Photoluminescence during the Catalysis of Water Decomposition on an Activated Europium(III)-Y Zeolite

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Summary Eu^{III} is easily reduced to Eu^{II} in Eu^{III}-Y zeolite when it is evacuated above 300 °C; activated Eu^{III}-Y has the ability to decompose water at low temperatures (25—50 °C).

THE rare earth ion-exchanged zeolites are well known as active catalysts for the cracking of fuel oil. However, the reduction–oxidation of the rare earth ion in the zeolite has apparently not been studied. We now report preliminary studies of this oxidation–reduction by photoluminescence measurements.

Eu^{III} ion-exchanged Y type zeolite [Eu^{III}-Y] was prepared from Linde NaY zeolite by conventional ion-exchange procedures. The sample was loaded into a quartz cell and was degassed at various temperatures for > 3 h ($< 10^{-2}$ Pa). After this pretreatment, emission spectra were recorded on a Shimadzu Recording Spectrofluorophotometer (RF-502) at room temperature.

The Figure shows the emission spectra under optimum excitation conditions after degassing at various temperatures. After evacuation at room temperature, the emission band produced by excitation with 390 nm radiation showed peaks at 590, 615, and 655 nm. This emission band is due to the transition between the ^5D and ^7F levels of the Eu^{3+} ion ($^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$, and $^5D_0$–$^7F_3$ transitions, respectively)[1] [Figure (b)]. When the Eu^{III}-Y zeolite was degassed at temperatures above 300 °C, and excited with 345 nm radiation the emission band for the Eu^{3+} ion decreased, while an emission peak at 455 nm appeared. This emission band in the short-wavelength u.v. region must be due to the Eu^{2+} ion ($4f$–$5d$ transition).[2] The relative intensity of this emission band increased as the temperature was increased [Figure (a)]. It is suggested that the reduction of Eu^{III} to Eu^{II} in the zeolite occurs as in equation (1).

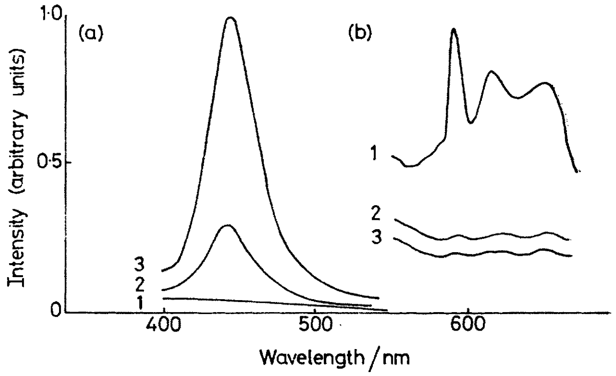

FIGURE. Emission spectra of the europium ion exchanged Y type zeolite after degassing at 1, 25, 2, 300, and 3, 500 °C. (a) Excitation with 345 nm radiation. (b) Excitation with 390 nm radiation.

$$[2Eu^{3+}, nH_2O]\text{-}Y \xrightarrow[>300\ ^\circ C]{-(n-1)H_2O} [2Eu^{2+}, 2H^+]\text{-}Y + 1/2\ O_2 \quad (1)$$

Mass-spectroscopic analysis of the noncondensable gaseous material evolved during evacuation above 300 °C indeed revealed that the gas was oxygen.

When the activated Eu^{III}-Y was subsequently exposed to degassed water at 25—50 °C, the emission band for Eu_2^+ disappeared and hydrogen was evolved. It is thought that reoxidation of Eu^{II} to Eu^{III} by water occurred in the zeolite, producing hydrogen [equation (2)]. This would

$$[2Eu^{2+}, 2H^+]\text{-}Y \xrightarrow[25\text{—}50\ ^\circ C]{nH_2O} [2Eu^{3+}, nH_2O]\text{-}Y + H_2 \quad (2)$$

seem to be similar to Kasai's results with Cr^{3+}-zeolon[3] because the reduction potential for the Eu^{3+}–Eu^{2+} cell is −0·43 V.

It was further observed that the emission band for Eu^{2+} regained 80% of its original intensity when the reoxidized sample was again degassed. The emission band for Eu^{2+} disappeared and the emission band for the Eu^{3+} ion returned to its original intensity when the activated Eu^{III}-Y was exposed to oxygen at temperatures above 300 °C and then degassed at the same temperature. This suggests that H$^+$ was consumed, equation (3).

$$[2Eu^{2+}, 2H^+]\text{-}Y \xrightarrow[>300\ ^\circ C]{1/2\ O_2} [2Eu^{3+}]\text{-}Y + H_2O \quad (3)$$

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