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Interaction between guest AgI and host zeolite FAU studied by optical spectra and EXAFS

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Abstract. AgI molecules were dilutely adsorbed into nano-cages of Na^+, K^+ and Cs^+ type FAU zeolites in order to understand the interaction between host zeolite and guest AgI. This interaction was investigated using optical absorption spectroscopy and extended X-ray absorption fine structure (EXAFS). The optical spectra strongly depend on the type of the alkali cations. Compared with the lowest absorption band of AgI molecules in gas phase, the spectra of AgI molecules adsorbed in the zeolite cages shifts to higher energy in the order of Cs^+, K^+, and Na^+. On the contrary, Ag-I bond lengths of adsorbed AgI molecules obtained from EXAFS were independent of the type of the alkali-cations. The bond length was very close to gas phase AgI molecules. Therefore, the interaction between AgI molecules and the zeolite, whose magnitude is $Na^+ > K^+ > Cs^+$, is important in the photo-excited electronic state.

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1 Introduction

The structures and electronic properties of nanoparticles and clusters depend on their sizes and their surface environments. When the size of the clusters is reduced, the number of surface atoms per volume increases. Therefore, the structure and the electronic properties of clusters that are reduced in size become sensitive to the environment.

We have studied the optical properties and structures of AgI and AgBr clusters in nano cages of the zeolites LTA and FAU [1,2]. (The structures and chemical compositions of the zeolites used here will be discussed below.) The AgBr bulk crystal shows an indirect transition at the lowest photo-excited state. Thus, the quantum effect on photo-excited state of AgBr clusters was of interest. With the decrease in the size of the AgI and AgBr clusters, the lowest photo-excitation energies of these clusters shifted to a higher energy side. This behavior could be qualitatively explained by the quantum confinement theory of excitons. However, the absorption bands assigned to the excitation of AgI and AgBr molecules have quite higher energies than the lowest photo excitation energies of AgI and AgBr molecules in the gas phase.

If we base our estimation of the maximum loading densities of AgI and AgBr molecules into the cages on simple calculations, the number of AgBr molecules becomes larger than that of AgI molecules, because the lattice constant of bulk AgI is larger than that of AgBr. In the case of AgI, ca. 10 molecules can be adsorbed per cage. The actual maximum loading densities of AgI and AgBr molecules in the FAU zeolite, however, were both four molecules per supercage [3]. The adsorption properties of the guest AgI and AgBr clusters in the cages appeared strongly dependent on the interaction between the constituent Ag atoms and the zeolite framework.

Previously, Kodaira and Ikeda reported that the arrangement of the AgI clusters in zeolite LTA depends on the type of alkali cations (Li^+, Na^+ and K^+) distributed in the space of the framework [4]. It was concluded that the effective inner size of the cages varied by changes in the type of cation. This variation in the type of alkali cation is thought to exert an effect on the adsorption and electronic properties of the clusters.

In the present paper, we discuss the host-guest interaction between Na^+-, K^+-, and Cs^+-type FAU zeolites and adsorbed AgI molecules based on the optical absorption spectra and extended X-ray absorption fine structure (EXAFS) data. We chose to adsorb AgI as molecules into the FAU zeolites, because we had already found some interactions between AgI and the host Na-type FAU which accounts for the higher optical transition energy of adsorbed AgI molecules than that of AgI molecule in the

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gas phase [2]. In this context, the interpretation of the EXAFS data is facilitated.

2 Experimental

Zeolite FAU, used in the present study, has a chemical composition of $M_{83}Al_{83}Si_{109}O_{384}$, where M indicates monovalent exchangeable cations. In the present case, M denotes Na^+, K^+, and Cs^+. For convenience, we will refer to this FAU zeolite as M-FAU(1.3), where the numeral in the parentheses indicates the Si-to-Al atomic ratio of the framework. FAU consists of two types of cages referred to as the sodalite cage and the supercage, with inner diameters of ca. 7 and 13 Å, respectively. Supercages arrayed in a diamond structure are connected directly to each other, sharing a window of ca. 7 Å. Cations are exchanged for K^+ and Cs^+ by soaking Na-FAU(1.3) in KCl and CsCl aq. solutions, respectively. In the case of Cs-FAU(1.3), not all of the Na^+ ions of the initial Na-FAU(1.3) zeolite were converted into Cs^+ ions. Nearly 70% of the Na^+ ions were estimated to be exchanged for Cs^+ ions.

AgI was adsorbed through the vapor phase into M-FAU(1.3). The fundamental procedures of the sample preparation have been described previously [3,5]. The loading density of AgI molecules per supercage was 0.3 for the three samples. The obtained samples were sealed in quartz glass tubes. We abbreviated the references to these samples as follows: AgI/M-FAU(1.3).

Optical absorption spectra were obtained transforming the diffuse reflection spectra measured under ambient conditions using the Kubelka-Munk function, $(1-r)^2/2r$, where r denotes the diffuse reflectivity. The absorption spectrum of Ag^+ ion-exchanged zeolite FAU(1.3) (Ag-FAU(1.3)) obtained by soaking Na-FAU(1.3) in $AgNO_3$ aq. solution was also measured for comparison.

In order to measure the X-ray absorption fine spectra (XAFS), the samples, sealed in glass tubes, were transferred and sealed in Al sample holders with Kapton film windows by using a He gas globe box to prevent the degradation of the samples by O_2 and H_2O gas adsorption. Ag and I K-edge XAFS of the samples, and bulk AgI crystals dispersed in a BN disk as a reference sample, were measured in transmission mode under ambient conditions using BL-01B1 at the SPring-8 synchrotron radiation facility in Japan. The k^3-weighted EXAFS data were Fourier-transformed (FT) from k-space into R-space.

3 Results and discussion

3.1 Optical absorption spectra

Figure 1 shows the optical absorption spectra of the AgI/M-FAU(1.3) samples. Spectral shapes and peak positions strongly depended on the type of alkali-metal cation, M, of the host zeolite FAU. In the case of AgI/Na-FAU(1.3), a notable absorption band appeared at 5.5 eV. Previously, this band was concluded originating from photo-excitation of AgI monomers (molecules) [2]. In case of AgI/M-FAU(1.3) of $M = K^+$ and Cs^+, peak positions of the lowest absorption bands were 4.9 and 4.8 eV, respectively. This finding indicated that the absorption band shifted to lower energy in the order of $M = Na^+$, K^+, and Cs^+. The shift did not originate from species larger than the AgI monomer, i.e., $(AgI)_n$ ($n \geq 2$) clusters, which induce weaker quantum confinement in the photo excited state [2]; instead, the shift was due to interactions with the cations Na^+, K^+, and Cs^+. These results can be accounted for in the following manner, namely, these three bands are from the smallest structural unit of adsorbed AgI, because these bands did not disappear, but merely were reduced in terms of their intensity in a manner proportional to the loading density, even when the AgI loading density was reduced to lower than 0.1 molecules per supercage.

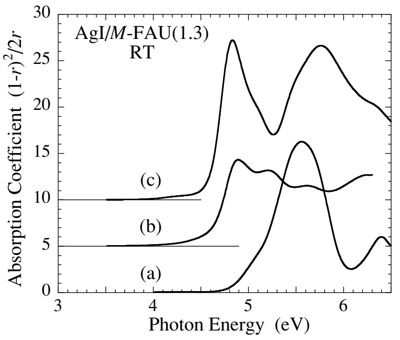

Fig. 1. Absorption spectra of AgI-loaded (a): Na-FAU(1.3), (b): K-FAU(1.3), and (c): Cs-FAU(1.3) at RT.

The HOMO-LUMO transition energy of gas-phase AgI molecules is 3.9 eV [6]. By changing the cation M from Na^+ into Cs^+ through K^+, the electronic state of the adsorbed AgI molecules becomes close to that of AgI molecules in gas phase. We propose a model in which the degree of the ionicity, δ, of the Ag and I atoms depends on the type of alkali cation, i.e., $Ag^{\delta+}$-$I^{\delta-} \cdots M$, because cation M will exert strong attractive Coulomb force, or chemical bonding with the iodine atom. Ionization energies, the definition of which is the energy required to remove one electron from a neutral atom, increased in the order of Cs, K, and Na. This finding suggests that the Na^+-ion has the largest electron affinity among these three kinds of ions. The value of δ will depend on the ionization energies of Na, K, and Cs, and will decrease in this order. Therefore, the bonding of the Ag and I atoms appears to vary from a convalent-like character to an ionic-like character when the cation M changes from Cs^+ to Na^+ through K^+.

The absorption spectrum of AgI/Na-FAU(1.3) was compared with that of Ag-FAU(1.3), as shown in Figure 2. Not only the spectrum of Ag-FAU(1.3) resembles that of AgI/Na-FAU(1.3), it is also similar to those of Ag^+-exchanged MFI (Ag-MFI) and LTA (Ag-LTA) zeolites [7,8]. These results indicate that the optical transition of Ag^+ ions is independent of the framework type. The origin of the photo excitation of Ag^+ ions in Ag-MFI

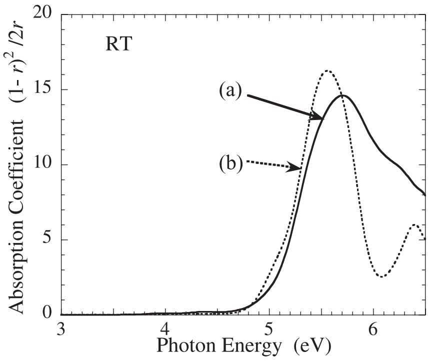

Fig. 2. Absorption spectra of (a): Ag-FAU(1.3) and (b): AgI/Na-FAU(1.3).

and Ag-LTA at 5−6 eV was interpreted on the basis of the $(4d)^{10}$ to $(4d)^9 5s$ atomic orbital transition. Dexter et al. reported that the observed absorption bands at 5−6 eV have an oscillator strength of ca. 0.2 per Ag^+ ion [8]. The $(4d)^{10}$ to $(4d)^9 5s$ transition is usually optically forbidden at isolated Ag^+ ions in a vacuum. Ag^+ ions embedded in alkali-halide crystals show weak oscillator strength at the order of 10^{-3}. The origin of the weak allowed transition is the coupling of Ag^+ orbitals with odd parity phonons of the host crystals [9]. To account for the substantial the large oscillator strength of Ag^+ in the zeolite LTA, further investigation will be necessary.

Adsorbed AgI molecules in the cages of Na-FAU(1.3) may be decomposed into Ag^+ and I^- ions, i.e., $\delta = 1$, in the worst case, because the absorption spectrum of the AgI/Na-FAU(1.3) sample shown in Figure 2 is identical to that of Ag-FAU(1.3). However, the optical transition includes information about both the electronic ground and the excited states. The electronic state that primarily contributes to the interaction between the guest AgI and the cation M remains unknown. EXAFS study only provides information about the local structure at the electronic ground state, as discussed in the next section.

3.2 EXAFS study

The FT data from Ag and I K-edge EXAFS are shown in Figures 3 and 4, respectively, for three AgI/M-FAU(1.3) samples and the bulk AgI crystal. The shortest distance between two atoms in bulk AgI with zincblende and wurtzite structures is 2.8 Å, which is the result of Ag-I chemical bonding. The scattering species observed at 2.5−2.6 Å, shown by open and closed circles at curve (a) in Figures 3 and 4, respectively, can be consistently assigned to I and Ag atoms, respectively. The observed distance of Ag-I bonding is slightly shorter than the actual bond length, because the phase-shift correction was not considered at the simple Fourier transformation. This shortened distance effect, with an error of ca. 0.2 Å between the Ag and I atoms, is also included in the data for the AgI/M-FAU(1.3) samples.

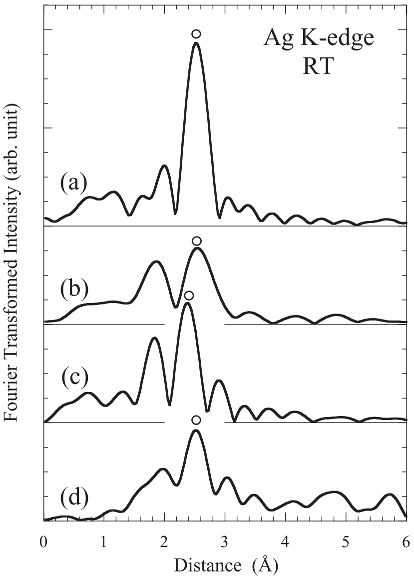

Fig. 3. FT-data of Ag K-edge EXAFS for (a): bulk AgI, (b): AgI/Na-FAU(1.3), (c): AgI/K-FAU(1.3), and (d): AgI/Cs-FAU(1.3). The structures indicated by open circles are from I atoms.

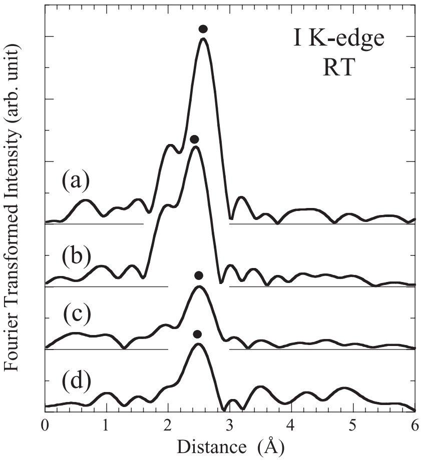

Fig. 4. FT-data of I K-edge EXAFS for (a): bulk AgI, (b): AgI/Na-FAU(1.3), (c): AgI/K-FAU(1.3), and (d): AgI/Cs-FAU(1.3). The structures indicated by closed circles are from Ag atoms.

We can clearly see scattering species at ca. 2.5 Å, as marked by the open circles in curves (b)−(d) of Figure 3. Scattering species at ca. 2.5 Å can also be observed in curves (b)−(d) in Figure 4 as indicated by the closed circles. Therefore, it was apparent that these scattering species were from the I and Ag atoms in Figures 3 and 4, respectively. The bond length was found to be independent of the type of cation M. If the guest AgI molecules have strong ionic bonding character ($\delta = 1$), the bond length is expected to be close to 3.42 Å, because the sum of the radii of Ag^+ (1.26 Å) and I^- (2.16 Å) ions gives this value. A length of an Ag-I bond in gas phase AgI molecules is 2.54 Å [6]. Thus, independent of the type of the alkali-cation M, the electronic ground states of adsorbed AgI into three types of host FAU have a character similar to that of the AgI molecule in gas phase. In particular, it was made clear that the AgI molecules in Na-FAU(1.3) did not decompose into Ag^+ and I^- ions.

In Figure 3, we can also see scattering species at a distance of 1.8−1.9 Å in the samples of AgI/M-FAU(1.3). These structures were not observed in the I K-edge EXAFS data shown in Figure 4. The origin of this scattering species may be the oxygen atoms of the FAU framework, because Ag-O bonding was observed at a distance of 1.7 Å in the Ag K-edge FT data of Ag-MFI [10]. Both bulk and gas phase AgO molecules have an Ag-O bond length of 2.0 Å. Therefore, it appears that the Ag atoms of adsorbed AgI molecules locate close to the framework oxygen atoms.

3.3 Electronic state of guest AgI in zeolite cages

The EXAFS study indicated that, independent of the type of cation M, the bonding character of the adsorbed AgI molecules in M-FAU(1.3) resembled that of gas phase AgI in the electronic ground state. Therefore, the large difference observed in the optical spectra originated from the effects of cation M in the electronic excited states. Ag atoms were situated near the framework O atoms, as described in Section 3.2. We did not observe any sign of cation M around Ag and I atoms in the present EXAFS FT-data. Therefore, in the electronic ground state, the configuration of the atoms can be roughly described as follows: =O ⋯ Ag-I ⋯ M, where "=O" indicates that the oxygen atoms have two strong covalent bonds with Si or Al atoms of the framework, and "⋯" indicates the weak interaction. In this configuration, the degrees of ionicity on the adsorbed Ag and I atoms are similar to those of AgI in the gas phase. The position of the cation M is a plausible one, as already discussed. The cation M can exist near the O atom, as well as at its initial site, prior to the adsorption of the AgI molecules.

On the contrary, as mentioned in Section 3.1, the degree of ionicity, i.e., the mixing level of electron wave functions between Ag and I atoms, is significant in the excited state. Furthermore, the large ionicity δ appears to induce an energy shift in the optical transition of the adsorbed AgI molecules. However, in order to account for the optical transitions of AgI/Na-FAU(1.3) and Ag^+ ion-exchanged zeolites, the contribution of the interaction between the Ag^+ ion and the framework O atom should be introduced, as explained below.

As regards the interaction between the Ag and O atoms in AgI-loaded M-FAU(1.3) and Ag-type zeolites, a weak but finite interaction with the O atom is thought to exist in the electronic ground state of Ag^+, because Ag clusters can be formed by the mere heating of Ag-type zeolite under atmospheric conditions [11]. Electrons are supplied to Ag^+ ions from the negatively charged framework through framework O atoms. Similarly, the substantial oscillator strength of the Ag^+ ions in Ag-LTA zeolite indicates that a further mixing of electron wave functions of Ag^+ and O atoms exists in the electronic excited state. This mixing, i.e., this interaction, is expected to induce the large oscillator strength of the optical transition. In the case when AgI is adsorbed into zeolite Na-FAU(1.3), no pure Ag clusters or atoms were detected in the optical spectrum. Therefore, the Ag-I bonding of adsorbed AgI molecules inhibits the interaction between the Ag and O atoms in the electronic ground state.

Finally, we will summarize the effect of the host-guest interaction on the AgI clusters in zeolites. Compared with the lowest photo absorption energy of the AgI bulk, the previously observed high energy shift of the absorption bands of AgI clusters with decreases in their size [1,2] includes not only the quantum-size effect but also the interaction between AgI clusters and the cation M in the electronic excited state. If the AgI clusters (molecules) exhibit a strong ionic character induced by the cation M, the Ag-O interaction will be indirectly enhanced. However, when the AgI clusters are large, these interactions become relatively weak, because the number of Ag-I bonds per cluster increases. If we expose the AgI loaded zeolite samples to air, the AgI is partially released from the cages and forms bulk AgI [3,5]. The adsorption potential for the guest AgI clusters is therefore shallow.

4 Summary

Based on the optical spectra and the FT-EXAFS data, it was revealed that guest AgI molecules and the host FAU zeolite undergo a notable interaction in the electronic excited state. The interaction can be controlled by changing the type of alkali-cation distributed in the space of the zeolite framework. The interaction in the electronic ground state is relatively weak. The interaction in the excited state increased in the following order: Cs^+, K^+, and Na^+. The type of cation appears to control the bonding character from covalent to ionic in the electronic excited state. The interaction between the Ag^+ ion and the O atom of the zeolite framework appears to be especially important for the optical properties of AgI/Na-FAU(1.3) and Ag^+-type zeolites.

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