Microenvironments in Faujasite-type Fe–Al Zeolites Probed by Europium Luminescence

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Europium was introduced into faujasite-type zeolites through ion exchange. The intensity ratio of the emission bands peaking at 590 and 614 nm changed depending on the amount of adsorbed water in zeolites. The results suggest that europium photoluminescence spectra could be a useful probe for providing information on a microenvironment in hydrated zeolites. The europium luminescence spectra of Fe–Al faujasite were measured as a function of the Fe content and compared with the water desorption temperatures to discuss the effect of Fe incorporation into the zeolite framework.

Rare earth metal/organic ligand complexes have been widely studied as an electroluminescence devices.[1] Europium can form complexes with various ligands such as 2,2′-bipyridyl. The Eu complexes emit an enhanced red luminescence via the excitation energy transfer from the ligands to Eu, as known as "antenna effect."[2] Several papers reported that zeolites allow to introduce not only Eu^{3+} but also Eu/ligand complexes as guest molecules into their micropores.[3–5] Although the bulkiness of the complexes often prevents the penetration into the zeolite pores. In this case, the locations of the complex molecules in the zeolite pores may be not well defined. On the other hand, Eu^{3+} can be readily introduced inside zeolites almost independent of the size of the zeolite cages via the ion exchange with sodium cation and can show a strong red photoluminescence even without ligands.[3]

We observed that the Eu luminescence spectrum drastically changed with the composition of water/methanol mixed solvent. In this paper, the microenvironments in the Fe–Al faujasite pores are discussed from the Eu spectral change. The purpose of the present work is to investigate the effect of the introduction of transition metals such as Fe into the zeolite frame work on the microenvironments in the pores.

Faujasite-type zeolite was prepared as follows: aluminum nitrate aqueous solution ($1.0\,\mathrm{mol\,dm^{-3}}$) was gradually added to the $1.0\,\mathrm{mol\,dm^{-3}}$ aqueous solution of sodium orthosilicate with a fixed mol ratio $Si/Al = 2.5$ at room temperature with continuous stirring. After 1 h, the homogeneous reaction mixture was poured into a polypropylene bottle and kept at $80 \pm 0.5\,^\circ\mathrm{C}$ in an air convection oven for 3 days. Fe–Al zeolites were obtained from iron(III) phosphate, sodium orthosilicate, and aluminum nitrate as reported previously.[6]

A narrow particle size range of faujasite (53–63 μm in diameter) was collected with sieves. The zeolites were ion-exchanged at 25 °C by the butch method using an aqueous $EuCl_3$ solution, and then washed thoroughly with water to remove an excess of $EuCl_3$ until no Cl^- is detected in the washings using an aqueous silver nitrate solution. The ion-exchanged zeolites were air-dried at 25 °C for 24 h. The extent of ion exchange $\mathrm{IE}\ (\%) = \{([Na^+]_0 - [Na^+])/[Na^+]_0\} \times 100$ where $[Na^+]_0$ and $[Na^+]$ denote the sodium ion concentration (in $\mathrm{mol\,g^{-1}}$) before and after ion exchange, respectively, ranged 63–68% from the inductively coupled plasma-analytical emission spectrography (ICP-AES) measurements. ICP-AES analysis also revealed that europium is present in the zeolites as the form of Eu^{3+} (no $EuCl_2{}^+$ and $EuCl^{2+}$ are included). For all samples, the mol ratios, $Na/(Al + Fe)$, were practically unity (0.99–1.00), suggesting that lattice defects such as nonbridged SiO^- are probably almost negligible in the present samples.

The Fe-free and Fe-containing zeolites synthesized in this work were characterized by X-ray diffraction, ICP-AES, atomic absorption spectrography (AAS), FT-IR spectroscopy, differential scanning calorimetry (DSC), and thermogravimetry-differential thermal analysis (TG-DTA). The corrected photoluminescence spectra of Eu^{3+}-exchanged zeolites, placed between quartz plates, were recorded on a Hitachi F-4500 fluorescence spectrophotometer in a reflection geometry at room temperature with a bandpass of 5 nm for both the excitation and detection monochromators.

Eu^{3+} is known to exhibit a red phosphorescence peaking at 590 nm ($^5D_0 \rightarrow {}^7F_1$, environment-insensitive magnetic dipole

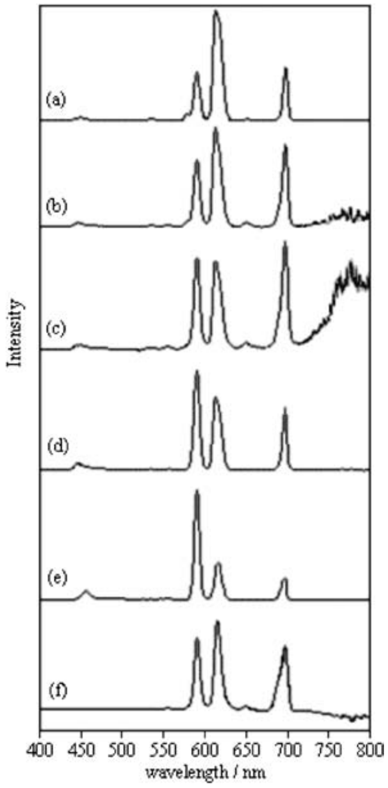

Figure 1. Photoluminescence spectra of $EuCl_3$ in solutions ($10^{-2}\mathrm{mol\,dm^{-3}}$, a–e): (a) pure methanol, (b) water/methanol (3/97, v/v), (c) 4/96, v/v, (d) 5/95, v/v, (e) pure water, and (f) Eu^{3+}-exchanged Fe-free faujasite.

transition) and 614 nm ($^5D_0 \rightarrow {}^7F_2$, environment-sensitive electric dipole transition).[7] Figures 1a–1e show the dependence of the Eu emission spectrum on the solvent composition.

In pure methanol, the band peaking at 590 nm is more intense than the 614-nm band. It should be noted that the addition of only a small amount of water into the methanol solution caused a drastic change in the intensity ratio, I_{590}/I_{614}. In water, the 590-nm band became stronger than the 614-nm band. This prominent solvent effect seems to be similar to the fact that the vibrational band intensity ratio, I_1/I_3, in pyrene fluorescence sensitively changes over a wide range of solvent polarity (from water to hexane).[8] But in case of pyrene, the difference between the I_1/I_3 in water and methanol is very small compared to the results in Figures 1a–1e. This suggests that the I_{590}/I_{614} in Eu is sensitive to the presence of water molecules around Eu^{3+} rather than the average solvent polarity.

If Eu^{3+} was introduced into the zeolite pores, one can obtain information on a local environment around Eu^{3+} bound onto the negatively charged sites in hydrated zeolites. Figure 1f exhibits the luminescence spectrum of Eu-exchanged faujasite. It should be noted that the I_{590}/I_{614} ratio is much lower than that in water, suggesting how the water molecules entrapped in zeolites differ from the bulk water. This corresponds to the fact that DSC measurements for hydrated faujasites show no freezing/melting peaks around 0 °C in both cooling/heating runs. Hydrated zeolites contain water coordinated in the zeolite lattice (coordinated water) and water adsorbed onto the coordinated water via hydrogen bonding (physisorbed water).[9] The decreased I_{590}/I_{614} ratio in Figure 1f most likely reflects the presence of the physisorbed water in faujasite, which is believed to be less polar than the bulk water.[10,11]

It is expected that partial desorption of physisorbed water from hydrated zeolites lowers the local polarity since the less polar coordinated water is consequently concentrated. A variation of the Eu luminescence spectrum was also monitored during vacuum–drying at 100 °C. Figure 2 shows that the I_{590}/I_{614} decreased gradually upon partial desorption of physisorbed water in Fe-free faujasite in accordance with the above prediction.

One of our interests is how transition metals synthetically introduced into the zeolite framework (not by ion exchange) influence the microenvironments such as local polarity, local acidity, mobility of some guest molecules, and catalytic reactivity. As the first step, we examined the local polarity in Fe–Al faujasite on the basis of the Eu luminescence spectral criterion mentioned above.

Figure 3 exhibits the relationship between the ratio I_{590}/I_{614} and the Fe content (%) = [Fe/(Al + Fe)] × 100.

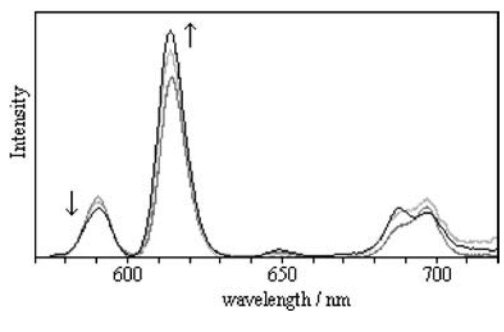

Figure 2. Change in the Eu photoluminescence spectrum measured at room temperature during vacuum-drying at 100 °C.

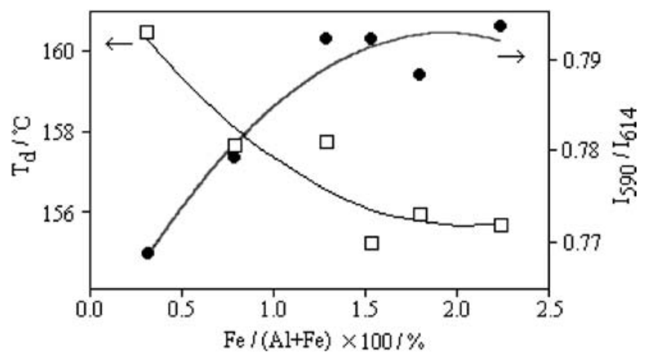

Figure 3. The Intensity ratio I_{590}/I_{614} and water desorption temperature as a function of Fe content in faujasite. The data for the Fe-free sample ($I_{590}/I_{614} = 0.72$ and $T_d = 163$ °C) were not plotted here since a slight difference of crystallinity was observed between Fe-free and Fe-containing faujasites from their XRD patterns.

The increase in the Fe content caused an increase in the intensity ratio, suggesting an enhanced local polarity, which is assumed to be based on a relative increase in physisorbed water. This assumption does not conflict with a decrease in the desorption temperature with increasing Fe content,[12] since the physisorbed water is desorbed in a much lower temperature range than the coordinated water.

The effects of Si/Al and other transition metals will be reported elsewhere.

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10 Similarly to hydrated zeolites, water-solubilized reverse micelles (W/O microemulsion) also include different types of water in the micellar core; water incorporated to ionic sites (bound water), water hydrogen-bonded to the bound water (intermediate water), and bulk-like water with the following order of polarity: bulk water > intermediate water > bound water (see ref 11).

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12 Physisorbed water in zeolites behaves as intermediate water between the bulk water desorbed below 100 °C and the coordinated water. The physisorbed water molecules are located between the coordinated water molecules in zeolites. An increase in the amount of physisorbed water most likely allows the formation of relatively weakly hydrogen-bonded water molecules with the coordinated water. This can cause a shift of desorption temperature toward lower temperatures.

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