

Preparation, Characterization and Optical Properties of Lanthanum-(Nanometer MCM-41) Composite Material

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Nanometer MCM-41 molecular sieve was prepared under a base condition by using cetyltrimethylammonium bromide as template and tetraethyl orthosilicate as silica source by means of hydrothermal method. Lanthanum(III) was incorporated into the nanometer MCM-41 by a liquid phase grafting method. The prepared nanocomposite materials were characterized by means of powder X-ray diffraction, spectrophotometric analysis, Fourier transform infrared spectroscopy, low temperature nitrogen adsorption-desorption technique, solid diffuse reflectance absorption spectra and luminescence. The powder X-ray diffraction studies show that the nanometer MCM-41 molecular sieve is successfully prepared. The highly ordered mesoporous two-dimensional hexagonal channel structure and framework of the support MCM-41 is retained intact in the prepared composite material La-(nanometer MCM-41). The spectrophotometric analysis indicates that lanthanum exists in the prepared nanocomposite materials. The Fourier transform infrared spectra indicate that the framework of the MCM-41 molecular sieve still remains in the prepared nanocomposite materials and some framework vibration peaks show blue shifts relative to those of the MCM-41 molecular sieve. The low temperature nitrogen adsorption-desorption indicates that the guest locates in the channel of the molecular sieve. Compared with bulk lanthanum oxide, the guest in the channel of the molecular sieve has smaller particle size and shows a significant blue shift of optical absorption band in solid diffuse reflectance absorption spectra. The observed blue shift in the solid state diffuse reflectance absorption spectra of the lanthanum-(nanometer MCM-41) sample show the obvious stereoscopic confinement effect of the channel of the host on the guest, which further indicates the successful encapsulation of the guest in the host. The La-(nanometer MCM-41) sample shows luminescence.

Keywords: Nanometer MCM-41 molecular sieve, Lanthanum, Nanocomposite material, Optical properties

INTRODUCTION

The ordered mesoporous materials have unique physical and chemical properties. In general case, they have large surface areas and the typical surface areas are above 1000 m² g⁻¹. The well-distributed pore diameter may be adjusted from 2 to 50 nm. The materials, whose surfaces are easy to be

decorated or modified, have a number of surface active centers.

The crystal or ordered mesoporous materials are new generation ones distinguishing from the disordered or amorphous mesoporous materials. They have the potential ability to be catalysts, adsorbents, *etc.* The MCM-41 discovered by the American Mobil Company represented a new family of mesoporous materials. From the atom level, these mesoporous materials are disordered and amorphous.

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However, the channels in the materials are regularly arranged, the pore diameters are narrowly distributed in size.

These mesoporous materials are long-range and highly ordered, thus they also have some characters of ordinary crystals and their structural information can be obtained by diffraction and other structural analytical methods [1]. The mesoporous molecular sieve hosts together with various guests, which can be incorporated into them, can form host-guest composite materials. These new materials showed abundant host-guest effects [2-4]. The rare earth modified molecular sieves belonged to well-catalytic materials. For instance the Y-zeolite modified by lanthanides can be used as a high efficiency petroleum refining catalyst. This kind of catalysts showed very high thermal stability.

Nanometer MCM-41 is a novel mesoporous material synthesized in 2001 [5]. In the present study, we selected rare earth element lanthanum(III), as a deputy, and dispersed it into the nanometer molecular sieve host and prepared La-(nanometer MCM-41) composite materials. Powder X-ray diffraction, spectrophotometric analysis, Fourier transform infrared spectroscopy, low temperature nitrogen adsorption-desorption technique, solid state diffuse reflectance absorption spectroscopy and luminescence studies were used to characterize the prepared materials. The nanocomposite materials prepared may possess high catalytic activity and the potential practical value in catalytic field.

EXPERIMENTAL

Chemicals

In this study, La_2O_3 (purity, 99.99%) was purchased from Beijing Chemical Plant and used for the preparation of a 0.10 M LaCl_3 solution. Cetyltrimethylammonium bromide (CTMAB) was purchased from Beijing Yili Fine Chemicals Co., Ltd., China. Tetraethyl orthosilicate (TEOS) was obtained from Fluka. Unless stated, the reagents used were of analytical grade. The water used was doubly deionized.

Preparation of Lanthanum-(Nanometer MCM-41) Composite Material

The synthetic conditions of nanometer MCM-41 were strong stirring with an extremely low surfactant concentration at 353 K. The synthesis procedure of nanometer MCM-41 was

as follows: 3.5 ml of 2 M sodium hydroxide solution was first mixed with 480 ml of water. Then, 1.0 g of CTMAB was added to the solution with stirring and heating. When the solution became homogeneous, 5 ml of TEOS was slowly dropped, so that a white slurry appeared. After 2 h, the resulting products were filtered, washed with water, dried at room temperature, and followed by calcination in air at 823 K for 4 h [5]. The size of the prepared sample MCM-41 was 110 nm [5].

In the next step, the La-(nanometer MCM-41) sample was prepared by a liquid phase grafting method as follows: 1.20 g of the calcined nanometer MCM-41 molecular sieve was dissolved in 60 ml of 0.10 M LaCl_3 solution and the mixtures were stirred for 24 h. The resulting products were filtered, washed with water, dried at ambient temperature, and followed by calcination in air at 823 K for 5 h. The prepared nanocomposite material was designed as La-(nanometer MCM-41).

Characterization of Samples

To investigate the structure and crystallinity of the samples, they were analyzed on a Siemens D5005 (Germany) diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm). The samples were scanned from 0.4° to 10° (2θ) with a tubular voltage of 30 kV and a tubular electric current of 20 mA. The spectrophotometric analysis was carried out on a 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China). The FTIR spectra were recorded on an American Nicolet 5DX-FTIR instrument using KBr wafers technique. The adsorption and desorption isotherms for nitrogen were obtained at 77 K using a Micromeritics ASAP-2010M. The samples were out-gassed at 573 K for 12 h before measurements. The data were obtained using the BdB model (Broekhoff and de Boer) [6]. The specific surface areas were obtained using the BET (Brunauer-Emmett-Teller) equation [7], and the pore structures were analyzed by BJH (Barrett-Joyner-Halenda) algorithm [8]. The UV-Vis absorption spectra of the samples were recorded on Shimadzu UV-3100 spectrophotometer over a wavelength range of 200-800 nm. Barium sulfate was taken as a standard background. The luminescence study was conducted on a SPEX-FL-2T-2 spectrofluorimeter (Spex Company, USA). The spectra were fully corrected for the spectral response of

the instrument.

RESULTS AND DISCUSSION

Chemical Analysis

The content of the host and guest in the nanocomposite material was spectrophotometrically analyzed with molybdsilicate blue for silicon [9] and with DBS-arsenazo for lanthanum [10]. The results showed that, in the La-(nanometer MCM-41) sample, the silicon and lanthanum contents are 41.36% and 0.77%, respectively. The ratio of silicon to lanthanum in the prepared nanocomposite material is 265.7, which indicates the incorporation of the guest lanthanum into the MCM-41 molecular sieve host.

Powder X-ray Diffraction

As shown in Fig. 1, for the diffractograms of the materials studied, the curve a exhibits four sharp Bragg peaks which can be indexed as (100), (110), (200) and (210) of the MCM-41 from 2° to 10° [5]. This shows that nanometer MCM-41 molecular sieve was successfully prepared. Figure 1b shows the X-ray diffraction pattern of the calcined nanometer MCM-41. After removing the template at 823 K, the strongest peak moves a little to a higher angle. Compared with curve a, the d value decreases slightly. In the framework of the molecular sieve calcined, thermal vibration action takes place and which remains the crystal lattice imperfection in the course of synthesis. The crystallinity of the framework of mesoporous molecular sieve MCM-41 was increased and, thus, the intensities of four diffraction peaks increase. Figure 1c shows the XRD pattern of the La-(nanometer MCM-41) sample, which shows three characteristic peaks for MCM-41. This shows that the framework of the molecular sieve in the La-(nano MCM-41) sample is still remained. However, the degree of ordering of the composite material decreases and a peak (210) disappears.

Fourier Transform Infrared Spectra

Figure 2 shows the Fourier transform infrared spectra of the samples over the region of $1400\text{--}400\text{ cm}^{-1}$. The calcined nanometer MCM-41 (Fig. 2a) exhibits a symmetric stretching vibration band at 803 cm^{-1} and two asymmetric stretching vibration bands at $1080, 966\text{ cm}^{-1}$ for the tetrahedral TO_4

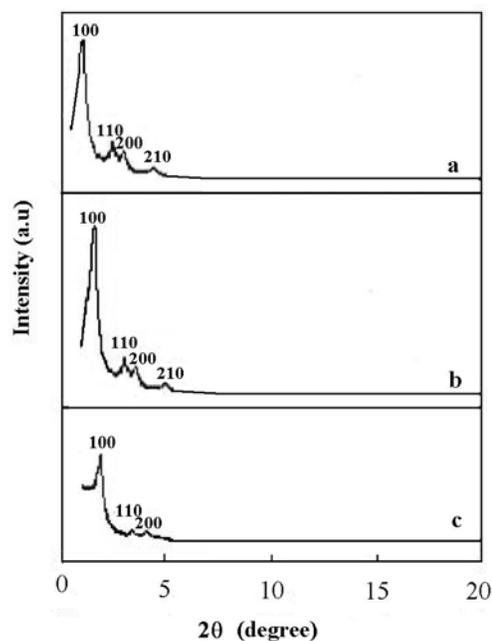


Fig. 1. X-ray diffraction patterns of samples: (a) nanometer MCM-41 (uncalcined); (b) nanometer MCM-41 (calcined); (c) La-(nanometer MCM-41).

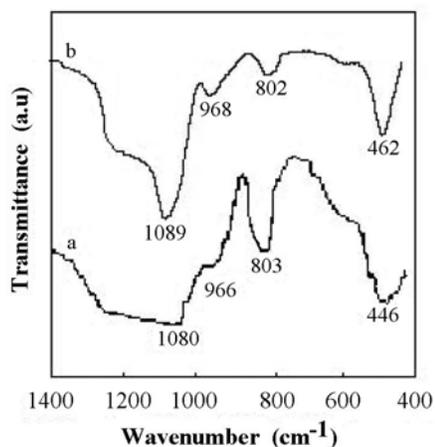


Fig. 2. Infrared spectra of samples: (a) nanometer MCM-41 (calcined); (b) La-(nanometer MCM-41).

structural units of silanol groups. The peak at 446 cm^{-1} results from the T-O bending vibration of the silanol groups.

Compared with the curve 2a, the infrared spectrum of the

La-(nanometer MCM-41) sample (Fig. 2b) shows the four corresponding characteristic peaks of the nanometer MCM-41. This indicates that the framework of the sample La-(nanometer MCM-41) is still remained intact and MCM-41 has kept its characteristic structure. The infrared characteristic peaks of the prepared nanocomposite material La-(nanometer MCM-41) have fluctuation and the positions of some characteristic peaks move towards the region of higher energy. Compared with the T-O bending vibration peak of silanol groups at 446 cm^{-1} and the asymmetric stretching vibration band of the tetrahedral TO_4 structural unit of the nanometer MCM-41 framework silanol group at 1080 cm^{-1} , in the case of La-(nanometer MCM-41), the corresponding peaks of the sample show blue shifts of 16 cm^{-1} and 9 cm^{-1} , respectively. The observed blue shifts of the infrared peaks is due to the fact that a part of the lanthanum incorporates into the framework of the molecular sieve.

Low Temperature Nitrogen Adsorption-Desorption Isotherms

The low temperature nitrogen adsorption-desorption isotherms and pore size distribution patterns of the samples are shown in Fig. 3, where the isotherms can be classified as typical mesopore adsorption Langmuir IV isotherms [11]. As is obvious from Fig. 3A, a gentle increase in the adsorbed volume at low pressures is followed by a steep increase at higher pressures, where the adsorbed phase nitrogen appears on the inner surface of the mesopore from monolayer to multilayer. With an H_1 hysteresis loop as defined by IUPAC, a sudden increase occurs at $P/P_0 = 0.25\sim 0.30$. The increase suggests the uniformity of the mesoporous size distribution and capillary absorption phenomenon. Although the slope of the La-(nanometer MCM-41) sample is smaller than the one of the host nanometer MCM-41, the slope of the composite material is still large. After this, the nitrogen appears on the external surface of the mesopore from monolayer to multilayer, where the curve does not show an obvious change. Because the particle gaps cause capillary condensation, another sudden increase occurs at $P/P_0 = 0.9$. From the adsorption-desorption isotherms, the average pore diameter and the specific surface area of the nanometer MCM-41 sample were found to be 2.29 nm and $961\text{ m}^2\text{ g}^{-1}$, respectively. The corresponding results of the La-(nanometer MCM-41) sample are 2.02 nm and 887

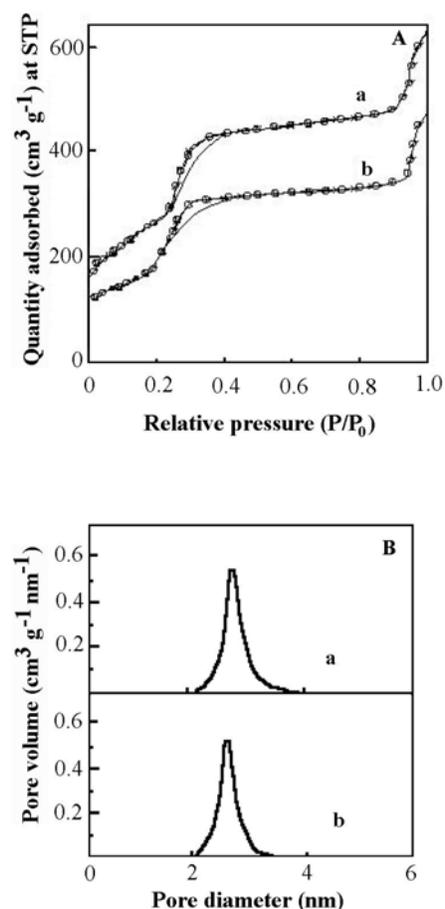


Fig. 3. Nitrogen adsorption-desorption isotherms (\circ , adsorption; \times , desorption) (A) and pore size distribution patterns (B) for nanometer MCM-41(calcined) (a) and La-(nanometer MCM-41) (b).

$\text{m}^2\text{ g}^{-1}$, respectively. The porous size distribution patterns of the samples are close to the Gaussian distribution (Fig. 3b). The framework of the MCM-41 molecular sieve in the La-(nanometer MCM-41) is still remained. However, the pore volume, the pore diameter and the specific surface area decrease due to the incorporation of lanthanum. The results show that, in the prepared nanocomposite material lanthanum-(nanometer MCM-41), a part of the guest is incorporated into the channels of the molecular sieve. The corresponding structure parameters are listed in Table 1.

Table 1. Pore structure Parameter of Samples

Sample	d_{100} (nm)	a_0 (nm) ^a	BET surface area (m ² g ⁻¹)	Specific pore volume (cm ³ g ⁻¹) ^b	Pore size (nm) ^c
Nanometer MCM-41	3.46	4.00	961	0.566	2.29
La-(nanometer MCM-41)	3.06	3.53	887	0.527	2.02

^a $a_0 = 2/\sqrt{3}$; d_{100} ; a_0 = unit cell parameter (the repeat distance between two pore centers in nanometer MCM-41 molecular sieve); d_{100} = crystal face spacing. ^bBJH adsorption cumulative surface area of pores. ^cPore size calculated from the adsorption branch.

Optical Properties

UV-Vis spectroscopy. In the theory of quantum mechanics, the change in quantity of a forbidden band is inversely proportional to the size of particle; the smaller the size of particle, the higher the energy of forbidden band. The energy of the electrons and holes produced by excitation is high in this case. The behavior in the UV-Vis solid diffuse reflectance absorption spectra is the blue shift of the absorption peak. The UV-Vis absorption spectra can characterize the photoabsorption ability of sample and the coordinate situation of some samples. As shown in Fig. 4a, the calcined nanometer MCM-41 does not have any absorption over the range of 200-800 nm in the solid UV-Vis diffuse reflectance absorption spectra. However, the La-(nanometer MCM-41) sample (Fig. 4c) has two absorption peaks. The peak at 223 nm is assigned to the UV-absorption of lanthanum molecule clusters. Compared with the absorption of bulk lanthanum oxide at 308 nm (Fig. 4b), the La-(nanometer MCM-41) shows the significant blue shift of 23 nm relative to the absorption band of 285 nm. It is attributed to the small size of guest particle, its large energy gap, and the increase of the energy of forbidden band. The peak at 285 nm is assigned to the characteristic absorption peak of the lanthanum oxide incorporated into the channels of the molecular sieve, due to quantum size effect.

Luminescence. The excitation and emission spectra of samples can provide the information on energy band, surface state and imperfection, *etc.* Figure 5 shows the excitation-emission spectra of the prepared lanthanum-(nanometer MCM-41) sample. The most remarkable character is that the spectrum bands are very wide. This shows that there are obvious imperfections in the sample. The emission of the

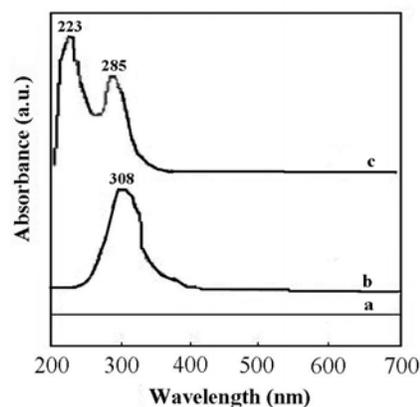


Fig. 4. Solid diffuse reflectance absorption spectra of samples (a) calcined nanometer MCM-41; (b) lanthanum oxide; (c) La-(nanometer MCM-41).

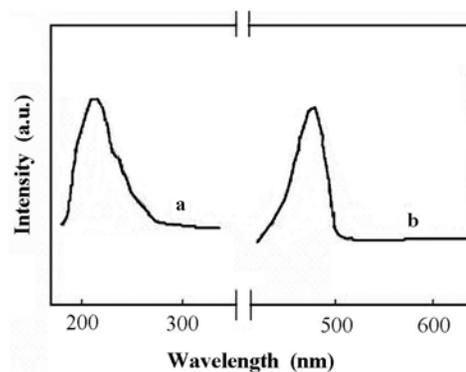


Fig. 5. Luminescence spectra of La-(nanometer MCM-41) sample: (a) Excitation spectrum, $\lambda_{em} = 468$ nm; (b) Emission spectrum, $\lambda_{ex} = 216$ nm.

La-(nanometer MCM-41) produces a weak steady-state luminescence because of its non-ordered character. The excitons, especially the surface excitons, are very easily formed in the prepared nanocomposite material. It contains different kinds of dangling bonds. Under the illumination of excitation light, the excitation peak at 216 nm results from the transition of electrons that have been excited into high energy level and go back into the low energy level and are captured.

CONCLUSIONS

The lanthanum-(nanometer MCM-41) nanocomposite material has been prepared by a liquid phase grafting method. The material prepared can not only introduce active centers into the mesoporous materials, but also keeps a high specific surface area, good structural ordered property and stability. The framework structure of the molecular sieve is retained in the lanthanum-(nanometer-MCM-41) sample. Some lanthanum locates in the channels of the molecular sieve. The solid diffuse reflectance absorption spectrum of the lanthanum-(nanometer MCM-41) sample shows a blue shift. The prepared lanthanum-(nanometer MCM-41) material shows a relatively strong luminescence.

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