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Study on the hydrothermal stability of MCM-41 via secondary restructure

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ABSTRACT

A series of MCM-41 mesoporous molecular sieves with different Si/Al molar ratio has been synthesized by hydrothermal crystalline method using cetyltrimethylammonium bromide as structural template, sodium silicate as silica source and sodium aluminate as aluminum source in alkaline solution. The results show that all the samples have hexagonal mesoporous structure. The secondary restructured materials exhibit well defined structure and the long distance order of the mesopores. The mesoporous structure for Si/Al = 25 MCM-41 with high specific area can be maintained after hydrothermal stability test in boiling water more than 12 h, showing that the secondary restructure can enhance the hydrothermal stability of MCM-41 with the pore diameter size of larger than 3.3 nm and BET surface area of more than 800 $m^2 \cdot g^{-1}$. Furthermore, MCM-41 with Si/Al = 25 has the optimal hydrothermal stability due to the introduction of Al atom.

1. Introduction

The ordered mesoporous molecular sieves, such as MCM-41, have attracted much attention since their discovery by Mobil Corporation [1,2]. There have been a great number of reports about the synthesis of these materials because of their large internal surface area, favorable uniformity and easily controlled size of the pore. These mesoporous materials have been found promising candidates for catalysts, absorbents and supports [3–6]. Of the particular interest is Al-containing MCM-41 materials which may be used as solid acid catalysts [7]. However, some disadvantages of these materials are their lower acidity and poorer hydrothermal stability compared with widely used zeolites [8–10]. The increase of acidity can be improved by the introduction of heteroatoms (e.g. Al, Ti), but low hydrothermal stability, attributing to the hydrolysis of Si—O—Si bond in the presence of adsorbed water, severely hinders their practical applications in catalytic reactions for the petroleum industry [11].

Many effective improvements such as pore wall thickening, silylation, stabilization by salt effect and hydrothermal restructuring process have been reported. The reasonably good hydrothermal stability has been achieved [12–19]. For example, Ryoo et al. [12] reported that the hydrothermal stability of MCM-41 can be greatly improved during the hydrothermal crystallization by adding different salts, such as sodium chloride, potassium chloride and sodium acetate; the obtained MCM-41 samples showed negligible structural losses after heating for 12 h in boiling water. Mokaya [13] reported that grafting Al onto calcined purely siliceous MCM-41 could increase the pore wall thickness and improve the hydrothermal stability of MCM-41. Chen et al. [18] found that MCM-41 with post-synthesis hydrothermal treatment method could also improve its hydrothermal stability. This method was carried out by replacing the mother liquor with pure water after the normal synthesis. The as-synthesized MCM-41 heated for 24 or 48 h was separated from the mother solution and mixed with a certain amount of pure water. The resulting samples heated in boiling water for 6 h caused little structure damage, and the hydrothermal stability was found to be enhanced by the post-synthesis hydrothermal treatment. M. Kruk et al. [19] synthesized MCM-41 at low temperature 343 K and subjected to post-synthesis hydrothermal treatment at 423 K. The hydrothermal stability of good quality and large pore MCM-41 obtained by restructuring at 423 K was found to be comparable with that for the most stable MCM-41 materials. It seems that the secondary restructure is superior to the direct hydrothermal method.

Despite much encouraging progress in recent years, to the best of our knowledge, there is less detailed study on the enhancement of hydrothermal stability of MCM-41 via secondary restructure. In this research, we introduced Al into reaction mixtures during the hydrothermal crystallization and investigated the hydrothermal stability of MCM-41 prepared by secondary restructure method with different Si/Al molar ratio. The results shows that the secondary restructure could lead to the increase of the quality and the hydrothermal stability of MCM-41. The MCM-41 with different Si/Al molar ratio could be heated in boiling water more than 12 h without significant structure damage.

2. Experimental

2.1. Synthesis of MCM-41

The Al-containing MCM-41 was synthesized with hydrothermal crystalline method [1]. The starting reaction mixture had a chemical

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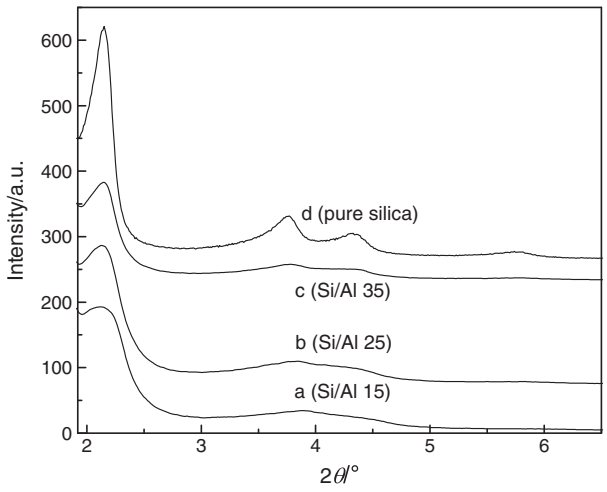

Fig. 1. XRD patterns of MCM-41 via direct hydrothermal method.

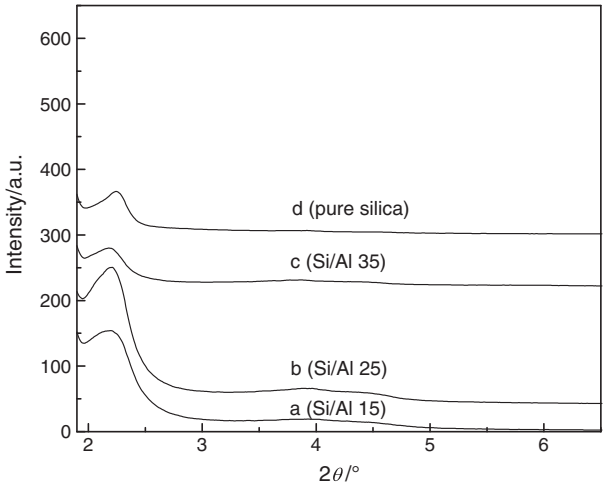

Fig. 3. XRD patterns after assessing the hydrothermal stability of MCM-41 via secondary restructure.

molar composition as 0.2 cetyltrimethylammonium bromide (CTAB, Tianjin Kermel Chemical Reagent Co. Ltd., China) –Na_2SiO_3–XAl_2O_3–$80H_2O$, where $X = 1/30,1/50,1/70$ and the general synthesis procedure was as follows: The set Na_2SiO_3 (Aladdin reagent Co. Ltd., China) was dripped into the CTAB solution and this mixture was stirred for 10 min. Then, the $NaAlO_2$ (Aladdin reagent Co. Ltd., China) solution was added into the mixture prepared above and stirred for another 10 min and the pH was adjusted by sulfuric acid solution (5 mol/L) to 10. After stirred at room temperature for 1.5 h, the resulting mixture was transferred into a stainless-steel autoclave reactor and synthesized at 130 °C for 48 h under autogenous pressure. Thereafter, it was taken out and cooled to room temperature. The solid product was obtained by filtration, washed with distilled water to neutral and dried at 90 °C overnight. Subsequently, the sample was calcined in the muffle furnace by heating from room temperature to 550 °C at 5 °C/min and then keeping at 550 °C for 5 h. Similarly, a series of mesoporous molecular sieve MCM-41 with different Si/Al molar ratio was obtained. The secondary restructure procedure was adopted that the obtained sample from direct hydrothermal method was put in sodium hydroxide solution with pH = 9 and stirred for several minutes, then placed into autoclave reactor to restructure again at 130 °C for another 24 h.

To assess the hydrothermal stability of MCM-41 with different Si/Al molar ratio, the calcined samples were mixed with distilled water and then placed in the closed bottle for 12 h at 105 °C.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were recorded using a RINT2000 Vertical Goniometer with Cu Kα radiation (40 kV, 200 mA), 0.01 step size. N_2 adsorption–desorption isotherms were conducted on a Micromeritics Tristar 3000 micropore analysis system and the calcined samples should be over dried at 150 °C for 12 h before analysis. Scanning electron micrographs (SEM) were obtained on a FEI Quanta-200 Scanning Electron Microscope using conventional sample preparation and imaging techniques.

3. Results and discussion

3.1. XRD analysis

Figs. 1 and 2 present XRD patterns of MCM-41 with different Si/Al molar ratios. All patterns show a very strong characteristic peak at 2.3° and several Bragg peaks at low reflection angles between 1.8 and 6.5°, which are typical of MCM-41 materials [12,13]. These indicate that MCM-41 materials with different Si/Al ratios can be well crystallized. As seen from Figs. 1 and 2, the intensity of the XRD patterns of MCM-41 increases significantly with the increasing of Si/Al

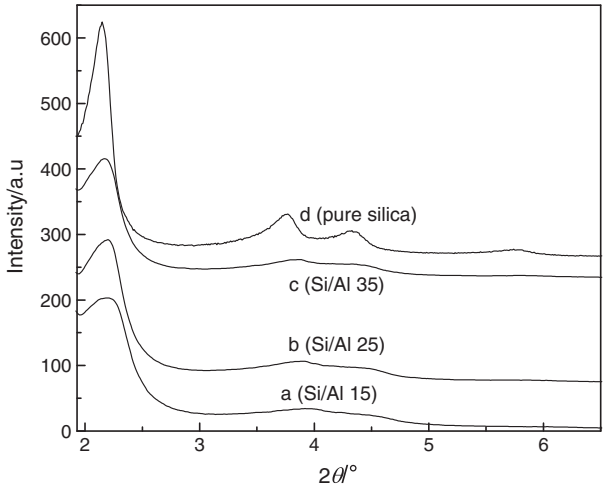

Fig. 2. XRD patterns of MCM-41 via secondary restructure.

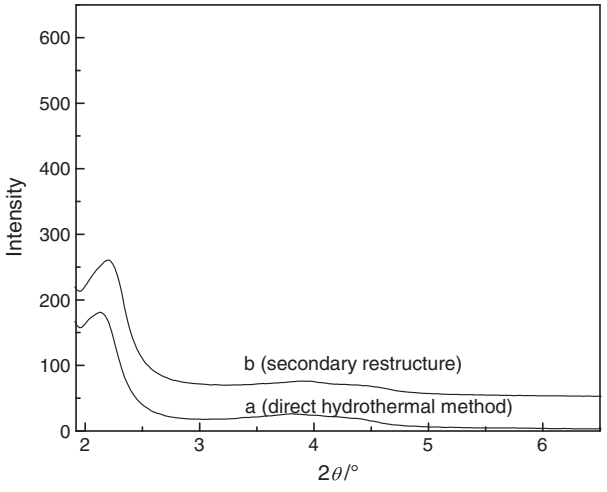

Fig. 4. XRD patterns after assessing the hydrothermal stability of MCM-41 with Si/Al = 25.