Synthesis of Ti-MCM-41 mesoporous materials using iron ore tailing as silicon source

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Ti-MCM-41 were synthesised by one-step method using sodium silicate extracted from iron ore tailing as silicon source, tetrabutyl titanate as titanium source and cetyltrimethylammonium bromide as the template. The effects of various experimental parameters, such as molar ratio of Si/Ti, reaction temperature and time, were investigated. The as-synthesised samples were further characterised by X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron micrographs, N2 absorption–desorption and transmission electron microscopy techniques. The results indicated that Ti-MCM-41 materials possessed the ordered hexagonal mesostructure and high surface area.

Keywords: Iron ore tailing, Ti-MCM-41, One-step method, Si/Ti ratio, Reaction temperature, Reaction time

Introduction

MCM-41-ordered molecular sieves have been widely used as highly efficient adsorbent and catalyst support because of highly uniform channel, large pore size and high surface area. However, pure siliceous mesoporous MCM-41 has relatively low activity and is of limited use for applications as heterogeneous catalysts and adsorbents in industry. The introduction of metals such as titanium, chromium and vanadium into the tetrahedral framework of MCM-41 can improve the activity and catalytic properties of pure MCM-41.1–3

In addition, the commercial silica sources such as tetraethylorthosilicate (TEOS), n-alkoxysilanes are expensive and toxic. Silica recovered from the solid wastes (such as fly ash, iron ore tailing) by using an alkali extraction route has been confirmed to be an effective and environmentally friendly silicon source in the synthesis of MCM-41.4,5

In this paper, Ti-MCM-41 mesoporous molecular sieves were synthesised by one-step method using sodium silicate extracted from the iron ore tailing as silicon source, tetrabutyl titanate (TBOT) as titanium source and cetyltrimethylammonium bromide (CTAB) as the template. The effects of various experimental parameters, such as molar ratio of Si/Ti, reaction temperature and time were investigated. The as-synthesised samples were further characterised by XRD, FT-IR, SEM, N2 absorption–desorption and TEM techniques.

Experimental

Materials

Iron ore tailing was obtained from Anhui Province, China. It contained 50.88% of SiO2, 13.62% of Al2O3, 13.62% of Fe2O3 and minor amount of other oxides. It was dried at 100°C and then ground. The other reagents such as sodium hydroxide, hydrochloric acid and CTAB were analytical reagents.

Extraction of silicon from the iron ore tailing

Thirty gram iron ore tailing and 65 mL HCl (1 mol L\(^{-1}\)) were mixed into a three necked flask and heated at 372 K for 1.5 h by stirring. Then, 20 g acid insoluble residue, 40 g NaOH and 130 g water were mixed into a three flasks and heated at 372 K for 6 h with vigorous stirring. To acquire sodium silicate solution, the mixture was departed by centrifugal separation, and the filtrate was diluted into a 500 mL volumetric flask. The sodium silicate solution was preserved in a sealed plastic beaker.

Synthesis of Ti-MCM-41

Ti-MCM-41 samples were synthesised with the following molar composition: Si: 0.01–0.08 Ti: 1.5 CTAB. About 50 ml of sodium silicate solution was added slowly to the aqueous solution of CTAB (0.69 g of CTAB dissolved in 15.00 g of deionised water) under vigorous stirring. The pH value of the reaction mixture was adjusted to 10 with HCl (1 mol L\(^{-1}\)). Then, TBOT and isopropoxide were added into the homogenous gel. The mixture was then transferred into a sealed beaker and heated at 333–373 K for 48–96 h after stirring for 30 min. The products were recovered by filtration, washed thoroughly with distilled water and dried at 373 K. To remove the template, the final products were roasted at 823 K for 5 h.
Characterisation

X-ray powder diffraction analysis of Ti-MCM-41 samples was taken on a DMX2000 with Cu Kα (λ = 1.5404 Å) radiation. The diffractometer was operated at 40 kV and 40 mA and scanned 1–10° with steps of 1° min⁻¹ and 10–80° with steps of 8° min⁻¹. FT-IR spectra were recorded on a Nicolet6700 FT-IR spectrometer using 0.5 mm KBr pellets containing 2.5 wt% samples. The SEM images of Ti-MCM-41 were using an S-4800 at 20.0 kV. The specific surface area was determined from N₂ adsorption–desorption isotherms using a Quadrasorb SI. Lower-resolution TEM images were obtained in a JEM-2100 (working voltage: 120 kV).

Results and discussion

Effect of Si/Ti molar ratio

Figure 1a presents the small-angle XRD patterns of Ti-MCM-41 with different Si/Ti molar ratios synthesised at 373 K for 72 h. The strong peak (100) at around 2.1° together with two weak peaks could be observed except for the sample with Si:Ti = 1:0.08. It was suggested that the hexagonally ordered array of mesoporous pores in MCM-41 was maintained after Ti loading. The small-angle XRD peak intensity decreases with the increase of Ti content, this is probably because that the radius of Ti⁴⁺ is bigger than that of Si⁴⁺, and it will cause the distortion of silicon-oxy tetrahedron. Figure 1b shows the wide-angle XRD spectra of Ti-MCM-41 samples. All
the samples exhibited a broad amorphous silica peak around 22.6°. No characteristic peaks of TiO₂ and other Ti species were observed, which suggested that titanium species might be incorporated into the lattice of the MCM-41⁷ or titanium species might be composed of amorphous small clusters and highly dispersed on the high surface area of silica support.⁷

FT-IR spectra of Ti-MCM-41 sample at different Si/Ti molar ratio synthesised at 373 K for 72 h are shown in Fig. 2. Four absorption bands were observed. Each sample exhibited the symmetric stretching vibration band of Si—O—Si bridges at around 810 cm⁻¹, and the anti-symmetric vibration band at around 1100 cm⁻¹ with a shoulder at 1220 cm⁻¹ for the tetrahedral SiO₄ structure units. The band at 960 cm⁻¹ was considered as a consequence of stretching vibrations of Si—O—Ti bonds,⁸ which was an evidence of the incorporation of titanium into the framework. It was also seen that the band intensity becomes stronger with the increase of Ti loading.

The SEM images of Ti-MCM-41 samples at different Si/Ti molar ratio synthesised at 373 K for 72 h are shown in Fig. 3. These images showed small particles with spherical-like morphology, which were reunited into larger particles.

**Effect of reaction temperature and time**

The SEM images of Ti-MCM-41 samples at different Si/Ti molar ratio synthesised at 373 K for 72 h are shown in Fig. 3. These images showed small particles with spherical-like morphology, which were reunited into larger particles.

Figure 4a shows the XRD patterns of Ti-MCM-41 (molar ratio of Si/Ti = 1/0.02) synthesised under different reaction temperatures for 72 h. It was seen that the long-range order of MCM-41 improved with the increase of reaction temperature. This is because that the improved temperature favour the hydrolysis, cross-link and uniform distribution of silicon. This is possibly arisen from that Si hydrolysed, cross-linked and distributed uniformly more with the increase of reaction temperature. Figure 4b shows the XRD pattern of Ti-MCM-41 (molar ratio of Si/Ti = 1/0.02) synthesised at 373 K for different time. With the increase of reaction time, the characteristic peaks became sharper owing to high crystallinity. The change in peak intensities indicated that reaction time played a crucial role in the formation of Ti-MCM-41. In addition, the (100) peak shifted to a higher value at a high reaction temperature and time, indicating that the lattice space d₁₀₀ of the pores decreased.

The N₂ adsorption–desorption isotherms for Ti-MCM-41 with Si/Ti = 1/0.02 synthesised at 373 K for 96 h were shown in Fig. 5. The sample exhibited type IV isotherms, which are characteristics of the mesoporous structures. The surface area was 677 m² g⁻¹ determined by the BET methods. The TEM micrograph of Ti-MCM-41 is shown in Fig. 6. It was seen that Ti-MCM-41 exhibited well-ordered hexagonal nanochannels of one-dimensional mesopores.

**Conclusions**

Ti-MCM-41 mesoporous molecular sieves were successfully synthesised by one-step method using sodium silicate extracted from the iron ore tailing and TBOT as Si and Ti source, respectively, under optimal conditions. Molar ratio of Si/Ti, reaction temperature and time played an important role in the synthesis of Ti-MCM-41. This
research provided a new method to convert a solid waste to a value-added material.

References


