Improvement in hydrophobicity of Ti-MCM-41 using a new silylation agent MSTFA

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A new silylation agent, N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), has been employed for the trimethylsilylation of Ti-MCM-41. The FT-IR spectra revealed that the hydrophobic trimethylsilyl group, $-Si(CH_3)_3$, in MSTFA can replace the hydrogen in the silanol at room temperature. By virtue of their high volatility, MSTFA and its derivative, N-methyl trifluoroacetamide, can be readily removed after silylation. The MSTFA silylated Ti-MCM-41 is found to be more hydrophobic than that silylated by BSTFA and to bring about a significant enhancement in the yield of epoxide from cyclohexene epoxidation with aqueous H_2O_2.

Keywords: silylation, MSTFA, hydrophobicity, Ti-MCM-41, epoxidation, cyclohexene

1. Introduction

Silylation of porous and non-porous silica has been widely used in the field of analytical chemistry and semiconductor industry [1]. In recent years, the silylation technique has been applied for the modification of mesoporous molecular sieves [2]. Tatsumi et al. [3] reported that trimethylsilylation could stabilize both MCM-41 and MCM-48. By applying it to the liquid-phase oxidation of alkenes with H_2O_2, Corma et al. [4] found that Ti-MCM-41 was much less active than Ti(Al)-beta and showed that the hydrophilic/hydrophobic property of Ti-MCM-41 played an important role in the activity for liquid-phase oxidations [5]. Since then, silylation of the hydrophilic silanol group has attracted a great deal of research interest.

Tatsumi et al. [6] silylated both Ti-MCM-41 and Ti-MCM-48 by using trimethylsilyl chloride (TMSCl) and hexamethyldisiloxane (HMDS), respectively. More recently, D'Amore and Schwarz [7] adopted bis(trimethylsilyl) trifluoroacetamide (BSTFA) to trimethylsilylate micro- and mesoporous titanosilicates. In order to improve the hydrophobicity of titanosilicates, the silylation agent is required to replace the active hydrogen in silanol with an alkylsilyl group efficiently under mild conditions, while the silylation agent and its derivatives should be volatile and removed readily.

In this study, Ti-MCM-41 was trimethylsilylated with a new silylation agent, N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA). The silylation efficiency of this new agent was compared with that of BSTFA. *In situ* FT-IR technique was employed to investigate the interaction between MSTFA and silanol. Subsequently, the silylated catalysts were applied to the epoxidation of cyclohexene with aqueous H_2O_2 and the effect of hydrophobicity on the epoxidation was examined.

2. Experimental

2.1. Preparations of catalysts

The Ti-MCM-41 sample (TM-1) was prepared by using TEOS, TBOT, TMAOH (20 wt%) and DTMABr (C_{12}). The synthesis method was the same as described by Koyano and Tatsumi [8]. Sample TM-2 was obtained by silylation of TM-1 with BSTFA (99%, Aldrich) following the method proposed by D'Amore and Schwarz [7]. The procedure for the silylation of TM-1 with MSTFA is as follows: a solution of 1 g MSTFA (99%, Aldrich) in 10 g of toluene was added to the sample TM-1 (0.5 g). The mixture was stirred at room temperature for 2 h, then the treated catalyst was filtered, washed with toluene and dried in air for 8 h to give the sample TM-3.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were collected on a Rigaku model D/Max-3C using Cu Kα radiation. UV-vis spectroscopic measurements were recorded on a Varian CARY 3E double-beam spectrometer. The elemental analysis of the samples was undertaken by inductive-coupled plasma atomic emission spectroscopy (ICP-AES). Nitrogen adsorption/desorption measurements were performed on a Micromeritics ASAP 2010 apparatus. The amount of water adsorbed on the sample was determined by the method reported by Kochkar and Figueras [9]. Framework FT-IR spectra were taken on the Nicolet Impact 410 FT-IR instrument. The sample dispersed in KBr (ratio of catalyst to KBr is 1/40) was pressed to a wafer.

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2.3. *In situ FT-IR study*

The *in situ* FT-IR experiment was implemented to monitor the silylation process with MSTFA. The sample TM-1 (20 mg) was pressed into a self-supporting wafer and placed in the sample holder of the IR cell, which is connected to a vacuum/sorption system with a residual pressure less than 10^{-4} Torr. This sample was first activated at 400 °C for 4 h and then 0.01 ml of MSTFA was introduced into the cell at room temperature. *In situ* FT-IR spectrum measurements were periodically recorded. All spectra were taken accumulating 100 scans with a spectral resolution of 2 cm^{-1}.

2.4. *Catalytic reaction*

The epoxidation of cyclohexene with H_2O_2 was carried out at 70 °C in a magnetically stirred three-necked flask equipped with a condenser. In practice, 0.05 g of catalyst was dispersed in the solution containing 0.02 mol of cyclohexene and 20 ml of acetonitrile (solvent). The mixture was then heated to 70 °C under stirring and 0.01 mol of H_2O_2 (35 wt% aqueous solution) was introduced in one lot. The sample was periodically collected and analyzed by gas chromatography (HP 5890 series II) equipped with FID and HP-1 capillary column.

3. Results and discussion

3.1. *Characterization*

The XRD pattern of synthesized Ti-MCM-41 (TM-1) is in accordance with that reported in the literature [8]. The UV-vis spectra of all the samples give no signal for anatase phase and indicate the presence of isolated Ti and oligomeric $(\mathrm{Ti{-}O})_n$ [10]. The BET surface area and pore volume were measured for three samples and are listed in table 1. Silylated samples have lower surface area and lower pore volume than the parent sample TM-1. It is similar to the earlier report of Tatsumi [6] and D'Amore and Schwarz [7] that the surface area and pore volume decreased as the silanol groups inside the pore of Ti-MCM-41 were trimethylsilylated by silylation agents.

Between the two silylated samples, the sample TM-3 has lower surface area and lower pore volume than TM-2, which indicates that MSTFA is more effective as a silylation agent. The adsorption of H_2O was studied and regarded as a measure of the relative hydrophobicity of materials. As presented in table 1, silylation improves the hydrophobicity of Ti-MCM-41, and TM-3 is found to be more hydrophobic than TM-2.

Figure 1 shows the FT-IR spectra of the samples dispersed in KBr. All the spectra display a strong band at 960 cm^{-1}. This band has been assigned to Si–O–Ti bonds [11] or to Si–OH groups [12,13]. Tatsumi et al. [6] observed that the intensity of the 960 cm^{-1} band decreased in the silylated Ti-MCM-48 or pure silica MCM-41 samples, while D'Amore and Schwarz [7] found a decrease in the IR intensity ratio, I_{960}/I_{1090}, of BSTFA silylated Ti-MCM-41. We also observed the same phenomenon in silylated Ti-MCM-41 samples. An interesting feature of our result is that the decrease in this ratio is more pronounced in MSTFA treated Ti-MCM-41. The I_{960}/I_{1090} ratio of TM-3 is less than one half of that of TM-2 (cf. table 1). In addition, the broad pattern between 3700 and 3000 cm^{-1}, originated from hydrogen-bonded surface OH groups as well as from adsorbed H_2O [14], decreases dramatically in the silylated samples. Therefore, one may conclude that the silylation of Ti-MCM-41 with MSTFA enhances the hydrophobicity more than that with BSTFA.

The silylation brings about additional bands to the IR spectra that may be regarded as important evidence for the alkylsilyl group ($\mathrm{SiMe_3}$) replacing the hydrogen in silanol. As depicted in figure 1, several new bands appeared after

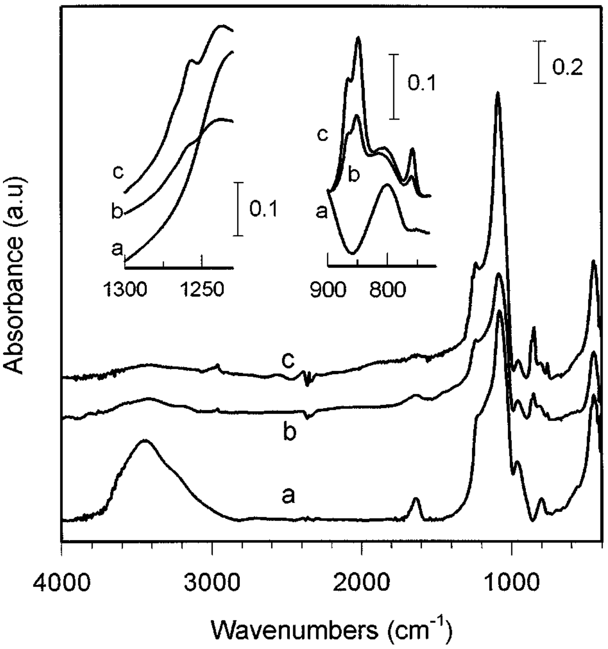


Figure 1. IR spectra of non-silylated and silylated Ti-MCM-41 catalysts: (a) TM-1, (b) TM-2, and (c) TM-3.

Table 1
Characterization of non-silylated and silylated Ti-MCM-41 catalysts.

Catalyst	Silylation agent	Si/Ti	BET surface area (m^2/g)	Pore diameter (Å)	Pore volume (ml/g)	I_{960}/I_{1090}	Adsorption of H_2O (g/g-cat)
TM-1	–	60.3	1405	26.1	0.915	0.167	0.301
TM-2	BSTFA	66.7	1213	23.1	0.831	0.115	0.157
TM-3	MSTFA	69.4	1153	22.4	0.853	0.054	0.110

silylation of TM-1 with MSTFA or BSTFA. The band at 2962 cm^{-1} is assigned to the C–H oscillation of the methyl group [15]. This band is also observed in the IR spectrum of the hydrophobic silica (AEROSIL R812), which was obtained from Degussa [16]. The $\mathrm{SiMe_3}$ group is also easily recognized by a band at ca. 1260 cm^{-1} together with one or more bands in the 870–750 cm^{-1} region originated from the $-\mathrm{CH_3}$ rocking and the Si–C stretching vibrations [17]. The bands at 845 and 760 cm^{-1} can be observed in both of the silylated samples. However, the band at 1260 cm^{-1} is clearly visible only on the sample TM-3, while it is a weak shoulder appearing on TM-2. These observations strongly suggest that a large amount of $\mathrm{SiMe_3}$ groups were bonded on the surface of MSTFA silylated catalyst to result in higher hydrophobicity for the sample TM-3.

3.2. *In situ FT-IR study on the silylation of Ti-MCM-41*

By the aid of the *in situ* IR technique, we could further investigate the interaction between MSTFA and silanol. As shown in spectrum (a) of figure 2, a sharp band at 3745 cm^{-1} appeared after degassing the sample TM-1 at 450 °C for 4 h. As this band has been assigned to the isolated silanol group [18,19], this is very indicative of the hydrophilic property of TM-1.

When the MSTFA (0.01 ml) was introduced into the sample at 35 °C, the band at 3745 cm^{-1} was completely vanished and several new bands appeared simultaneously as can be seen in the spectrum (b) of figure 2. The band at 1420 cm^{-1} has been assigned to the asymmetric $-\mathrm{CH_3}$ deformation of $\mathrm{Si{-}Me_3}$ [7,17], while the 2962 and 2905 cm^{-1} bands corresponded to $-\mathrm{CH_3}$. These new bands match well the IR spectra of MSTFA and N-methyl trifluoroacetamide ($\mathrm{CF_3CONHCH_3}$) characterized by Aldrich [20,21]. The broad band in the range of 3180–3490 cm^{-1} can be attributed to the N–H group [15]. We also observe a band in the range of 1640–1830 cm^{-1} assigned to the stretch of C=O [15], which typically represents the amide group contained in both MATFA and $\mathrm{CF_3CONHCH_3}$.

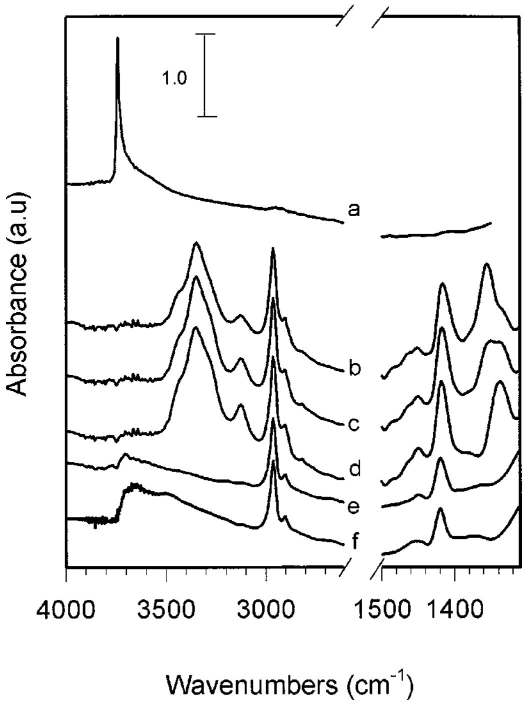


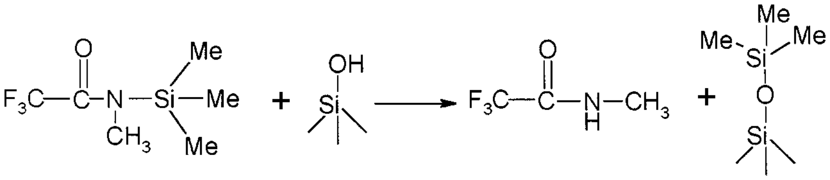
Figure 2. *In situ* IR spectra of Ti-MCM-41 before and after silylation with MSTFA: (a) after evacuation at 450 °C for 4 h, (b) after introduction of MSTFA at 35 °C for 5 min, (c) after introduction of MSTFA at 35 °C for 30 min, (d) after introduction of MSTFA at 35 °C for 100 min, (e) after evacuation at 60 °C for 30 min, and (f) after exposure to wet air for 4 h.

Two bands observed at 1364 and 1335 cm^{-1} cannot be assigned with certainty. However, we tentatively assign them to the characteristics of MSTFA and $\mathrm{CF_3CONHCH_3}$, as they are identical with the bands from these compounds. The band at 1364 cm^{-1} tends to disappear whereas the intensity of the band at 1335 cm^{-1} increases with the exposure time. This indicates that MSTFA is converted to $\mathrm{CF_3CONHCH_3}$ (derivative) as the silylation reaction proceeds. It may be noticed from the spectra (e) and (f) of figure 2 that those bands corresponding to the residual MSTFA and derivative vanished when the sample was evacuated at low temperature, exposed to the wet air, or dried at room temperature after silylation (cf. figure 2). Only the bands at 2962, 2905 and 1420 cm^{-1} remained. These varieties in IR spectra strongly suggest that the $\mathrm{SiMe_3}$ groups in MSTFA irreversibly replace the silanol groups by a chemical reaction at room temperature. Thus, one may conclude that MSTFA and $\mathrm{CF_3CONHCH_3}$ are volatile and can be readily removed.

On the basis of the differences in the amount of adsorbed water (cf. table 1) and intensities of the bands assigned to $\mathrm{SiMe_3}$ (cf. figure 1), MSTFA is considered to be superior to BSTFA under identical silylation conditions. According to the suggestion of D'Amore and Schwarz [7], BSTFA contains two $\mathrm{SiMe_3}$ groups, so it can react with two Si–OH groups and produce $\mathrm{CF_3CONH_2}$ (derivative). On the other hand, the silylation of silanol with MSTFA may proceed by the reaction shown in scheme 1; that is, one MSTFA molecule replacing one silanol group results in the formation of one $\mathrm{CF_3CONHCH_3}$ molecule, so the reaction rate with MSTFA may be faster than that with BSTFA.

3.3. *The effects of silylation on cyclohexene epoxidation*

Four different products were detected from the epoxidation of cyclohexene; they are epoxide, cyclohexanediol (diol), 2-cyclohexene-1-ol (1-ol), and 2-cyclohexene-1-one (1-one). This observation is in accordance with the report in the literature [6,22]. Table 2 presents the results of cyclohexene epoxidation over hydrophilic Ti-MCM-41 (TM-1) and silylated catalysts (TM-2 and TM-3). Apparently, the non-silylated TM-1 gave the lowest values of the turnover number (TON), conversion, and the selectivity to epoxide. The epoxide yield was substantially increased over the silylated catalysts and this is in good agreement with the results of Tatsumi et al. [6] and D'Amore and Schwarz [7]. The hydrophobic nature of catalyst either increases the access



Scheme 1.

Table 2
Cyclohexene epoxidation with H_2O_2 over non-silylated and silylated Ti-MCM-41 catalysts.

Catalyst	Conversion[a] (mol%)	TON[b] (mol-oxide/mol-Ti h)	Selectivity[a] (%)			Epoxide yield[c]
			Epoxide	Diol	1-ol + 1-one	
TM-1	14.2	4.5	13.2	17.6	69.2	1.87
TM-2	24.4	13.4	22.1	15.4	62.5	5.39
TM-3	32.3	31.1	36.9	17.8	45.3	11.9

[a] Reaction conditions: catalyst 0.05 g, substrate 20 mmol, H_2O_2 0.01 mmol, solvent 20 ml, 70 °C, 4 h.

[b] Turnover number (TON) estimated after 1 h reaction.

[c] Yield = selectivity to epoxide × conversion/100.

of the olefin to the active sites or suppresses the inhibitory effect of water [6,23]. In other words, the more hydrophobic the catalyst, the higher the activity. This is strongly supported by the experimental result that the MSTFA silylated Ti-MCM-41 (TM-3) gave a larger value of turnover number and higher activity than TM-2.

In addition, the recent kinetic model proposed by Figueras and Kochkar [9,24] may explain the influence of hydrophobicity on the selectivity. These authors suggested that cyclohexene can undergo either epoxidation yielding epoxide or allylic attack yielding 1-ol, which can be further oxidized to form 1-one. They found that the hydrophobic catalyst attacked preferentially the C=C bond in the olefin. This is in agreement with our experimental observation that a higher selectivity to epoxide was obtained over MSTFA silylated catalyst (TM-3) than over TM-2.

Recently, Corma et al. [25] pointed out that the presence of water is responsible for the ring opening of the epoxide to form diol, which acts as a catalyst poison to the Ti sites. According to the experimental results shown in table 2, the amount of diol produced over TM-3 remained nearly the same as over other catalysts while the production of epoxide was considerably increased. The hydrophobic nature of TM-3 reduced the amount of water adsorbed on the surface, so we speculate that the influence of diol poisoning may not be serious after silylation. Indeed, the catalytic activity of TM-3 remained fairly constant over the reaction period of several hours.

4. Conclusions

The new agent MSTFA is proven more effective than BSTFA for the silylation of Ti-MCM-41. The IR spectra of silylated Ti-MCM-41 show that the hydrophobic $SiMe_3$ group in MSTFA replaces the hydrogen in Si–OH at room temperature. It is found that the MSTFA silylated Ti-MCM-41 becomes more hydrophobic than that silylated by BSTFA under identical conditions. Experimental results of cyclohexene epoxidation with aqueous H_2O_2 indicate that the hydrophobic catalyst enhances the yield of epoxide and suppresses the formation of by-products with insignificant influence upon the selectivity to diol. The more hydrophobic nature of MSTFA silylated catalyst gives rise to a substantial increase of the epoxide yield.

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