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Synthesis of TS-1 by microwave heating of template-impregnated SiO_2–TiO_2 xerogels

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TS-1 was prepared by microwave heating of a SiO_2–TiO_2 xerogel dry-impregnated with the template, TPAOH. A highly crystalline product was obtained within 30 min after microwave irradiation with yields over 90%. These are significant advantages over the TS-1 obtained by conventional oven heating using alkoxide precursors in liquid phase, which requires 1–2 day crystallization time with low product yields. Characterization of the TS-1 obtained was carried out using XRD, SEM, FT-IR, and UV-vis spectroscopy, and catalytic activity was examined for 1-hexene epoxidation using H_2O_2 as oxidant. These studies revealed that the material obtained by microwave heating of the mixed oxide gel shows essentially identical physicochemical properties to those prepared by conventional means.

KEY WORDS: TS-1; SiO_2–TiO_2 xerogel; microwave heating

1. Introduction

TS-1 (titanium silicalite-1) discovered by Enichem [1] is a redox molecular sieve with MFI structure in which isolated titanium sites in the zeolite framework act as active sites for oxidation of a variety of organic substrates using H_2O_2 as oxidant. TS-1 is known to catalyze aromatic hydroxylation, alkene epoxidation, ketone ammoximation, alcohol and alkane oxidation, and initiated an intense research activity on redox molecular sieves in general. Whilst several reviews on the synthesis, characterization, and catalytic applications of TS-1 have been reported already [2–4], additional information about the physicochemical properties of the catalytic material is still being actively sought [5,6]. Recently, microwave heating of the clear liquid substrate mixture was reported to produce TS-1 in substantially reduced crystallization time [7]. Referring to earlier work by Padovan [8] and Uguina et al. [9], who reported TS-1 preparation by a sol–gel route with enhanced crystal yield, it seems useful if advantages of these attempts can be combined to produce TS-1 in high yields in shortened crystallization time. In this work, we report TS-1 synthesis by microwave heating of the TPAOH (tetrapropyl ammonium hydroxide) impregnated SiO_2–TiO_2 xerogel. A series of characterizations performed established that the products obtained possess essentially identical properties to TS-1 prepared by conventional methods.

2. Experimental

SiO_2–TiO_2 cogel was prepared via a two-step acid/base sol–gel process by following the literature procedure of Uguina et al. [9]. The mole ratio of Si/Ti was controlled to 50. The gel obtained was dried overnight at 383 K and subsequently ground to give a fine powder. The cogel was dry impregnated by adding 1.6 g TPAOH (Aldrich 20% aqueous solution) per 1 g xerogel. The impregnated gel was transferred to a 200 ml Teflon autoclave for microwave heating. The microwave equipment used was a CEM MDS-2100 model equipped with a fiber optic temperature and pressure controller as well as an adjustable power output (maximum 950 W at 2450 MHz). The sample was heated to 443 K for various heating periods between 10 min and 5 h. Initially, the sample was quickly heated to 443 K in 3 min using full power and subsequently adjusted to constant power of 500 W to maintain isothermal condition. The crystalline product was filtered, washed several times with distilled water, dried overnight at 383 K, and calcined in air at 823 K for 5 h.

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 samples was examined by SEM (Hitachi, X-650). FT-IR spectra were recorded in air at room temperature on a Bomem MB 104 spectrometer using a diffuse reflectance cell. UV-vis diffuse reflectance spectroscopy was performed under ambient conditions using dehydrated MgO as a reference in the range of 190–800 nm on a Varian CARY 3E double-beam spectrometer. The catalytic activities of all samples were tested for 1-hexene epoxidation 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 using 2.02 g of substrate, 150 mg of catalyst, 25 ml methanol as a solvent, and 0.65 g of 35 wt% H_2O_2. The reaction was performed at 313 K for 2 h and the products were analyzed using a GC equipped with a SUPELCO fused silica capillary column and a FID.

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3. Results and discussion

Figure 1 shows the XRD patterns of the crystalline materials obtained at different synthesis times and plots of crystallization kinetics for TS-1 prepared in microwave and in conventional oven heating at 443 K. All TS-1 samples obtained after 30 min microwave irradiation showed peaks characteristic of MFI structure and virtually identical peak intensities to those of TS-1 prepared by conventional oven heating for 24 h. Apparently, the faster and more homogeneous heating achieved by microwave heating led to enhanced nucleation and crystal growth, and proved to be a significant advantage in the preparation of inorganic oxide materials [10]. The heating rate to the final synthesis temperature is very critical determining the overall synthesis time, and special care was taken not to overshoot the preset synthesis temperature of 443 K as a consequence of increasing the heating rate. The crystal yield of TS-1 achieved by microwave heating of the TPAOH-impregnated SiO_2–TiO_2 was over 90% compared with the ca. 50% reported with the TS-1 prepared with liquid substrate mixture of silicon and titanium alkoxides [9]. SEM micrographs of the TS-1 samples are shown in figure 2. The average crystal size of all the samples was ca. 500 nm independent of the synthesis methods. Fully-grown crystals were already apparent after 30 min microwave irradiation and crystals of virtually the same dimension were obtained after 5 h microwave heating. Figure 3

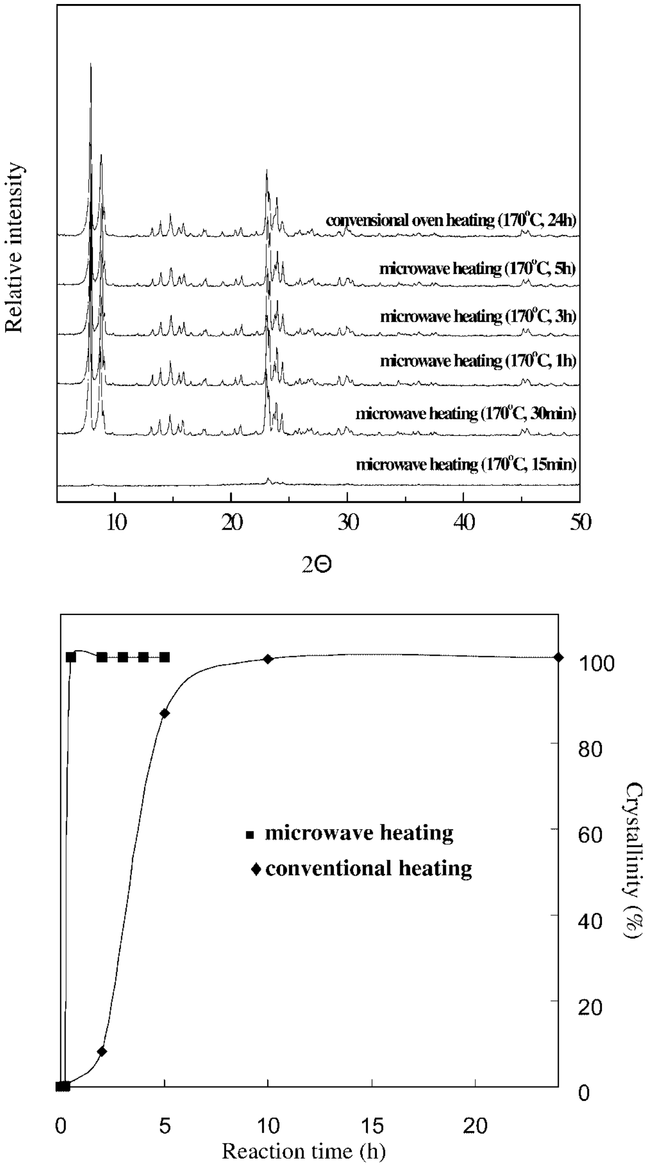

Figure 1. XRD spectra and crystallization kinetics of TS-1 prepared using TiO_2–SiO_2 xerogel precursors.

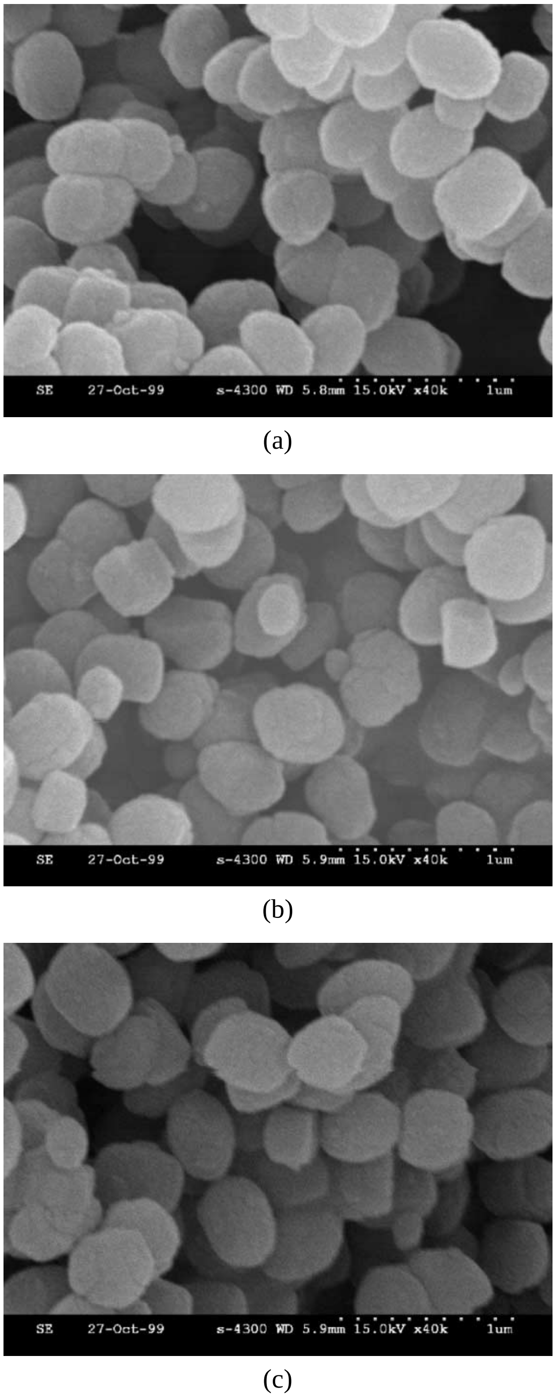

Figure 2. SEM micrograph of TS-1: (a) microwave heating for 3 min, (b) microwave heating for 5 h, and (c) conventional heating for 24 h.

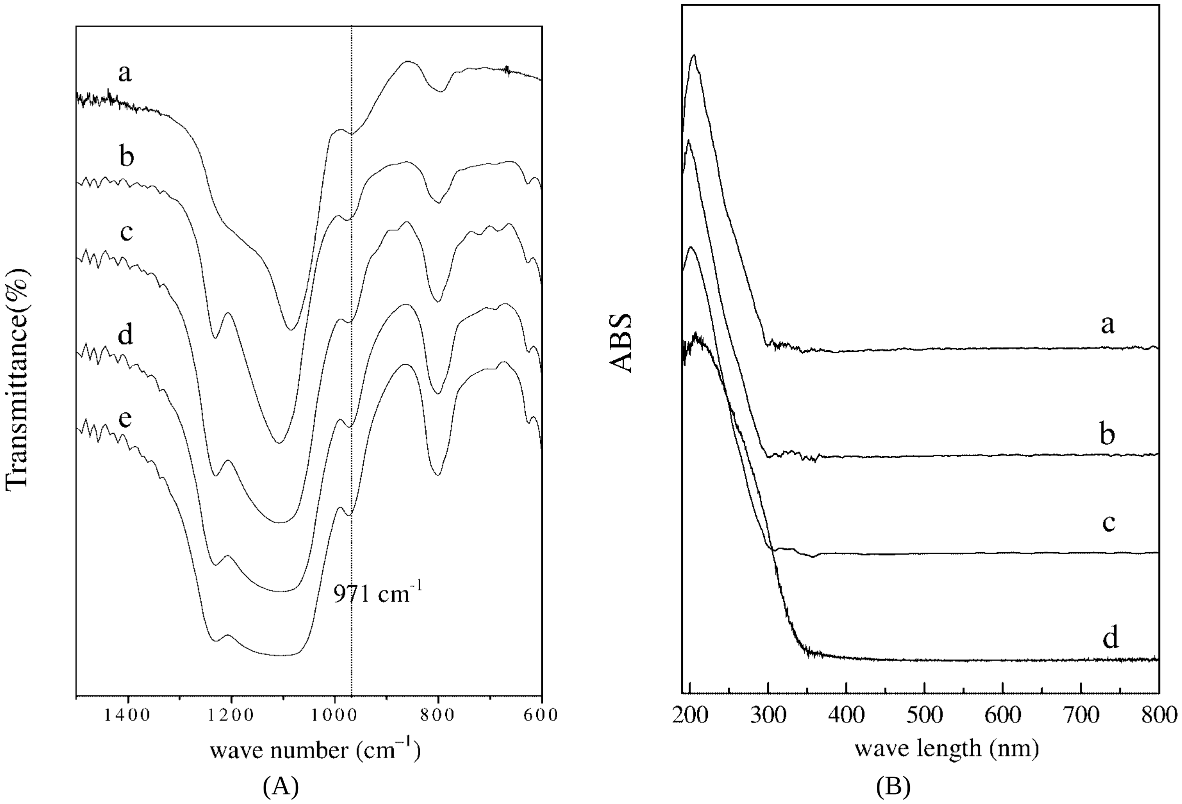

Figure 3. IR and UV-vis spectra of TS-1. (A) IR: (a) conventional heating for 24 h, (b) microwave heating for 30 min, (c) microwave heating for 1 h, (d) microwave heating for 5 h, and (e) SiO_2–TiO_2 xerogel; (B) UV-vis: (a) conventional heating for 24 h, (b) microwave heating for 30 min, (c) microwave heating for 5 h, and (d) SiO_2–TiO_2 xerogel.

Table 1
1-hexene epoxidation with H_2O_2 over TS-1 samples.[a]

TS-1 sample	Si/Ti (gel)	Si/Ti[b] (solid)	1-hexene conversion	H_2O_2 selectivity	Product selectivity 1,2-epoxyhexane
TS-1 (conventional heating for 24 h)	50	71	18.1	90	100
TS-1 (microwave heating for 30 min)	50	74	17.5	87	100
TS-1 (microwave heating for 2 h)	50	71.4	18.4	90	100
TS-1 (microwave heating for 5 h)	50	72	17.9	89	100
TS-1[c]	40	–	20.2	89	100

[a] Reaction conditions: 150 mg catalyst, 2.20 g 1-hexene, 0.65 g 35% aqueous solution H_2O_2, reaction temperature 313 K, reaction duration 2 h, 25 ml solvent (methanol).

[b] ICP analysis.

[c] Hydrothermally prepared by oven heating using Si-,Ti-alkoxide precursors.

shows IR and UV-vis spectra of the TS-1 samples prepared by different microwave heating. A characteristic IR band at 960 cm^{-1} corresponding to the Si–O–Ti bond [11] is observed for all TS-1 samples, and its peak intensity remains almost constant after 30 min microwave heating. The relative intensity of the 960 cm^{-1} band to 800 cm^{-1} peak has often been used to estimate the titanium incorporation in TS-1 samples [9]. Since IR spectra in this study have been obtained using hydrated samples, the characteristic IR band is slightly blue-shifted to ca. 971 cm^{-1}, as reported earlier by Boccuti et al. [12]. This peak was also observed for SiO_2–TiO_2 xerogel, but at a slightly shifted position from the TS-1 samples. UV-vis spectra of the TS-1 samples show an absorption band at ca. 220 nm indicating titanium in tetrahedral coordination [13], and again peaks with almost the same intensity were obtained after 30 min microwave heating. No peaks corresponding to anatase phase at 330 nm or nanophase TiO_2 at 270 nm were observed. The corresponding UV-vis absorption peaks for SiO_2–TiO_2 xerogel were very similar to those for calcined TS-1 samples but the spectrum was wider than for TS-1, probably due to varying titanium environment in the hydrophilic amorphous gel. These IR and UV-vis spectral data indicate that a favorable environment for titanium to take tetrahedral coordination in the subsequent hydrothermal treatment is already achieved in the xerogel precursors. Finally, the catalytic property of the TS-1 prepared by microwave heating of the SiO_2–TiO_2 xerogel was tested by 1-hexene epoxidation, and the results are summarized in table 1. 1-hexene conversions after 2 h reaction were virtually identical for all samples tested. These results demonstrate that TS-1 prepared by microwave heating of the TiO_2–SiO_2 mixed gel in accelerated crystallization has no detrimental effects in catalytic oxidation reactions compared with the TS-1 catalysts prepared using conventional oven heating. This microwave heating of the mixed oxide xerogel precursors was found equally effective in preparing high quality niobium or tantalum incorporated silicalite-1 [14]. Further investigation is being progressed to apply the synthesis method to prepare TS-1 using nano-sized mixed oxide precursors prepared in thermal plasma process.

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