Electronic states and arrangements of AgI and CuI clusters incorporated into zeolite LTA

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Both AgI and CuI clusters were successfully incorporated into the cages of Na-type LTA. The maximum loading densities of the AgI and CuI molecules per [-cage were 4.0 and 6.3, respectively. In the optical spectra, the lowest absorption bands of both kinds of clusters show a large shift to the higher energy side compared to that of the original bulks. It was found that the space group of the original Na-LTA, Fm3c, changed to lower symmetry ones by incorporation of both kinds of clusters. These are determined by the appearance of new reflections in the X-ray powder diffraction patterns. The physical properties of these two kinds of clusters seem to be slightly different. CuI molecules adsorbed sparsely into the cage have the property to aggregate and form a cluster. The CuI clusters have large electron-vibration interaction.

1. INTRODUCTION

We have studied the electronic states and arrangements of the AgI and AgBr clusters incorporated into LTA and FAU [1-3]. There are several reports on the adsorption of AgI onto zeolites[4-6]. The electronic states, however, of the guest material have been not discussed in detail. We discussed and compared the electronic states of the AgI and AgBr clusters in FAU from the viewpoint of quantum confinement on the photoexcited states of semiconductors which are the direct and indirect type in bulk[3]. With the increasing loading densities of the guest molecules of AgI and AgBr, the lowest absorption band shifts to the lower energy side in the absorption spectra. This can be interpreted by using the model of quantum confinement on the photoexcited state of semiconductor nano-particles [7] whose size become larger with the increasing loading density.

From a simple calculation using the bulk crystal structures and their lattice constants of the Ag-halides[8], it is possible to fill the supercage of zeolite FAU with ca. ten Ag-halide molecules or more. However, the actual maximum loading densities of the AgI and AgBr clusters per supercage of Na-type FAU with an Si-to-Al atomic ratio of 1.3 (Na-FAU(1.3))
were both four[3]. The saturated loading density of the incorporated AgI clusters into Na-
type LTA with an Si-to-Al ratio of unity (Na-LTA(1)) was also four molecules per []-cage[2].
It seems that the guest adsorbed Ag-halide molecules are not adsorbed by a simple physical-
adsorption, e.g., dipole-dipole or van der Waals attractive interactions. Some preferred sites
for the adsorption may exist on the wall of the cages.

In this paper, we mainly discuss the difference in the optical properties and arrangements
between the AgI and Cul clusters in Na-LTA(1). It was found that the maximum loading
densities of Cul depend on the type of the frameworks, LTA and FAU, which were 6.2 and 9.3
molecules per supercage, respectively. The absorption spectra measured at room
temperature (RT) and 77K had very small differences for the AgI clusters, but a large one for
the Cul clusters. This indicates that the intensities of the electron-vibration interaction in a
cluster are different in these two kinds of clusters.

2. EXPERIMENTAL

The method of incorporating AgI clusters into Na-LTA(1) and Na-FAU(1.3) has already
been described in Ref. 1. Cul clusters are successfully incorporated into Na-LTA(1) and Na-
FAU(1.3) by 1) distillation of bulk Cul, 2) dehydration of Na-LTA(1) and Na-FAU(1.3) at
500°C for 15h to completely remove the water molecules, 3) adsorption of Cul onto zeolites
in a vacuum at 400°C. The loading densities of the guests are selected by the weights of the
zeolites and the bulk semiconductors before the adsorption.

Diffuse reflection spectra of the samples were measured at RT and 77K. They were
converted into absorption spectra using the Kubelka-Munk function, (1-r)^3/2r, where r is the
diffuse reflectivity, and the X-ray powder diffraction (XRD) patterns were obtained at RT
using CuKα radiation in a high vacuum and in air.

3. RESULTS AND DISCUSSION

3.1. Loading densities of AgI and Cul in Na-LTA(1) and Na-FAU(1.3)

The number of adsorbed AgI and Cul molecules per supercage ([])-cage) at saturated
loading densities in Na-LTA(1) and Na-FAU(1.3) are summarized in Table 1. For reference,
the saturated loading density of AgBr in Na-FAU(1.3) is also shown. Comparing the value

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<th>AgI</th>
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<tr>
<td>Na-LTA(1)</td>
<td>4.0</td>
<td>-</td>
<td>6.2</td>
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<tr>
<td>Na-FAU(1.3)</td>
<td>4.1</td>
<td>4.0</td>
<td>9.3</td>
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of AgI to that of AgBr in both Na-FAU(1,3), they are almost the same. In both kinds of zeolites, Na-LTA(1) and Na-FAU(1,3), the saturated number of CuI molecules has larger values compared to that of AgI. This means that not a halogen atom but a silver atom plays an important role in the adsorption of the guest onto the zeolite cage. On loading CuI molecules, we can easily understand that the clusters are formed not in the \(\[\) cage but in the supercage of FAU or in the \(\square\)-cage of LTA, because the arrangements and inner diameters of the supercages or \(\square\)-cages and window sizes are different in these two framework structures. On the contrary, the number of AgI molecules in LTA and FAU is almost the same. Previously, we reported that the formed AgI clusters are in the \(\square\)-cage of Na-LTA(1)[1]. In the case of using the bulk AgI lattice constant, \(a = 6.473 \text{Å} \) (zincblende type)[8], it is estimated from a geometrical calculation that \(ca.\) ten AgI molecules can be introduced into the \(\square\)-cage. This means that the maximum size of the AgI clusters is not determined by the volume of the \(\square\)-cage, and they seem to be located next to the wall of the \(\square\)-cage. The AgI clusters, with some magic number, which depends on the host matrix, may have a relationship to the saturated loading density[9]. Of course, the possibility that the clusters are in the \(\square\)-cage, which is common unit of LTA and FAU framework, cannot be completely excluded at this stage.

3.2. XRD patterns of AgI and CuI clusters in Na-LTA(1)

Previously, we reported the XRD patterns of the AgI loaded Na-LTA(1)[1,2]. An XRD pattern of AgI_{4.0}/Na-LTA(1) (4.0 molecule per \(\square\)-cage) measured in a high vacuum is shown in Fig. 1(a). Reflections indexed as A and B, which are not allowed in the space group of the original Na-LTA(1), \(\text{Fm}3\overline{\text{c}}\), newly appeared by incorporation of the AgI clusters. For the present, these were interpreted as 111 and 211 reflections with a lattice constant \(ca. 24.7 \text{ Å}\) and systematic absence in a cubic symmetry[1]. Especially, reflection A has a large integrated intensity with a broad width. It seems that there are three possibilities for the origin of this reflection: 1) a Bragg peak originates from the incorporation of the AgI clusters, 2) thermal diffuse scattering (TDS) derived from fluctuation of the cluster size, and 3) some amorphous phase formed by the destruction of the framework upon incorporating the clusters. The oscillated background due to the TDS is also observed in the diffraction pattern of AgBr in bulk[10].

To clarify the origin of structure A, an XRD pattern of this sample was also measured in the air as shown in Fig. 1(b). Reflection A disappeared, but B still exists. The origins of new reflections labeled by W and Z can be assigned by the diffraction peaks from AgI in bulk with wurtzite and zincblende structures, respectively. This indicates that some of the guest AgI is reduced on the surface of the zeolite powder and forms bulk AgI through aggregation by the adsorption of molecules in air, \textit{e.g.}, water molecules. Disappearance of the reflection A with appearance of the reflections from AgI in bulk indicates that this structure is not from some amorphous phase, because once the framework is destroyed, it never returns to a zeolite structure. The possibilities of 1) and/or 2) can not be determined by this experiment. Reconstruction on the atomic arrangement of AgI may lead to a new space group which does
Fig. 1 XRD patterns of AgI_{4}/Na-LTA(1) at RT. (a): in a vacuum, (b): in air. Reflections A and B appeared by the incorporation of AgI clusters. Reflections marked W and Z correspond to the reflections of AgI in bulk with Wurtzite and Zincblende structures, respectively.

not allow the appearance of the 111 reflection, or TDS may not occur due to the adsorption of atmospheric molecules. If reflection A is a Bragg reflection, the large integrated intensity with a wide width of the 111 reflection indicates that the array of the AgI cluster on the [111] plane has a small domain. The diffraction patterns should be measured at low temperature in the future to clarify the origin of reflection A.

An XRD pattern of Na-LTA(1) with CuI at a saturated condition is shown in Fig. 2. There are large humps, which may be from TDS, in the background. The Cu and/or I atoms are postulated to be fluctuating with correlation between the neighboring guest atoms in the cage. This phenomenon has a relationship to the mobility of atoms or ions in the space of zeolite cages[11] and to the temperature dependence on the optical spectra discussed in the next section. The low angle region is expanded in the inset of Fig. 2. No 111 but 211 reflections were observed. Reflection of the 200 splits into two reflections which suggest the space group was degraded to a lower symmetry, e.g., tetragonal or rhombohedral symmetry. A specific space group, however, has not yet been determined yet.
Fig. 2 XRD pattern of CuI_{3/2}/Na-LTA(1) at RT. The inset shows the pattern of the low 2\theta region with reflection indices based on cubic symmetry.

3.3. Optical spectra of AgI and CuI clusters in Na-LTA(1)

Absorption spectra of the AgI clusters in Na-LTA(1) with a systematic change in the loading densities were reported\[2\]. With increased loading densities, the observed lowest absorption bands shifted to the lower energy side. This behavior can be interpreted by the model of quantum confinement in the photoexcited state of semiconductor clusters with a larger size. Even if the loaded AgI molecules are in the \([\text{I}^-]\)-cage, they form clusters with localization somewhere inside the \([\text{I}^-]\)-cage, because the \([\text{I}^-]\)-cage is not fully occupied by the AgI cluster at the maximum loading density. The localized clusters may produce the stacking faults on an arrangement of the clusters leading to the broadening of the 111 reflection in the XRD pattern. The possibility exists that the localized cluster may be in motion at room temperature leading to the TDS in the low 2\theta region of the XRD pattern.

In comparison to the AgI clusters, the CuI clusters in Na-LTA(1) shows a notable temperature dependence on the optical spectra. First, the absorption spectra of the CuI loaded Na-LTA(1) at RT are shown in Fig. 3. Their loading densities are 6.2 (saturated, curve (a)) and 0.15 molecules per \([\text{I}^-]\)-cage (curve (b)). In curve (a), there is a broken line area where the diffuse reflectivity is not correctly converted, because the Kubelka-Munk function is not available due to the strong photo-absorption. Anyway, the strong absorption at around 3.9 eV indicates that the guest CuI is located in the \([\text{I}^-]\)-cage with a strong quantum confinement, because the energy of the Z_{1,2} exciton in the bulk \([\text{I}^-]\)-CuI is 3.06 eV\[12\]. As shown in Fig. 2, the framework of Na-LTA(1) is not destroyed by the incorporation of the CuI clusters. Therefore, the cluster size is smaller than the inner diameter of the \([\text{I}^-]\)-cage, 1.1 nm.
Previously, exciton states of the CuI microcrystals, whose size are a few nm, in an alkali-halide crystal can also be successfully explained by the exciton confinement theory [13]. Comparing to the exciton band of the CuI microcrystals in alkali-halide, observed absorption band of CuI δ/Na-LTA(1) has larger energy. This behavior is consistent with relationship between the quantum confinement theory and the size of the semiconductor particle. Namely, the smaller size semiconductor particle has a larger excitation energy.

In curve (b) of Fig. 4, a notable band exists at 5.6 eV. This band originates from the CuI molecule with interaction of the host zeolite, because the isolated CuI molecule in the gas phase has a HOMO-LUMO transition at 2.45 eV[14]. On the contrary, Cu⁺ ions embedded in potassium-halide crystals show an absorption at 4.7 – 4.8 eV[15]. The difference in the absorption energies indicates that the quantum confinement theory based on solid state physics[7] cannot explain well the experimental results. Effective mass approximation is not available on the photo-transition of the very small clusters and the molecules[16]. The absorption energy of these clusters and molecules also depends on their surrounding environments. In this curve (b), a weak absorption exists at 4.1 eV. This transition is a common one observed in curve (a). This means that even if CuI molecules are dilutely
adsorbed, they have a tendency to concentrate to form a cluster. In other words, the cohesive energy of Cul molecules is stronger than the adsorption energy into the zeolite cage.

Figure 4 shows the absorption spectra of CuI$_{50}$/Na-LTA(1) at RT and 77K. Roughly, there are notable absorption bands at ca. 4 eV in both spectra. This energy is almost the same as in Fig. 3. However, we can clearly see that there are differences in the spectral shape and the intensity. The change in the spectral shape means that there is a strong electron-vibration interaction in a CuI cluster. Concerned with the absorption intensity, there is generally a sum rule on the oscillator strength. In other words, the total area on each spectrum should be independent of the temperature. The experimental result that there is more than a ten times difference between the two spectra, seems to be inconsistent with the sum rule. As mentioned above, due to the existence of the strong absorption, absorption coefficient obtained by the Kuboleka-Munk transformation does not have accuracy at strong absorption region in photon energy. At 77K, the damping factor is smaller than at RT due to the electron-vibration (EV) interaction. Namely, photoexcited electronic state couples with the thermally activated vibration of the clusters or their consisting atoms. The small damping factor leads to absorption bands with a narrow but intense one to conserve the total area in a spectrum. In the diffuse reflection spectrum with a strong absorption, we cannot neglect the direct reflection from the surface of the powder crystals[17]. Anyway, the existence of the EV interaction on the CuI clusters in Na-LTA(1) is apparently consistent with
the possibility of TDS guessed from the XRD pattern as mentioned in section 3.2. The intensity of the vibration on the Cu and I atoms depends on the temperature because of the EV interaction observation. Therefore, if the TDS truly exists on this sample, there will be a difference in the background humps in the XRD pattern at low temperature compared to that at RT.

4. SUMMARY

From the optical spectra and the XRD patterns, it was concluded that the AgI and CuI clusters can be successfully incorporated into the cages of Na-LTA(1). Both clusters seem to be in the \[ \square \]-cage. The maximum loading density of AgI does not depend on the type of framework structures, LTA and FAU, and the type of halogen atoms. The loading density of CuI depends on the framework structure. In the XRD pattern of the CuI loaded Na-LTA(1), humps exist in the background. The origin of these humps may be due to the TDS. The temperature dependence on the optical spectra of the CuI clusters in Na-LTA(1) will have a relationship with the observed humps in the background of the XRD pattern. Na-LTA(1) with AgI clusters has a cubic symmetry. On the contrary, Na-LTA with CuI clusters has a lower symmetry than the cubic symmetry.

REFERENCES

8. Landolt-Börnstein New Series III/22a, pp. 299.