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Microwave synthesis and textural property of europium substituted mesoporous molecular sieves

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ABSTRACT

Using cetyltrimethyl ammonium bromide (CTAB) as the template and sodium silicate as the silicon source, the MCM-41 mesoporous molecular sieves with Eu incorporated in the framework were synthesized under microwave irradiation condition and the influence of the Si/Eu molar ratio on the crystalline structure, textural properties and the long-range ordering of the resulting sample was investigated by various physicochemical techniques such as X-ray diffraction (XRD), transmission electron microscope (TEM), diffuse reflectance ultraviolet–visible spectroscopy (UV–vis), thermal gravimetric–differential scanning calorimeter (TG–DSC) and N_2 physical adsorption. The results of N_2 adsorption and XRD reveal that the synthesized sample has the ordered hexagonal mesoporous structure. UV–vis spectra provide the strong evidences that most of europium ions were incorporated into the framework of the MCM-41 sample. The crystalline structure, textural properties and mesoporous ordering of the resultant mesoporous materials are related to the amount of europium incorporation. Small amount europium incorporated into the silica-based MCM-41 does not strongly modify the structure of mesoporous molecular sieve. An increase of the Eu content in sample led to reduction of the specific surface area and the deterioration of the long-range ordering.

1. Introduction

The discovery of a new family of mesoporous molecular sieves (M41S) [1] opened new perspective and created new challenge in the areas of the catalysis and materials. They have attracted much attention among worldwide researchers owing to their outstanding textural characteristics such as uniform pore size and high specific surface area. Recently, the MCM-41 mesoporous molecular sieve has brought about the growing interest in some potential applications of synthesis of the nanometer cluster, adsorbent, fine chemical industries, catalysis, medicine and environment protection [2–9]. Nevertheless, it is the fact that the pure silica-based MCM-41 mesoporous molecular sieve exhibits low catalytic activity, weak surface acidity and poor stability, which limits its application in many acid-catalyzed reactions. The bottle-neck has not been overcome completely. In order to obtain better catalytic performance and to improve its potential application in many fields, various kinds of mesoporous molecular sieves have been synthesized [10–12]. It is well known that the hexagonal MCM-41 mesoporous molecular sieve has excellent characteristics of strong metal support interactions, high specific surface area, unique pore structure and tunable pore size varying from 2 to 10 nm. These characteristics of MCM-41 enables itself a potential candidate for inclusion of guest species inside its mesopores, offering the possibility to incorporate the transition metal ions into the silica framework. Over the last decades, the incorporation of heteroatoms into mesoporous silica framework has been widely investigated [13–18] and the resultant mesoporous materials have remarkable catalytic performance [13,14,17]. As a vital promoter, the rare earth elements have been used widely in catalysts and the new functional materials [19,20]. Eu-incorporated materials have been investigated extensively due to the photoluminescence properties of europium ion trapped in various host materials [21–23]. Recently, many efforts on the synthesis of europium doped MCM-41 mesoporous molecular sieve have been reported. To our knowledge, most of the previous reports focused on the hydrothermal synthesis of EuMCM-41 [24,25]. The hydrothermal synthesis process requires a long crystallization time and high crystallization temperature, which greatly increases the cost of the synthesis process. Compared with hydrothermal method, microwave irradiation technique has some advantages such as microwave dielectric heating, short crystallization time and environmentally friendly. By far, synthesis of EuMCM-41

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mesoporous molecular sieve through microwave irradiation methods was seldom reported.

Therefore, in present work, we report the synthesis of Eu-substituted MCM-41 mesoporous molecular sieves via the microwave irradiation method. We aimed at the investigation on the effect of the Si/Eu molar ratio in the synthesis gel on the specific surface areas, pore volume and the mesoporous ordering of the resulting EuMCM-41 mesoporous materials. At the same time, several modern techniques like XRD, TEM, UV–vis, TG–DSC and N_2 physical adsorption were utilized to evaluate the structure and adsorption characteristics of the resultant mesoporous materials.

2. Experimental

2.1. Materials

The chemicals used for the synthesis of Eu-substituted mesoporous molecular sieves were sodium silicate and europium oxide. They were used as the source of silicon and europium, respectively. Cetyltrimethyl ammonium bromide (CTAB) was used as template and concentrated sulfuric acid (H_2SO_4) was used to adjust the pH of the mixture solution. They were purchased from Shanghai Chemical Reagent Corporation, PR China. All reagents were of analytical grade.

2.2. Synthesis of EuMCM-41

The EuMCM-41 mesoporous molecular sieves were synthesized via microwave irradiation method according to the molar ratio of Si:CTAB:Eu:H_2O in the synthesis gel was $(1-x)$:0.25:x:100 (x=0.01, 0.02, 0.04, respectively). First of all, a given amount of Eu_2O_3 was dissolved in the superfluous 6 mol/l of hydrochloric acid solution while stirring and warming at about 343 K, and then the solution was condensed time after time to remove the superfluous hydrochloric acid controlling the pH value of the solution in the range 5–5.5. After that, 30 ml of distilled water was added in the solution and the aqueous solution of the $EuCl_3$ was obtained. A given amount of $Na_2SiO_3 \cdot 9H_2O$ was dispersed into 100 ml distilled water, and 9.11 g of CTAB was dissolved in 50 ml distilled water under stirring, obtaining a transparent gelatinous solution. The resultant $EuCl_3$ solution and the sodium silicate solution were slowly added in the gelatinous solution of CTAB. After 10 min of vigorous agitating, the pH value of the mixed solution was adjusted to 11 by drop by drop addition of sulfuric acid (5 mol/l). The stirring was continued for the next 80 min, the resulting suspension was transferred into a 250 ml round-bottomed quartz flask, and then the round-bottomed flask was placed into a microwave oven with a refluxing condenser and heated at boiling point for 2.5 h under continuous microwave irradiation with a power of 220 W (National NN-S570MFS). After cooling to room temperature, the sample was filtered, washed with deionized water and dried at 100 °C for 24 h to remove water present in sample. As a result, the dried sample was obtained, denoted as s-EuMCM-41(X), where X stands for the sample number from 1 to 3, according to europium content added in the synthesis procedure. The s-EuMCM-41(X) sample was heated to 550 °C at a heating rate of 2 °C/min and calcined at 550 °C in air for 10 h in order to remove the template. The calcined sample was named as EuMCM-41(X).

2.3. Characterization

The X-ray diffraction (XRD) patterns of samples were recorded with a powder XRD instrument (Rigaku D/max 2500PC) with Cu K_α radiation (λ=0.154 18 nm). It was operated at 40 kV and 50 mA. The experimental conditions corresponded to a step width of 0.02° and a scan speed of 1 °/min. The diffraction patterns were recorded in the 2θ range 1–10°.

The specific surface area, total pore volume and pore size were measured by the N_2 adsorption/desorption method with a NOVA2000e analytical system made by Quantachrome Corporation (USA). Samples were degassed at 300 °C for 3 h prior to the analysis. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method. The pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) method and the desorption branch.

The transmission electron microscopy (TEM) morphologies of samples were observed on a Philips TEMCNAI-12 with an acceleration voltage 100–120 kV.

The TG–DSC was analyzed by a NETZSCH-STA499 thermal gravimetric–differential scanning calorimeter (Germany).

The diffuse reflectance UV–vis spectra were recorded on a UV-3100 spectrophotometer made by Shimadzu Corporation (Japan) with spherical diffuse reflectance accessory, using $BaSO_4$ as a reference. The effective wavelength range was from 200 to 500 nm.

3. Results and discussion

3.1. XRD analysis

Fig. 1 presents the XRD patterns of the three calcined samples (EuMCM-41(1), EuMCM-41(2) and EuMCM-41(3)). The unit cell parameters a_0 and d spacing corresponding to (1 0 0) reflection are listed in Table 1. All samples have a strong diffraction peak at 2θ value of ca. 2.2°, which corresponded to (1 0 0) reflection of the mesoporous material [1], indicating that the EuMCM-41 samples synthesized by microwave irradiation method possess the mesoporous framework. Furthermore, with the increase in europium content, the diffraction peak (1 0 0) of the EuMCM-41 sample gradually weakened and broadened, and the main peak intensity decreased, suggesting that the mesoporous ordering gradually deteriorated with the increase in europium content. This probably owes to an increasing number of defect sites and bond strain in these materials [26]. As shown in Fig. 1a, other (1 1 0), (2 0 0) and (2 1 0) reflections of high order for EuMCM-41(1) sample appear at 2θ=4.0°, 4.62° and 6.03°, respectively, indicating that the channels are hexagonally organized and the ordered MCM-41 structure is formed because the typical Bragg reflections of hexagonal MCM-41 mesoporous material appear at low angles [1]. At the same time, the results also show that the substitution of Si ions in the MCM-41 framework by a small amount of Eu ions does not significantly modify the crystalline structure. The XRD pattern in Fig. 1b exhibits high-intensity (1 0 0) and two low-intensity reflections (110 and 200). However, from Fig. 1c, it can be observed that the EuMCM-41(3) sample has only one weak diffraction peak (1 1 0) except for the main diffraction peak (1 0 0) and the other planes could not be observed. This indicates that a gradual loss of long-range ordering occurs with increasing incorporation of Eu in the EuMCM-41 samples. This is probably attributed to the replacement of Eu ions for Si^{4+} in the framework of MCM-41, resulting in the deterioration of the symmetry of MCM-41. On the other hand, by increasing europium content, the main peak position shifts to lower 2θ value, indicating that d_{100} and a_0 values increase and the pore size enlarges, which is consistent with the data summarized in Table 1. A similar situation has been observed in MCM-41 containing other metals [27].

3.2. TEM analysis

The TEM images of the synthesized EuMCM-41 samples calcined at 550 °C are displayed in Fig. 2. It is clearly observed that these samples have mesoprous structure, indicating that the EuMCM-41 mesoporous molecular sieves were successfully synthesized under