Fast Synthesis of Si- and Ce-MCM-48 Mesoporous Molecular Sieve with Hydrothermal Stability

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A novel route for reducing crystallization times of Si- and Ce-MCM-48 mesoporous molecular sieves and simultaneously endowing them with hydrothermal stability has been developed.

Since the discovery of M41S mesoporous molecular sieves,[1] these materials have drawn tremendous attentions from various research fields. Among them, MCM-48 seems more attractive because of its unique three-dimensional pore structure. However, the synthesis for MCM-48 is hard since it is an intermediate of hexagonal MCM-41 and lamellar MCM-50. It generally takes 3 days to synthesize cubic MCM-48 to finish a slow phase-transformation process.[2–4] Gallis et al.[5] and Kim et al.[6] reported that increasing crystallization temperature could greatly reduce the synthesis time for MCM-48. However, a rapid synthesis process will engender poor pore ordering or inferior framework stability. Hydrothermally stable MCM-48 mesoporous molecular sieve has an important role in catalysis, photochemistry, and adsorption, especially for those which are metal doped. However, most of current researches are concentrated on improving the hydrothermal stability of pure silica MCM-48 and fewer dealt with its metal-doped counterparts owing to the rigorous requirement for synthesis. The hydrothermal stability of mesoporous materials can be improved by silylation,[7] post treatment in water,[8] and adding salts during crystallization process.[9] Nevertheless, silylation treatment will lead to inactivity of pore surface, and adding salts during crystallization process will interrupt the high pressure crystallization reaction repeatedly. Xia et al. reported that the one-pot synthesis of hydrothermally stable MCM-48 can be achieved by adding HF to sol mixture before crystallization process, but it still needs a long crystallization time and similar studies involved with metal doping have not been presented.[10] On the other hand, the substitution of Al on Si can also increase the hydrothermal stability of MCM-48. Nevertheless, the cubic *Ia*3*d* mesophase of Al-MCM-48 transforms to an amorphous phase only after being boiled in water for 12 h although the framework does not collapse.[11] So up to now, it generally needs a tedious and long process to synthesize hydrothermally stable Si-MCM-48, and it is more difficult to form a metal-doped MCM-48 with hydrothermal stability.

In this letter, we first balance the purpose of reducing crystallization time with obtaining hydrothermal stability at the same time for MCM-48 mesoporous material. We succeeded in rapidly synthesizing Si-MCM-48 by making a simple modification on previous report, which reduces crystallization time by increasing temperature to 423 K.[5] We set the crystallization temperature at 393 K instead of 423 K, selected strong dehydrating SO_4^{2-} as a promoter and added it to the reaction mixture before, not after hydrothermal crystallization process. Such slight changes not only greatly reduce the crystallization time, but also improve the hydrothermal stability of MCM-48 material. Besides, in consideration of the absence of research on lanthanide cerium-doped MCM-48 and its important role as heterogeneous catalyst, we apply the above method to the synthesis of cerium doping and successfully prepare hydrothermally stable Ce-MCM-48 with Si/Ce = 100 within a short time. This is also the first report on improving the hydrothermal stability of metal-doped MCM-48 with the aid of Na_2SO_4 by one-step synthesis.

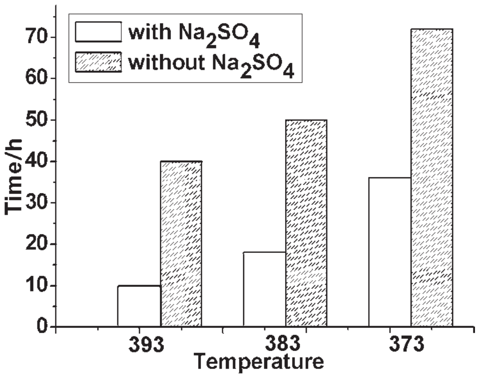

Figure 1. The common influences of crystallization temperature and Na_2SO_4 addition on the formation time of MCM-48.

In a typical synthesis, 4.65 g of tetraethyl othosilicate (TEOS) was added to 25 mL of 0.45 M NaOH solution at room temperature, then 0.32 g of sodium sulfate and 5.3 g of cetyltrimethylammonium bromide (CTAB) were successively added to above mixtures under vigorous stirring. The sol mixture was transferred to an autoclave and crystallized at 393 K after stirring for 1 h. The molar composition of the reactants mixture is $1SiO_2$:$0.25Na_2O$:0.65CTAB:$62H_2O$:$0.1Na_2SO_4$. For the synthesis of Ce-MCM-48 with Si/Ce = 100, 0.097 g of $Ce(NO_3)_3 \cdot 6H_2O$ was added dropwise after TEOS. Finally, the solid product was collected by filtration and dried in air, and the as-synthesized sample was calcined at 923 K for 6 h to remove CTAB templates.

Figure 1 shows the common influences of crystallization temperature and Na_2SO_4 addition on the formation time of Si-MCM-48. The white and shaded blocks denote the synthesis process with and without Na_2SO_4 addition, respectively. The formation time of MCM-48 gradually decreases from reported 72 to 40 h when we increase the temperature from 373 to 393 K in the absence of Na_2SO_4. The influence of varying crystallization temperature on the reaction time seems not so obvious, whereas the crystallization time can be decreased as

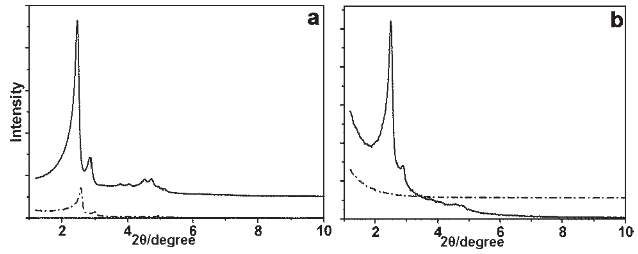

Figure 2. XRD patterns of calcined pure silica MCM-48 materials (a) and after being boiled in water for 12 h (b). Solid and dotted lines denote samples synthesized with the aid of Na_2SO_4 for 10 h and without the aid of Na_2SO_4 for 40 h at 393 K, respectively.

short as to 10 h at 393 K when we added Na_2SO_4 to reaction mixture before crystallization treatment. Further increasing temperature resulted in no solid gel precipitation because of abnormal behavior of high-concentration CTAB. The as-synthesized sample obtained within such a short time is robust enough to endure calcination and hydrothermal treatment in boiling water.

Figure 2 shows XRD patterns of calcined pure silica MCM-48 materials (a) and after being boiled in water for 12 h (b). Solid and dotted lines denote samples synthesized with the aid of Na_2SO_4 for 10 h and without the aid of Na_2SO_4 for 40 h at 393 K, respectively. X-ray powder diffraction (XRD) patterns of all samples were recorded on a Rigaku D/MAX-2550 diffractometer (40 kV, 100 mA) by using Cu Kα radiation. The crystallization time of sample synthesized without Na_2SO_4 is longer than that with Na_2SO_4, but its XRD intensity seems much weaker. So, the addition of Na_2SO_4 not only reduces the synthesis time, but also greatly increases the pore ordering of MCM-48. The framework stability is greatly improved with the addition of Na_2SO_4, which still preserves the cubic structure after being boiled in water for 12 h. MCM-48 material can not endure the hydrothermal treatment either by only increasing the crystallization temperature from 373 to 393 K (Figure 2b, dotted line), or by just adding Na_2SO_4 to the synthesis system at 373 K (see Supporting Information), which are both completely collapsed in boiling water. So, both of adding Na_2SO_4 and increasing crystallization temperature are indispensable for the synthesis of hydrothermally stable MCM-48 within a short time.

Figure 3 shows XRD patterns of calcined cerium-doped MCM-48 materials (a) and after being boiled in water for 12 h (b). Solid and dotted lines denote samples synthesized with the aid of Na_2SO_4 for 18 h and without the aid of Na_2SO_4 for 48 h at 393 K, respectively. The synthesis time are both prolonged since the incorporation of metal to the silica wall will decrease the pore ordering. The hydrothermal stability of MCM-48 is slightly increased by introducing cerium, which is not absolutely collapsed. The addition of Na_2SO_4 further improves the wall stability, and the crystallization time is more than half reduced compared with that in the absence of Na_2SO_4. The UV–vis absorption spectrum (see Supporting Information) of calcined cerium-doped MCM-48 material synthesized with the aid of Na_2SO_4 at 393 K for 18 h shows a single peak between 250–300 nm and is assigned as well-dispersed tetrahedral $O^{2-} \rightarrow Ce^{4+}$ charge-transfer absorption.[12] There is no absorption at 400 nm, indicating the absence of hexacoordinated Ce^{4+} species.

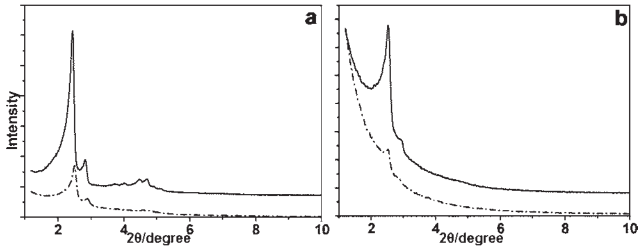

Figure 3. XRD of calcined cerium-doped MCM-48 materials (a) and after being boiled in water for 12 h (b). Solid and dotted lines denote samples synthesized with the aid of Na_2SO_4 for 18 h and without the aid of Na_2SO_4 for 48 h at 393 K, respectively.

Corma et al. reported that increasing crystallization temperature can improve the effective packing parameter, g value, of CTA^+ ($g = V/a_0l$), leading to the formation of MCM-48 at an earlier stage.[13] On the other hand, $SO_4{}^{2-}$ anion has low hydration energy of -241 kJ/mol and it tends to self-hydrate in water.[14] The addition of $SO_4{}^{2-}$ anion to the sol–gel synthesis system for MCM-48 causes the dehydration of cationic CTAB and anionic silicates, which accelerates the following behaviors in the synthesis system: 1) the formation and growing of CTAB micelle; 2) the condensation between anionic silicates; 3) electronic interaction between CTAB and silicates. Simply increasing crystallization time can not effectively accelerate the silicates condensation. Similarly, only adding Na_2SO_4 can not improve the effective g value for CTA^+ ions within a short time either and the silicates condensation becomes slower at lower crystallization temperature. Therefore, these two factors must be combined together to contribute the successful synthesis of hydrothermally stable MCM-48 within a short time.

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