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Hydrophobicity and catalytic properties of Ti-MFI zeolites synthesized by microwave and conventional heating

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Abstract

Ti-incorporated MFI zeolite (Ti-MFI-MW) has been synthesized with microwave heating. Their physicochemical properties such as surface hydrophobicity, and adsorption and catalytic properties have been compared with those of Ti-incorporated MFI zeolite (Ti-MFI-CH) prepared by conventional hydrothermal method. Competitive adsorption measurements with toluene and water revealed that the hydrophobicity index of Ti-MFI-MW (8.0) is higher than that of Ti-MFI-CH (6.2). IR spectra showed that Ti-MFI-MW also has a lower content of surface hydroxyl groups and adsorbs a larger amount of 1-hexene than Ti-MFI-CH. These results pointed out that Ti-MFI-MW is more hydrophobic than Ti-MFI-CH. Epoxidation reactions of 1-hexene and styrene with hydrogen peroxide have been conducted to investigate catalytic properties of the Ti-MFI zeolites according to the synthesis method. The conversions and epoxide selectivities over Ti-MFI-MW are higher than those over Ti-MFI-CH due to the enhanced surface hydrophobicity.

Keywords: Ti-MFI zeolite; Microwave heating; Hydrophobicity; Modified hydrophobicity index; Epoxidation

1. Introduction

A titanium silicalite zeolite having a MFI structure (TS-1 or Ti-MFI) has shown excellent catalytic properties in a wide range of selective oxidation reactions [1,2]. The oxidant used in oxidation reactions with Ti-MFI is often aqueous hydrogen peroxide, which is a green oxidant because its final product is water. Therefore, Ti-MFI is widely used as catalyst in selective oxidation reactions under mild conditions [3–5], such as the hydroxylation of phenol to hydroquinone and catechol, the epoxidation of olefins to epoxides, the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones, the oxidation of alkanes to alcohols and the ammoxidation of ketones to oximes. In view of these potential industrial applications, the synthesis of Ti-MFI has received considerable interest during the last few years.

Microwave heating has lately become popular in the crystallization of materials such as zeolites [6–8] and other inorganic materials [9,10], due to its higher yields, cleaner synthetic method and shorter crystallization time compared with the conventional method. The synthesis of porous material with microwave heating has many advantages such as fast crystallization [11–14], increased phase purity and selectivity [15,16], narrow particle size distribution [17] and facile morphology control [18,19]. Microwave heating has also been successfully applied in the synthesis of Ti-MFI [20–22]. Ahn et al. [23,24] have developed the microwave synthesis of titanium silicalite-1 using solid phase precursors, and obtained a highly crystalline product in a short time.

The framework Ti ions with tetrahedral coordination are the catalytic active sites in Ti-MFI, and their content is an important factor to affect the catalytic property of Ti-MFI. It has been reported that the hydrophobicity of Ti-containing zeolites is important for the epoxidation and the increased

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hydrophobicity has the positive effect on their activities [5–10,25,26]. Many researchers have reported that the hydrophobicity increases with decreasing the amount of surface hydroxyl groups [10,27–31]. The hydrophobicity index (HI) [27,32] can be used for the characterization of Ti-MFI zeolites. It is measured by the competitive adsorption of organic compounds and water on molecular sieves. HI is defined as the mass ratio of the final loadings of toluene and water over the molecular sieve. Thus, the higher HI value indicates the higher hydrophobicity.

Very recently, we have reported the synthesis of Ti-MFI-MW with a fibrous morphology using microwave heating [33]. The fibrous morphology was ascribed to the condensation of the terminal hydroxyl groups between crystal surfaces to induce multiple stacking of flat crystals. In the present work, we report the epoxidation reactions of styrene and 1-hexene with H_2O_2 over Ti-MFI zeolite catalysts synthesized with microwave heating (Ti-MFI-MW) and conventional electric heating (Ti-MFI-CH). The improved performance of Ti-MFI-MW compared with Ti-MFI-CH was explained with the increased hydrophobicity.

2. Experimental

2.1. Synthesis of Ti-MFI zeolites

The Ti-MFI samples were synthesized using tetraethyl orthosilicate (TEOS, Aldrich), tetrapropylammonium hydroxide (TPAOH, TCI), tetrapropyl orthotitanate (TPOT, Aldrich), isopropyl alcohol and water. The molar composition of the reaction mixture was 1 TEOS:0.2 TPAOH:0.014 TPOT:22.2 H_2O. The synthesis mixtures were stirred at room temperature for 1 h and then at 70–80 °C for 2 h with vigorous stirring so as to remove alcohol with later replacement by the doubly distilled water. The crystallization of Ti-MFI-MW was performed in a Teflon autoclave, which was placed in a microwave oven (MARS-5, CEM, maximum power of 1200 W). Microwave heating steps were divided into three stages: the first step at 80 °C for 30 min under irradiation power of 300 W, the second step at 165 °C for 5 min under 1200 W and the third step at 165 °C for 55 min under 300 W and autogenous pressure. The resulting crystallized solids were recovered by centrifugation. The materials were then extensively washed with distilled water, dried at 120 °C and calcined at 550 °C for 6 h in air. For the preparation of the conventional Ti-MFI (denoted as Ti-MFI-CH), the same gel as above was transferred into a Teflon flask and put in a preheated electric oven at 170 °C for about 5 days without agitation. The other treating processes were the same as those for the preparation of Ti-MFI-MW.

In the synthesis using microwave heating, the reaction temperature was controlled using EST-300 Plus system (Electronic Sensor–Temperature) that monitored and controlled temperature conditions inside sample vessels. In this system, a microwave transparent fiber-optic temperature probe was inserted into a thermowell of a sample vessel. The temperature sensor was a phosphor located at the tip of the probe. The decay rate of fluorescent light emitted from the phosphor is temperature dependent, allowing a precise determination of temperature. For safety, the temperature of the reaction vessel in the microwave oven was measured using an optional TempGuard^{TM} system. An infrared lens and sensor were located in the microwave oven and the temperature of each vessel was measured as the vessels rotated over the sensor. If the temperature in any vessel was higher than the maximum pre-set temperature, the TempGuard^{TM} stopped microwave generation.

2.2. Characterization of Ti-MFI zeolites

The titanium content of Ti-MFI samples was determined by the ICP-AES technique. X-ray powder diffraction (XRD) was performed with a Rigaku powder diffractometer using Cu Kα radiation. XRD measurements were run between an angle 2θ of 3° and 50° with a step size of 0.02°. FT-IR spectra were recorded by using compressed KBr pellets containing 1 wt% Ti-MFI sample on a Nicolet Magna-IR 560 spectrophotometer in the range of 500–4000 cm^{-1}. For the measurements of surface hydroxyl groups and adsorbed 1-hexene, the IR spectra of the Ti-MFI sample using a self-supported wafer were recorded in a quartz cell equipped with CaF_2 window after the samples were treated at 400 °C in vacuo ($\leq 10^{-5}$ Torr). UV–vis spectra in the range of 200–800 nm were obtained on a Shimadzu UV-2501 PC spectrometer equipped with a diffuse reflectance attachment using $BaSO_4$ as a reference. To determine the hydrophobicity index, we first put 1.0 g of adsorbent Ti-MFI sample into a fixed bed absorber and then pretreated it at 500 °C for 1 h using a N_2 flow. The absorption temperature was fixed at 25 °C. A mixture of water and toluene ($P_{water} = P_{toluene} = 3.33$ kPa) was passed through the zeolite adsorbent in a fixed bed reactor and nitrogen was used as carrier gas with a flow rate of 50 cm^3/min. The gas stream was analyzed using a capillary gas chromatograph equipped with a thermal conductivity detector. The final loadings (L_i) of toluene and water were calculated directly from the measured breakthrough curves. The hydrophobicity index was then calculated as $HI = L_{Toluene}/L_{Water}$ according to Weitkamp et al.'s method [27,28]. SEM micrographs were taken with a JEOL scanning electron microscope (model JSM-840).

2.3. Epoxiation reactions with H_2O_2

Epoxidation reactions of styrene and 1-hexene with H_2O_2 were performed in a 50 ml glass round-bottom flask immersed in a thermostated bath and fitted with a condenser, a magnetic stirrer and a thermometer. For styrene epoxidation, a standard reaction was carried out as follows: 0.35 g catalyst, 18 ml acetone as solvent, 5 ml styrene (99%, Aldrich) and 1.3 ml 30 wt% H_2O_2 aqueous solution were charged into the flask. The reaction was conducted at 70 °C under ambient atmosphere. 1-Hexene epoxidation was carried out with 4 ml 1-hexene, 4 ml acetonitrile as a solvent, 1.12 ml 30 wt% H_2O_2 at 60 °C. During the reaction, small aliquots were carefully withdrawn from the mixture using a syringe at certain time intervals and the liquid mixture was separated from the catalyst through a septum.

The analysis of the products in both reactions was then performed using a gas chromatograph (Acme 6000GC, Korea) equipped with a FID and a capillary column (CP-Sil-5 CB, 50 m × 0.32 mm × 0.40 μm, USA).

3. Results and discussion

3.1. Titanium incorporation of Ti-MFI zeolites

The powder XRD patterns of Ti-MFI-MW and Ti-MFI-CH samples show the characteristic peaks for the fully crystalline MFI structure without any impurity (Fig. 1). As shown in Fig. 2, framework IR spectra of the calcined Ti-MFI-MW samples exhibit an absorption band at 960 cm^{-1} for the stretching mode of a [SiO_4] unit bonded to a Ti^{4+} ion (O_3SiOTi). This absorption band has been generally assigned to the Ti incorporated into the zeolite framework and its relative intensity was reported to be proportional to the framework Ti content [9,32]. Considering the relative intensity of the absorption band at 960 cm^{-1}, it is presumed that the concentrations of the framework Ti species are similar in two samples. Actually, the Si/Ti ratios determined with ICP-AES are 81 and 82 for Ti-MFI-MW and for Ti-MFI-CH, respectively. In Fig. 3, UV–vis diffuse reflectance spectra of Ti-MFI zeolites, collected after evacuation ($\leq 10^{-5}$ Torr) at 400 °C, reveal a strong peak around 210–240 nm, assignable to the ligand to metal charge transfer absorption band from oxygen to tetrahedral titanium(IV) in the zeolite framework [33]. This result indicates that most of titanium species are incorporated into the framework regardless of the synthesis method. The Ti-MFI zeolites from the microwave and conventional hydrothermal syntheses also showed practically the same XRD, IR and UV–vis data, indicating that the difference in the synthesis methods did not influence the identity of the final products.

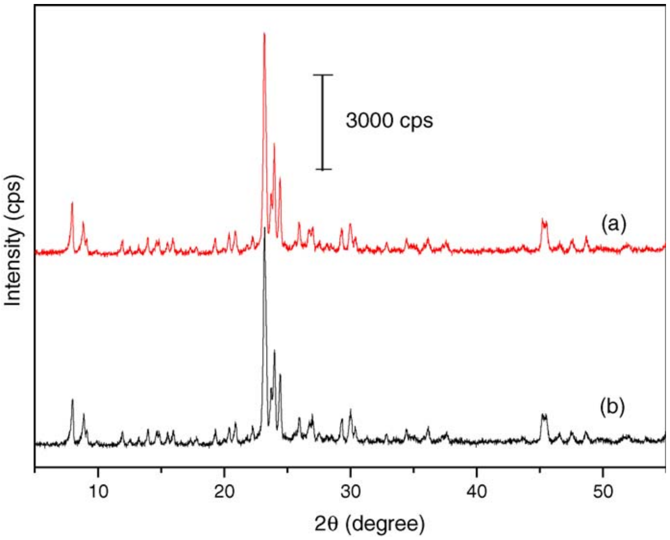

Fig. 1. X-ray diffraction patterns of (a) Ti-MFI-MW and (b) Ti-MFI-CH.

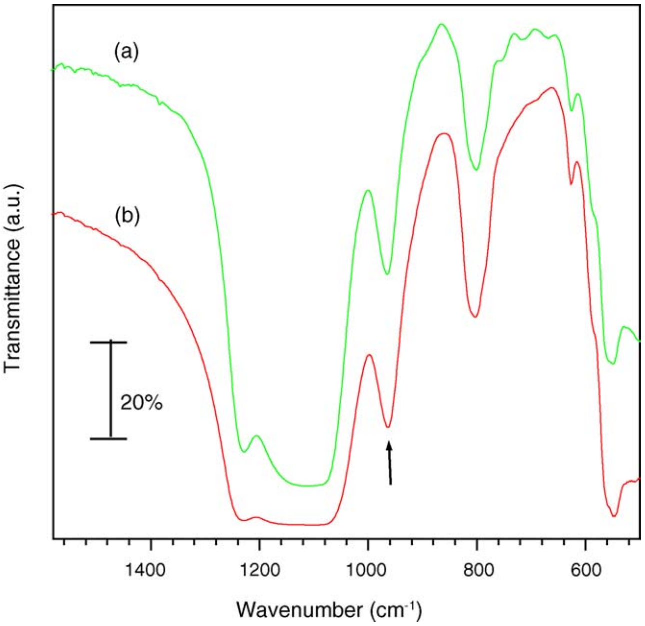

Fig. 2. FT-IR spectra of (a) Ti-MFI-MW and (b) Ti-MFI-CH.

However, we observed a dramatic change in the morphology depending on the synthesis methods. Ti-MFI-CH reveals ellipsoidal crystals of submicrometer size as presented in Fig. 4a. However, Ti-MFI-MW exhibits a fibrous morphology through the stacking of flat crystals on top of one another along their [0 1 0] direction. The fibrous morphology was ascribed to the condensation of the terminal hydroxyl groups between crystal surfaces to induce multiple stacking of flat crystals [33]. This stacking is sufficiently robust so as not to be destroyed by a sonication treatment for more than 1 h, indicating that this morphology is not a result of simple aggregation but of strong chemical bonds between the crystals. However, the BET surface areas and micropore volumes from N_2 adsorption experiments show that Ti-MFI-MW ($S_{BET} = 429\ m^2/g$,

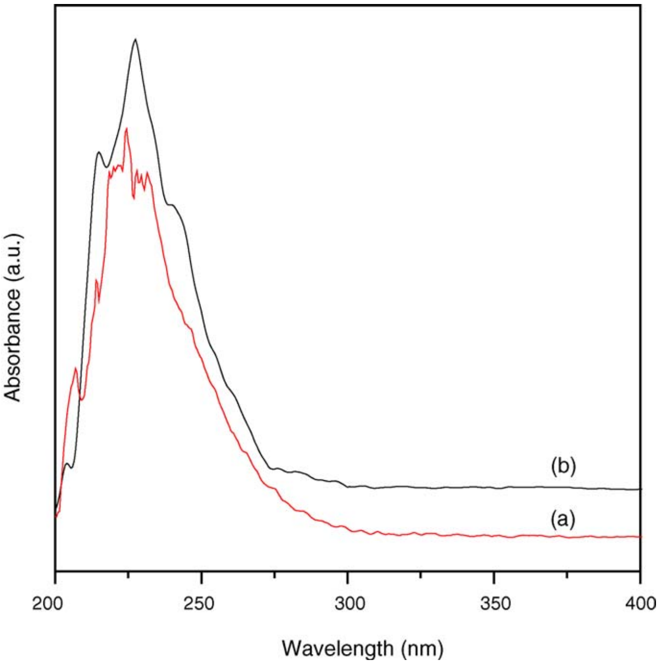

Fig. 3. UV–vis diffuse reflectance spectra of (a) Ti-MFI-MW and (b) Ti-MFI-CH.

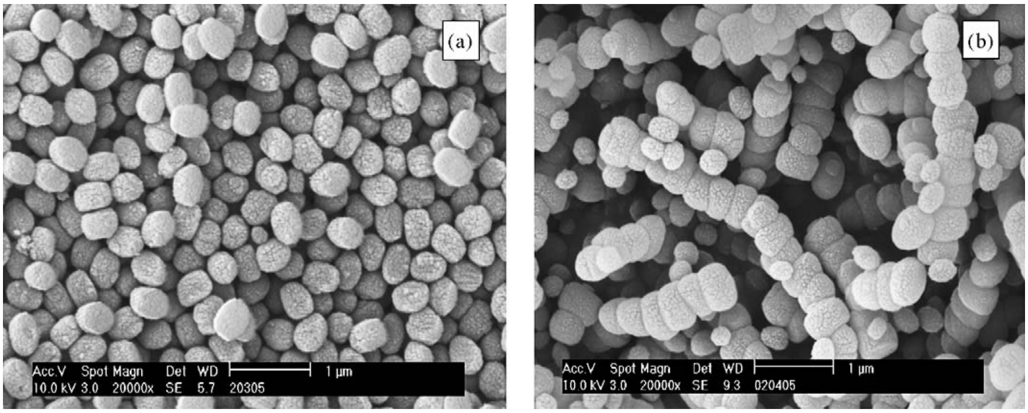

Fig. 4. SEM images of (a) Ti-MFI-CH and (b) Ti-MFI-MW.

$V_{\mathrm{pore}} = 0.21$ ml/g) and Ti-MFI-CH ($S_{\mathrm{BET}} = 448$ m^2/g, $V_{\mathrm{pore}} = 0.24$ ml/g) have the comparable pore characteristics, suggesting that the crystal stacking hardly affects the intracrystalline pore structure and that the reduced density of Ti-MFI-MW is a result of the fibrous morphology.

3.2. Hydrophobicity

The HI is an important guideline to characterize the surface properties of titanium-incorporated zeolites. We measured HI values of Ti-MFI zeolites using the typical breakthrough curves for the competitive adsorption of toluene and water. The final loading amounts of adsorbates (L_i) were obtained from the area of the region enclosed by the corresponding breakthrough curve, the line $P_i/P_{i,\mathrm{in}} = 1$ and the y-axis. Based on the measured breakthrough curves, HI values of Ti-MFI-MW and Ti-MFI-CH were estimated to be 8.0 and 6.2, respectively, indicating that Ti-MFI prepared by the microwave method exhibits a higher hydrophobic character.

The difference in hydrophobicity indices of the Ti-MFI zeolites can be rationalized in terms of the different amount of surface hydroxyl groups (T–OH, herein T represents Ti and Si atoms). The surface hydroxyl groups of Ti-MFI-MW and Ti-MFI-CH were investigated by FT-IR measurements of their self-supported wafers (10 mg cm^{-2}) after sequential evacuation treatments at 22 °C for 2 h, and 400 °C for 2 and 12 h, respectively. The IR spectra of the surface hydroxyl groups are presented in Fig. 5. After the evacuation at 22 °C for 2 h, Ti-MFI-MW and Ti-MFI-CH show a sharp peak at 3741 and 3734 cm^{-1}, respectively. These peaks can be attributed to the presence of terminal and defective isolated T–OH groups including Si–OH and Ti–OH [9,33–37]. At the same time, a broad absorption band in the range of 3720–2800 cm^{-1} was observed. This broad absorption band is assignable to hydrogen-bonded T–OH groups or strongly adsorbed water on the surface [33]. After further dehydration under vacuum, the broad band disappears owing to the removal of water and the breakage of the hydrogen-bonded species, leading to the presence of only isolated T–OH groups. Moreover, the peak

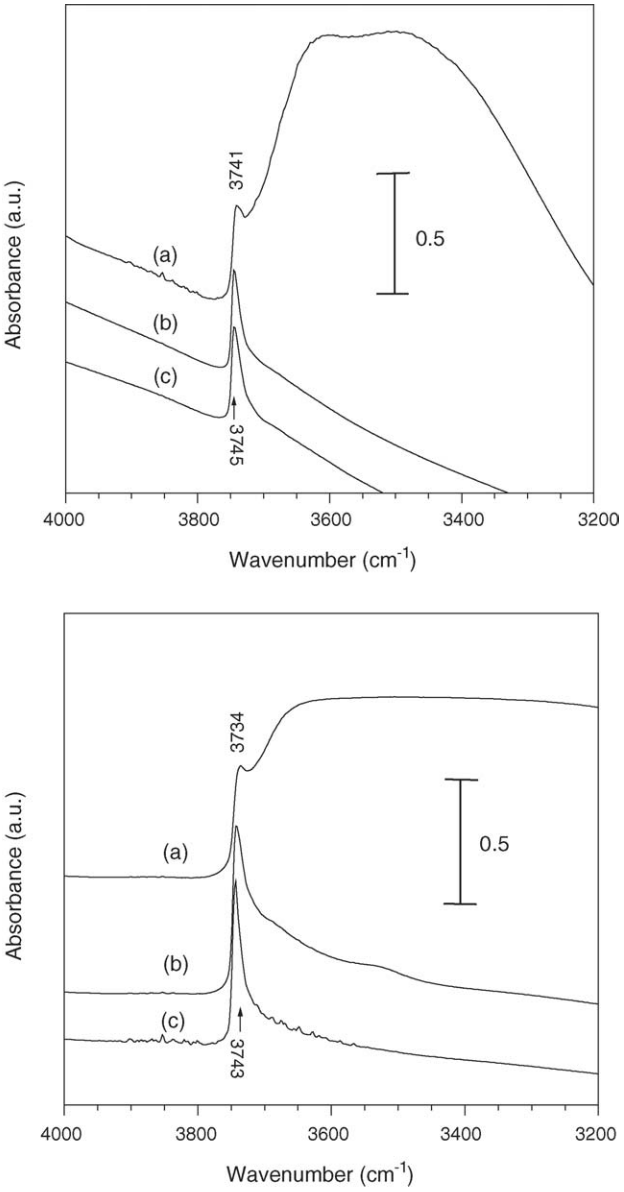

Fig. 5. FT-IR spectra of Ti-MFI-MW (upper) and Ti-MFI-CH (lower) after evacuation at (a) 22 °C for 2 h, (b) 400 °C for 2 h and (c) 400 °C for 12 h.

Table 1
IR analysis results on T–OH groups of dehydrated Ti-MFI zeolites and 1-hexene adsorbed on Ti-MFI zeolites

Samples	IR signals	After dehydration at 400 °C in vacuo ($<10^{-5}$ Torr)		After adsorption of 7.5 Torr 1-hexene at RT for 20 min	
		T–OH (2 h)[a]	T–OH (12 h)[a]	T–OH[a]	1-hexene[b]
Ti-MFI-CH	Peak areas (a.u.)	44.6	19.6	9.5	123.1
Ti-MFI-MW	Peak areas (a.u.)	7.6	6.5	6.9	226.7

[a] Peak area values at 3743 or 3745 cm^{-1}.

[b] Peak area values at 2780–3110 cm^{-1}.

intensity and peak area of the isolated terminal hydroxyl groups (T–OH) decrease with the heating time, indicating the partial condensation of adjacent T–OH groups. However, the peak areas of the isolated T–OH groups of Ti-MFI-CH always remain much larger than that of Ti-MFI-MW under the identical heating conditions (Table 1). The intensity of the isolated terminal hydroxyl groups on Ti-MFI-CH depends on heating time in vacuo at 400 °C; thus, the intensity upon 2 h treatment is two times higher than that upon 12 h treatment. However, almost no significant difference is noticeable for Ti-MFI-MW after the same treatment procedures, resulting from the consumption of terminal hydroxyl groups by the microwave-induced stacking of Ti-MFI-MW crystals, as illustrated in Fig. 5.

It is expected that a hydrophobic zeolite have a strong preference for adsorption of organic compounds. Therefore, we also investigated the adsorption of 1-hexene on Ti-MFI zeolites using FT-IR technique. 1-Hexene is mainly adsorbed on the pore walls of the zeolite. The IR spectra of 1-hexene adsorbed on Ti-MFI zeolites give a series of new absorption bands in the region 3100–2780 cm^{-1} (Fig. 6). From Table 1 and Fig. 6, it is clearly observed that the intensity and the total area of adsorption bands for Ti-MFI-MW in the range of 3100–2780 cm^{-1} are larger than those for Ti-MFI-CH. This indicates that Ti-MFI-MW has a higher adsorption capacity of 1-hexene and thus Ti-MFI-MW is more hydrophobic than Ti-MFI-HT. Additionally, the IR absorption area of T–OH groups for the Ti-MFI-CH decreases from 19.6 to 9.5 a.u. after adsorption of 1-hexene, while almost no change is observed for Ti-MFI-MW.

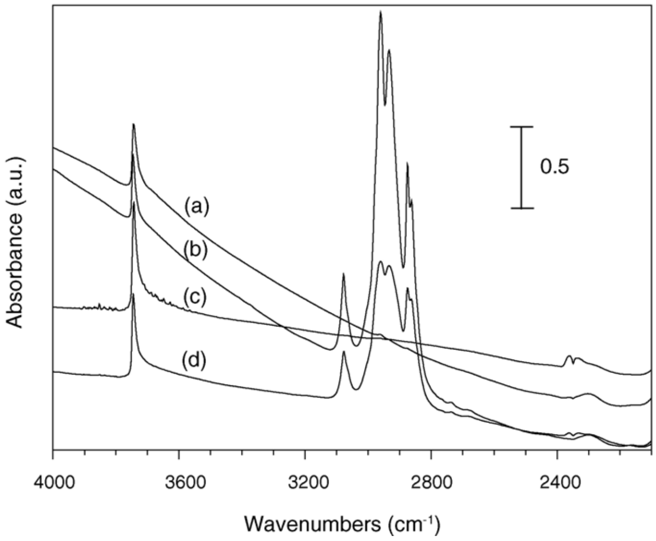

Fig. 6. FT-IR spectra of Ti-MFI-MW (a) before and (b) after 1-hexene adsorption, and Ti-MFI-CH (c) before and (d) after 1-hexene adsorption. Ti-MFI zeolites were dehydrated in vacuo at 400 °C for 12 h followed by adsorption of 7.5 Torr 1-hexene at room temperature for 20 min.

3.3. Catalytic activity

The enhanced surface hydrophobicity affects the catalytic properties of Ti-MFI-MW. Table 2 lists the catalytic results on the epoxidation reactions of 1-hexene and styrene with H_2O_2 over Ti-MFI zeolites synthesized by microwave and conventional heating. Fig. 7 presents styrene conversions and selectivity for styrene oxide against the reaction time. It is confirmed that Ti-MFI-MW is catalytically active than Ti-MFI-CH for both epoxidation reactions. According to the results presented in Section 3.2, we conclude that the difference in their catalytic properties results from their different hydrophobicity. Although the fibrous structure of Ti-MFI-MW may limit the diffusion of reactants and products, this drawback is more than offset by the positive effect of the increased hydrophobicity for this reaction [5]. Organic reactant molecules are easily adsorbed on the more hydrophobic Ti-MFI-MW so that the probability of adsorbed reactants to contact the Ti active sites might increase, leading to the higher catalytic activity. However, the Ti active sites of the more hydrophilic Ti-MFI-CH can be easily covered by the water molecules from the competive adsorption of organic reactants [9,37], resulting in a situation that the organic molecules are hindered to approach the active centers and therefore the lower catalytic activity is achieved.

Two Ti-MFI zeolites show similar epoxide selectivities in the epoxidation of 1-hexene despites different hydrophobicity. However, the effect of the hydrophobicity of Ti-MFI on its catalytic properties can be clearly seen from the different trends of the epoxide selectivities in the styrene epoxidation reaction. In the Ti-MFI-catalyzed styrene epoxidation, three main products styrene oxide (SO), β-phenylacetaldehyde (PA) and benzaldehyde (BA) were detected in agreement with previous studies [33,37]. Kumar et al. reported that about 70–80% β-phenylacetaldehyde in the product was obtained from the rearrangement of styrene oxide on the weakly acidic centers provided by T–OH groups of Ti-incorporated zeolite [38]. As presented in Fig. 7, the styrene oxide selectivities on Ti-MFI-MW as a function of reaction time exhibit higher

Table 2
Catalytic properties of Ti-MFI zeolites for epoxidation reaction of 1-hexene and styrene with hydrogen peroxide

Substrate	Catalyst	Reaction time (h)	Conversion (mol%)	Distribution of products (mol%)			
				Epoxide	Diols	PhCHO	$PhCH_2CHO$
Styrene[a]	Ti-MFI-MW	6	65.2	63.0	1.6	30.0	5.4
		15	69.2	55.0	2.3	25.0	17.7
	Ti-MFI-CH	6	46.1	48.0	4.2	40.0	7.8
		15	58.0	16.0	5.6	35.0	43.4
1-Hexene[b]	Ti-MFI-MW	3	23.2	89.1	10.9		
		9	36.1	88.8	11.2		
	Ti-MFI-CH	3	17.3	93.8	6.2		
		9	25.4	93.1	6.9		

[a] *Reaction conditions*: 70 °C, 5 ml styrene, styrene/H_2O_2 = 4, 12 ml acetone (solvent), 0.35 g catalyst.

[b] *Reaction conditions*: 60 °C, 4 ml 1-hexene, 1-hexene/H_2O_2 = 4, 4 ml acetonitrile (solvent), 0.35 g catalyst.

selectivities of styrene oxide than Ti-MFI-CH. Thus, for Ti-MFI-MW the selectivity of styrene oxide increases slowly with increasing reaction time in the beginning and reaches a maximum value for 63 mol% at about 4 h. However, for Ti-MFI-CH the selectivity of styrene oxide first increases and reaches a maximum at 5 h and then decreases rapidly with increasing reaction time to give 20 mol% after 15 h in agreement with previous results in literature [33,37]. The rapid decrease of styrene oxide selectivity might be due to its rearragement to β-phenylacetaldehyde. Based on the above results, it is thought that the more hydrophilic Ti-MFI-CH gives rise to the easy absorption for water, which leads to the production of weakly acidic sites on the molecular sieves.

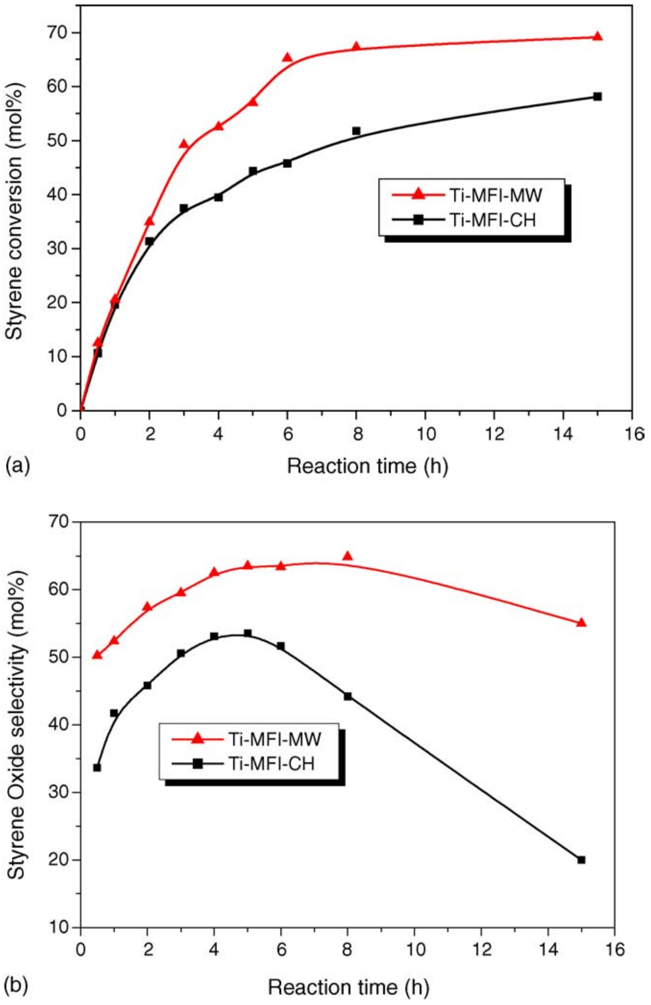

Fig. 7. (a) Conversion and (b) styrene oxide selectivity as a function of reaction time in epoxidation of styrene with H_2O_2 on Ti-MFI-MW and Ti-MFI-CH catalysts. *Reaction conditions*: see Table 2.

4. Conclusions

Ti-MFI-MW (Si/Ti = 81), synthesized by microwave heating, exhibited the higher hydrophobicity than the conventional Ti-MFI-CH (Si/Ti = 82). SEM results revealed a stacking between the adjacent crystals of Ti-MFI-MW, which came from the condensation of the terminal hydroxyl groups. This consumption of terminal hydroxyl groups led to the enhancement of the hydrophobicity, showing the higher selectivity in the epoxidation of styrene as well as the higher catalytic activities in the epoxidation reactions of 1-hexene and styrene.

Acknowledgements

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