Catalysis Letters 66 (2000) 245–249

Silylation of Ti-MCM-41 by trimethylsilyl-imidazole and its effect on the olefin epoxidation with aqueous H_2O_2

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Received 10 December 1999; accepted 11 April 2000

Ti-MCM-41 catalyst was silylated with a new silylating agent, N-trimethylsilyl-imidazole (TMSI). TMSI was found to be more effective to improve the hydrophobicity and the catalytic performance of Ti-MCM-41 than other silylating agents. Different levels of silylation were obtained by varying the silylation time. A linear relationship was observed between the degree of silylation and each of the intensity ratios I_{1260}/I_{1083}, I_{845}/I_{1083} and I_{760}/I_{1083} of $SiMe_3$ spectra bands detected by FT-IR or the intensity ratio $SiMe_3/SiO_2$ of the ^{29}Si-MAS-NMR signals. High level of silylation degree significantly enhances both the catalytic activity and the selectivity to epoxide.

Keywords: silylation, trimethylsilyl-imidazole, hydrophobicity, Ti-MCM-41, cyclohexene epoxidation

1. Introduction

After the discovery of M41S mesoporous molecular sieves [1,2], a significant effort has been made to engineer their structural and surface properties [3]. Due to their mesoporous natures (20–100 Å), the titanium-substituted MCM-41 [4] or MCM-48 [5] molecular sieves showed a good potential as epoxidation catalysts for larger molecules [6]. Corma et al. [7], however, found that Ti-MCM-41 was much less effective than Ti(Al)-beta for liquid phase oxidation, and the hydrophilic/hydrophobic property of Ti-MCM-41 plays an important role with respect to the activity [8]. Consequently, Corma et al. [9] further proposed that the silylation of Ti-MCM-41 or removal of water from the reaction media could improve the epoxidation activity and selectivity of Ti-MCM-41.

In recent years, the silylation technique applied to the modification of mesoporous molecular sieves has received much attention. Several authors reported that some silylating agents, such as TMSCl, HMDS [9–11] and BSTFA [12], were effective to silylate Ti-MCM-41 or Ti-MCM-48. In the previous work [13], we adopted a new silylating agent, N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA), to modify Ti-MCM-41 and observed an increased hydrophobicity and epoxidation activity. In this study, it is aimed to report a simple and yet effective silylation method for the silylation of Ti-MCM-41 with a new silylating agent, N-trimethylsilyl-imidazole (TMSI). The silylation efficiency of this new agent was compared to those of BSTFA and MSTFA. Different levels of silylation were obtained by varying the reaction time. TGA, FT-IR, ^{29}Si MAS NMR and BET techniques were employed to determine the degree of silylation. Subsequently, the silylated Ti-MCM-41 catalyst was applied to the cyclohexene epoxidation with aqueous H_2O_2 to investigate the effects of silylation degree on the catalytic activity and on the selectivity to each product.

2. Experimental

2.1. Preparation of catalysts

Ti-MCM-41 was synthesized by the method of Koyano and Tatsumi [6]. The molar composition of the gels used was as follows: $SiO_2 : 0.0167TiO_2 : 0.75DTMA : 0.26 TMAOH : 84H_2O$. The sample TM-B was obtained by silylation with BSTFA (99%, Aldrich) following the method proposed by D'Amore and Schwarz [12]. The sample TM-M was also prepared by silylation with MSTFA, for which the procedure was the same as described in our previous work [13]. The ratio of BSTFA or MSTFA to catalyst was 10 mmol/g and the silylation time was 2 h. The procedure for the silylation of TM with N-trimethylsilyl-imidazole (TMSI) is as follows: A solution of 1 mmol TMSI (ACROS) in 60 ml of acetonitrile was added to the calcined Ti-MCM-41 (0.5 g). The mixture was stirred in a closed reactor at 25 °C for a desired period of time, and then the treated catalyst was filtered, washed with acetonitrile (100 ml) four times and dried at 60 °C in air for 4 h. The characterization results of the samples are presented in table 1.

2.2. Characterization

X-ray powder diffraction data were obtained on a Rigaku model D/Max-3C using Cu K radiation. UV-visible spectra

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

Sample	Ti (wt% TiO_2)	Silylation time[a] (min)	BET surface area (m^2/g)	Pore diameter (nm)	Weight loss[b] (%)
TM	2.10	–	1250	2.30	16.5
TM-T1	1.94	12	1130	2.11	11.1
TM-T2	1.88	16	1090	2.10	9.12
TM-T3	1.85	26	1030	2.00	6.44
TM-T4	1.85	60	990	1.90	4.13

[a] Silylation conditions: TMSI/catalyst = 2 mmol/g_{cat}, 0.5 g of catalyst and 60 ml of acetonitrile (solvent), temperature 25 °C.

[b] Measured for hydrated samples at 150 °C on TGA analyzer.

were recorded on a Varian CARY 3E double beam spectrometer. The composition of the samples was determined 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 a thermogravimetric analyzer (Perkin–Elmer TGA-7) using a heating rate of 5 °C/min (to 150 °C) and an N_2 flow rate of 20 ml/min. The FT-IR spectra were collected on a Nicolet Impact 410 FT-IR instrument. Powder containing 2 wt% of catalyst in KBr was pressed to a wafer. ^{29}Si-MAS-NMR spectra were measured on a Bruker AM-300 NMR spectrometer at ambient temperature.

2.3. Catalytic reaction

The cyclohexene epoxidation has been conducted at 70 °C, in a magnetically stirred three-necked flask immersed in a thermostat bath and equipped with a condenser. In practice, 0.05 g of catalyst was dispersed in a 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 a gas chromatograph (HP 5890 series II) equipped with FID and a HP-1 capillary column.

3. Results and discussion

3.1. Characterization and determination of silylation degree

The XRD pattern of non-silylated Ti-MCM-41 is in accordance with that reported in the literature [6], while the XRD patterns of other silylated samples remain unchanged after silylation. The UV-vis spectra of all the samples give no signal for anatase phase and indicate the presence of isolated Ti and oligomeric $(Ti–O)_n$ [14]. The BET surface area and pore size are presented in table 1. Silylated samples have lower surface area and smaller pore size than the non-silylated sample TM. It is in agreement with the previous reports that both the surface area and pore size decreased, as the silanol groups inside the pore of Ti-MCM-41 were trimethylsilylated [11–13].

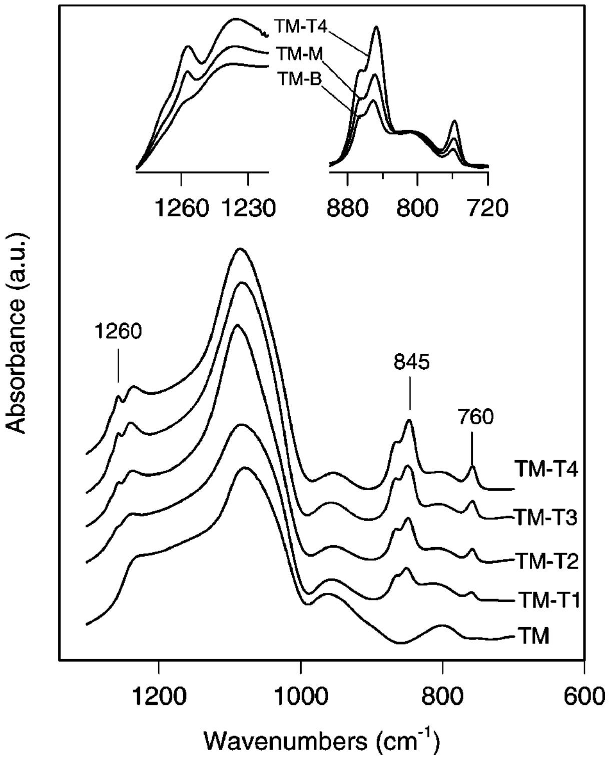


Figure 1. IR spectra of non-silylated and silylated Ti-MCM-41 catalysts.

Corma et al. [9] estimated the hydrophobicity of Ti-MCM-41 from the weight loss of the fully hydrated sample at 150 °C. In this study, we also determined the hydrophobicity of each sample based on the measurement of weight loss. As shown in table 1, the weight loss of silylated samples is decreased as the silylation time increases, which indicates that the hydrophobicity of the samples is improved during silylation.

The substitution of trimethylsilyl groups ($SiMe_3$) for silanol H atoms can be monitored by FT-IR [12,13]. The distinctive band at 1260 cm^{-1} is always accompanied by one or more bands in the 870–750 cm^{-1} region from the $–CH_3$ rocking and the Si–C stretching vibrations. This region is useful for characterizing the presence of trimethyl-substituted silicon. $SiMe_3$ gives the bands at 845 and 760 cm^{-1} [15]. The FT-IR spectra of non-silylated and TMSI-silylated catalysts are presented in figure 1. Three new FT-IR bands appear at 1260, 845 and 760 cm^{-1}, re-

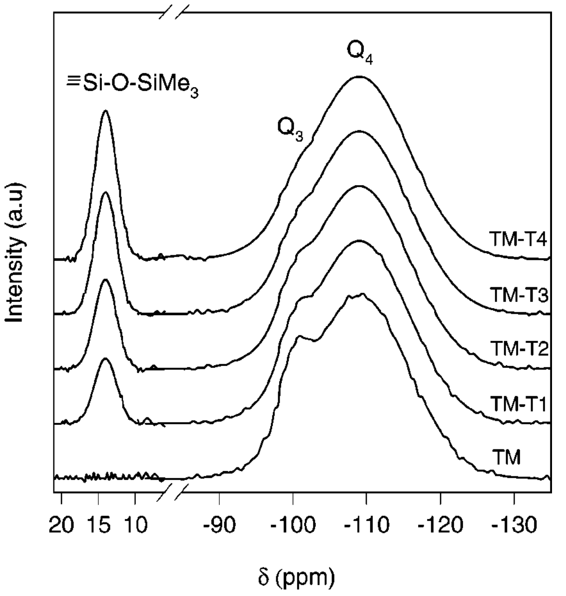


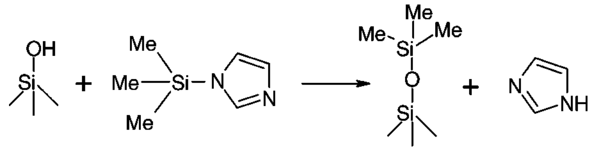
Figure 2. ^{29}Si-MAS-NMR spectra of non-silylated and silylated Ti-MCM-41 catalysts.

spectively, after silylation and they become stronger with the silylation time. This confirms that the amount of $SiMe_3$ groups bonded on the catalyst surface is increased with the silylation time.

An important feature of our result is that the intensities of the three new FT-IR bands on the TMSI-treated sample, TM-T4, are stronger than those on the BSTFA- and MSTFA-treated catalysts (cf. figure 1). It was reported that the MSTFA-silylated Ti-MCM-41 was more hydrophobic than that silylated by BSTFA under identical conditions [13]. However, TMSI is found to be more effective than either MSTFA or BSTFA, because the silylation with TMSI proceeded in a more dilute solution during a shorter period of reaction time, e.g., 1 h for TM-T4, as shown in table 1. These observations strongly suggest that TMSI can be regarded as a very effective silylating agent.

In addition, the ^{29}Si-MAS-NMR spectra may also be regarded as an important evidence for –$SiMe_3$ groups bound to the surface of Ti-MCM-41 [11]. As presented in figure 2, two signals are observed at −108 ppm (Q_4) and −100 ppm (Q_3), respectively, on TM (non-silylated). After silylation, a new signal at 14 ppm, which is assigned to Me_3Si–(OSi) [10,16,17], appears and its intensity increases with the hydrophobicity. The ^{29}Si-MAS-NMR spectra are in agreement with the FT-IR and TGA characteristics and clearly show that the TMSI reacts with silanol groups yielding Me_3Si–(OSi) groups on the surface, which improves the hydrophobicity of the samples. Furthermore, different levels of silylation can be obtained by varying the silylation time.

On the basis of the above arguments, the silylation of silanol with TMSI may be considered to proceed by the reaction shown in scheme 1.



Scheme 1.

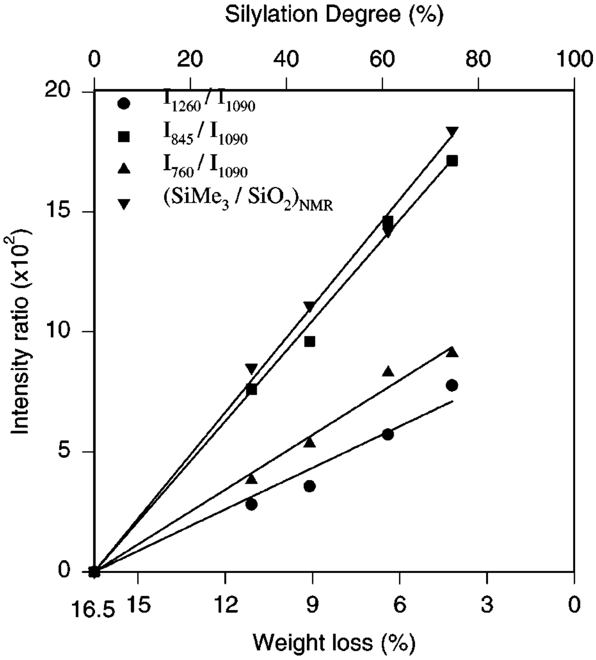


Figure 3. Correlation between the hydrophobicity and each of the intensity ratios I_{1260}/I_{1083}, I_{845}/I_{1083} and I_{760}/I_{1083} of $SiMe_3$ IR spectra or the intensity ratio $SiMe_3/SiO_2$ of the ^{29}Si-MAS-NMR signals.

Further analysis of the FT-IR and ^{29}Si-MAS-NMR spectra for silylated samples provides a quantitative correlation between the spectra ratio and the silylation degree. Corma et al. [9] observed that there was a linear correlation between the hydrophobicity and the surface coverage with $SiMe_3$ groups determined by the carbon content. As shown in figure 3, it was found that each of the IR spectra intensity ratios, I_{1260}/I_{1083}, I_{845}/I_{1083} and I_{760}/I_{1083}, has a linear relationship with the hydrophobicity (weight loss). Therefore, one may conclude that the above intensity ratios of the IR bands are proportional to the degree of silylation and the higher level of silylation makes more of –$SiMe_3$ groups linked to the surface. The linear plot of the ^{29}Si-MAS-NMR signal intensity ratio of $SiMe_3/SiO_2(Q_4)$ against the silylation degree further supports this conclusion. The intensity of the IR spectra at 960 cm^{-1} was also observed to decrease on silylated samples, as described by Tatsumi et al. [11] and D'Amore and Schwarz [12], but the ratio of I_{960}/I_{1083} did not give a linear correlation with the silylation degree. The reason may be that the 960 cm^{-1} band is assigned to Si–O–Ti [18] or to silanol groups in Ti-MCM-41 [19,20].

3.2. Effect of silylation degree on cyclohexene epoxidation with H_2O_2

Over all the catalysts tested, four different products were detected from the epoxidation of cyclohexene with H_2O_2; they are epoxide, cyclohexanediol (diol), 2-cyclohexene-1-

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

Catalyst	Silylating agent[a]	Conversion[b] (mol%)	TON[c] (mol oxide/mol Ti)	Selectivity[b] (%)			
				Epoxide	Diol	1-ol	1-one
TM-B	BSTFA	24.4	13.4	22.1	15.4	23.9	38.6
TM-M	MSTFA	32.3	31.1	36.9	17.8	16.4	28.9
TM		13.6	5.1	13.7	18.3	26.8	41.2
TM-T1		15.2	13.2	16.6	17.6	24.3	41.5
TM-T2	TMSI	22.4	18.9	24.1	17.2	21.5	37.2
TM-T3		30.8	29.7	36.7	17.4	16.2	29.7
TM-T4		34.7	37.5	40.3	17.1	15.5	27.1

[a] Silylation conditions: BSTFA or MSTFA/catalyst = 10 mmol/g_{cat}, 0.5 g of catalyst and 10 g of toluene, temperature 25 °C, silylation time 2 h [13].

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

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

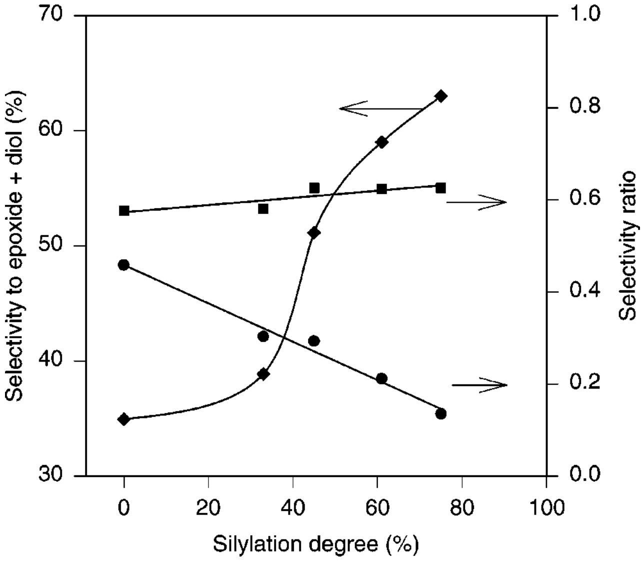


Figure 4. Effects of the silylation degree on the product selectivities in epoxidation of cyclohexene after 1 h reaction: (●) diol/(epoxide + diol) and (■) 1-one/(1-ol + 1-one).

ol (1-ol) and 2-cyclohexene-1-one (1-one). This observation is in accordance with reports in the literature [11,13]. The results shown in table 2 clearly indicate that both the catalytic activity and selectivity to epoxide increase with the silylation degree. The yield of epoxide is promoted more than seven-fold. When compared with the reported results of epoxidation [13], the sample TM-T4 obtained by silylation with dilute TMSI at room temperature for 1 h gave higher values of turnover number (TON), conversion and selectivity to epoxide than those observed on the BSTFA- and MSTFA-treated Ti-MCM-41 catalysts, which were prepared by silylation with above two silylating agents for 2 h. The experimental results clearly indicate that the silylating agent TMSI improves the catalytic performance of Ti-MCM-41 more significantly than the previously reported agents, BSTFA and MSTFA.

In addition, figure 4 presents an interesting result that the total selectivity to epoxide and diol is enhanced dramatically. On the other hand, the ratio of diol to the sum of epoxide and diol decreases as the silylation degree increases, while the ratio of 1-one to the sum of 1-ol and 1-one slightly increases with the silylation degree.

These effects of hydrophobicity may be considered to provide direct evidence for the mechanism of olefin epoxidation with aqueous H_2O_2. The nature of the products demonstrates that cyclohexene can undergo either epoxidation yielding epoxide and diol or allylic attack yielding 1-ol, which can be further oxidized to form 1-one [21,22]. Silylation improves the hydrophobicity of a catalyst, which either increases the access of the olefin to the active sites or suppresses the inhibitory effect of water [11,12,23]. Thus silylation promotes the attacking of the C=C in olefin to produce more epoxide. Since the presence of water on the surface is responsible for the ring opening of the epoxide to form diol [9], the relative amount of diol decreases almost linearly with the hydrophobicity (cf. figure 4). On the other hand, the hydrophobicity suppresses the formation of 1-ol, but it appears to give less influence on the oxidation of 1-ol than on the hydrolysis of epoxide.

4. Conclusions

The new agent, TMSI, turns out to be more effective for the silylation of Ti-MCM-41 than the previously reported agents, BSTFA and MSTFA, and improves the catalytic performance of Ti-MCM-41 more significantly. The silylation with TMSI could proceed in dilute TMSI solution under mild conditions, and different levels of silylation can be obtained by adjusting the silylation time. It is found that there is a linear relationship between the silylation degree and each of the intensity ratios I_{1260}/I_{1083}, I_{845}/I_{1083} and I_{760}/I_{1083} of the additional FT-IR bands or the intensity ratio $SiMe_3/SiO_2$ of ^{29}Si-MAS-NMR signals. Silylation of Ti-MCM-41 with TMSI promotes the production of epoxide and suppresses the formation of by-products in cyclohexene epoxidation with aqueous H_2O_2.

Acknowledgement

We are thankful for the financial aid from the Brain Korea 21 Program supported by the Ministry of Education.

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