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Short-time formation of well-ordered cubic mesoporous MCM-48 molecular sieve with the aid of fluoride ions

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Abstract

The crystallization time for cubic Ia3d mesoporous MCM-48 molecular sieve was first reduced by combining slight increase of reaction temperature with addition of tiny fluoride ions to the synthesis system. The reaction time reduces with the increasing F^-/Si ratio, but the high ratio of 0.4 will only lead to a disordered structure with poor crystallinity. The pore ordering is also considerably improved with the aid of fluoride ions even the reaction time is much shorter than those without any fluorides. The time-reduction action of fluoride ions on the synthesis of MCM-48 is attributed to the accelerated hydrolysis speed of silica source and condensation degree of silicates by fluoride ions.

Keywords: MCM-48; Fluoride; Promote; Time-reduction

1. Introduction

Since the discovery of M41S in 1992 [1], most attentions have been paid on MCM-41 or other mesoporous materials such as HMS and SBA-15 [2–4]. However, fewer researches have dealt with MCM-48 mainly due to its difficult synthesis. It is known that the formation of cubic MCM-48 with most molar composition ratios generally needs long reaction time to finish slow phase transformation processes [5–7]. However, it was reported that increasing crystallization temperature could reduce the synthesis time for MCM-48. For example, Corma et al. reported that higher reaction temperature such as 423 K could reduce synthesis time to 24 h using the widely used CTAB as templates. Unfortunately, the synthesis should strictly restrict reaction temperature and surfactant/silicon ratio [8]. It was also reported that MCM-48 could be obtained within 6 h using temperature modification, but it still needs high temperature of 423 K to accelerate the phase transformation process from MCM-41 to MCM-48 and post-treatment to increase crystallinity [9]. Therefore, it seems that high-temperature synthesis route is tedious and inconvenient, which is not suitable for most synthesis systems at present. Besides, higher temperature means more invested cost and is disadvantageous to future extensive applications. MCM-48 has an attractive three-dimensional interwoven structure and is expected to have tremendous application prospects. This motivates us to find a new way synthesizing well-ordered MCM-48 quickly and easily under milder and more controllable conditions. In this paper, for the first time we achieved the purpose of reducing reaction time for MCM-48 by combining slight increase of crystallization temperature to 393 K with introduction of F^- to the synthesis system advanced by Monnier et al. [10], which originally needs 3 days at 373 K. The product obtained is well-developed and needn't any post-treatment.

2. Experimental

In a typical synthesis, 5 ml TEOS was first dropwised to 25 ml of 0.45 M NaOH solution at room temperature, then 5.3 g CTAB was gradually added under vigorous stirring.

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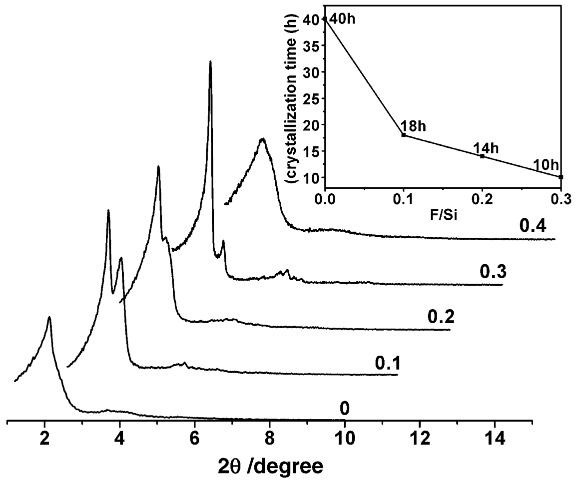

Fig. 1. XRD patterns obtained after reaction for 10 h at F / Si = 0, 0.1, 0.2, 0.3 and 0.4. Insert: the crystallization time for the initial formation of well-developed MCM-48 structure at various F / Si ratio.

Finally, 0.094–0.376 g NaF was added to the gel mixture and the mixture was transferred to an autoclave and crystallized at 393 K with different time after stirring for 1 h. The molar composition of the gel mixture is $1SiO_2:0.25Na_2O:0.65CTAB:62H_2O:x$NaF where x is 0–0.4.The solid products were collected by filtration and dried in air. The as-synthesized sample was calcined at 550 °C for 6 h to remove the templates.

3. Results and discussion

Fig. 1 shows XRD patterns obtained after reaction for 10 h at F / Si = 0, 0.1, 0.2, 0.3 and 0.4. It can be distinctly observed that the formation time for MCM-48 is largely dependent on F / Si ratio. At F / Si = 0, only an amorphous product is obtained after crystallization for 10 h. When F / Si reaches 0.1, the mesophase of MCM-48 begins to appear and mixed phases of the lamellar and cubic are acquired after reaction for the same time. The cubic phase is gradually enhanced and the lamellar one slowly disappeared at F / Si = 0.2. A cubic Ia3d mesophase with a strong XRD intensity is formed at F / Si = 0.3 and further increasing F / Si ratio to 0.35 (not shown) can't lead any significant time-reduction. But when F / Si reaches 0.4, only a disordered structure is produced. Therefore, there is an optimum F / Si ratio for the formation of MCM-48. Moreover, from the insert of Fig. 1 it is obvious that the approximate time for the initial formation of MCM-48 decreases sharply with the increasing F / Si ratio, which defines the effect of fluoride ions once again. It was reported using reactant compositions of TEOS: 0.64NaOH : 0.55CTAB : 0.18HF : $113H_2O$, the hydrothermal stability of MCM-48 can be improved after reaction for 4 days at 369 K. However, they found increasing HF / Si ratio from 0.18 to 0.27 will result in a phase transformation from cubic MCM-48 into disordered hexagonal MCM-41 [11]. In this paper, we obtained a well-ordered MCM-48 within 10 h by combining slight increase of reaction temperature to 393 K at F / Si = 0.3, but we found that further reaction for 2 days will only produce a lamellar phase. Therefore, the method of this work which uses a more commonly used synthesis system can quickly form well-developed MCM-48 with a more wide F / Si range. The channel structure of the fast crystallization product is analogous to the reported MCM-48 and is well-defined. Taking TEM images (Fig. 2) of the calcined sample synthesized for 10 h at F / Si = 0.3 as a sample, a uniform pore structure along [100] direction (a) and an apparent hexagonal array on cubic [111] plane (b) clearly show that the channel structure of MCM-48 is well-developed. So, it is undoubted that fluoride ions are really advantageous to the formation of cubic MCM-48 mesophase. The subsequent researches will be focused on the specific influence of tiny fluoride ions on the phase transformation process of MCM-48 by varying the F / Si ratio.

Fig. 3 shows XRD patterns of the as-synthesized samples obtained after various crystallization time at (a) F / Si = 0 and (b) F / Si = 0.1, respectively. It can be found that both samples experience a phase transformation process from disordered MCM-41 to cubic MCM-48. It is obvious that fluoride ions indeed play an active role in promoting the hydrolytic condensation of silicates since the sample at F / Si = 0.1 obtained without hydrothermal reaction shows a stronger XRD intensity than that at F / Si = 0. The phase transformation at F / Si = 0.1 initiates earlier than that at F / Si = 0 and finished approximately after 18 h, which is only the beginning time for the phase transition of the sample at F / Si = 0. The peak intensity of the product obtained at F / Si = 0.1 is much improved after crystallization for another 10 h, though the cubic MCM-48 mesophase of the sample at F / Si = 0 is just beginning to be dominant after reaction for the same time. Further hydrothermal reaction of the sample at F / Si = 0 for 40 h leads to improvement of

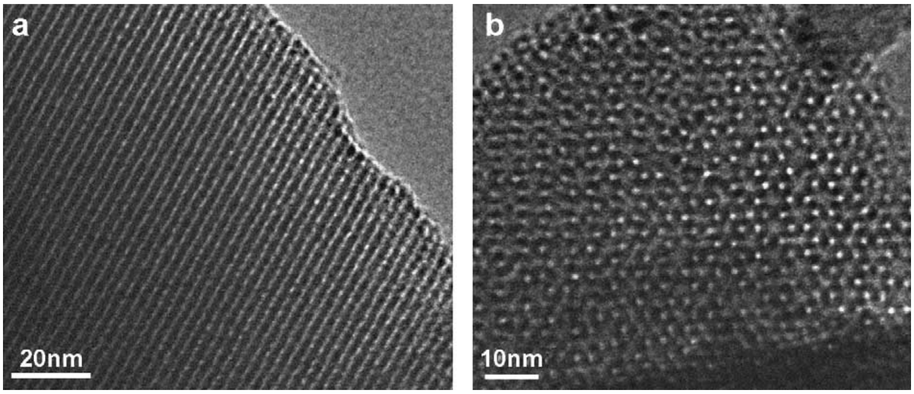

Fig. 2. TEM image of calcined MCM-48 molecular sieve synthesized at 393 K for 10 h at F / Si = 0.3.