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Luminescent properties of RE–silicalite-I and RE–ZSM-5 zeolites synthesized by direct hydrothermal crystallization

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Abstract

Rare earth ions were introduced into silicalite-I and ZSM-5 by direct hydrothermal crystallization either in a non-alkaline aqueous medium containing fluoride or in an alkaline medium. The excitation and emission spectra of europium, cerium and terbium ions in the zeolites were investigated.

1. Introduction

Owing to the very low framework negative charge and ion exchange ability of zeolite ZSM-5, it is difficult to exchange rare earth ions into its structure. Rare earth ions cannot be exchanged into silicalite-I, since it has no capacity for ion exchange. We have developed a novel synthesis method, using direct hydrothermal synthesis, which successfully crystallizes these rare earth molecular sieve zeolites. Single crystals were obtained both in a non-alkaline medium (in the presence of fluoride) and in an alkaline medium. The rare earth component was added to the starting mixture, which was gelled and crystallized at temperatures between 443 and 473 K for 2–30 days in a Teflon-lined hydrothermal pressure vessel.

2. Experimental details

Tetraethyl orthosilicate, metallic aluminium (99.99%), ammonium fluoride (guaranteed reagents), tetrapropylammonium bromide (TPABr) and rare earth (RE) oxides (99.99%) were used as the main starting materials. For acidic reactions the pH value was adjusted in the range 5.0–6.5 with HF; for alkaline reactions the pH was adjusted in the range 12–14 with NaOH. After reaction the crystalline product was separated from the reacted mixture by washing with water in a supersonic washer, filtering and drying. X-ray diffraction (XRD), IR and far-IR spectroscopy, scanning electron microscopy (SEM),

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energy-dispersive analysis by X-rays (EDAX), electron probe microanalysis (EPMA), photoelectron spectroscopy (XPS), and thermogravimetry–differential thermal analysis (TG–DTA) were used to characterize the structures and determine the chemical components of products. The luminescent properties of the RE–zeolites were studied via excitation and emission spectra and diffuse reflection spectra, which were obtained on a Hitachi F-4000 fluorescence spectrophotometer and a Shimadzu UV-365 spectrophotometer. One or at the most two ions selected from the group Ce^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+} have been introduced into silicalite-I and ZSM-5 by direct hydrothermal crystallization; the sizes of crystals containing RE ions reached 300 μm×150 μm in the fluoride medium and 120 μm×40 μm in the alkaline system. The contents of RE ions in the zeolites are about 4 wt.%, as determined on sections of crystals by EPMA.

3. Results and discussion

The excitation spectrum of the crystalline powder of Eu–silicalite-I zeolite has the characteristic lines of europium fluoride [1] (Fig. 1c), while that of a calcined sample shows a charge transfer band of (Eu^{2+}–0^{-})* [2] at 250 nm (Fig. 1a); the zeolites emit bright red fluorescence under a UV lamp (254 nm). In the emission spectra the main emission lines (587 and 593 nm) of the primary sample originate from the $^5D_0$–$^7F_1$ transition (Fig. 1d) when excitation is performed at 393 nm, while those of the calcined sample arise from the $^5D_0$–$^7F_2$ transition (613 and 622 nm) (Fig. 1b) corresponding to excitation at 254 nm. In fact, the intensities of the $^5D_0$–$^7F_2$ transition for excitation to the Eu^{3+} ion are different from those for excitation to the charge transfer state (Fig. 1b). The appearance of the charge transfer band in the calcined samples results from replacement of the F$^-$ ions coordinated to the Eu^{3+} ion by O^{2-} ions as a consequence of heating in air.

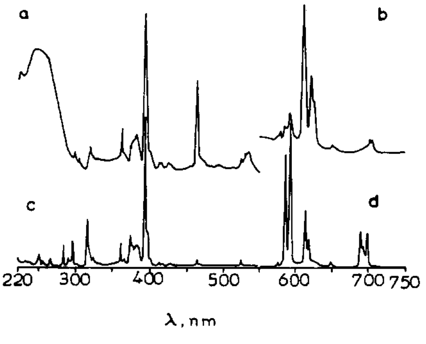


Fig. 1. Excitation (a, c) and emission (b, d) spectra of Eu–silicalite-I synthesized in fluoride medium: a,b calcined, $\lambda_{em}=613$ nm, $\lambda_{ex}=250$ nm; c,d, uncalcined, $\lambda_{em}=593$ nm, $\lambda_{ex}=393$ nm.

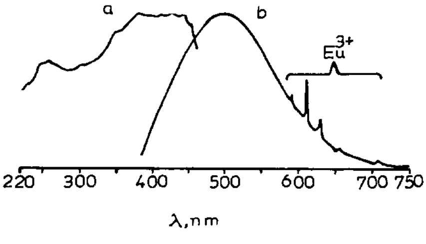
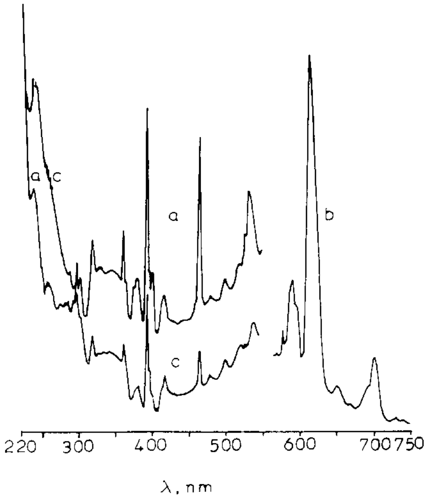


Fig. 2. Excitation (a) and emission (b) spectra of slightly calcined Eu–silicalite-I.

Another interesting luminescence is the wide emission band at a maximum of 500 nm as well as the lines of the Eu^{3+} ion in the emission spectrum of a slightly calcined sample (Fig. 2b). This emission band, which corresponds to a complex excitation spectrum (Fig. 2a), moves towards longer wavelengths and eventually disappears if the sample is calcined sufficiently. This broad band emission may be related to the dissociation of the organic template during calcination.

For the Eu–ZSM-5 zeolite synthesized in the alkaline system the excitation spectrum (Fig. 3a) exhibits lines and a charge transfer band (240 nm) of the Eu^{3+} ion. The energy of the charge transfer band is higher than that for samples synthesized in the fluoride system and the maximum moves towards lower energies after calcination (Fig. 3c). On the basis of the diffuse reflectance spectra, the band may originate by charge transfer from framework oxygen ions to Eu^{3+} ions. It is very interesting to note that there are fine structures in the excitation and emission spectra (Fig. 3). The fine structures of the emission lines of the Eu^{3+} ion do not appear when exciting to the Eu^{3+} ion at 393 nm.

There are two bands in the excitation spectrum of Ce–silicalite-I; their maxima are situated at 235 and 252 nm. The emission spectrum of the Ce^{3+} ion is composed of two broad bands peaking at 289 and 304 nm. All the wavelengths for Ce^{3+} ion luminescence in silicalite-I molecular sieves are shorter than those in other hosts, *e. g.* oxides or oxysalts [3], but approximate to those reported for fluorides [4]. The excitation (a) and emission (b) spectra of (Ce,Tb)–silicalite-I are presented in Fig. 4. The most intense emission of the Tb^{3+} ion is at 542 nm ($^5D_4$–$^7F_5$), corresponding to excitation of the



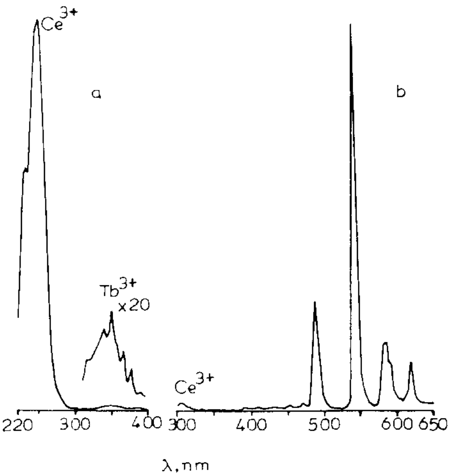


Fig. 3. Excitation (a, c) and emission (b) spectra of Eu–ZSM-5 synthesized in alkaline medium: a, uncalcined, $\lambda_{em}=613$ nm; b, calcined, $\lambda_{ex}=242$ nm; c, calcined, $\lambda_{em}=613$ nm.

Fig. 4. Excitation (a) and emission (b) spectra of (Ce,Tb)–silicalite-I: a, $\lambda_{em}=542$ nm; b, $\lambda_{ex}=250$ nm.

Ce^{3+} ion (250 nm); the excitation lines of Tb^{3+} are very weak. Besides Tb^{3+} ion emissions, there is a weak emission band (305 nm) from the Ce^{3+} ion. These results show that Ce^{3+} ions can transfer excitation energy to the Tb^{3+} ions in the crystalline silicalite-I and the sensitizing effect is very good. Under excitation by a 254 nm UV lamp, (Ce,Tb)–silicalite-I shows bright green luminescence.

For Tb–silicalite-I the excitation spectrum is composed of the transition lines of the Tb^{3+} ion, with the main emission at 542 nm ($^5D_4$–$^7F_5$). As in Eu–silicalite-I, some fine structures also appear in the excitation and emission spectra of Tb–silicalite-I. Considering that the zeolites silicalite-I and ZSM-5 have straight and Z-type channels rather than cages, the rare earth complex ions have to be bound linearly in the zeolite channels, which are about 560 pm in diameter. This should be regarded as the reason for the appearance of fine structures in the spectra.

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