1290 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *57, 1290—1294 (1984)* [Vol. 57, No. 5

Physicochemical Studies of an Activated Europium Ion-exchanged Mordenite

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(Received September 5, 1983)

The physicochemical properties of an activated Eu(III) ion-exchanged mordenite (Eu-M) have been studied by the measurement of the fluorescence of the europium ion. When Eu-M (the exchanged level; 3.7%) was degassed only above 300 °C, a band emission which peaked at 488 nm appeared. This band emission was associated with the Eu^{2+} 5d-4f transition. The peak of the band emission shifted linearly to a shorter wavelength with the increase in the exchanged level of the Eu ions. For the Eu-M sample, which was reduced by H_2 at 500 °C, the peak position of the band emission was almost 499 nm in all cases, and the quantum yield for a reduced sample was larger than that for a dehydrated sample. The quantum yield for a reduced sample fell off extremely above the exchanged level of 6%. Moreover, the Eu^{2+}–Eu^{2+} energy transfer in the reduced samples was discussed.

Several attempts have been made to identify the structures and chemical properties of europium-exchanged zeolites. The presence of Eu^{4+} in zeolite A has been postulated by X-ray analysis.1) Electron-paramagnetic resonance has been applied to study the ligand coordinations of europium-exchanged mordenite, zeolite Y, and zeolite A.2,3) A Mössbauer study of europium-exchanged zeolite has been reported.4,5) These techniques are, however, of restricted applicability. On the other hand, fluorescence spectroscopy can be helpful for rare-earth ion-exchanged zeolites, though the rare-earth mordenites have rarely been studied by the use of fluorescence techniques.6) We ourselves have previously studied the physicochemical properties of rare-earth ion-exchanged zeolites from the measurement of the fluorescence of the rare-earth ions in an attempt to clarify the catalytic properties of these compounds.7) Especially, it has been found that a part of the Eu^{3+} ion in zeolite Y and mordenite is reduced to the Eu^{2+} ion by dehydration in a vacuum or inert gases. That is, on Eu^{3+} ion-exchanged zeolites, the emission band for Eu^{3+} decreased and the band emission due to Eu^{2+} appeared as Eu^{3+} ion-exchanged zeolites were degassed above 300 °C. The fluorescence of Eu^{2+} has been studied, and a number of Eu^{2+}-containing phosphors emitting in the blue or ultraviolet region have been described.8–10) In general, the Eu^{2+}-doped phosphors are made by the reduction of the Eu^{3+}-doped samples at higher temperatures (800 °C$<T$) in an hydrogen atmosphere. Therefore, it is noteworthy that the reduction of Eu^{3+} to Eu^{2+} in zeolites takes place easily upon degassing at low temperatures.

In this paper, the fluorescence properties of Eu^{2+} for an activated Eu ion-exchanged mordenite (Eu–M) will be reported in more detail.

Experimental

Materials. The Eu–M samples were prepared starting from Na-mordenite which had been supplied by the Norton Company. The parent mordenite had the following composition: $Na_8(AlO_2)_8\cdot(SiO_2)_{40}\cdot 24H_2O$. The mordenite was ion-exchanged in solutions containing $EuCl_3$, washed, dried at 100 °C, and calcined in air at 450 °C. The close correspondence between the decrease in the sodium content and the increase in the europium content indicated that a simple ion-exchanged process had occurred. The exchanged mordenites were analyzed for europium by means of X-ray fluorometry and for sodium by means of flame photometry. Thus, the exchanged levels (100*x* (%); $Na_{8(1-x)}\cdot Eu_{8\ 3\cdot x}(AlO_2)_8\cdot(SiO_2)_{40}\cdot 24H_2O$) of the europium ion were found to be 0.1, 0.5, 1.4, 3.7, 5.8, 6.7, and 8.0%.

Methods and Procedures. The emission and excitation spectra were measured using a Shimadzu Recording Absolute Spectrofluorophotometer (RF-502) at room temperature. The UV spectra were taken with a Shimadzu UV-180 apparatus, using MgO as the reference. The particle size of the Eu–M samples was made to fall in the range of 10^{-5}—10^{-4} m so that the light-scattering would be as uniform as possible. The UV spectra in the region from 200 to 400 nm were recorded using a glass filter (UV-D25), since the UV spectra in the region of 250—400 nm were affected by the fluorescence of the divalent europium ion as will be described below, Prior to the measurement, the samples in a quartz cell were dehydrated at the desired temperature for 4 h under a pressure of 10^{-5} Torr (1 Torr=133.322 Pa) and then cooled at room temperature. The reduced samples were obtained by treatment at 500 °C for 1 h in a hydrogen atmosphere. The quantum yield (Q_0) of fluorescence was derived from the following equation:11)

$$Q_0 = \frac{Q_{\mathrm{sample}}}{Q_{\mathrm{CaWO_4:Pb}}} \times \frac{I_{\mathrm{CaWO_4:Pb}}}{I_{\mathrm{sample}}}, \tag{1}$$

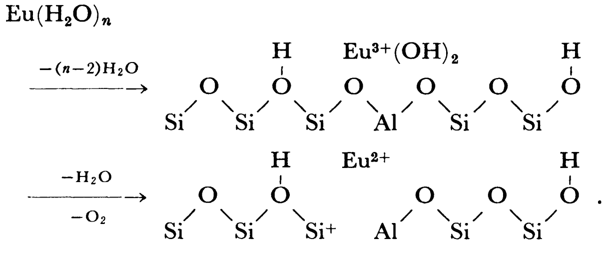
where Q_{sample} and $Q_{\mathrm{CaWO_4\ Pb}}$ are the photoluminescence outputs where, therefore, I_{sample} and $I_{\mathrm{CaWO_4\ Pb}}$ are the numbers of absorbed photons, as obtained from the UV spectra.

Gas-consumption Experiments. When the Eu–M sample was reduced by hydrogen, the amount of hydrogen consumption was accurately determined as a function of the time by measuring the pressure drop. Reoxidation was also investigated by measuring the oxygen-pressure drop in the same apparatus, which consisted of a closed circuit containing a circulation pump in series with a quartz tube reactor and a cold trap. The volume of the system was 180 cm³; the rate of circulation of the gas was 1000 cm³ min⁻¹. The pressure drop was monitored on a digital manometer (Validyne CD-23). The accuracy of the gas-uptake measurements was better than ±0.002 mmol.

Lifetime Measurement. The fluorescence lifetimes were measured using a Nitrogen Laser (337 nm) with a lifetime of less than 5 ns. Also, for the measurement of the lifetimes a monochrometer was used to enable us to select the emission wavelength. The lifetimes were determined from the oscilloscope trace as the slope of log *I* *vs.* *t*.

Results and Discussion

Europium Spectra for the Dehydrated Samples. When the Eu-M sample (exchanged level: 3.7%) was degassed above 300 °C, the band-emission (Curve 1), peak at 488 nm newly appeared, as is shown in Fig. 1. The optimum excitation wavelength was 315 nm. The quantum yield was 4.3%. A new band emission in the short-wavelength UV region must be due to the $4f^6 5d$-$4f^7$ transition for the Eu^{2+} ion, as has been described elsewhere.[9] In the dehydrated Eu-M samples, the emission band for the Eu^{3+} ion under excitation with 300-nm radiation, which has its peaks at around 572 ($^5D_0$-$^7F_0$), 580 ($^5D_0$-$^7F_1$), and 624 nm ($^5D_0$-$^7F_2$), was observed (*cf.* Fig. 2). When Eu-M was dehydrated at 500 °C, the emission lines were observed on the foot of the band emission for the Eu^{2+} ion. No position of the emission lines changed between before and after the dehydration. However, the relative intensity of the $^5D_0$-$^7F_0$, $^5D_0$-$^7F_1$, and $^5D_0$-$^7F_2$ emissions varied with an elevation of the temperature. This fact is mainly attributable to the change in the local environment of the Eu^{3+} ion, with a loss of coordinated water molecules, as has been described elsewhere.[12] The mass-spectroscopic analysis of the noncondensable gaseous material evolved during the evacuation above 300 °C for Eu-M revealed that the gas was oxygen. The amount of oxygen evolved from Na-M was negligibly small. The evolved oxygen for Eu-M samples increased, though, with the increase in the exchange level of Eu ions. The degree of reduction for Eu^{3+} to Eu^{2+} in mordenite during the evacuation at 500 °C for 4 h was about 30%, judging from the measurement of the magnetic susceptibility, as has been described elsewhere.[12] Moreover, the total evolved oxygen amounted to one oxygen molecule desorbing per Eu^{2+} ion. Although we no clear data of the dissociation of adsorbed water,[12] it is probable that the dissociation of adsorbed water occurs as follows, in a manner similar to that occurring on the other rare-earth ion-exchanged zeolites; $Ln(OH_2)_2^{+3} \rightarrow Ln(OH)_2^{+} + 2H^{+}$.[13] Thus, it can be considered that the reduction of Eu^{3+} in mordenite proceeds mainly according to Eq. (2):



(2)

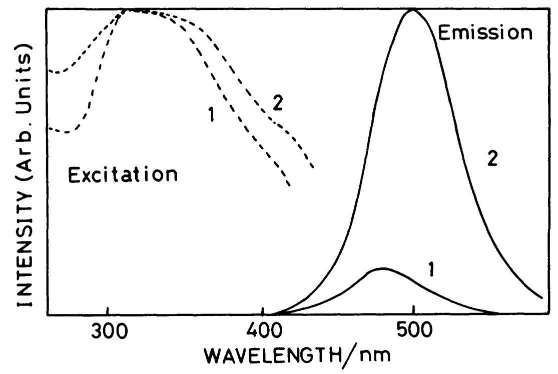


Fig. 1. Fluorescence spectra of Eu-M (3.7%) after degassing at 500 °C for 4 h (1) and reducing at 500 °C for 2 h (2).

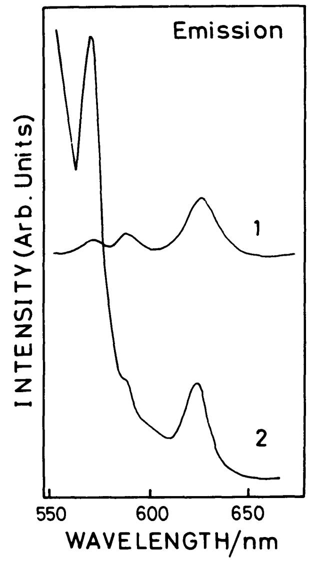


Fig. 2. Emission spectra of the Eu^{3+} ion in Eu-M (3.7 %). Excitation with 300 nm radiation. (1) After degassing at 25 °C for 2 h. (2) After degassing at 500 °C for 4 h.

The peak position of the band emission of Eu^{2+} in dehydrated samples changed with the concentration of europium ions in mordenite. However, the optimum excitation wavelength was 315 nm in all cases. Therefore, the excitation process of Eu-M may be thought to be relatively unimportant. Figure 3 gives the relationship between the wavelength of the peak position and the exchanged level of the europium ion. The peak position of the band emission shifts linearly to a shorter wavelength as the exchanged level increases. Similar behavior has been observed for the system of $SrMgP_2O_7$: Eu^{2+} or $Sr_{1-x}Ba_xAlF_5$:Eu^{2+}.[14] The wavelength for the band emission in Eu^{2+} ions is determined by two factors: on the one hand, the splitting of the 5d levels by the crystal field of the surrounding oxygen ions, and, on the other hand, the energy gap between the 4f ground state and the center of gravity of the 5d excited levels. The UV spectra of dehydrated samples with different exchanged levels are shown in Fig. 4. The peak of the absorption spectra in the UV region was about 300 nm in all cases. The split of the absorption bands attributable to the allowed electric dipole transitions between the 4f and 5d states was not clearly observed. Therefore, it

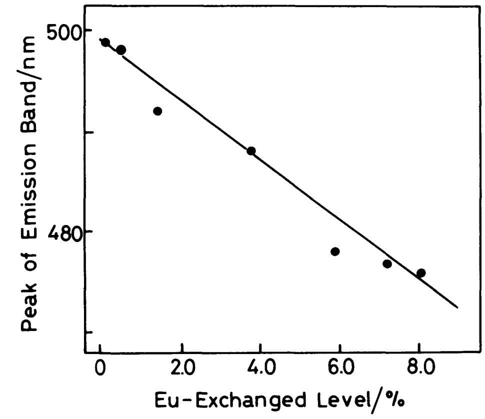


Fig. 3. The relationship between the peak position of the emission band for Eu^{2+} and the exchanged level of europium ion.

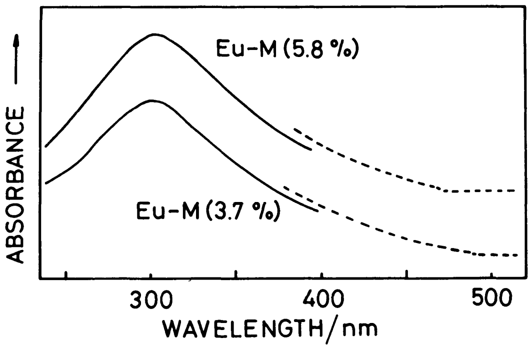


Fig. 4. The absorption spectra of the dehydrated samples. The solid lines are the spectra with a glass filter (UV-D25). The dotted lines are the spectra without the filter.

can be anticipated that the possibility of the peak shift is rarely present. The absorption edge, however, shifted to a shorter wavelength with the increase in the exchanged level of the europium ion. These results were consistent with the results for the shift of the band emission. The peak shift may be attributed to an increase in the fraction of Eu^{2+} ions which interact with each other in dipolar coupled pairs.[3] In this case, the exchanged sites will play an important part in the formation of dipolar coupled pairs.

The structure of Na mordenite has the space group Pbcn, a=17.92 (1), b=20.31 (1), and c=7.48 (7) Å.[15] Only the I′, IV, and VI sites are occupied by Na cations in a dehydrated Na mordenite. The percentages of occupancy for the sites are 43% (I′), 36% (IV), and 21% (VI). Jacobs *et al.*[16] have pointed out that, in Cu-Y, a small number of supercage oxygen ions were capable of causing a rupture or considerable weakening of the Si(Al)-O bond under evacuation at 623 K. In Na-M, the VI site faces the large channel, much like the supercage in the Y-type zeolite. Thus, it appears that the Eu^{3+} ions which occupy the VI site are easily reduced to Eu^{2+} ions during the dehydration, according to Eq. (2). The VI site is a wall site in the large channel, and the cation on the VI site sticks out of the wall somewhat. That is, the Eu^{2+} ions on the VI site are able to interact directly with each other. Also, the fraction of Eu^{3+} ions for the VI site is 21% if the Eu^{3+} ions are ion-exchanged according to the percentage of occupancy for each site. Since the degree of the reduction of the Eu^{3+} ions was about 30% under the evacuation, it is thought that the Eu^{3+} ions are slightly localized to the VI site. Therefore, the fraction of the Eu^{2+} ions which interact with each other in dipolar coupled pairs will be enhanced as the concentration of the Eu ions increases. Thus, in dehydrated Eu-M samples, a shift of the peak position would be observed as the Eu^{2+} concentration increased. Further physicochemical evidence should be collected to support the phenomena of the peak shift.

Europium Spectra for the Reduced Sample. The emission spectrum after the treatment at 500 °C in a hydrogen atmosphere is shown in Fig. 1 (Curve 2). The emission spectrum of Eu^{2+} for the reduced sample was distinct from that for the dehydrated sample. For Eu-M (3.7%), the peak position of the band emission is 499 nm under the optimum excitation of 315 nm, and the quantum yield (27.2%) is larger than that for the dehydrated sample (4.3%).

The stoichiometry of the reduction-reoxidation of dehydrated and reduced Eu-M samples at 500 °C can be derived from the data of Table 1. For Na-M, an oxygen or hydrogen pressure drop was rarely observed. After the dehydration of Eu-M, the small amount of oxygen was consumed. The amount of oxygen corresponds to 30% of the total Eu ions. The degree of reduction for Eu^{3+} to Eu^{2+} in mordenite was about 30%, as has been described elsewhere.[12] Also, we have concluded from the experiments of the thermal-programmed desorption (TPD) of oxygen that one oxygen molecule is adsorbed to an Eu^{2+} ion in mordenite.[17] Thus, the amount of oxygen estimated from the pressure drop is consitent with the amount of oxygen needed to reoxidize. On the other hand, the amount of oxygen needed to reoxidize after the reduction of hydrogen is consistent with the total number of Eu ions. The amount of hydrogen consumed, however, was 1.4 times the total amount of Eu ions in all cases. After the reduction at 500 °C, the sample was degassed and then exposed to oxygen at the same temperature. It was subsequently cooled to 25 °C under an oxygen atmosphere and then degassed for 1 h at the same temperature. After these operation, the TPD spectroscopy was done; the results

TABLE 1. GAS CONSUMPTION (mmol g^{-1}) AT 500 °C

Exchanged level (%)	Eu^{3+} ion (mmol g^{-1})	Cycle No.	H_2	O_2
5.8	0.044	1		0.013[a]
		2	0.058	0.043[b]
		3	0.060	0.044[b]
7.2	0.055	1		0.016[a]
		2	0.075	0.050[b]
		3	0.078	0.052[b]

a) Oxygen uptake at 500 °C for 2 h after dehydration.
b) After the reduction of H_2, the circular system was evacuated for 1 h and then the reduced sample was reoxidized by O_2; reoxidation time: 0.5 h.

will be described elsewhere.[17)] Thus, it was clear from the TPD experiment that the amount of desorbed oxygen from the reduced sample was almost consistent with that for the dehydrated sample described above. Also, the degree of reduction was about 100%, judging from the measurement of magnetic susceptibility, as has been described elsewhere.[12)] Therefore, the amount of hydrogen consumed should be twice the amount of oxygen needed to reoxidize if oxygen does not desorb under the evacuation at 500 °C after oxygen exposure. As has been described above, it appears that the Eu^{3+} ions which occupy the VI site are easily reduced to Eu^{2+} ions during the dehydration, while other Eu^{3+} ions which exist on the I′ or IV site are reduced only under the reducing atmosphere. Since the I′ and IV sites are shaded by the (Si, Al)O_4 network,[15)] the increase in the quantum yield for the reduced sample may be attributed to the increase in the isolated Eu^{2+} ions. That is, it is considered that, in the emission spectrum for the reduced sample, the emission band with a peak at 488 nm is concealed in the foot of the emission band with a peak at 499 nm.

Concentration Dependence. In Fig. 5, we plot the quantum yield *vs.* the exchanged-Eu-ion concentration for the reduced samples in comparison with that for the dehydrated samples. The quantum yield stays relatively constant up to almost 6%, but above that point it decreases abruptly. This phenomenon may be recorded in terms of the concentration-quenching effect. In order to discuss the concentration-quenching phenomenon in more detail, we have considered the Eu^{2+}—Eu^{2+} energy transfer in an reduced Eu-M. Since the transfer occurs mainly *via* dipole-dipole interaction,[18)] the probability, $P_{Eu^{2+}-Eu^{2+}}$, of energy tranfer between Eu^{2+} ions by means of this interaction has been given as;

$$P_{\mathrm{Eu}^{2+}-\mathrm{Eu}^{2+}} = 6.3\times10^{27}\frac{Q_{\mathrm{A}}}{R^6\tau_{\mathrm{Eu}}}\frac{1}{E^4}\int f_{\mathrm{Eu}}(E)F_{\mathrm{Eu}}(E)\mathrm{d}E, \quad (3)$$

where Q_A is the absorption cross-section of the Eu^{2+} ions (in cm^2 eV); R, the distance between the Eu^{2+} ions (Å); τ_{Eu}, the decay time of the fluorescence (in s); E the energy transferred (in ev), and $\int f_{Eu}(E)F_{Eu}(E)dE$, the overlap between emission and excitation bands. Blasse defined a critical distance, R_c, between two luminescent centers, S and A, as the distance for which the probability of transfer from S to A equals the probability of the radiative emission of S. This means that $P_{Eu^{2+}-Eu^{2+}}\cdot\tau_{Eu^{2+}}=1$ in terms of Eq. (3). Thus, R_c can be found from this equation;

$$R_c^6 = 6.3\times10^{27}\frac{Q_{\mathrm{A}}}{E^4}\int f_{\mathrm{Eu}}(E)F_{\mathrm{Eu}}(E)\mathrm{d}E. \quad (4)$$

Also, the critical distance R_c (in Å) can be estimated by geometrical considerations as follows:

$$R_c \simeq 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3}, \quad (5)$$

where V is the volume of the unit cell (in Å^3); x_c the activator atom fraction (the concentration) at which the quenching starts, and N, the number of sites per unit cell at which the activator atoms enter. In this paper, we assume that, for the critical concentration, the average shortest distance between nearest activator ions is equal to the critical distance, R_c. Thus, the R_c value for the reduced sample, 22 Å, is derived from Eq. (5), as V is 2.72×10^3 Å^3, x_c is 0.06, and N is 8. This value is the same as that in the system of $BaBPO_5$; Eu^{2+} (22 Å).[18)] 22 Å is the distance separating one Eu^{2+} ion and another Eu^{2+} ion when the quenching starts in Eu-M. If the Eu^{2+}-Eu^{2+} distance is expressed in terms of 3.4 Å×n, where 3.4 Å is the mean interatomic distance between Na nearest neighbors in Na mordenite, as has been described above and n is the number of exchanged sites, n is 6.5. $P_{Eu^{2+}-Eu^{2+}}$ is varied by the factor of $\left(\frac{R_c}{R}\right)^6\frac{1}{\tau_{\mathrm{Eu}}}$, which is derived from Eqs. (3) and (4). Since τ_{Eu} is $\simeq10^{-6}$ s, as is shown in Table 2, in the reduced Eu-M the transfer probability for the separation of 3.4 Å is $\simeq10^{10}$ s^{-1}.

The concentration-quenching effect was also observed at a low concentration of Eu^{2+} ions in the dehydrated Eu-M, as is shown in Fig. 5. If Eu^{2+} ions disperse statistically, R_c is 46 Å, as x_c is 0.006 (the effective Eu^{2+} fraction is 0.02×0.3, since the degree of reduction is about 30%). The R_c value of 46 Å is much larger than the maximum R_c (27 Å).[10,19)] Since the concentration-quenching effect is observed at a low concentration, it is probable that a Eu^{2+} ion, which is easily produced by the dehydration, is present at the specific site and in the neighborhood of another Eu^{2+} ion to be able to affect the concentration quenching as has been described above.

Since the fluorescence is a phenomenon depending on many variables, such as the concentration of the luminescent activator, its coordination, and the host lattice, the interpretation of results is not always easy. However, it is specific in the sence that it can solve certain problems which are very difficult to solve with

TABLE 2. DECAY TIME OF THE REDUCED Eu-M SAMPLES AT ROOM TEMPERATURE

Exchanged level (%)	Pretreatment	$\tau/10^{-6}$ s
3.7	500 °C, Reduced	3.5
5.8	500 °C, Reduced	3.5

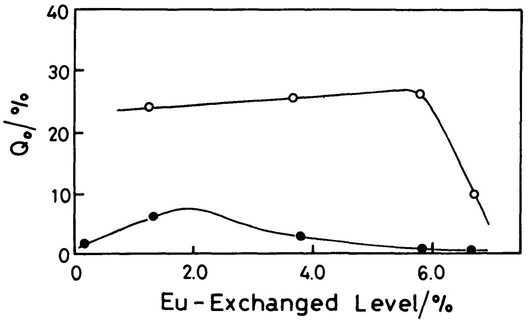


Fig. 5. Concentration quenching of the Eu^{2+} emission of the reduced samples (—○—) and the dehydrated samples (—●—).

other techniques, *e.g.*, the prediction of dipole-dipole interaction. Thus, it is considered that the results in this paper lead to a method of investigating the physicochemical properties of rare-earth ion-exchanged zeolites, although fluorescence spectroscopy is by no means a new technique. Further detailed studies to investigate these problems are now in progress.

We are grateful to Professor H. Mikawa and Dr. Y. Shirota of Osaka University for their support in the measurement of the decay time.

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