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Synthesis of Fe-loaded MFI zeolite using silatrane as precursor and its CO activity

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Fe-MFI zeolite was successfully synthesized using silatrane as precursor and tetrapropyl ammonium bromide as template via the sol–gel process and microwave heating technique. The effects of ageing time, heating temperature, heating time and iron concentration were investigated, and it was found that Fe-MFI synthesis favors higher heating temperatures, but is limited by the degradation of the incorporation of a template molecule. Moreover, longer ageing and heating times promote the incorporation of higher amounts of iron atom in the MFI structure. However, too long an ageing time decreases the incorporation of iron. The lower the percentage Fe loading, the greater the percentage of Fe^{3+} ions incorporated into the MFI framework. The catalytic activity of Fe-MFI catalyst for the oxidation of CO was studied and it was found that these synthesized catalysts catalyzed the oxidation of CO very well. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: Fe-loaded MFI zeolite; tetrapropyl ammonium bromide (TPA); sol–gel process; silatrane

INTRODUCTION

MFI zeolites, with their high silica content, are of interest owing to their many applications, such as catalysis, separation process and ion exchange. This type of zeolite is not found in nature owing to its unique pore structure, thus, it needs an organic molecule to act as a template to form certain structures. The most effective organic templates are alkylammonium derivatives, such as tetrapropyl ammonium bromide (TPA).[1,2] Phiriyawirut *et al*.[3,4] have found a way to synthesize MFI zeolite via the sol–gel process and microwave technique, using silatrane as precursor, and either TPA or tetrabutyl ammonium bromide (TBA) as template. They also found that the tendency towards MFI formation can be improved by increasing the ageing and heating times.

Synthesis of Fe-MFI zeolites has received much interest in view of their excellent catalytic performance.[5] However, incorporation of iron in the zeolite framework appears to occur only via in the directly synthesized route.[6] The first attempt at synthesis of this material was carried out in alkaline media based on the hydrothermal crystallization.[7] Recently, the synthesis of Fe-MFI zeolite using different inorganic salts under fluoride media has also been reported.[8]

CO oxidation is of interest due to its considerable environmental toxicity; only small exposures (ppm) can be lethal. A number of investigations have therefore been focused using gold-based catalysts for CO oxidation.[9–12] It is also found that the activity of CO is greatly influenced by the catalyst preparation methods.[13–15] Owing to the scarcity and high cost of these catalysts, and uniform as well as homogeneous MFI synthesized by Phiriyawirut *et al.*,[3,4] in this work, Fe-MFI zeolite catalysts were used to study the oxidation activity of CO.

Synthesis of iron-loaded MFI zeolite was carried out using silatrane as a zeolite synthesis precursor and sodium hydroxide as a hydrolysis agent and the source of sodium ions via the sol–gel process, followed by the microwave heating technique. Various parameters were studied to find the optimum condition to incorporate Fe atoms into MFI zeolite. The influence of the preparation method on the catalytic activity in the oxidation of CO was investigated.

EXPERIMENTAL

Materials

Fumed silica (SiO_2) and iron(III) chloride ($FeCl_3$) were supplied from Aldrich Chemical. The ethylene glycol

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($HOCH_2CH_2OH$) reaction solvent was obtained from J.T. Baker. Triethanolamine (TEA, $N[CH_2CH_2OH]_3$) and acetonitrile (CH_3CN) were purchased from Labscan Co. Ltd. Sodium hydroxide (NaOH) and potassium nitrate (KNO_3) were purchased from EKA Chemicals. Tetrapropyl ammonium bromide (TPA) was obtained from Fluka Chemical AG. All chemicals were used as received. Carbon monoxide (CO) 24.85% in helium was supplied from Thai Industrial Gases (Public) Co. Ltd. Oxygen in helium at a ratio of 20 : 80 was supplied from Praxair (Thailand) Co. Ltd. High-purity helium was supplied from Thai Industrial Gases (Public) Co. Ltd.

Instrumentation

The crystal morphology was studied using a Jeol 5200-2AE scanning electron microscope (SEM). The crystal structure was characterized using a Rigaku X-ray diffractometer (XRD) at a scanning speed of 5 deg/s using Cu$K\alpha$ as incident radiation and a filter. The working range was 3–50° $\theta/2\theta$ with 1°, 0.3 mm setting of the divergent, scattering and receiving slits, respectively. UV–visible spectroscopy was performed on a Shimadzu UV-2550 with ISR-2200 integrating sphere attachment, using $BaSO_4$ as a reference sample. The Si : Fe ratio was determined by X-ray fluorescence (XRF) spectroscopy (Bruker model SRS 3400). Electron spin resonance (ESR) spectroscopy was measured at X-band, ~9 GHz, on an ESPRIT-425 vol. 604 spectrometer.

Catalyst preparation procedure

Silatrane synthesis (Si-TEA)

The procedure utilized followed previous work[16] by heating a mixture of TEA (0.125 mol), SiO_2 (0.1 mol) and EG (100 mL) at 200 °C under nitrogen atmosphere. The reaction was complete within 10 h, and the mixture was cooled to room temperature before distilling off the excess EG under vacuum (8 mmHg) at 110 °C. The brownish white solid was washed three times with dried acetonitrile to obtain a fine white powder. The silatrane product was characterized using XRD, TGA and FTIR.

FT-IR bands observed were 3000–3700 cm^{-1} (weak, intermolecular hydrogen bonding), 2860–2986 cm^{-1} (strong, νC–H), 1244–1275 cm^{-1} (medium, νC–N), 1170–1117 (broad-strong, νSi–O), 1093 (strong, νSi–O–C), 1073 (strong, νC–O), 1049 (strong, νSi–O), 1021 (strong, νC–O), 785 and 729 (strong, νSi–O–C) and 579 cm^{-1} (weak, Si ← N). TGA shows one sharp mass loss transition at 390 °C with 19% ceramic yield corresponding to $Si[(OCH_2CH_2)_3N]_2H_2$ having the theoretical yield 18.58%.

Fe-MFI synthesis

Following previous studies,[3,4] silatrane and TPA were dispersed in water using the SiO_2 : 0.1 TPA : 0.4 NaOH : 144 H_2O : 0.01 $FeCl_3$ formula, and continuously stirred before adding iron(III) chloride. To establish the optimum reaction conditions for loading 1% Fe in the gel, the effects of ageing time, heating time and temperature were studied. Additionally, the effect of percentage Fe loading was also studied by varying the percentage from 1 to 6. The synthesized Fe-MFI products were calcined in an electronic furnace set at 550 °C with a heating rate of 0.5 °C/min. The calcined products were characterized using XRD, SEM, DR-UV, XRF and ESR. The framework and the extra framework of Fe-MFI were also determined using ion-exchange technique to confirm the results from these spectroscopic techniques. The Na^+ counter ion in the synthesized Fe-MFI product was exchanged with 0.1 M KNO_3, and the percentage extra framework was calculated from the K^+ : Fe ratio.

Gas blending system

The reactant mixture consisted of 1% carbon monoxide and 0.45% oxygen balanced in helium. To obtain a desired component of the typical reactant mixture, a mass flow controller (Sierra Instrument Inc., model 840) was applied to control the flow rate of each reactant gas. The reactant mixture was passed through a check valve to protect reverse flow before being passed to the reactor.

Catalytic reactor

Catalyst (200 mG) was packed in the middle of a 1 cm outside diameter borosilicate glass reactor containing glass wool. The experiment was performed at atmospheric pressure with a space velocity of 42 000 h^{-1}. The reaction temperature studied ranged from 323 to 723 K, controlled by a PID controller equipped with K-type thermocouple (Yokohama, model UP27). The final product gas was quantitatively and qualitatively analyzed using Hewlett Packard 3365 series II Chemstation with a molecular sieve 13× column for O_2 and N_2 mixture concentration.

RESULTS AND DISCUSSION

Fe-MFI characterization

In this study, TPA was used as the template for producing Fe-MFI. Following previous studies,[3,4] the formulation was SiO_2 : 0.1 TPA : 0.4 NaOH : 144 H_2O for producing small and perfect MFI crystals. To load Fe into the MFI structure, it was necessary to investigate the effects of parameters such as ageing time, heating temperature, heating time and Fe concentration in precursors on the amount of iron in the MFI framework.

Effect of ageing time

To investigate the effect of ageing time, the heating temperature and time were fixed at 150 °C and 10 h, respectively. The iron concentration was fixed at 1 mol% $FeCl_3$. SEM results of samples aged at various times are shown in Fig. 1. When the mixture was aged for 36 h [Fig. 1(a)], amorphous material was obtained. On increasing the ageing time to 60 h [Fig. 1(b)], no amorphous phase was observed, and fully grown crystals were obtained. The crystal size decreased with increase in the ageing time, due

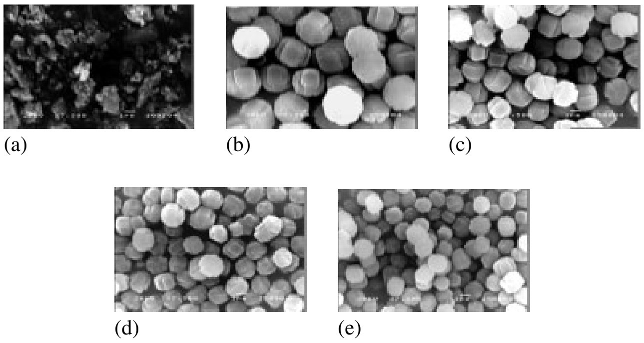

Figure 1. Effect of the ageing time on the product morphology at 150 °C for 10 h: (a) 36, (b) 60, (c) 84, (d) 108 and (e) 132 h.

to increased nucleation. However, the crystal sizes are not significantly different at ageing times between 84 and 132 h. As seen in SEM, the particles of Fe-MFI zeolites obtained are nicely uniform and homogeneous when compared with those Fe containing MFI zeolites synthesized in other works.[17,18]

To confirm the SEM results, XRD analysis was performed and indeed shows a broad amorphous peak at $2\theta = 23°$ [Fig. 2(B)] when the sample was aged for 36 h. This broad XRD peak disappeared when the sample was further aged for 60 h [Fig. 2(B)], which agrees with the SEM results. In addition, the DR-UV results shown in Fig. 3 indicate mainly the intense absorption band at 200–245 nm, which is characteristic of Fe^{3+} charge transfer associated with iron incorporated in the MFI framework.[18] The absorbance bands at 277 and above 300 nm, assigned to the octahedral complex of iron and the extra-framework cluster of Fe_2O_3,[18] respectively, were barely observed.

XRF analysis was used to confirm the total amount of Si and Fe in the zeolite (both inside and outside the framework), as listed in Table 1. The percentage Fe incorporation (in calcined samples) increases as the ageing time increases to 84 h, and then decreases again, probably due to the limitation of the MFI structure in allowing a certain amount of iron to be incorporated. At too short an ageing time, the diffusion of

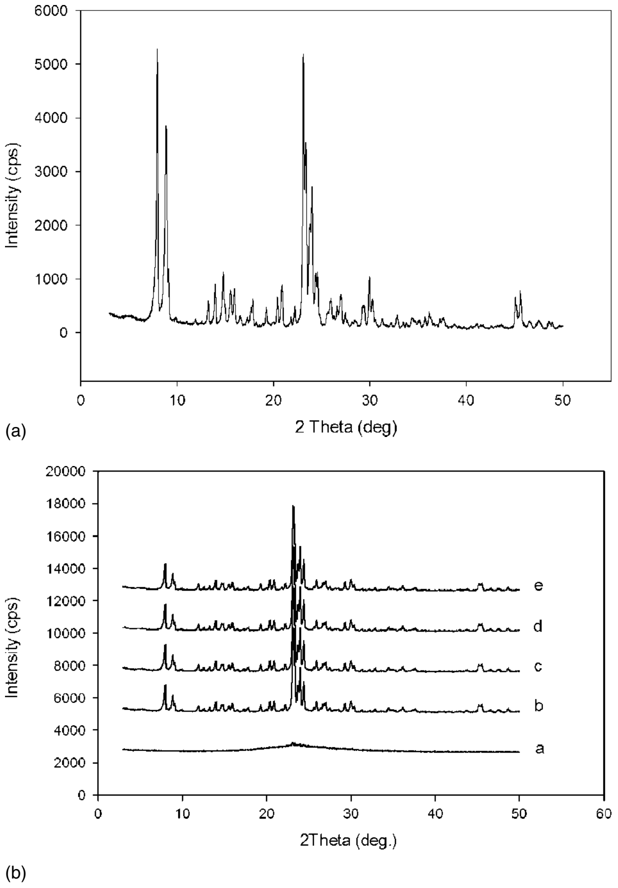

Figure 2. XRD spectra of (A) MFI zeolite and (B) Fe-MFI at various ageing times of: (a) 36, (b) 60, (c) 84, (d) 108 and (e) 132 h.

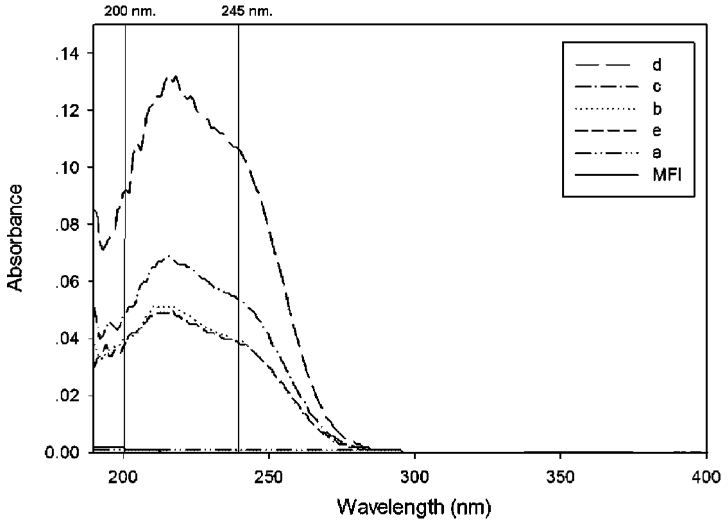

Figure 3. DR-UV spectra of Fe-MFI at various ageing times of: (a) 36, (b) 60, (c) 84, (d) 108 and (e) 132 h and MFI zeolites.

Table 1. Effect of ageing time on the % Fe incorporated in Fe-MFI samples determined using XRF analysis

Ageing time (h)	Fe load (%)	Fe incorporated (%)
36	1	—
60	1	0.72
84	1	0.99
108	1	0.86
132	1	0.81

Fe to be incorporated in the zeolite framework may not be complete, while at too long an ageing time, the reverse reaction may occur.[19] It can be seen that the iron content is lower than the actual loading in every condition, reflecting part of the iron being washed out during the cleaning process.

Effect of heating temperature

From studies of the effect of ageing time, the sample aged for 84 h gives homogeneous MFI crystals, and also provides the highest amount of iron in the solid sample. Thus, in this experiment, the ageing and heating times were fixed at 84 and 10 h, respectively. It is known that increasing temperature affects not only the growth rate and the product morphology,[3] but also enhances condensation of the transition metal. SEM and XRD (not shown) results showed the same patterns as Figs 1 and 2, and a crystalline phase was formed after heating at 130 °C. The crystal size increased with increased heating temperature owing to an increase in the growth rate. Moreover, similar DR-UV spectra were obtained. However, the absorbance peak in the range of 200–245 nm ultraviolet regions, assigned to Fe^{3+} in a tetrahedral environment, increased when the heating temperature was increased. These results were confirmed by the XRF data in Table 2, showing an increase in the percentage Fe incorporation of the solid when the temperature was increased, indicating that increasing the temperature increased the condensation of Fe into the MFI structure.[20] However, at 170 °C, percentage Fe incorporation decreased again, possibly due to degradation of the template molecule.[21]

Effect of heating time

To obtain fully grown crystals and the highest amount of iron incorporated in the MFI structure, the ageing time and heating temperature were set at 84 h and 150 °C, respectively. In this study, the heating time was varied from 5 to 20 h using the microwave technique. The SEM, XRD and DR-UV results (not given) showed similar profiles to Figs 1–3, indicating an increase in Fe-MFI crystal size and crystallinity with heating time. However, DR-UV results indicated that the heating times of 15 and 20 h gave a lower absorbance intensity, characteristic of iron incorporated in the MFI framework, than a heating time of 10 h. The reason appears to be that some iron cannot tolerate long heating conditions, thus it is released from the structure, and becomes extra-framework, as indicated by the XRF results (Table 3). In summary, a heating time of 10 h is optimal, resulting in the largest amount of iron incorporated in MFI.

Table 2. Effect of the heating temperature on the % Fe incorporated in Fe-MFI samples aged and heated for 84 and 10 h, respectively, using XRF analysis

Heating temperature (°C)	Fe load (%)	Fe incorporated (%)
110	1	0.85
130	1	0.87
150	1	0.99
170	1	0.71

Table 3. Effect of the heating time on % Fe incorporated in Fe-MFI samples aged for 84 h and heated at 150 °C using XRF analysis

Heating Time (h)	Fe loaded (%)	Fe incorporated (%)
5	1	0.88
10	1	0.99
15	1	0.74
20	1	0.75

Effect of iron concentration

The effect of Fe loading on the crystal morphology was studied at percentage Fe loadings of 1, 2, 3, 4, 5 and 6, while fixing the ageing time at 84 h, and with microwave heating at 150 °C for 10 h. SEM results (Fig. 4) showed a change in the morphology of crystals from the cubic MFI shape with increase in iron content. As iron loading increased, the crystal size seemed to decrease and the crystal shape became

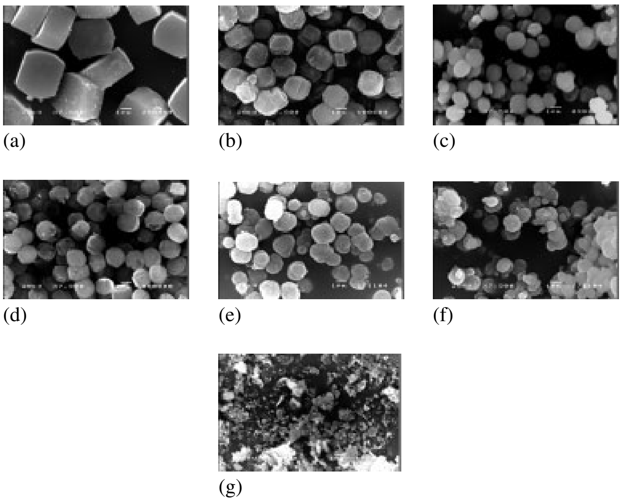

Figure 4. Effect of the iron concentration at various Fe loadings on the product morphology aged at room temperature for 84 h, and heated at 150 °C for 10 h: (a) MFI, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5 and (g) 6%.

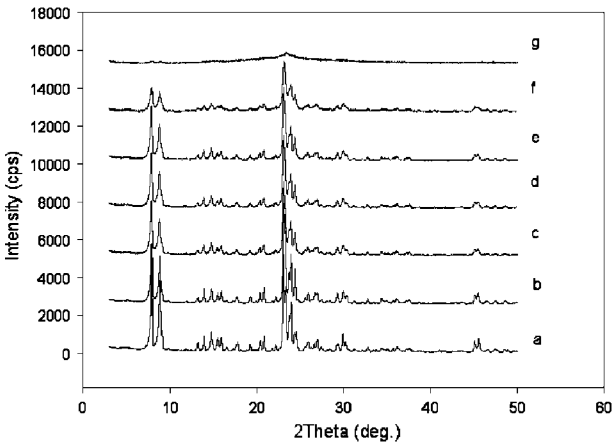

Figure 5. XRD spectra of Fe-MFI at various Fe loadings: (a) MFI, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5 and (g) 6%.

rounder and less homogeneous, reflecting distortion of the MFI lattice due to the difference in size between iron and silicon atoms, as also observed in previous work.[17] However, at an Fe loading of 6%, amorphous phase was observed since the zeolite structure collapsed. This was confirmed by XRD analysis, which showed a broad amorphous peak at $2\theta = 23°$ (Fig. 5).

Table 4 shows that the amount of iron in calcined samples was almost the same as the amount of iron loaded. However, the samples at Fe loadings of 1, 2 and 3% were white in color, whereas the samples at Fe loadings of 4, 5 and 6% were yellow-white, slightly yellow and yellow in color, respectively. This probably reflects the deposition of extra-framework Fe outside the crystallites.[22] To confirm the presence of both framework and extra-framework Fe in MFI structure, qualitative study using ESR was carried out. ESR results (Fig. 6) of the samples at the different Fe loadings of 1, 2, 3, 4, 5 and 6% showed two main signals at $g = 4$ and $g = 2$, which were assigned to Fe^{3+} in lattice and cationic positions, and/or oxide of Fe [such as α-Fe_2O_3, γ-Fe_2O_3 and FeO(OH)], respectively, as discussed by Phu *et al.*[22] From these results, it can be confirmed that both framework and extra-framework Fe appear together in the Fe-MFI samples.

To quantitatively determine the distribution of framework and extra-framework Fe, ion-exchange technique experiments were conducted.[22] The Na^+ counter ion in the synthesized Fe-MFI zeolite was exchanged with K^+ from KNO_3. The incorporation of iron in MFI framework can be determined from the K^+:Fe ratio where K^+ is the number of exchanged K^+ ions, and Fe is the overall amount of Fe in the zeolite. If the K^+:Fe ratio is equal to 1, all iron in the gel is incorporated into the crystalline lattice of the zeolite, and for ratios <1, a fraction of iron must be located outside the zeolite framework. The results are summarized in Table 5, indicating the incorporation of iron into the zeolite lattice at various iron concentrations of Fe loadings between 1 and 6%. The results show that, when Fe loading increased, the amount of iron incorporated in the crystalline lattice diminished. This incorporation varied from 98 to 42%. The percentage of extra-framework Fe was approximately 58% for 5% Fe loading, and 2% for 1% Fe loading. According to Phu *et al.*,[22] our synthesized Fe-MFI contained a higher amount of Fe in the framework.

Table 4. Effect of iron concentration on the percentage Fe incorporated in iron-MFI samples aged for 84 h and heated at 150 °C for 10 h using XRF analysis

Fe loaded (%)	Fe incorporated (%)	Color
1	0.99	White
2	0.96	White
3	0.94	White
4	0.96	Yellow-white
5	0.87	Slight-yellow
6	—	Yellow

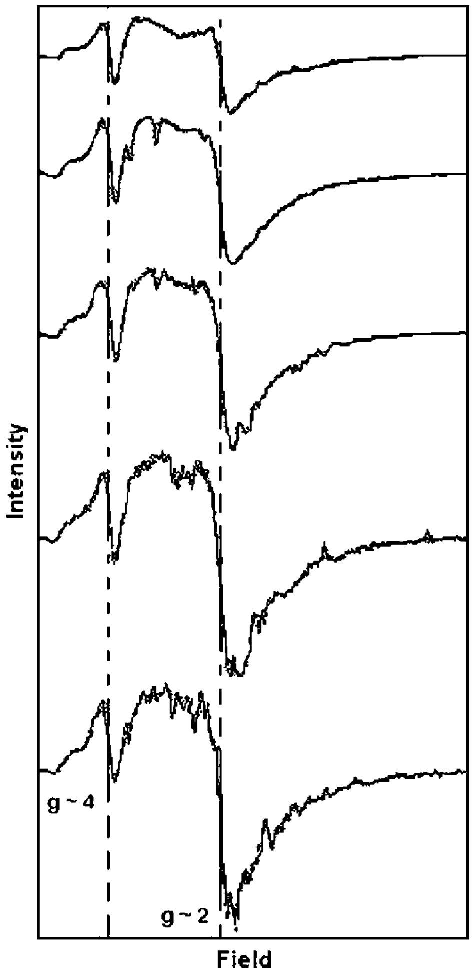

Figure 6. ESR spectra of Fe-MFI at various Fe loadings: (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5%.

Catalytic activity testing

The Fe-MFI samples synthesized at Fe loadings of 1, 3 and 5% were selected as representative catalysts to evaluate the

Table 5. Ion-exchange over Fe-MFI zeolites

Sample	Fe loaded (%)	Fe overall amount (%mmol)	K^+ exchanged ion amount (%mmol)	K^+ : Fe	Fe intra-framework fraction (%)
1	1	13.48	13.20	0.98	98
2	2	59.55	41.70	0.70	70
3	3	47.40	28.23	0.60	60
4	4	61.84	29.46	0.48	48
5	5	67.81	28.45	0.42	42

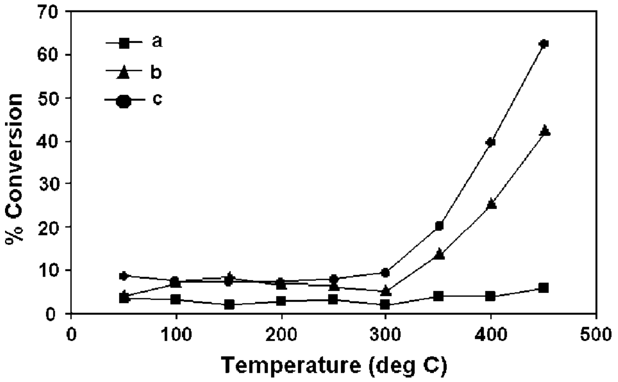

Figure 7. CO conversion profiles over Fe-MFI at various Si : Fe ratios: (a) 1, (b) 3 and (c) 5%.

catalytic activity for oxidation of CO. The experimental results indicate that CO oxidation profiles for the synthesized Fe-MFI catalysts in $CO + O_2 \rightarrow CO_2$ in Fig. 7, presented as a function of reaction temperature from 50 to 450 °C for Fe-MFI catalysts synthesized at 5% (curve a), 3% (curve b) and 1% (curve c), show that at 5% Fe Fe-MFI catalyst provided the highest activity, around 62.29% CO conversion at a temperature of 450 °C. This result is coincident with Malero *et al.*[18] and Lobree *et al.*,[23] who also found that the higher the Fe loadings, the higher the Fe^{3+} charge transfer, resulting in the higher oxidation reaction. The synthesized Fe-MFI catalysts at the 3 and 1% Fe loadings gave lower CO conversions of around 24.54 and 5.95%, respectively.

CONCLUSIONS

Fe-MFI zeolite was successfully synthesized via the sol–gel process and microwave technique, using silatrane and TPA as the precursor and template, respectively. A higher heating temperature was preferred for Fe-MFI synthesis due to higher promotion of iron condensation into the zeolite structure. However, this statement is limited by the degradation of the template molecule. In addition, increase of ageing and heating times promoted increased incorporation of iron into the MFI structure. However, too long times decreased the incorporation of iron. All synthesized Fe-MFI zeolites contained iron in two different forms: framework and extra-framework. The fraction of framework Fe increased proportionally with decrease in the Fe loading. The synthesized Fe-MFI zeolite catalyzed the oxidation of CO in this reaction.

Acknowledgments

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