Microwave preparation of a titanium-substituted mesoporous molecular sieve

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A titanium-containing redox material with disordered wormhole-like mesoporous structure was prepared using microwave heating. Substantially accelerated crystallization was achieved using microwave heating compared with the conventional oven heating. Development of the mesopore structure was confirmed by XRD, TEM, and N_2 physisorption. Incorporation of titanium into the mesopore structure was confirmed by UV-vis spectroscopy. A laser light particle size analyzer showed that smaller particle size and narrower particle size distribution were obtained with microwave heating than with oven-heated hydrothermal synthesis. These mesoporous titanosilicates were equally active as catalysts for liquid-phase oxidation of 2,6-di-*tert*-butylphenol with hydrogen peroxide as an oxidant.

Keywords: titanium, mesoporous molecular sieve, microwave synthesis, 2,6-di-*tert*-butylphenol oxidation

1. Introduction

There has been growing interest in the utilization of the microwave heating method for inorganic and organic synthesis [1]. Microwave energy can be directly and uniformly absorbed throughout the entire volume of an object, causing it to heat up evenly and rapidly. For microporous molecular sieves, this advantage led to homogeneous nucleation and substantial reduction in crystallization times compared to conventional oven heating. Such has been demonstrated for zeolite A [2], Y [3], ZSM-5 [3,4], Beta [4] as well as several $AlPO_4$ type materials [5,6]. Recently, MCM-41, a pure silicate mesoporous material with a hexagonal arrangement of 1D mesopores with diameters ranging from 20 to 100 Å, was prepared using microwave-assisted heating [7,8]. In this study, the microwave heating technique was extended to the preparation of titanium-substituted M41S type material, which can be a very useful redox catalyst for large organic molecules in the liquid-phase reactions utilizing hydrogen peroxide (H_2O_2) as an oxidant [9]. Conventionally, Ti-MCM-41 can be synthesized hydrothermally at 373 K by heating a synthesis gel with adequate formulation in a conventional oven for 1–10 days. We have attempted a synthesis of titanium-substituted MCM-41 using the microwave heating method, and a comparison was made with a sample prepared using conventional oven heating. Essential characterization works were carried out and, for a catalytic activity study, liquid-phase oxidation of 2,6-di-*tert*-butylphenol (2,6-DTBP) was chosen as a probe reaction.

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2. Experimental

A synthesis gel for the mesoporous Ti-MCM-41 sample was prepared using a method similar to that described by Franke et al. [10]. Ludox AS-40 (SiO_2 40 wt% colloidal silica in water, Dupont) was added under vigorous stirring to a 40 wt% tetraethylammonium hydroxide (TEAOH) solution. This solution mixture and titanium butoxide which is dissolved in isopropyl alcohol were then combined with a 25 wt% cetyltrimethylammonium chloride (CTMACl) solution. The composition of the resultant gel was $SiO_2 : 0.02TiO_2 : 0.2TEAOH : 0.25CTMACl : 31H_2O$. The gel obtained was stirred at room temperature for 1 h. Half of the gel was placed in an autoclave for hydrothermal reaction in a conventional oven, and kept at 373 K for 24 h. The other half was transferred to a 200 ml teflon autoclave for microwave heating. The microwave equipment used in this work was a CEM MDS-2100 sample preparation system equipped with a fiber optic temperature and a pressure controller as well as an adjustable power output (maximum 950 W at 2450 MHz). Synthesis of titanium-containing mesoporous material by microwave heating was carried out at 373–393 K for various heating periods between 10 min and 5 h. Initially, the substrate mixture was quickly heated to the final synthesis temperature in less than 3 min using full power and subsequently adjusted to constant power of 500 W to maintain isothermal condition. The solid products obtained were separated by filtration, dried at 373 K, and calcined at 813 K for 1 h under flowing nitrogen and subsequently for 6 h under an air flow.

The crystallinity of the samples prepared was measured by X-ray diffraction using Ni-filtered Cu K_α radiation (Philips, PW-1700), and the morphology of the sam-

ples was examined by TEM (Philips, CM200). Framework IR spectra were recorded in air at room temperature on a Perkin–Elmer 221 spectrometer with sample wafers mixed with dry KBr. The specific surface areas and average pore diameters were determined by nitrogen physisorption with the BET method at liquid-nitrogen temperature using a Micromeritics ASAP 2000 automatic analyzer. UV-vis diffuse reflectance spectroscopy was performed on a Varian CARY 3E double-beam spectrometer connected to a computer and dehydrated MgO as a reference in the range of 190–750 nm. Particle size distribution was measured using a laser scattering particle size analyzer (Malvern, laser light particle size SYS 4700). The catalytic activities of all samples were tested for the liquid-phase oxidation of 2,6-DTBP to quinone using H_2O_2 as an oxidant. Reactions were carried out under vigorous stirring in a two-neck glass flask equipped with a condenser and a thermometer. The oxidation of 2,6-DTBP was conducted using 10 mmol of substrate, 100 mg of catalyst, 10 g acetone as a solvent, and 30 mmol of 35 wt% H_2O_2. The reaction was performed at 333 K for 2 h and the products were analyzed using a HP 5890 series II GC equipped with a HP-5 capillary column and a FID.

3. Results and discussion

Synthesis of Ti-MCM-41 was attempted in the absence of alkali cations as they hinder the incorporation of titanium to the mesoporous pore walls [11]. XRD patterns of the titanium-containing samples obtained at different synthesis time intervals are shown in figure 1. Well-defined (100) reflections in their XRD patterns were demonstrated in all the samples shown. But (110), (200) and (210) peaks which indicate the long range order of the hexagonal MCM-41 structure were absent, and these XRD patterns were similar to those of HMS type materials showing a wormhole-like pore structure [12]. The disordered wormhole-like pore structure of the microwave-prepared sample was confirmed by TEM, as shown in figure 2. As reported by others [13–16], the introduction of a heteroatom such as titanium usually resulted in less well-resolved X-ray diffractograms with poor long-range orders than were obtained for the pure silica MCM-41 counterpart. It is mentioned that the intensity of XRD peaks increases as the template size increases, showing a maximum, and then decreases again [17], and only Ti-MCM-41 samples prepared with C_{12} templates show the XRD patterns closely matching the hexagonal MCM-41 structure [17,18].

For titanium-containing mesoporous material prepared using microwave heating at 373 K, the (100) peak started to grow after 2 h synthesis time and virtually identical diffraction patterns were obtained after 5 h. For those prepared at 393 K, on the other hand, the (100) peak began to grow only after 30 min and its size remained constant after 2 h reaction. The corresponding FT-IR spectra of the samples showed the concurrent steady increases of the absorption band at ca. 960 cm^{-1}, which may indicate the growth of surface silanol groups and gradual incorporation of titanium into the structure [13,16] as crystallization progresses.

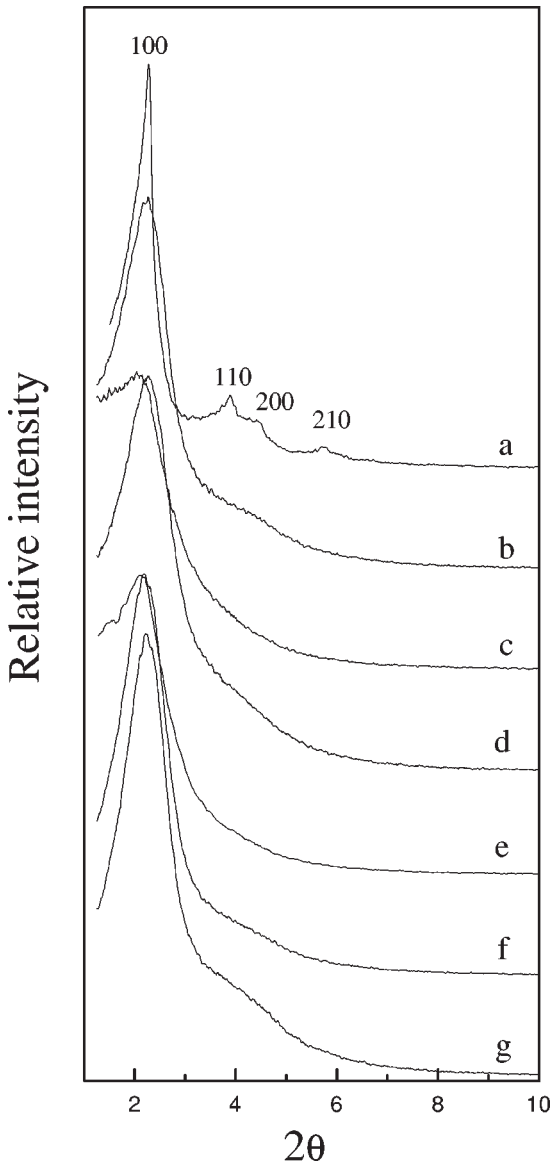

Figure 1. XRD patterns of calcined titanium-containing mesoporous samples: (a) pure silica MCM-41 conventional heating (373 K, 24 h); (b) conventional heating (373 K, 24 h); (c) microwave heating (373 K, 2 h); (d) microwave heating (373 K, 5 h); (e) microwave heating (393 K, 0.5 h); (f) microwave heating (393 K, 2 h); and (g) microwave heating (393 K, 5 h).

Figure 3 shows UV-vis spectra of the titanium-containing mesoporous samples synthesized in a microwave and conventional oven. A broad band centered at ca. 210 nm is observed in all the samples, and this band is usually assigned to a low-energy charge-transfer transition between tetrahedral oxygen ligands and central Ti^{4+} ions, indicating framework incorporation of titanium [13,16,19]. An anatase-like TiO_2 phase at 330 nm was absent in these samples, but some polymeric Ti species suspected coexist at 280 nm. It is worth mentioning that the 210 nm absorption peak was observed only after 10 min microwave heating, and some

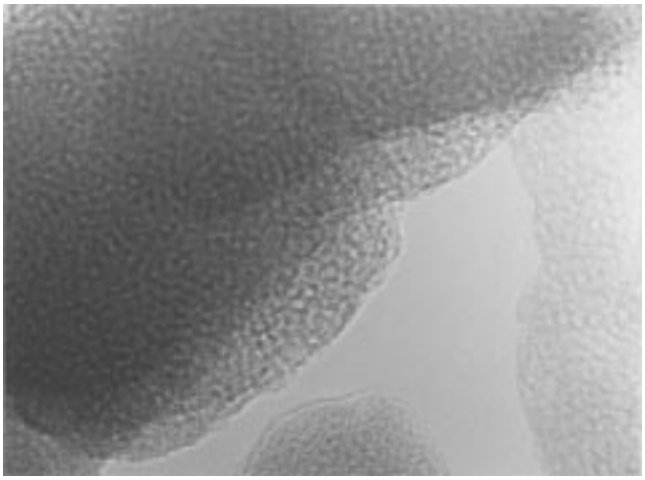

Figure 2. TEM micrograph of a calcined titanium-containing mesoporous sample: microwave heating, 373 K, 5 h.

catalytic activity for 2,6-DTBP oxidation was confirmed for this amorphous sample (see table 1). Prolonged treatment in the microwave oven led to the growth of the shoulder peak at ca. 280 nm, which corresponds to polymeric Ti species.

Figure 4 shows the particle size distribution curves of the titanium-containing mesoporous materials. The average particle size of the sample prepared by microwave heating was ca. 400–440 nm, whilst that prepared by hydrothermal synthesis was ca. 590 nm. On top of the substantially smaller particle size, preparation of the material using microwave heating rendered narrower particle size distribution and this effect was more pronounced at higher synthesis temperature. Apparently, these are a consequence of homogeneous heating achieved in the microwave heating method [3].

Peroxide oxidation of 2,6-DTBP was carried out in a Pyrex flask at 337 K for 2 h, and 2,6-DTBP conversion and quinone selectivity obtained are summarized in table 1. The sample prepared using microwave heating at 373 K for 5 h resulted in somewhat higher conversion, possibly due

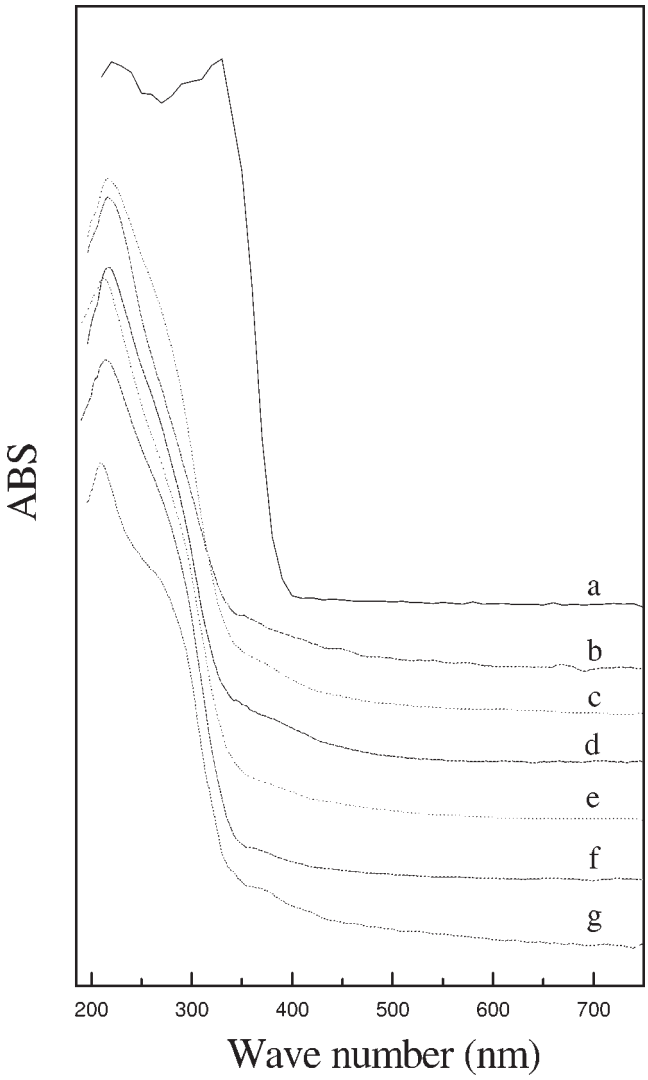

Figure 3. UV-vis spectra of calcined samples: (a) TiO_2 anatase; (b) conventional heating (373 K, 24 h); (c) microwave heating (373 K, 2 h); (d) microwave heating (373 K, 5 h); (e) microwave heating (393 K, 0.5 h); (f) microwave heating (393 K, 2 h); and (g) microwave heating (393 K, 5 h).

Table 1
Physical properties of titanium-containing mesoporous materials and their catalytic activity for 2,6-DTBP oxidation.[a]

Sample	BJH average pore size (Å)	BET surface area (m^2)	Average particle size (nm)	2,6-DTBP conversion	Quinone selectivity
Hydrothermal synthesis (373 K, 24 h)	32.6	917.1	590.5	14.4	>99
Microwave heating (373 K, 5 h)	36.4	944.4	442.5	17.7	>99
Microwave heating (393 K, 2 h)	29.7	894.9	408.8	14.3	>99
Microwave heating (393 K, 5 h)	30.0	938.8	442.4	13.0	>98
Amophorous TiO_2–SiO_2	–	–	–	5.6	>99
TiO_2 powder	–	–	–	0.9	77

[a] Reaction conditions: 10 mmol 2,6-DTBP, 30 mmol H_2O_2 (35 wt% in aqueous solution), 100 mg catalyst, 10 g acetone (as solvent), 337 K, 2 h.

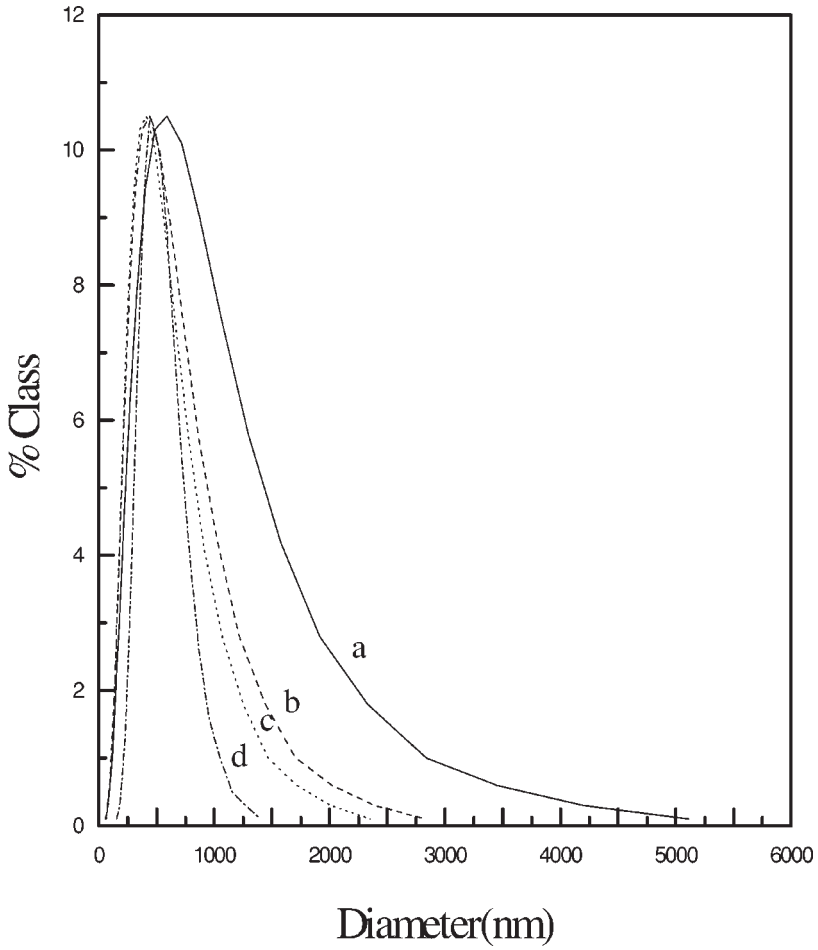

Figure 4. Particle size distribution of titanium-containing mesoporous samples: (a) conventional heating (373 K, 24 h); (b) microwave heating (373 K, 5 h); (c) microwave heating (393 K, 2 h); and (d) microwave heating (393 K, 5 h).

to larger average pore diameter and larger BET surface area of the sample. Smaller particle diameters would be advantageous in liquid-phase reactions in which diffusion plays an important role, but this particle size effect seems minor in this case due to the relatively large pore diameters of the catalysts used in the reaction.

In conclusion, substantially accelerated crystallization for titanium-containing mesoporous materials was achieved using microwave compared with the conventional oven heating. Whilst the samples prepared by microwave heating showed an average pore diameter of ca. 3 nm with very narrow pore size distribution, their morphology was disdordered and wormhole-like, lacking long-range order of MCM-41 structure. Incorporation of titanium into the mesoporous structure was confirmed by UV-vis spectroscopy. A laser light particle size analyzer showed that smaller particle size and narrower particle size distribution were obtained with microwave heating. These mesoporous titanosilicates were active as catalysts for liquid-phase oxidation of 2,6-DTBP with aqueous H_2O_2. This work showed that transition-metal-substituted mesoporous molecular sieves can be prepared efficiently with substantial reduction in synthesis time using the microwave heating technique.

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