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Study of the influence factors on the synthesis of Fe-MCM-48 with binary mixed cationic and anionic surfactants

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Abstract

Highly ordered Fe-MCM-48 was synthesized by a mixed template method under low molar ratio (0.17:1) of mixed surfactants to silica. The effect of various factors, such as Fe sources, the amount of Fe salt, Si sources, surfactant/SiO_2, crystallization temperature and crystallization time on the synthesis were discussed in detail. The Debye-Huckel theory, the theory of salts formation, the local effective surfactant packing parameter theory and the charge balance theory were used to explain the reason that various factors can affect the product structure reasonably. The optimum synthesis conditions for Fe-MCM-48 were obtained.

Keywords: Fe-MCM-48; Hydrothermal synthesis; Mixed surfactants; Crystallization; Mesoporous materials

1. Introduction

In the beginning of the 1990s, a new family of ordered M41S mesoporous silica was discovered and immediately received great attention because of its uniform channels, high surface area and good thermal stability [1]. Among this M41S family, MCM-48 with three-dimension channel system has several advantages over MCM-41 with one-dimension channel system when they were applied to the adsorption and catalytic reaction. However, the formation of MCM-48 required very special synthesis conditions and large amount of surfactant if the cationic surfactant was used as the sole template [2]. In order to resolve this problem, we developed a new pathway to synthesize Si, Al-MCM-48 with the binary mixed cationic–anionic surfactants method [3]. This method enabled the synthesis of MCM-48 easily under the low molar ratio of surfactant to silica (Surf/SiO_2) and low surfactant concentration. And we further extended this method to synthesize the Fe-MCM-48 with good catalytic performance on the phenol hydroxylation [4]. Meanwhile, the proofs that Fe^{3+} ion had been introduced into the MCM-48 framework were set up by the XRD, ^{29}Si MASNMR, ESR and UV–visible results. However, the function of different synthesis factors only referred a few in these reports. In the present paper, we systemically studied the effects of Fe source, Si source, Fe salt amount, surfactant/SiO_2 and other hydrothermal conditions on the product structure and the optimum synthesis conditions for Fe-MCM-48 were obtained. Especially, the reason that various factors could affect the product structure was discussed in detail. We believe this work not only can help us to recognize the synthesis chemistry of Fe-MCM-48 deeply but also is useful to synthesize other high quality mesoporous silica containing transition metals.

2. Experimental

2.1. Synthesis

The synthesis mixture of Fe-MCM-48 was prepared as follows: Si source and Fe source were added to the mixture

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solution of cetyltrimethylammonium bromide ($C_{16}H_{33}$-Me_3NBr, CTAB, imported from Denmark), sodium laurate ($C_{11}H_{23}COONa$, SL, First Chemical Co., Shanghai), NaOH (First Chemical Co., Shanghai) and H_2O. If there is not any special notice in this paper, the molar composition of the above mixture was 1.0 SiO_2:0.153 CTAB:0.017 SL:0.25 Na_2O:0.002–0.003 Fe_2O_3:100 H_2O. This solution was stirred at 30 °C for 1 h. After that, the mixture was placed in a static autoclave at 100 °C for four days. The solid product was recovered and calcined at 550 °C in air (5 °C/min) for 4 h. The Si sources included tetraethylorthosilicate (TEOS, First Chemical Co., Shanghai), water glass (Jiangpu Chemical Co., Shanghai) and fumed silica (Electrochemical Co., Shanghai). The Fe sources were $Fe_2(SO_4)_3 \cdot xH_2O$ (the content of Fe is 22 wt%, First Chemical Co., Shanghai), $FeCl_3 \cdot 6H_2O$ (First Chemical Co., Shanghai), and $Fe(NO)_3 \cdot 9H_2O$ (First Chemical Co., Shanghai), respectively.

2.2. Characterization

The powder X-ray diffraction patterns were recorded on the Rigaku D/Max-II A diffractometer (Ni-filtered Cu-Kα radiation with $\lambda = 1.542$ Å) operated at 40 kV and 20 mA. The TEM images were obtained on the JEM-2010 Transmission Electron Microscope operated at 200 kV. The SEM images were obtained on the Philips XL-30 Scan Electron Microscope.

3. Results and discussion

3.1. The XRD, TEM and SEM image of Fe-MCM-48 sample

Fig. 1 is the XRD pattern of Fe-MCM-48 sample synthesized using $Fe_2(SO_4)_3 \cdot xH_2O$ and TEOS as Fe source and Si source, respectively. It corresponds well to those reported for purely siliceous MCM-48 [1]. Fig. 2 is the TEM image of this sample. The order arrangement of lattice dot along [1 1 0] direction means the sample has excellent textural uniformity. The SEM image (Fig. 3) of this sample suggests that the sample is composed of sphere particles and there is no other structure phase. All of these results show that the sample is high quality Fe-MCM-48 material.

3.2. The effect of Fe sources

The effect of different Fe sources, such as $Fe_2(SO_4)_3 \cdot xH_2O$, $FeCl_3 \cdot 6H_2O$ and $Fe(NO)_3 \cdot 9H_2O$ on the product structure was studied under the condition that TEOS was used as the constant Si source. From Fig. 4, one can see that the XRD patterns of the two samples synthesized by $Fe(NO)_3 \cdot 9H_2O$ and $FeCl_3 \cdot 6H_2O$ are similar. Besides the main peak at 2.6°, there also exist two peaks at 2.2° and 5.1°, respectively (Fig. 4, left b and c). Because

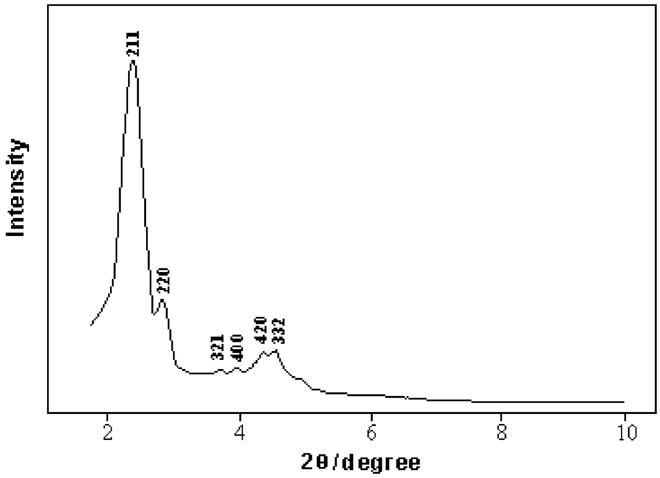

Fig. 1. XRD pattern of Fe-MCM-48 sample.

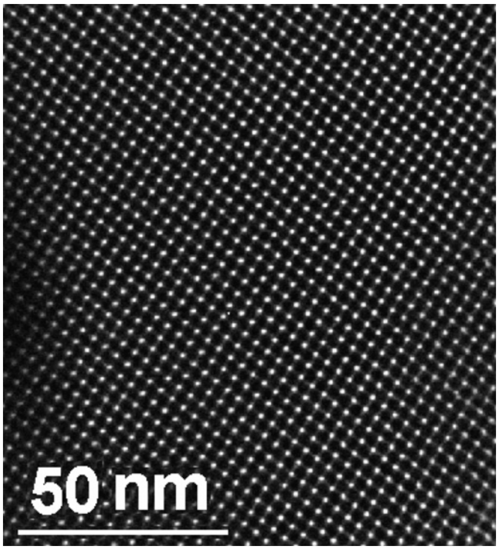

Fig. 2. TEM image of Fe-MCM-48 on the (1 1 0) cubic plane.

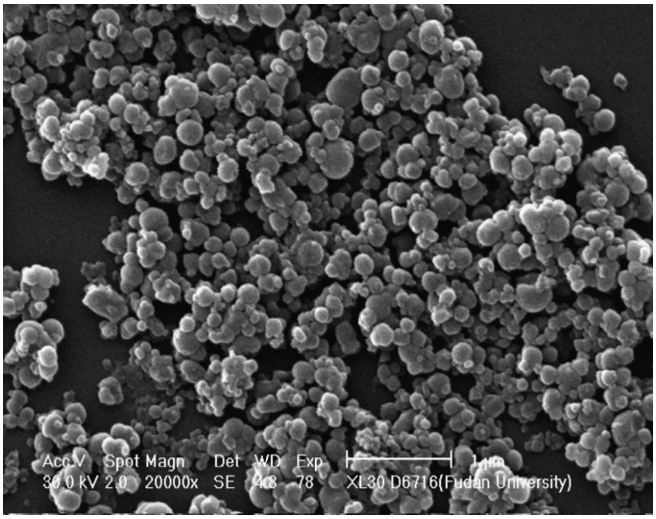

Fig. 3. SEM image of Fe-MCM-48 sample.