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PHOTOLUMINESCENCE DURING ADSORPTION OF AMMONIA AND OTHER SIMPLE MOLECULES ON AN ACTIVATED EUROPIUM ION-EXCHANGED MORDENITE

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It has been studied the adsorption of simple molecules on an activated Eu(III) ion-exchanged mordenite by the measurement of the luminescence of Eu^{2+} ion which was produced by the evacuation at 500°C. The emission peak for Eu^{2+} ion shifts to shorter wavelength on the exposure of ammonia and other simple molecules. The magnitude of the shift is correlated to the specific dielectric constant of adsorbates.

There are a number of studies for the adsorption of various gases on the transition metal ion-exchanged zeolites. Especially the formation of carbonyl, nitrosyl or copper(II) - ammine complex in the zeolite has been reported from adsorption measurement and from ESR spectroscopy.1), 2) However, the adsorption of ammonia and other simple molecules on an europium ion-exchanged mordenite (Eu-M) has been rarely studied. In this communication, the unique features that were only observed in an activated Eu-M during adsorption of some gases are presented.

Eu(III)-M was prepared from Na-mordenite, $Na_8(AlO_2)_8\cdot(SiO_2)_{40}\cdot 24H_2O$, by conventional ion-exchange procedures. The exchange level of Eu^{3+} ion was 5.8%. Anhydrous ammonia, 99.9% purity, supplied from Seitetsu Kagaku Co., Inc., was used for the adsorption study without further purification. The other adsorbates were degassed by a freeze-pump-thaw technique before use. The emission and excitation spectra were taken on a Shimazu Recording Absolute Spectrofluorophotometer (RF-502) at room temperature. The UV spectra were measured using a Shimazu UV-180. The UV spectra in the region of 200 to 400 nm were recorded using a glass filter (UVD-25). Prior to the adsorption, the sample in a quarz cell was dehydrated in vacuo at 500°C for 4 h, and then the adsorbates were introduced on dehydrated samples at room temperature. The adsorption of NH_3 was carried out at about 400 Torr (1 Torr = 133.322 Pa) of equilibrium pressure. Other gases were adsorbed at 25°C and at the saturated vapor pressure. Except for ethyleneglycol, the adsorption was rapid and equilibrium was always attained within 1 h.

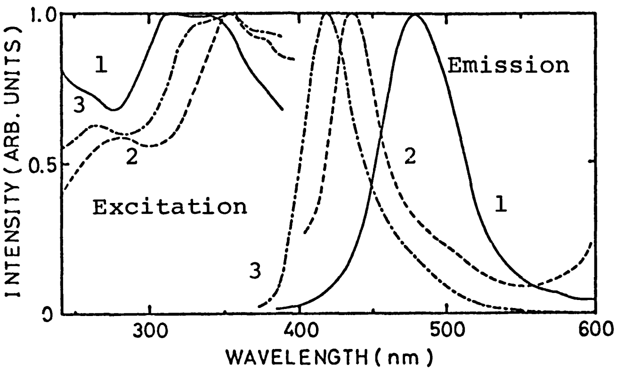

Fig. 1 The emission spectra for Eu^{2+} of Eu-M. (1) degassed at 500°C for 4 h and then cooled in vacuum to 25°C. (2) after the introduction of NH_3 to (1). (3) after the introduction of CH_3OH to (1).

Table 1 The peak position of emission band for Eu^{2+}–adsorbate system in mordenite.

Adsorbate	Peak Position (nm)
none	478
CH_3COOH	415
CH_3OH	418
H_2O	420
$(CH_2OH)_2$	418
$(NH_2CH_2)_2$	432
NH_3	438
NH_2CH_3	430
CH_3CN	452

The compounds activated with Eu^{2+} or Eu^{3+} ion generally exhibits the fluorescence.[3)] In the case of the Eu-M which was degassed at 500°C, the band emission for Eu^{2+} (peak at 478 nm) and emission lines for Eu^{3+} ion, which had the peaks at around 570($^5D_0$–$^7F_0$), 590($^5D_0$–$^7F_1$) and 620 nm($^5D_0$–$^7F_2$), were observed.[4)] However, the variation of the fluorescence for Eu^{3+} ion under gas adsorption was not discussed in this paper as the relative intensity of emission lines were extremely smaller than that of the band emission for Eu^{2+} and the peak position of emission lines did not change after the adsorption of various gases. While, the band emission for Eu^{2+} ion drastically changed after gas adsorption. The typical excitation and emission spectra for Eu^{2+} ion in mordenite are shown in Fig. 1. Curve 1 is the band emission for Eu^{2+} ion which was produced in the course of evacuation at 500°C. Curve 2 and 3 is the emission band when the dehydrated sample was exposed to ammonia or methanol, respectively. The results of other adsorbates are summarized in Table 1. The optimum excitation wavelength after gas adsorption was 355 nm in all cases. In this way, the emission band shifted to shorter wavelength under gas adsorption. These shifts will be attributed to the fact that the adsorbate molecules are coordinated to Eu^{2+} ion in mordenite which is bound to framework oxygen ions.

The band emission for Eu^{2+} ion is normally associated with $4f^65d$ to $4f^7$ transitions, where $4f^65d$ is the excited state of Eu^{2+}. Also, it is well known that the 5d orbitals in the excited $4f^65d$ is split by the crystal field into t_{2g} and e_g orbitals and the magnitude of the splitting depends on the strength of the crystal field.5), 6) Succeedingly, the effect of adsorbated molecules to the crystal splitting for Eu^{2+} ion in mordenite has been discussed by the measurement of UV spectra. Figure 2 shows the typical absorption spectra before and after adsorption of ammonia or methanol. Although the single band was only observed under dehydration, the two bands appeared after gas adsorption. The degree of splitting is dependent on the adsorbates. It is generally accepted that for highly ionic compounds such as containing Eu^{2+} ion, the two broad absorption bands seen in the UV spectra are due to the allowed electric dipole transitions between the 4f and 5d states.7) The existence of two peaks in Fig. 2 may be a result of the splitting of the 5d orbitals in the excited state as the crystal field is increased after gas adsorption. Moreover, it should be noted that the adsorption edge in the system for all of Eu^{2+}– adsorbated molecule, which is the lowest energy edge (or the longest wavelength), is almost agreed with the emission peak in Fig. 1 as the Stokes shift occurs. Thus, it would seem that the emission for Eu^{2+} in mordenite after gas adsorption depends on the adsorbed molecules.

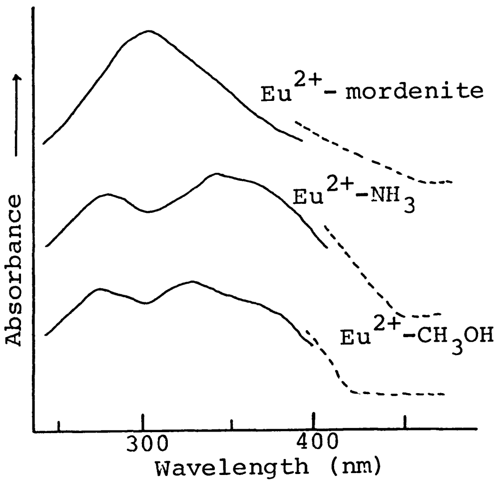

Fig. 2 Absorption spectra of Eu^{2+}- M , Eu^{2+}- NH_3 and Eu^{2+}- CH_3OH. The solid lines are the spectra with a glass filter (UVD-25).

From Table 1, we discussed above the relationship between the magnitude of the shifts of emission before and after gas adsorption and the specific dielectric constant (ε) of adsorbates. The relationship can be classified into two groups (oxygen - and nitrogen - donor group) as shown in Fig. 3. The magnitude of the shift ($\Delta\sigma_F$) predicted by the approximate equation,8)

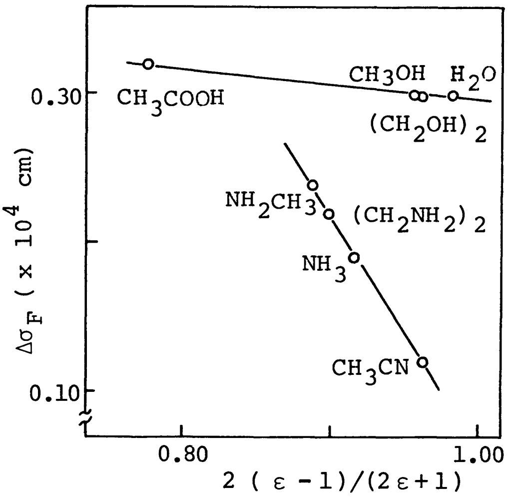

Fig. 3 The relationship between the dielectric constant of adsorbates and the shift of emission peaks for Eu^{2+}- adsorbated molecule in mordenite.

$\Delta\sigma_F = \frac{2(\varepsilon - 1)}{2\varepsilon + 1} \cdot \alpha$, where α is the constant which is determined by the photoexcited process of Eu^{2+}- adsorbated molecule. As can be seen from the results that the optimum excitation level after the adsorption rarely changed, the variation of the chemical environment around Eu^{2+} ion under various gas adsorption seems to be relatively unimportant in causing variations of excitation process. Further detailed studies to investigate these interesting problems are in progress.

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