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Synthesis and Characterization of Mesoporous Materials MCM-41 Incorporated by Yttrium, Neodymium and Samarium*

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Abstract: Using cetyl-trimethyl-ammonium bromide (CTMAB) as template agent and tetraethylorthosilicate (TEOS) as silica source, the MCM-41 mesoporous materials were synthesized with Y, Nd and Sm incorporated in the framework under hydrothermal conditions. The structure and the micro-morphology of the materials and the state of Y, Nd and Sm were investigated through the analyses of XRD, nitrogen adsorption-desorption isotherm, SEM, IR and TG-DTA. The XRD results indicate that the synthetic samples are of typical structure of mesoporous MCM-41 with ordered hexagonal arrangements, and Y, Nd and Sm can be incorporated into the framework of these mesoporous materials. Nitrogen adsorption-desorption isotherms show that the samples possess the typical mesopores character. SEM micrographs reveal that the incorporated samples show a well-defined spherical morphology with the diameter ranging 0.10~0.15 μm. The occurrence of two different template sorption sites in the framework as revealed by TG-DTA analysis further suggests the presence of Y, Nd and Sm in siliceous framework.

Key words: MCM-41 mesoporous materials; incorporate; template; synthesis; characterization; rare earths
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Zeolite molecular sieves, with the uniform channel structure and shape selective property, are widely used as catalysts in industries of oil-refining, petrochemicals, fine-chemicals and so on. However, the pore sizes of zeolite molecular sieves usually are smaller than 2 nm, it greatly prevents large molecules into the pores for effective reactions.

In 1992, researchers at the Mobil Company first synthesized a family of ordered mesoporous materials, known as MCM-41[1,2]. This novel material possesses regular mesoporous channels in a hexagonal array, with the adjustable pore size between 2 and 50 nm, and the large internal surface area, high sorption capacities and thermal stability, believed to be a potential catalyst in oil and chemical industry, especially those involving larger molecules[3~6]. However, few lattice defect, low surface acidity and low catalytic activity inhibit the practical use of MCM-41 materials[7~9]. Inorder to solve these problems, active metal elements are usually introduced into the silica-based framework of MCM-41 mesoporous material[10~12].

Rare earth elements can catalyse many chemical reactions, such as hydrocarbon cracking, isomerization, aromatization, arene alkylation, disproportionation and inorganic compounds[13,14].

The synthesis of MCM-41 mesoporous materials was studied in this paper. The yttrium, neodymium and samarium were incorporated in the framework under hydrothermal conditions through the use of CTMABr as template agent.

1 Experimental Methods

1.1 Materials

The materials used in the preparation were listed below. The template agent was cetyl-trimethyl-ammonium bromide (CTMABr, 99%) from Kermel. The tetrathylorthosilicate (TEOS) containing 27.9% (mass fraction) SiO_2 from Tongxin Chemical Inc was used as silica source. The yttrium oxide (Y_2O_3, 99.99%), neodymium oxide (Nd_2O_3, 99.99%), samarium oxide (Sm_2O_3, 99.99%) and tetramethyl ammonium hydroxide (TMAOH, 25% in solution) were

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commercial products from SINOPHARM. The nitric acid, sodium hydroxide and de-ionized water were used in the synthetic process.

1.2 Synthetic procedures

1.2.1 Synthesis of siliceous MCM-41 The pure siliceous MCM-41 mesoporous material (denoted as SiMCM-41) was prepared according to the following synthetic procedures. As much as 62.5 g TEOS and 16.4 g TMAOH were dissolved into de-ionized water. 21.87 g CTMAB and 2.64 g NaOH were sequentially added into the solution with the vigorous stirring by a magnetic stirrer. After adjusting the pH to 9~ 10 and further stirring for about 30 min at room temperature, the gel mixture was transferred into a stainless steel autoclave and crystallized in static conditions at 373 K for 2 d. The final molar composition of the gel mixture was 1TEOS: 0.20CTMAB: 0.15TMAOH: 0.22NaOH: 60H_2O. The solid products SiMCM-41 were obtained by filtration, washed with plenty of de-ionized water, dried at 353 K and calcined at 823~ 853 K for 7 h to remove template agent.

1.2.2 Svnthesis of YMCM-41. NdMCM-41 and SmMCM-41 The synthesis of Y, Nd and Sm-incorporated MCM-41 samples, abbreviated as YMCM-41, NdMCM-41 and SmMCM-41, were carried out as follows: (1) Three different nitrate solutions were prepared by dissolving proper quality of Y_2O_3, Nd_2O_3 and Sm_2O_3 in excessive nitric acid, respectively, with the molar ratio of Si/Ln (Ln= Y, Nd, Sm) to be 100. (2) The three solutions were dripped into prepared gel mixture described above by 1.2.1. (3) The samples of YMCM-41, NdMCM-41 and SmMCM-41 were synthesized on the basis of similar procedures as SiMCM-41.

1.3 Analytic methods

The low-angle X-ray power diffraction (XRD) measurements were performed on a Riga KuD/max- III A X-ray diffractometer using the Cu Kα radiation (40 kV, 35 mA) over a 2θ rang from 1° to 10°. Nitrogen adsorption isotherms were measured at 77.35 K on a Micromeritics ASAP-2010 model adsorption analyzer, the pore size distribution was calculated by BJH method. SEM images were taken on an ESEM-30 scanning electron microscope operated at 25.0 kV. The infrared spectra were recorded on a TJ270-33 FT-IR spectrometer using KBr pellets. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on 15 mg synthetic sample using a TGA-50 thermal analyzer with the temperature program from 373 to 1173 K at 15 K•min^{-1}.

2 Results and Discussion

Fig. 1 shows the XRD patterns of the calcined samples. All the samples exhibit an intense d_{100} characteristic peak at 2θ= 2°~ 2.5°, and several weak diffraction peaks indexed to (110) and (200) planes in the 2θ range from 3° to 8°, consistent with the typical MCM-41 mesoporous material[1,2]. The similarity of the peak location with the known XRD of MCM-41 suggests an ordered hexagonal array in the synthetic samples. When Si is replaced by Y, Nd and Sm, the characteristic peaks of d_{100} become wide in association with the variation of other peaks in the 2θ range from 3° to 8°. This infers that incorporation of Y, Nd and Sm can, to a certain degree, affect the long-range ordered arrangement but not change the hexagonal mesoporous structure.

XRD data and the synthesis parameters of all the four samples are listed in Table 1. YMCM-41, NdMCM-41 and SmMCM-41 shift to the low values in the 2θ of the d_{100} peak, and high values in d_{100}-spacing and unit cell parameter a_0 in comparison with SiMCM-41. This is possibly due to the replacement between Si

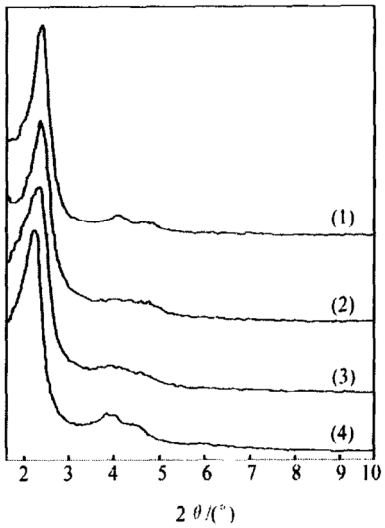

Fig. 1 XRD patterns of calcined samples
(1) SiMCM-41; (2) YMCM-41; (3) NdMCM-41; (4) SmMCM-41

Table 1 XRD results and synthesis parameters of samples

Samples	CTMAB/SiO_2 (molar ratio)	Si/Ln* (molar ratio)	d_{100}**/ nm	a_0***/ nm
SiMCM-41	0.20	∞	3.616	4.176
YMCM-41	0.20	100	3.757	4.338
NdMCM-41	0.20	100	3.778	4.363
SmMCM-41	0.20	100	3.895	4.498

* Si/Ln, molar ratio in the gel mixture, Ln= Y, Nd or Sm;
** d_{100}, XRD d_{100}-spacing; *** $a_0= 2d_{100}/3^{1/2}$, unit cell parameter

and the rare earth elements Y, Nd and Sm which possess larger ionic radius. The replacement indirectly indicates the occurrence of the incorporation of these rare earth elements in the framework of MCM-41.

The nitrogen adsorption isotherm of sample YMCM-41 is displayed in Fig. 2. According to the IUPAC classification, it is of typical type Ⅳ isotherm, a characteristic for materials containing uniform mesopore. As the relative pressure P/P_0 goes up, nitrogen-adsorbed volume linearly increases caused by the monolayer adsorption of nitrogen at low relative pressure ($P/P_0 < 0.2$). When the relative pressure varies between 0.2~ 0.5, there is a noticeable increase in nitrogen-absorbed volume accompanied by a small loop, corresponding to the capillary condensation within mesopores. At P/P_0 of 0.9, a sharp increase associated with a large loop was observed, indicating capillary condensation of N_2 among particles[15]. The B_{JH} pore size of YMCM-41 displays a very narrow distribution with a mean value of 3.24 nm, further illustrating the mesoporous nature.

The crystal morphology can be shown by scanning electronic microscope. The SEM images of MCM-41 mesoporous materials incorporated by Y, Nd and Sm are shown in Fig. 4. All the incorporated samples appear to be well-defined spherical in particle morphology with a diameter of 0.10~ 0.15 μm, agreeing with the previously reported data of MCM-41 materials[1,2]. This fitness indicates that incorporation of Y, Nd and Sm does not substantially change the morphology of mesoporous samples.

The infrared spectra for the synthesized materials are shown in Figs. 5 and 6. The strong absorbing bands observed at ca. 2921, 2851 and 1480 cm^{-1} respectively correspond to asymmetric stretching υ_{as}(C–H), symmetric stretching υ_s(C–H) and bend vibration δ(C–H) in template agent[16]. After calcinations at 550~ 580 ℃, these bands disappear, indicative of the complete decomposition of template species.

In the calcined samples, the strong absorbing bands at 3440 and 1640 cm^{-1} probably result from the vibration of Si–O–H or H–O–H groups[17,18]. The broad vibrational bands at ca. 1086 cm^{-1}, and two relatively weak bands at ca. 810 and 460 cm^{-1}, can be attributed to υ_{as}(Si–O–Si), υ_s(Si–O–Si) and δ(Si–O), respectively. These are the typical adsorption bands for the mesoporous materials. Additionally, a weak vibrational bands at ca. 960 cm^{-1} is assigoed to the Si–O stretching vibration in Si–O–H SiMCM-41 samples[19], buu it is considered as a signature of the introduction of metal ions into siliceous frameworks in TiMCM-41, VMCM-41 and WMCM-41 and so on[10,20,21]. Comparably, the smaller vibrational

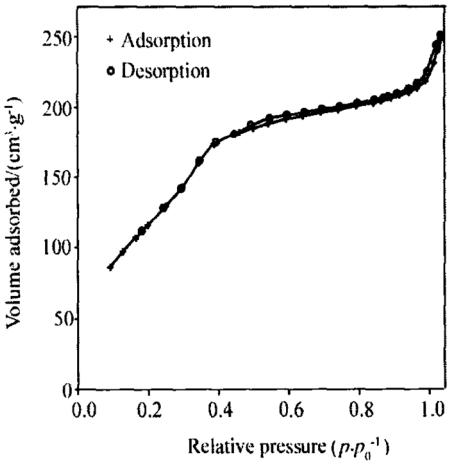

Fig. 2 Nitrogen adsorption isotherm of YMCM-41

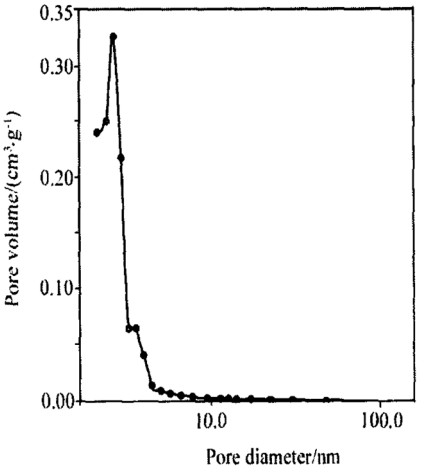

Fig. 3 BJH pore size distribution curve of YMCM-41

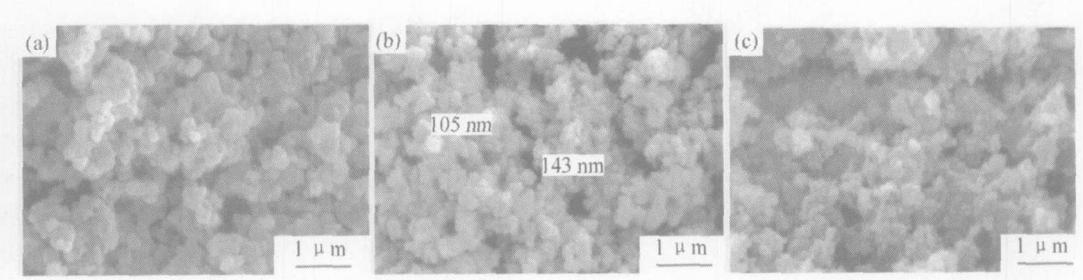

Fig. 4 Scanning electron micrographs of incorporated samples (× 20000)
(a) YMCM-41; (b) SmMCM-41; (c) NdMCM-41

bands at 960~ 985 cm^{-1} in YMCM-41, NdMCM-41 and SmMCM-41 than those in SiMCM-41 may indicate the replacement of Si by Y, Nd and Sm.

After calcinations, all the absorbing bands shift to the great wavenumbers in YMCM-41, NdMCM-41 and SmMCM-41. This is probably due to the formation of more Si- O- Ln (Ln= Y, Nd or Sm) boods in addition to lattice condensation[16]. Furthermore, the bands in YMCM-41, NdMCM-41 and SmMCM-41 shift to the low frequency regions in comparison with SiMCM - 41,

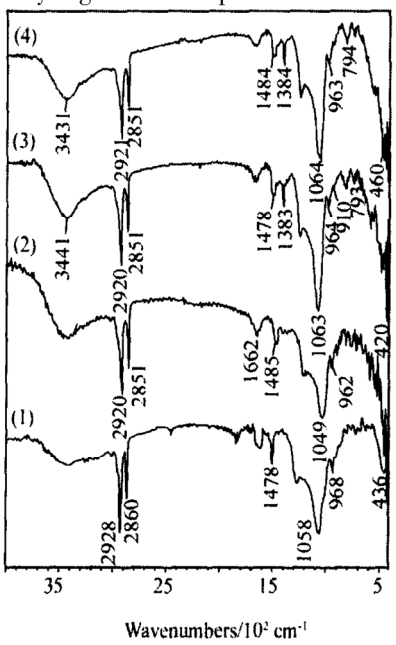

Fig. 5 Infrared spectra of uncalcined samples
(1) SiMCM-41; (2) YMCM-41; (3) NdMCM-41; (4) SmMCM-41

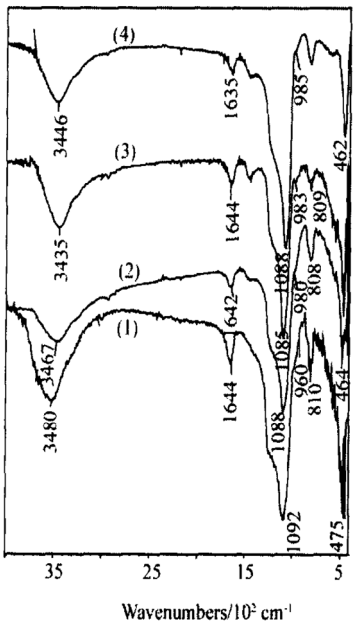

Fig. 6 Infrared spectra of calcined samples
(1) SiMCM-41; (2) YMCM-41; (3) NdMCM-41; (4) SmMCM-41

inferring Y, Nd and Sm were incorporated into the framework of samples[22,23].

Thermogravimetry (TG) and differential thermal analysis (DTA) are the effective tool to investigate the framework composition of MCM-41 mesoperous materials[2]. Fig. 7 lists the TG and DTA curves for the synthetic SiMCM-41, YMCM-41, SmMCM-41 and NdMCM-41. There are two main weight losses for SiMCM-41. The first weight loss between room temperature and 423 K is due to desorption of physical adsorbed water, and a second weight loss between 423 and 673 K results from the decomposition of template molecules. The TG data of the incorporated samples YMCM-41, SmMCM-41 and NdMCM-41 display a comparable weight loss of adsorbed water under 423 K with SiMCM-41, in line with the occurrence of an endothermic peak at 373 K in the DTA curves (Fig. 7 (b)). Different from SiMCM-41, there appear respectively new exothermic peaks at 624.2, 655.5 and 640.2 K in the DTA curves of samples YMCM-41, SmMCM-41 and NdMCM-41, believed to be the decomposition of Si- O- Ln (Ln= Y, Nd and Sm) groups in template agent. These results demonstrate that a proportion of Y, Nd and Sm have already been incorporated into the silica framework of MCM-41 mesoporous materials. The weight loss at 423~ 603 K in TG curves and the exothermic peaks at ca. 573 K correspond to the removal of the template agent associated with Si- O- Si bond in [SiO_4] group. This is not contradictory with the observation of Beck et al.[1,2] showing a much higher decomposition temperature of Si- O- Al bond associated with the template agent than Si- O- Si bond. The decomposition of temperate agent in our samples incorporated by Y, Nd and Sm occurs at two distinct stages. This is also a strong evidence of the presence of Y, Nd and Sm in the framework.

Finally, a weight loss upon 600 ℃ is ascribed to dehydrogenization in Si-O-H and Ln-O-H (Ln= Y, Nd and Sm) groups.

3 Conclusions

1. MCM-41 mesoporous materials are successfully synthesized with the incorporation of Y, Nd and Sm into the siliceous framework under hydrothermal conditions. The analyses of XRD, nitrogen adsorption isotherms and SEM images indicate that the synthetic samples are typical mesoporous. The XRD results also reveal the structure regularity of the incorporated samples decrease to some extent.

2. The XRD, IR spectra and TG-DTA curves suggest that Y , Nd and Sm species are incorporoated

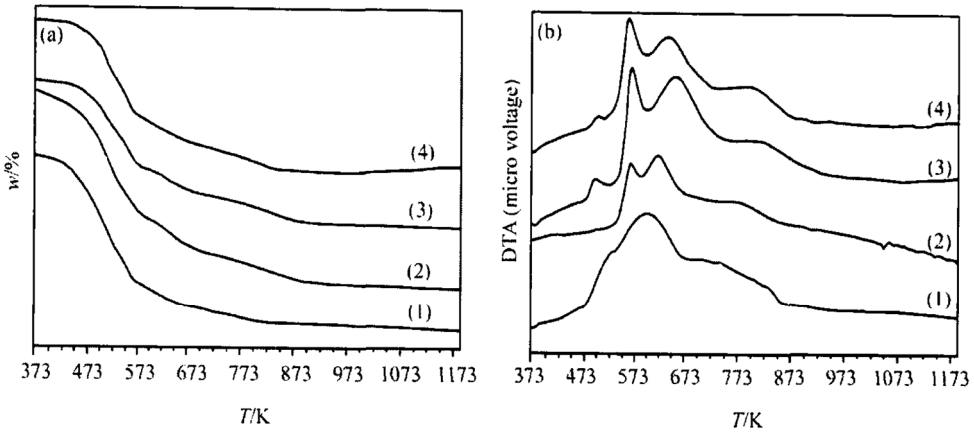

Fig. 7 TG and DTA curves for synthetic samples
(a) TG curve; (b) DTA curve
(1) SiMCM-41; (2) YMCM-41; (3) SmMCM-41; (4) NdMCM-41

into the siliceous frameworks of MCM-41 mesoporous materials.

3. Different from the pure silica-based MCM-41 mesoporous materials, the incorporated samples of Y, Nd and Sm have two different template adsorption sites and two distinct decomposition stages.

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