contained in the framework in the alminosilicate zeolite. The AlO_4 sites are negatively charged compared with SiO_4 sites, and charge-compensated with zeolite cations, such as Na^+. These cations are distributed in the space of framework. The pair of AlO_4 and cation has a permanent dipole moment which acts as the attractive potential for guest materials. Usually, Al- and Si-rich zeolites are hydrophilic and hydrophobic, respectively. The hydrophilic zeolite adsorbs Se depending on the Al content[1]. Se has the linear chain structure and the ring one in bulk crystals. Hence, Se can have a similar structure in the nanospace of zeolite, for example, linear chain in MOR[2,3] and cluster with closed ring structure in LTA[4].

PbI_2 clusters are generated in zeolite LTA and FAU[5,6]. Some strange indication has been observed in the structure. Most striking one is the appearance of the extra-reflection spot of electron diffraction pattern in PbI_2-saturated LTA[7]. This appearance indicates that the combination between PbI_2 and LTA shows superstructure with the symmetry different from the original LTA-framework. A rough image of the superstructure is given by the double period ordering of PbI_2 clusters. In this model, we assume different sizes of cluster, such as $(PbI_2)_5$ and $(PbI_2)_3$. BiI_3 molecule is incorporated into the channel of zeolite MOR. According to the polarized optical absorption spectrum by the microoptical measurement, BiI_3 molecule is sitting depending on the cation potential[8].

In alkali metal cluster, situation is quite different from above ones. When alkali metal vapor is adsorbed into dehydrated zeolite, *s*-electrons are shared with zeolite cations as well as guest atoms. When Na is dilutely adsorbed into Na-form FAU with the higher Si-to-Al ratio, called NaY, cationic cluster Na_4^{3+} is known to be generated in β-cage[9,10]. In this cluster, one 3*s*-electron is shared with four Na^+ cations. In the present paper, we overview the electronic state of alkali metal cluster and their structure. In K clusters generated in LTA, a ferromagnetism has been observed at a certain electron density, although no magnetic element is contained[11]. It is very important for the novel synthesis of cluster material to find a suitable combination of the host zeolite and guest material.

2. Zeolite framework and the effective potential for guest *s*-electrons

The quality of zeolite crystal is recently further improved, and zeolite increasingly plays an important role as the container of guest materials as well as the molecular sieve, catalysis, adsorbent, builder, etc. Many types of zeolite crystals are synthesized under various growth conditions. The most typical zeolite is alminosilicate. A general chemical formula of alminosilicate zeolite is given by

$$M_{m/r}\cdot Al_mSi_nO_{2(m+n)}\cdot xH_2O, \quad (m \leqq n),$$

where $Al_mSi_nO_{2(m+n)}$ constructs the framework of zeolite, and M is an r-valent cation which is sitting at the site near the framework.

The framework material of alminosilicate zeolite is transparent between infrared and ultraviolet regions. This point is very important in the optical study of guest materials. Zeolite is stable at rather high temperatures. Structurally unstable clusters can be supported in nanometer size cages. Besides the cage type zeolite, there are a lot of channel type zeolite. One dimensional chain structure can be stabilized there.

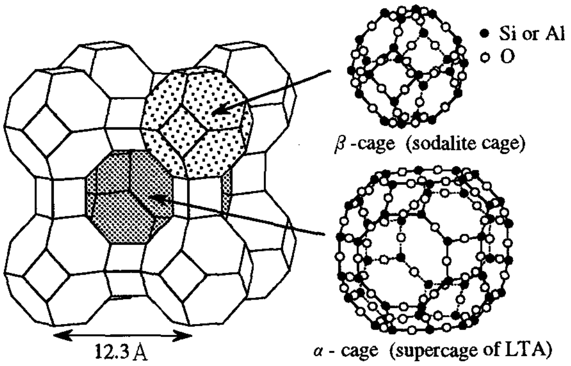

Fig. 1 Framework structure of zeolite LTA. Closed and open circles indicate (Si or Al) and O, respectively. The β-cages are connected at the 4-membered rings in a simple cubic structure with the lattice constant of 12.3 Å. The α-cage (or the supercage of LTA) is formed among β-cages. In the figure, cations are not shown.

LTA is one of the most typical zeolites. In Fig. 1, LTA framework structure is shown schematically, where cations are neglected. Open and closed circles indicate O and (Si, Al) atoms, respectively. A basic unit cage is called the β-cage or the sodalite cage. The β-cage has the effective inner size of 6 Å. The β-cages are connected at double 4-membered rings, and arrayed in a simple cubic structure. Among β-cages, a new cage, called the α-cage (or the supercage of LTA), exists. In other words, the α cages are connected by the sharing of 8-membered rings in a simple cubic structure. The α cage has the effective inner size of 11 Å. The 8-membered ring is called the window of α-cage. We denote Na type zeolite LTA with Si to Al ratio of unity as Na-LTA(1), hereafter.

Besides LTA, there is FAU (faujasite) zeolite which has the β-cage as the basic unit cage. In FAU, β-cages are connected at 6-membered rings, and arrayed in a diamond structure. Zeolite MOR (mordenite) has a different type of framework, and has parallel channels with an inner diameter of about 7 Å.

The cation in zeolite is located at the potential minimum which is given by the interaction with the framework and other cations. In Fig. 2, the total Coulomb potential is calculated for an electron according to the structural data of the dehydrated Na-LTA(1)[12]. The abscissa is the distance on the [111]-line ($x=y=z$) in units of Å, where the origin is taken at the center of the β-cage. The Na cation at the center of 6-membered ring is located at $x=y=z=0.20a$, where $a = 12.3$ Å. The pseudopotential is assumed for Na cations. The total pseudopotential (solid curve) has the peak around $x=0.20a$. The potential at the center of β-cage is nearly the same as that at the center of α-cage. When the cation position at the center of 6-membered ring is shifted to the centers of α-cage and β-cage, a remarkable up-and-down of potential occur at the center of α- and β-cage.

Above calculation suggests that the cation is located at the subtle balance of the attractive and repulsive interaction. The shift of cation position leads to the remarkable up-and-down of potential for the guest *s*-electrons. The situation in cation-less zeolite, such as $AlPO_4$-5 type zeolite, is quite different from above one, because of the neutral framework[13]. K atoms do not come in through the channel of AFI zeolite, although the channel is large enough for the incorporation of K atom. The reason is tentatively assigned to the repulsive interaction with 4*s*-electron of K atom. The O atoms of $AlPO_4$-5 type zeolite are facing to the interior surface of channel. Hence, the potential for electron is repulsive inside the channel.

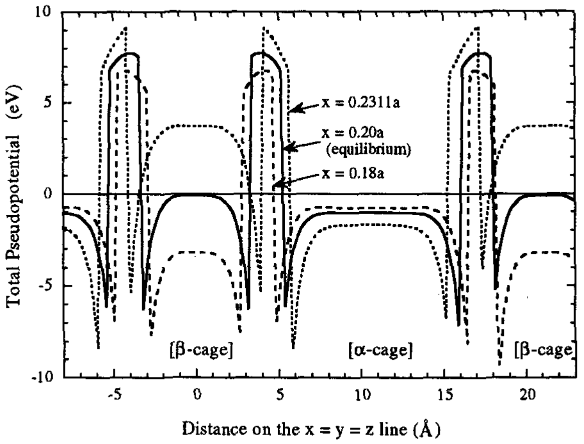

Fig. 2 Calculated total pseudopotential in dehydrated Na-LTA(1). The abscissa is the distance from the center of the β-cage on the [111]-line. The position of the Na cation at the center of 6-membered ring is set at $x = y = z = 0.2311a$, $0.20a$, $0.18a$, where $x = 0.20a$ in the dehydrated Na-LTA(1).

In *p*-nitroaniline molecules are expected to be arrayed in the AFI channel with the head-to-tail connection, and this orientation is thought to enhance the second harmonic generation of incident later light[14]. 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 of above structure 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.

When the Si-to-Al ratio is changed in the common zeolite framework, cluster formation is found to change. The spectral difference is shown for K clusters generated in FAU with different Si-to-Al ratio in Fig. 3. In K-FAU(2.8), remarkable absorption band is seen at 2.4 eV. According to the rough estimation of the quantum electronic state of cluster, the resonance energy 2.4 eV indicates that the cluster is generated in the β-cage[15]. In K-FAU(1.1), however, the spectral shape is quite different from that in K-FAU(2.8). This clusters is generated in the supercage, and electrons are in the extended state, because of the wide band width and different structural shape extended to lower energies. Hence, the difference in the cation density leads to the difference in the intercluster interaction as well as the site of cluster.

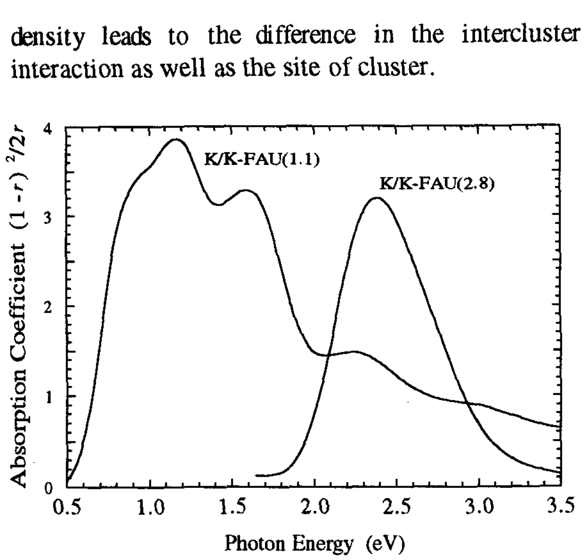

Fig. 3 Absorption spectra of dilutely K-loaded K-FAU(2.8) and K-FAU(1.1).

3. Structural instability of cluster and magnetic state

Diamagnetic clusters are generated in β- and α-cages in dilutely and densely Na-loaded Na-LTA(1)'s, respectively. When the light is irradiated for the absorption peak of the diamagnetic Na clusters generated in the β-cage, a remarkable photochromism occurs[16]. Simultaneously, a photoinduced ESR signal is observed as shown in Fig. 4[16]. This cluster is assigned to the Na_4^{3+} cluster with the C_{3v} symmetry by the analysis of the hyper-fine structure of the ESR spectrum. Hence, the light irradiation to the diamagnetic cluster leads to the generation of paramagnetic cluster. This is a reminiscent of the lattice instability in the Na clusters in LTA.

When K metal is adsorbed into K-form LTA, a ferromagnetism has been observed, although no magnetic element is contained[11]. The ferromagnetism strongly depends on the average electron concentration per cluster. An *ac* magnetic susceptibility at 2 K increases and decreases in several orders as a function of the electron concentration per cluster. Around the five electrons per cluster, the *ac* susceptibility is saturated. The observed huge value is a manifestation of ferromagnetism. The observed *M-H* curve shows a very soft ferromagnetism.

The magnetization at 1.7 K under the external magnetic field of 100 Oe increases above the electron concentration of 2, and has the peak around 5 and decreases at higher concentrations[11]. The electron concentration at which a significant magnetization is observed is in the region between 2 and 8 electrons per cluster. This region well corresponds to the condition that the 1*p* state of quantum electronic state of cluster is partly occupied with electrons. The 5 electrons per cluster just coincides with the two electrons for 1*s* state and three electrons for 1*p* state. In this electron configuration, the maximum spin state is expected, because of the Hund rule for 1*p*-state electrons. The stability of the ferromagnetic state is calculated by the introduction of the second neighbor electron transfer term[17].

The ferromagnetism and diamagnetism observed in alkali metal clusters indicate that slight difference in the electronic parameter changes the magnetic phase dramatically.

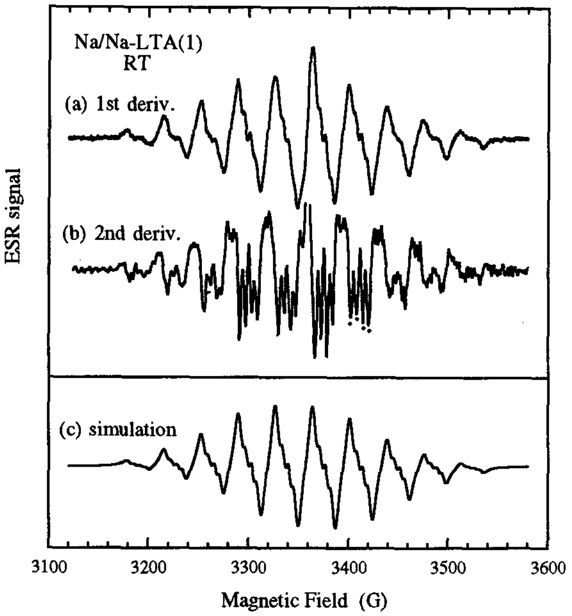

Fig. 4 Photoinduced ESR spectrum of Na loaded Na-LTA(1). Curves (a) and (b) are 1st and 2nd derivative, and curve (c) is the result of simulation.

Summary

We can expect wide variety in the electronic properties as well as the structure of the nanoscale materials in the various combination of guest materials and host zeolites. The host-guest interaction plays an important role in the stability of the new structure.

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