Research Article

Synthesis of Fe-MCM-41 from silatrane and FeCl₃ via sol–gel process and its epoxidation acivity

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An iron-containing mesoporous molecular sieve, or Fe-MCM-41, was successfully synthesized the via sol–gel technique using silatrane and FeCl₃ as the silicon and iron sources, and was characterized using various techniques. Many factors were investigated, namely, reaction temperature and time, calcination rate, and iron amount in the reaction mixture. It was found that the optimum conditions in which to synthesize Fe-MCM-41 was to carry out the reaction at 60 °C for 7 h using a 1 °C min⁻¹ calcination rate and a 550 °C calcination temperature. The catalytic activity and selectivity of styrene epoxidation using hydrogen peroxide showed that the selectivity of the styrene oxide reached 65% at a styrene conversion of 22% over the 1%wt catalyst. Copyright © 2008 John Wiley & Sons, Ltd.

Introduction

MCM-41, possessing a hexagonal arrangement of channels, is one of the most important members of the M41S family,[1] and has attracted the attention of scientists owing to its elevated specific surface area, high thermal and hydrothermal stability, and the possibility of controlling its pore size, hydrophobicity and acidity. These characteristics have made MCM-41 a promising material as a catalyst and/or catalyst support to be used in industrial processes of adsorption, ion exchange, environmental control and as hosts for the inclusion of compounds and nanosize clusters, and as molecular sieves for large molecules.[2]

However, pure silica MCM-41 has limited catalytic application. Metal ion-incorporated MCM-41 has attracted much attention as an oxidation catalyst. For example, Ti-MCM-41 was reported to catalyze various oxidation reactions with H₂O₂,[3] but the epoxidation of cyclohexene could not proceed selectively over the catalyst with diluted H₂O₂.[4] Also, Mn-MCM-41 has shown high selectivity for the epoxidation of stilbene with tert-butyl peroxide or TBHP.[5] Iron, one of the most significant transition metals, has also been studied and introduced onto MCM-41 using iron salts such as iron nitrate [Fe(NO₃)₃ · 9H₂O] as iron source.[6,7] In terms of activity, a study of iron-immobilized MCM-41 modified with organic silane exhibited activity in the oxidation of cyclohexane to cyclohexanol and cyclohexanone at 373 K with H₂O₂.[8] The highest conversion of styrene over the Fe-MCM-41 via the direct hydrothermal technique showed 14% conversion over a 1.1 wt% Fe catalyst.[9] Moreover, Su and coworkers indicated that the activity and the efficiency of H₂O₂ increased with the metal content and reaction temperature.[10]

In this work, high surface area MCM-41 and Fe-MCM-41 were synthesized using moisture-stable silatrane and FeCl₃ as precursors. The synthesis conditions were studied to obtain the optimal conditions for high oxidation activities on styrene.

Experimental

Synthesis method

Following the method of Wongkasemjit, silatrane, as the silicon source, was synthesized directly from inexpensive and widely available starting materials, fumed silica (SiO₂, Aldrich Chemical Co.) and triethanolamine (TEA, Labscan), via the oxide one pot synthesis (OOPS) process.[11] Fe-MCM-41 was synthesized via the one-step synthesis using silatrane and ferric chloride (FeCl₃, Aldrich Chemical Co.) as silicon and iron sources, respectively. The composition of the reactants followed the previous study on the synthesis of extremely high surface area MCM-41.[12] A 1.29 g aliquot of silatrane precursor was added to a solution containing y% of FeCl₃, 182 g of hexadecyltrimethyl ammonium bromide (CTAB, Aldrich Chemical Co.), 0.04 g of sodium hydroxide (NaOH, Aldrich Chemical Co.) and 2.09 g of TEA. A 6.48 g aliquot of water was then added with vigorous stirring. To study the optimal condition for Fe-MCM-41 synthesis, iron concentration, synthesis time, reaction temperature, calcinations rate and metal amount were varied.

Characterization

FTIR spectroscopic analysis was conducted on a Bruker Instrument (Equinox55) with a scanning resolution of 4 cm⁻¹. Thermal properties were analyzed by thermogravimetric analysis (TGA) on

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a Du Pont Instrument TGA 2950 with an N_2 flow rate of 50 ml/min. The mesoporous product was characterized using a Rigaku X-ray diffractometer at a scanning speed of $2°\ s^{-1}$ and a CuK_α source. Diffuse reflectance UV–vis (DR-UV) spectra were recorded on a Shimadzu UV-2550 UV–vis spectrophotometer. The powdery sample was loaded in a Teflon cell and the spectra were collected in the 190–600 nm range using $BaSO_4$ as the reference. The surface area and average pore size were measured by BET on a Quantasorb Jr. (Autosorb-1). The product was degassed at 250 °C for 10 h before analysis. ESR spectra were measured at X-band, $\sim$9 GHz, on an Esprit-425 vol. 604 spectrometer. The sample was placed in a quartz tube with an inner diameter of 3 mm and measured at ambient temperature. X-ray fluorescence spectroscopy, or XRF (Bruker Model SRS 3004), was used to determine the amount of Fe.

Catalytic activity study

The epoxidation of styrene (Labscan) was carried out using a batch-type reactor. The catalyst (0.1 g), styrene (10 mmol), hydrogen peroxide (H_2O_2, Carlo Erba, 10 mmol of 30 wt% aqueous solution) and dimethylformamide (DMF, Labscan, 10 ml) were added to a glass flask. The reactant mixture was stirred vigorously at 60 °C reaction temperature for 2 h. All liquid products were quantified using a gas chromatograph with a capillary column (DB-Wax, 30 m × 0.25 mm) and a FID detector. The consumption of H_2O_2 was determined by iodometric titration.

Results and Discussion

Fe-MCM-41 catalyst

Wang *et al*.[9] synthesized a good quality Fe-MCM-41 with a surface area of 1100 $m^2\ g^{-1}$ at 1% iron loading using a sodium silicate precursor, via the direct hydrothermal and template ion exchange method. The reaction took more than 2 days for aging the sample, and provided more extra-framework species. Recently, Wongkasemjit's method using CTAB as a template and a silatrane precursor synthesized from an inexpensively starting material,
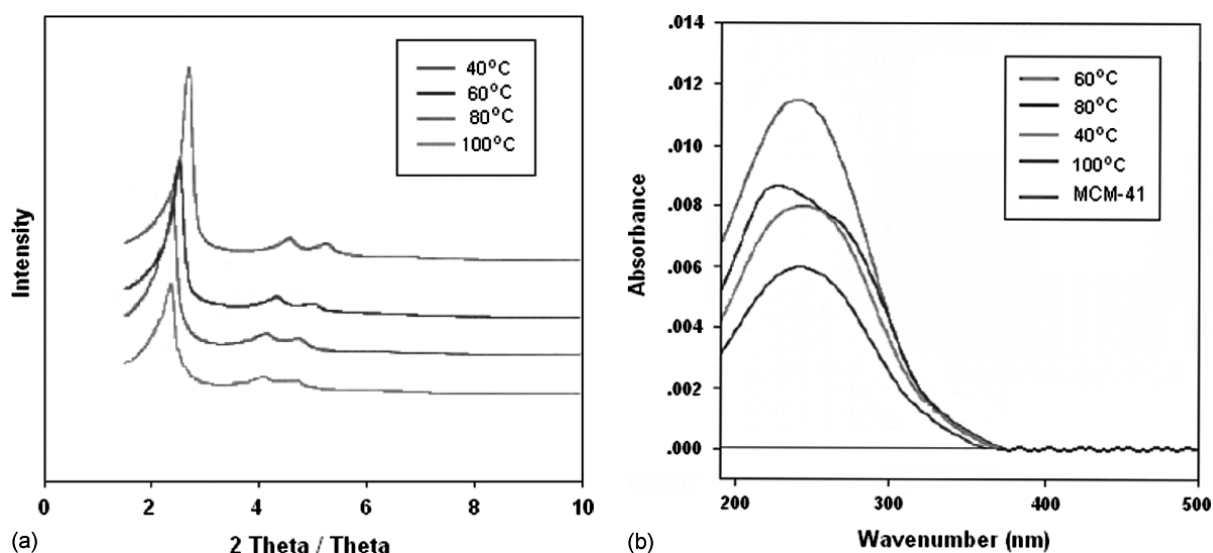

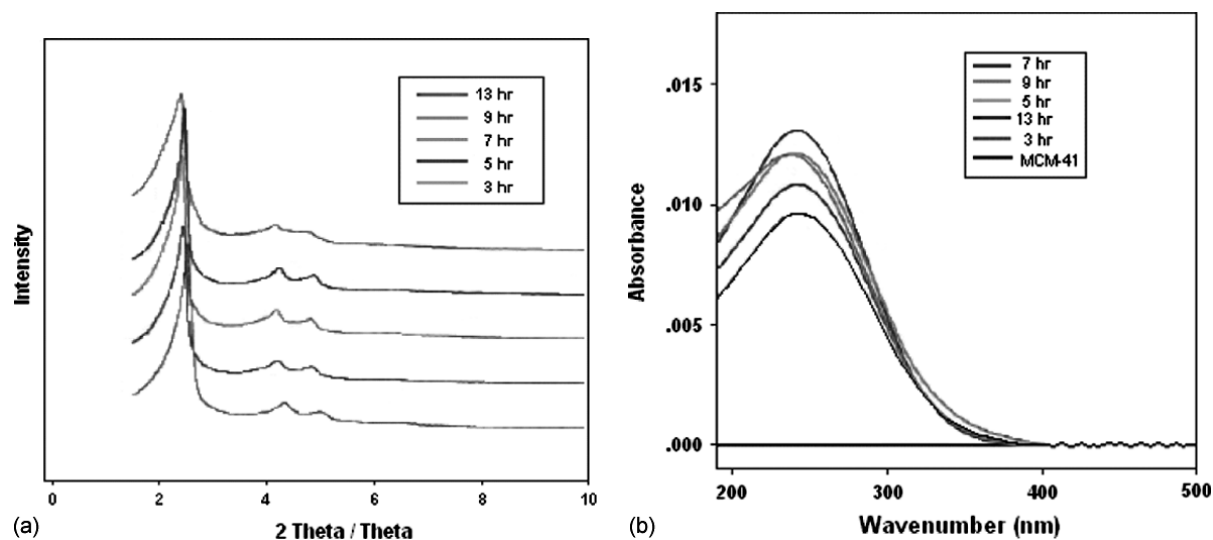**Figure 1.** (a) XRD and (b) DRUV spectra of the synthesized Fe-MCM-41 at different temperatures.

Figure 2. (a) XRD and (b) DRUV spectra of the synthesized Fe-MCM-41 at different aging times.
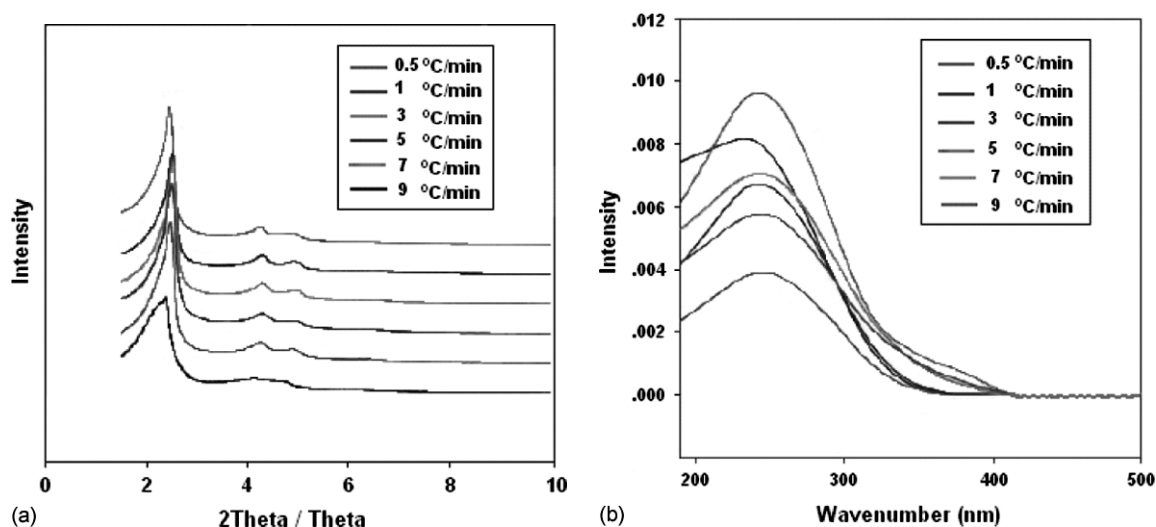
Figure 3. (a) XRD and (b) DRUV spectra of the synthesized Fe-MCM-41 at different calcination rates.

Table 1. BET and XRF analyses of Fe-MCM-41 synthesized at different temperatures

Temperature (°C)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Fe content by XRF (%)
40	1314	1.06	2.1	0.893
60	1625	1.21	2.2	0.991
80	1553	1.40	3.0	0.943
100	1290	1.09	3.2	0.804

Table 2. BET and XRF analyses of Fe-MCM-41 synthesized at different aging times

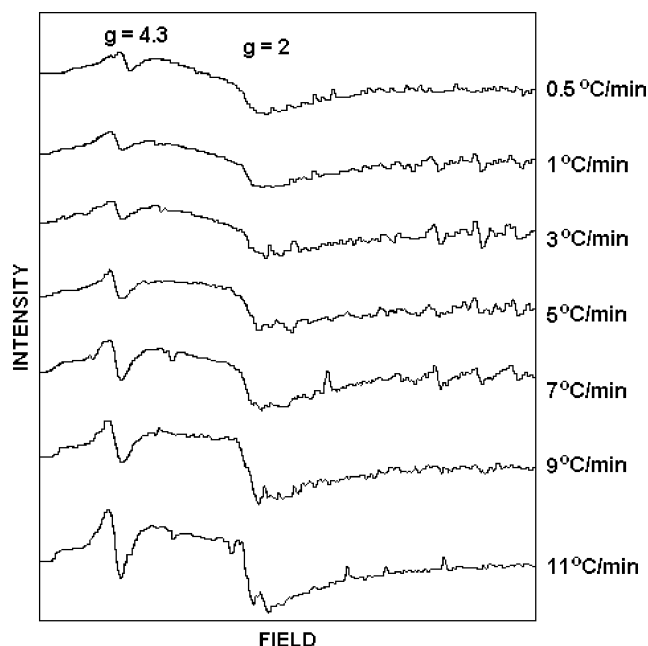| Time (h)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Fe content by XRF (%)
3	1504	1.12	2.6	0.87
5	1568	1.09	2.6	0.937
7	1698	1.12	2.7	1.078
9	1407	1.12	2.7	0.993
11	1395	1.14	2.8	0.956
13	1309	1.08	2.7	0.945

Figure 4. ESR spectra of synthesized Fe-MCM-41 at different calcinations rates.

SiO$_2$, successfully provided extremely high surface area MCM-41.[12] Fe-MCM-41 was synthesized by using CTAB as a template.[12] Following this method, a high-quality Fe-MCM-41, having a remarkable surface area up to ~1800 m^2 g^{-1} at 1% iron loading, was satisfyingly synthesized at lower reaction temperature and shorter aging time.

Generally, the XRD pattern of MCM-41 shows the diffraction lines of (100), (110) and (200), indexing to the hexagonal regularity of MCM-41.[12] Those three characteristic lines were also observed in our study of the Fe–MCM-41 samples. Moreover, DR-UV, employed to determine the site of the iron and also the presence of the Fe extra-framework, showed that all samples exhibited a peak at around 240–300 nm, similar to ferrisilicate containing tetrahedrally coordinated iron species.[9] This band is assigned to the dπ–pπ charge transfer between the Fe and O atoms in the framework of the Fe–O–Si bond. The contribution at long

wavelength to this band became larger with an increase of the Fe content. However, the presence of the extra-framework iron or the aggregated Fe oxide clusters of Fe$_2$O$_3$ at the high Fe content at around 385 and 510 nm suggests that there is an upper limit of the iron content incorporated inside the framework of MCM-41.[9]

Effect of temperature

It is known that temperature affects liquid crystal formation.[12] When increasing the mixing temperature from 40 to 100 °C at 1% Fe loading for 3 h aging time, the XRD spectra in our case showed a sharper peak, referring to bigger pore sizes, with a small shift of peaks to the lower degree of 2θ, as shown in Fig. 1. This is due to the fact that the higher temperature makes the surfactant tail more flexible to move or vibrate more freely,

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causing more occupied space of the surfactant in the pore and, as a result, causing a larger pore after removing the surfactant.[12] The diameters at 40 and 100 °C are 21 and 32 Å, respectively. This size is close to that of the CTAB micelle, ~39 Å.[12] Coincidentally, Cheng used the same sorption technique as our work and showed the increase in channel diameter from 27.1 to 36.5 Å when increasing temperature from 70 to 165 °C for 48 h reaction time.[13] However, in this work, when increasing the temperature up to only 60 °C, the XRD spectrum clearly showed the pattern of MCM-41, giving distinguishable peaks of the 110 and 200 reflections owing to the long-range order of the hexagonal array. As a result, the surface area and pore volume of the Fe-MCM-41 obtained from using silatrane are impressively high, and much higher (see Table 1) than atrane synthesized from another route,[9,10] probably due to our purer silatrane product obtained. In addition, the DR-UV results in Fig. 1 show the peak of the framework around 260–300 nm, indicating Fe incorporation in the MCM-41 framework, without the extra-framework peak. At a temperature lower than 60 °C, less iron can be incorporated inside the framework due to the smaller pore size, making it more difficult for an iron atom to be incorporated. At too high a temperature, ~100 °C, a smaller amount of iron can be incorporated due to the degradation of TEA generated from the silatrane; thus, the hydrolysis and condensation reactions are chaotic.[14] The results were also confirmed by XRF to determine the amount of iron, as shown in Table 1.

Effect of aging time

In this study, aging time is another important factor. For alkoxide-derived gel, a condensation reaction between surface functional groups continues to occur after the gel point. During aging, there are changes in most texture and physical properties of the gel. The strength of the gel, thereby, increases with aging. When increasing the aging time from 3 to 13 h at 1% Fe loading and 60 °C mixing temperature, XRD spectra are slightly different, as also indicated in previous work.[12] The 110 and 200 reflections were not obviously separated (see Fig. 2) when the aging time reached 13 h, meaning that the hexagonal array cannot be formed perfectly.[12] DRUV results show that the highest amount of iron was incorporated inside the framework at 7 h aging time (Fig. 2). At a shorter aging time, less than 7 h, less iron was incorporated inside the framework because there was not enough time for the Fe to be incorporated.

At an aging time longer than 7 h, a smaller amount of iron was also incorporated due to the reverse condensation reaction.[14] The results were confirmed by XRF, providing the amount of the iron in the sample, as listed in Table 2. BET surface area, pore size and pore volume are also summarized in Table 2. It was also found that the aging time had no effect on the surface area or pore volume, in agreement with the XRD results.

Effect of calcination rate

The major problem with iron atoms is the formation of an extra-framework iron species during template removal by calcination. Some works have reported that iron oxide clusters colored the materials in shades of brown, whereas framework iron is colorless, as discovered by Crowther and coworkers.[6] They also found that iron could be incorporated in the silica framework through direct synthesis by introducing an appropriate iron precursor in the synthesis gel. Using this technique, iron atoms at the edge of the pore walls are likely to represent resistant active centers. A substitution technique is more difficult than simple contact with the surface and there is often a mixture of both framework and extra-framework metal species.[9] Thus, the calcination rate was studied to find the condition for the least amount of extra-frameworks while the structure and surface area remain.

Calcination rate was varied from 0.5 to 11 °C min^{-1} at 1% Fe loading and 60 °C mixing temperature for 7 h aging time. As expected, the XRD patterns showed lower crystallinity with increased calcination rate, as shown in Fig. 3. The DRUV spectra in Fig. 3 show the extra-framework observed at 360 nm wavenumber and it is even more obvious when the calcinations were increased at a rate higher than 3 °C min^{-1}. The results were also confirmed using the ESR technique shown in Fig. 4. There were two signals at $g = 2.0$ and 4.3. It was reported that the signal at $g = 4.3$ could be attributed to Fe(III) in the tetrahedral coordination with strong rhombic distortion or framework form, and at $g = 2.0$ in the octahedral coordination or extra-framework form.[15–17] When increasing the calcination rate, the signal at $g = 2.0$ became strong and broad, indicating that more of the octahedral coordinated iron exists in the structure. Surprisingly, in terms of the surface area, the calcination rate did not have a significant effect (not shown).
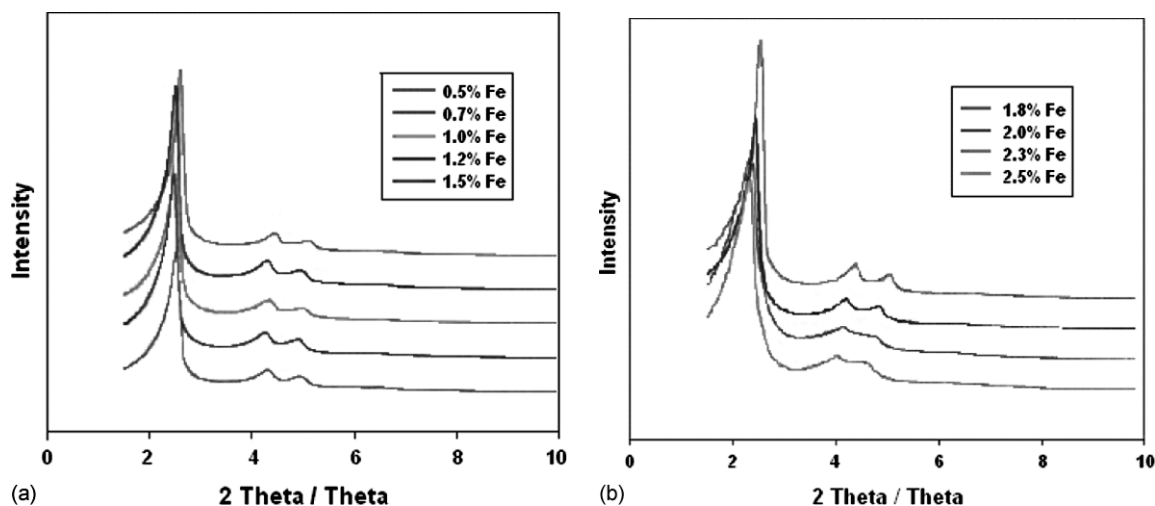

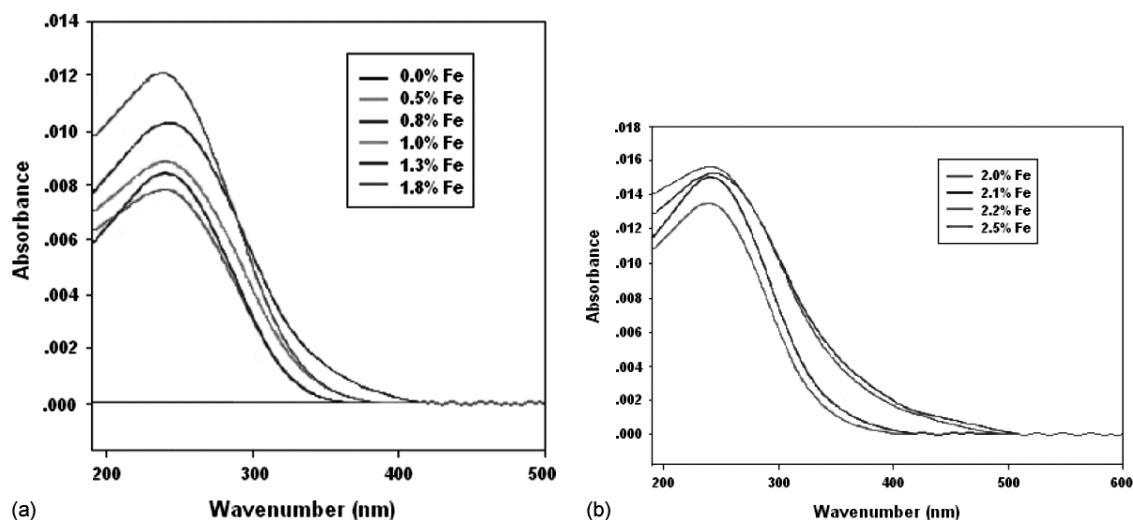**Figure 5.** XRD spectra of the synthesized Fe-MCM-41 at different amounts of Fe loading.

Figure 6. DRUV spectra of the synthesized Fe-MCM-41 at different amounts of Fe loading.
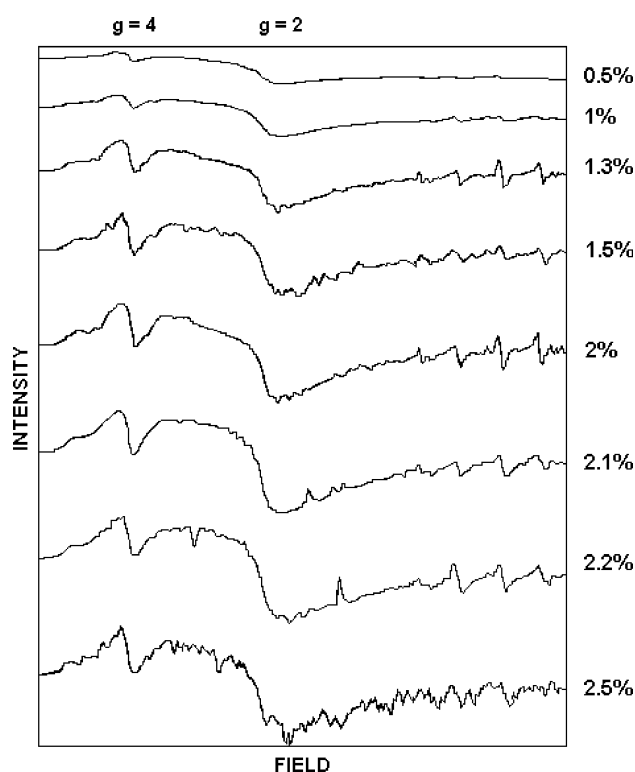

Figure 7. ESR spectra of the synthesized Fe-MCM-41 at different amounts of Fe loading.

Table 3. BET and XRF analyses of Fe-MCM-41 synthesized at different amounts of Fe loading

Loaded Fe (%)	BET surface area (m²/g)	Pore volume (cm³/g)	Average pore size (nm)	Fe content by XRF (%)
0	1885	1.16	2.4	0
0.5	1823	1.16	2.5	0.544
1	1724	1.20	2.8	1.078
1.3	1588	1.21	2.8	1.332
1.5	1539	1.21	3.0	1.495
2.0	1208	1.24	3.2	2.005
2.5	989	1.31	3.4	2.465

the amount of Fe, the signal at $g = 2.0$ became strong and observable. The XRF results in Table 3 show that the amount of iron in the samples is close to the amount of the actual loading. It was found that most of the iron loaded exists in the framework and the extra-framework. Thus, when increasing the amount of iron loading, the color of the sample was changed from white to brown (not shown). For the BET results in Table 3, the surface area was decreased, but the pore size and the pore volume were increased due to the large ionic radius of Fe^{3+}.[9]

Catalytic activity in styrene epoxidation reaction

Various factors, namely reaction temperature and time, and amount of the Fe-MCM-41 catalyst, were studied (not shown). We found that the optimal condition for styrene epoxidation over synthesized Fe-MCM-41 was at 0.1 g of the catalyst and 60 °C reaction temperature for 2 h reaction time. The factor presented here is the amount of Fe loaded. Figure 8 shows the results of the epoxidation of the styrene with diluted H_2O_2. Conversion of styrene was very low over pure MCM-41, although the conversion of H_2O_2 reached 50%, suggesting that iron was mainly responsible for the conversion of styrene with H_2O_2. The increase in the Fe content up to 1% improved the conversion of styrene observably and the selectivities of both styrene oxide and benzaldehyde were 64.68 and 35.31%, respectively, without any styrene glycol and benzoic acid. When the Fe content was higher than 1%, the conversion of styrene was slightly decreased, although the
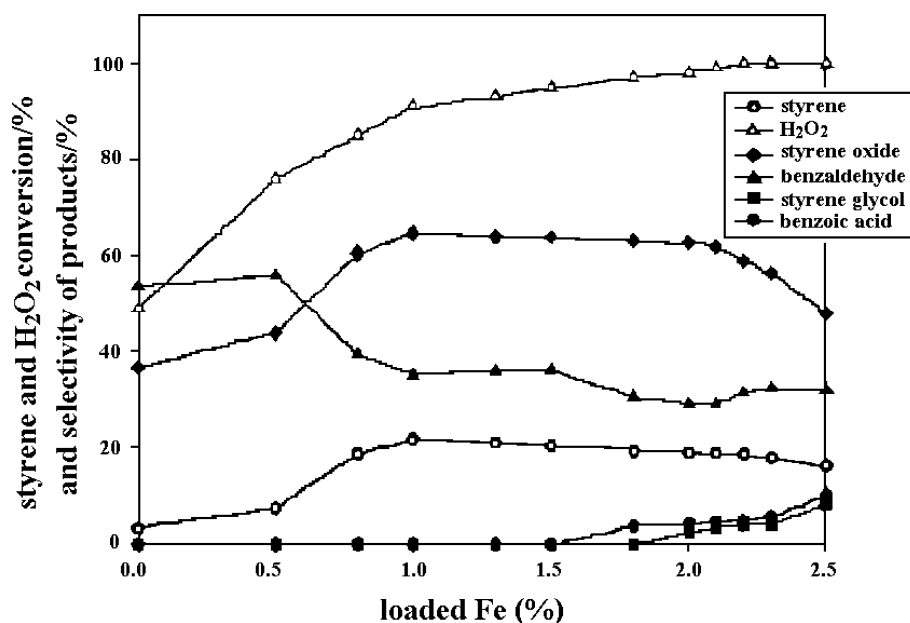
Effect of amount of Fe loaded

The calcined products at 0.5–2.5% Fe loading showed a well-resolved pattern of the hexagonal mesostructure (see Fig. 5). However, at high %Fe loading, the XRD patterns showed lower crystallinity, as indicated at the 100 reflection peak, and less isolation of the 110 and 200 reflection peaks. The DRUV spectra in Fig. 6 also show an increase in the extra-framework at 380 nm wavenumber with increased %Fe loading, and this was more obvious when the %Fe loaded was higher than 2.1%. The results were confirmed using the ESR technique (Fig. 7). When increasing

Figure 8. Change of catalytic performance with amount of loaded Fe.

Table 4. Comparison of catalysts for epoxidation of styrene

Catalyst (%)	Styrene conversion (%)	H_2O_2 conversion (%)	Selectivity (%)				H_2O_2 efficiency (%)
			Styrene oxide	Benzaldehyde	Styrene glycol		Benz â
0% Fe (s–g)	3.32	49	36.77	53.75	–	–	2.54
1% Fe (s–g)	21.89	91	64.68	35.31	–	–	15.88
2% Fe (s–g)	19.12	98	62.79	29.33	3.56	4.32	12.5
1% Fe (imp)	9.23	100	41.05	44.76	3.21	10.98	3.87
2% Fe (imp)	11.26	100	43.06	32.84	5.67	18.43	4.95

conversion of H_2O_2 still went up. Moreover, styrene glycol and benzoic acid were also observed.

In addition, the Fe-impregnated MCM-41 catalyst was also studied to compare it with the catalyst synthesized via the sol–gel technique. It was found that conversion of H_2O_2 was very high, but the conversion of styrene and the selectivity of the products was very low. The results summarized in Table 4, combined with the characterization results, suggest that the iron sites incorporated inside the framework of MCM-41 probably account for the epoxidation of styrene with H_2O_2, whereas the iron oxide clusters or iron species in the extra-framework position seem to accelerate the decomposition of H_2O_2.

Conclusions

Silatrane synthesized via the OOPS process is an excellent precursor for the synthesis of Fe-MCM-41. The optimal condition maintaining the hexagonal array of the MCM-41 structure is at 60 °C reaction temperature for 7 h, 550 °C calcination temperature and 1 °C/min calcination rate. When increasing the amount of Fe loading, the XRD patterns showed lower crystallinity. However, the obtained Fe-MCM-41 kept the structure of MCM-41 even when using 2.5% Fe loading. The extra-framework was observed when the %Fe loading was more than 2.1%. The iron cations could exist either outside or inside the framework of MCM-41, but the iron inside the framework was responsible for the conversion of styrene with H_2O_2 aqueous solution. The selectivity of styrene oxide reached 65% at a styrene conversion of 22% over 1% loaded Fe. Moreover, when compared with the impregnated catalyst, the sol–gel synthesis catalyst showed much better performance for the epoxidation of styrene.

References

[1] Liu SH, Wang HP. *Int. J. Hydrogen Energy* 2002; **27**: 859–862.
[2] Ryoo R, Jun S. *J. Phys. Chem. B* 1997; **101**: 317–320.
[3] Thanabodeekij N, Tanglumlert W, Gulari E, and Wongkasemjit S. *Appl. Organometal. Chem.* 2005; **19**: 1047–1054.
[4] On DT, Desplantier-Giscard D, Danumah C, and Kaliaguine S. *Appl. Catal. A: General* 2003; **253**: 545–602.

[5] Zhang Q, Wang Y, Itsuki S, Shishido T, and Takehira K. *Chem. Lett.* 2001; **CL-010566**: 946–947.

[6] Crowther N, Larachi F. *Appl. Catal. B: Environ.* 2003; **46**: 293–305.

[7] Tuel A, Gontier S, and Teissier R. *Chem. Commun.* 1996; **32**: 651–660.

[8] Carvalho A, Wallau M, and Schuchardt U. *J. Mol. Catal. A* 1999; **144**: 91–99.

[9] Wang Y, Zhang Q, Shishido T, and Takehira K. *J. Catal.* 2002; **209**: 186–196.

[10] Su B-L, Parvulescu V. *Catal. Today* 2001; **69**: 315–322.

[11] Piboonchaisit P, Wongkasemjit S, and Laine RM. *Science-Asia, J. Sci. Soc. Thailand* 1999; **25**: 113–119.

[12] Thanabodeekij N, Gulari E, and Wongkasemjit S. *Mater. Chem. Phys.* 2006; **98**(1): 131–137.

[13] Cheng FC, Zhou W, Klinowski J. *Chem. Phys. Lett.* 1996; **263**: 247–252.

[14] Yilmaz VT, Topcu Y, and Karadag A. *Thermchimica Acta* 2002; **383**: 129–133.

[15] Derouane EG, Mestsdagh M, and Vielvoye L. *J. Catal.* 1974; **33**: 169.

[16] Bordiga S, Buzzoni R, Geobaldo F, Lamberti C, Giamello E, Zecchina A, Leofanti G, Petrini G, Tozzola G, and Vlaic G. *J. Catal.* 1996; **158**: 486.

[17] Kritchayanon N, Thanabodeekij N, Jitkarnka S, Jamieson AM, and Wongkasemjit S. *Appl. Organometal. Chem.* 2006; **20**: 155–160.

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