CHAPTER IV

RESULTS AND DISCUSSION

The characteristics of the prepared catalysts and their catalytic activity on methanol conversion to olefins were investigated. The results and discussion are shown as follows.

4.1 Characterization of the Fe-MFI Catalysts

4.1.1 Effect of pH of Gel on Formation of Fe-MFI

4.1.1.1 XRD Results

XRD patterns of as-synthesized Fe-MFI (Si/Fe ratio in gel of 90) prepared at different pH are 8.0, 9.0, 9.5, 10.0, 10.5, and 11.0 in the small-scale preparation are shown in Figure 4.1. The characteristic pattern of MFI structure is comparable to those of all catalysts without any other impurity phase. The intensity of the highest XRD peak (2 theta of 23.1) slightly decreases (intensity = 14,056, 11,785, 11,366, 10,439, 11,421, and 10,231 for the gel pH value of 8.0, 9.0, 9.5, 10.0, 10.5, and 11.0, respectively). This indicates that the crystallinity of these catalysts is affected by the pH of gel, at least in the case of Si/Fe ratio of 90.
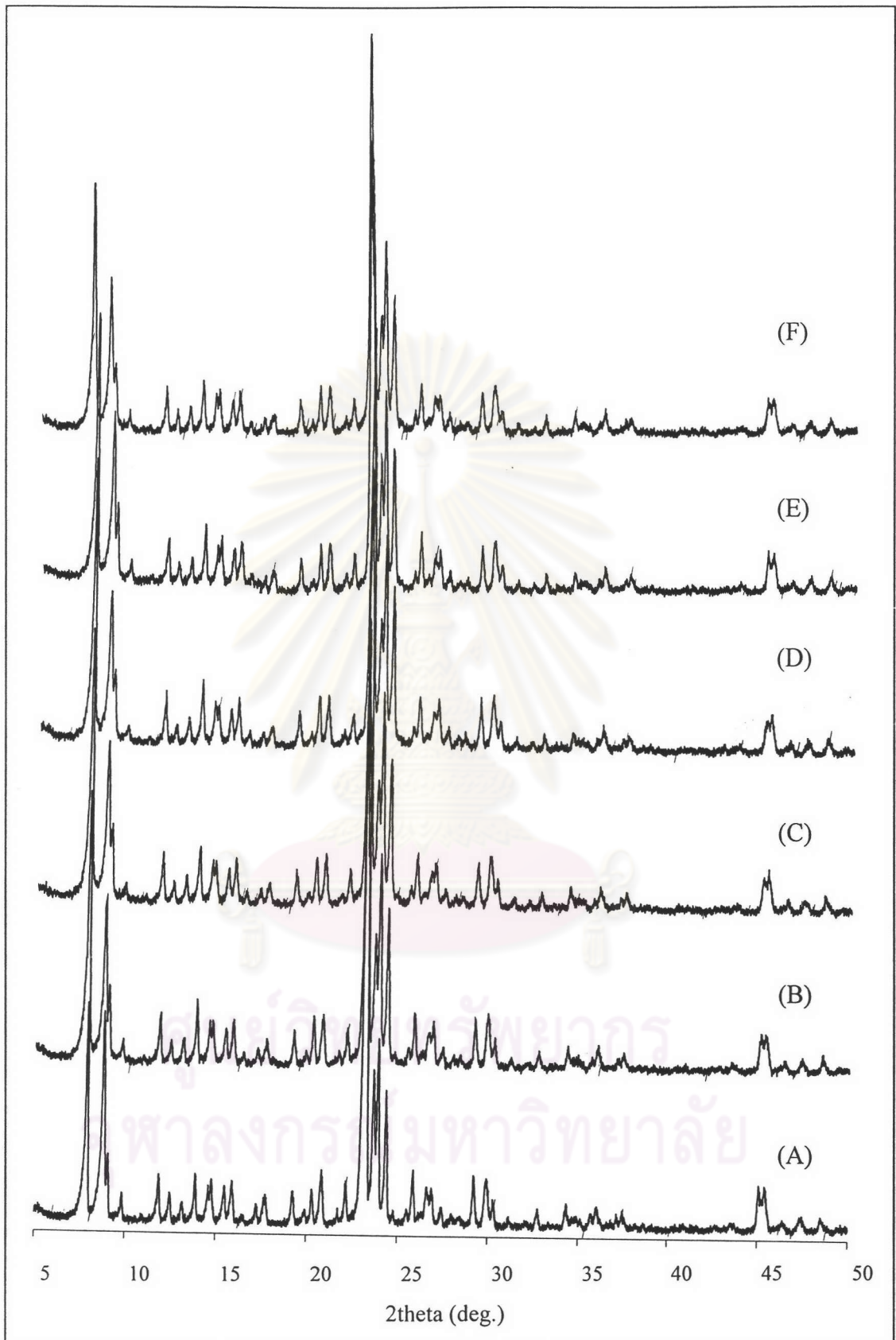
Figure 4.1 XRD patterns of as-synthesized Fe-MFI (the Si/Fe ratio in gel of 90) prepared at the small scale and different pH gel value, (A) pH = 8.0, (B) pH = 9.0, (C) pH = 9.5, (D) pH = 10.0, (E) pH = 10.5, and (F) pH = 11.0.

4.1.1.2 SEM Images

SEM images of as-synthesized Fe-MFI (the Si/Fe ratio in gel of 90) prepared at different pH are 8.0, 9.0, 9.5, 10.0, 10.5, and 11.0 in the small-scale preparation shown in Figure 4.2. The particle size and morphology are affected by the pH of gel. All six catalysts have in general varied uniform size distribution, and no amorphous matter is observed on external surface. Specifically, polycrystals with cylindrical shape are observed at the pH value of 8.0. When the pH of gel increases to 9.0 and 9.5, the particle size decreases and uniform twinned plus-like crystals are formed. Parts of them are inflated and become tomato-like, and the particle size increases when the pH value increases to 10.0. Large particle size and regular spherical shape of polycrystals are obtained at the pH value of 10.5. At the pH value of 11.0, the small spherical shape and, in addition, fan-like polycrystals are formed and the particle size decreases again. The reason may be due to more nuclei are formed in the higher alkalinities in the synthesis of the MFI catalyst.[73] The relation of the particle size and morphology of Fe-MFI with the pH of gel are revealed in Table 4.1 and Figure 4.3. The particle size decreases with increasing the pH of gel from 8.0 to 9.5, and increases beyond this point, and finally decreases again.

Kyu-Wan *et al.*[73] studied the effect of pH of gel (pH = 8.0 to 11.0) on the crystal size and morphology of Fe-MFI (the Si/Fe ratio in gel of 300). It was found that the crystal size decreased with increasing the pH of the starting gel mixture. Moreover, the twinned crystals shrinked and became cubic-shape at the pH value of 11.0. The results are different from this work. The reasons may be due to different iron content and Si sources. In this work, sodium silicate was used as Si source for the synthesis of Fe-MFI with the Si/Fe ratio in gel of 90, while tetraethylorthosilicate (TEOS) was used as Si source for the synthesis of Fe-MFI with the Si/Fe ratio in gel of 300. Similar study regarding the pH of gel in case of galloaluminosilicate (Ga-MFI) was also reported.[96]
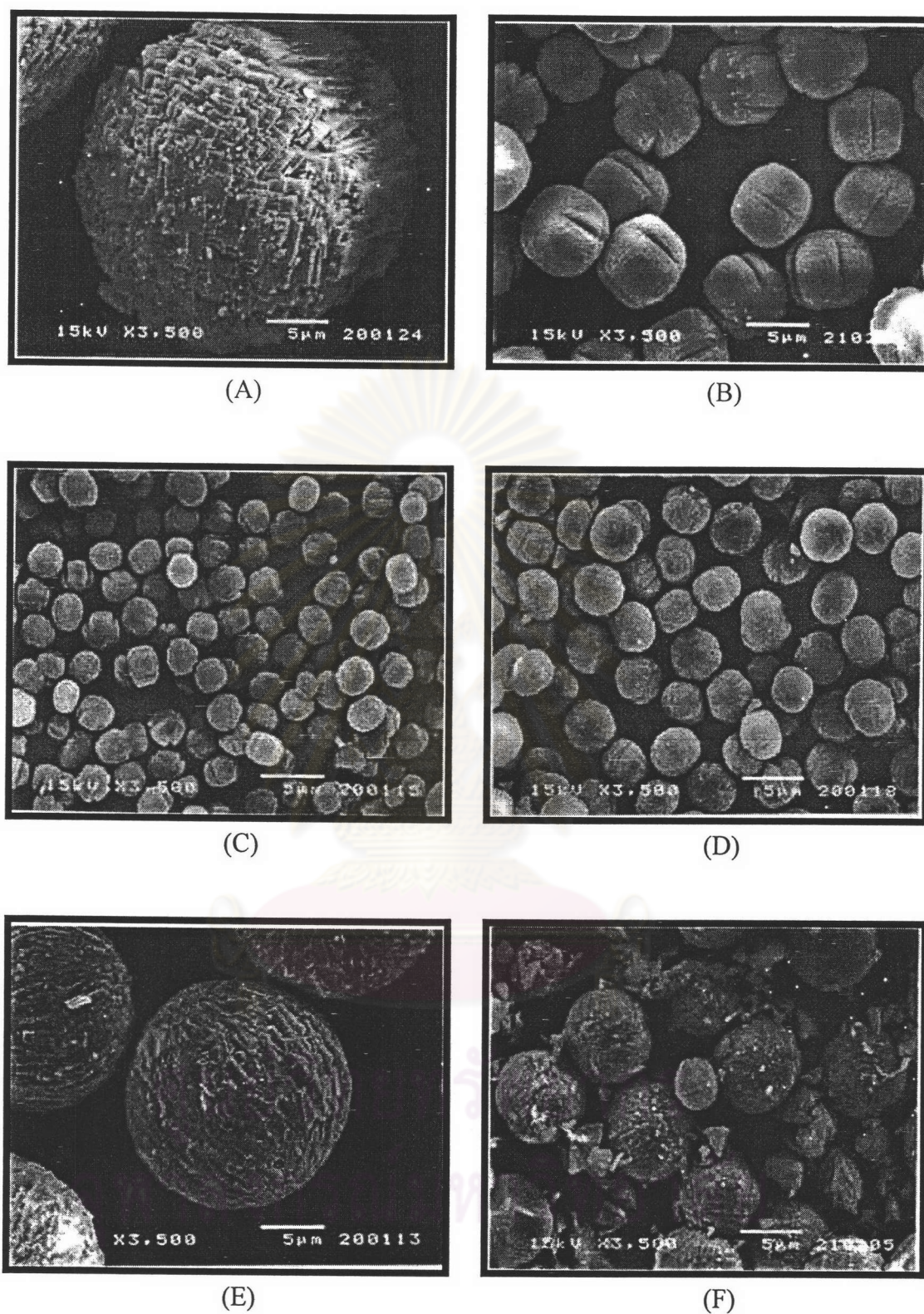
Figure 4.2   SEM images of as-synthesized Fe-MFI (the Si/Fe ratio in gel of 90) prepared

at the small scale and different pH gel value, (A) pH = 8.0, (B) pH = 9.0, (C)

pH = 9.5, (D) pH = 10.0, (E) pH = 10.5, and (F) pH = 11.0.

Table 4.1 The relation of the pH of gel on the mean particle size and morphology of as-synthesized Fe-MFI with the Si/Fe ratio in gel of 90 in the small-scale preparation

pH of gel	Mean particle size (μm)	Morphology
8.0	29[a]	Cylindrical shape
9.0	7.6[b]	Twinned plus-like
9.5	2.6[a]	Twinned plus-like
10.0	4.3[a]	Inflated twinned plus-like (tomato-like)
10.5	18[a]	Spherical shape
11.0	6.8[a]	Spherical shape and fan-like

[a] *The mean particle size of catalysts are estimated from SEM images.*
[b] *The mean particle size of catalysts are estimated from particle size analyzer.*
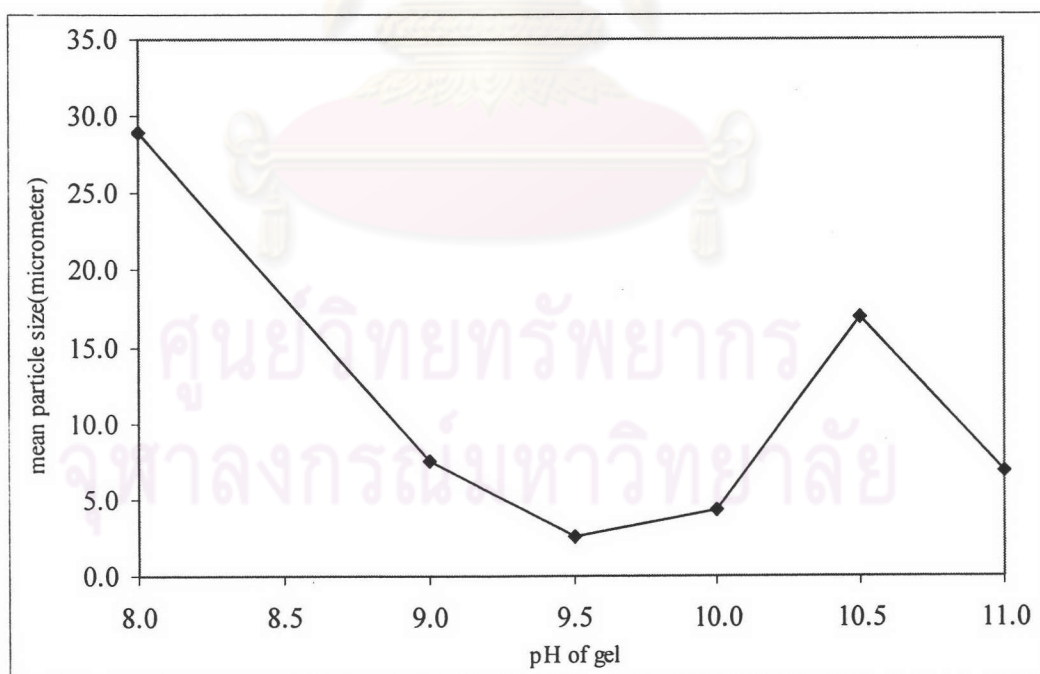

Figure 4.3 Effect of the pH of gel on the particle size of as-synthesized Fe-MFI with the Si/Fe ratio in gel of 90 in the small-scale preparation.

4.1.1.3 ESR Results and Chemical Analysis

ESR spectra recorded at room temperature for calcined Fe-MFI with the Si/Fe ratio in gel of 90 prepared at different pH of gel in the small-scale preparation are revealed in Figure 4.4. Two signals appeared at the g value of 1.9 and 5.3 for all cases of the catalysts. These signals have been commonly accepted as Fe^{3+} in cationic sites located at non-framework iron sites, and Fe^{3+} framework iron sites, respectively.[39,47-68] ESR data and Si/Fe ratio in catalyst of the Fe-MFI catalyst (the Si/Fe ratio in gel of 90) prepared at the small scale obtained from different pH are shown in Table 4.2. There is no significant difference in the ESR peak relative intensity of framework iron site from synthesis at the pH value of 9.0 to 10.5, while the synthesis at the pH value of 8.0 and 11.0, result in the lower relative intensity. It indicates that the incorporation of iron to framework of silicate is affected by the pH of gel. This results are different from these reported by Kyu-Wan *et al.*[73] who studied the effect of pH (pH = 8.0 to 11.0) of the synthesis gel on the preparation of Fe-MFI with the Si/Fe ratio of 300. They found that the ESR spectra showed two signals with a broad signal at g = 2.0 (non-framework) and sharp signal at g = 4.3 (framework) and the intensity of the ESR signal for framework iron site decreased with increasing the pH of the synthesis gel. The relative intensity of the two signals is different from what has been found in this work can be explained by the different of the Si/Fe ratio and Si sources as mentioned in Section 4.1.1.2.

The actual Si/Fe ratio in catalysts are always less than that in the starting materials and it increases with decreasing the pH of gel except one at pH 8.0. This indicates that the iron content in Fe-MFI catalysts is affected by the pH of gel.
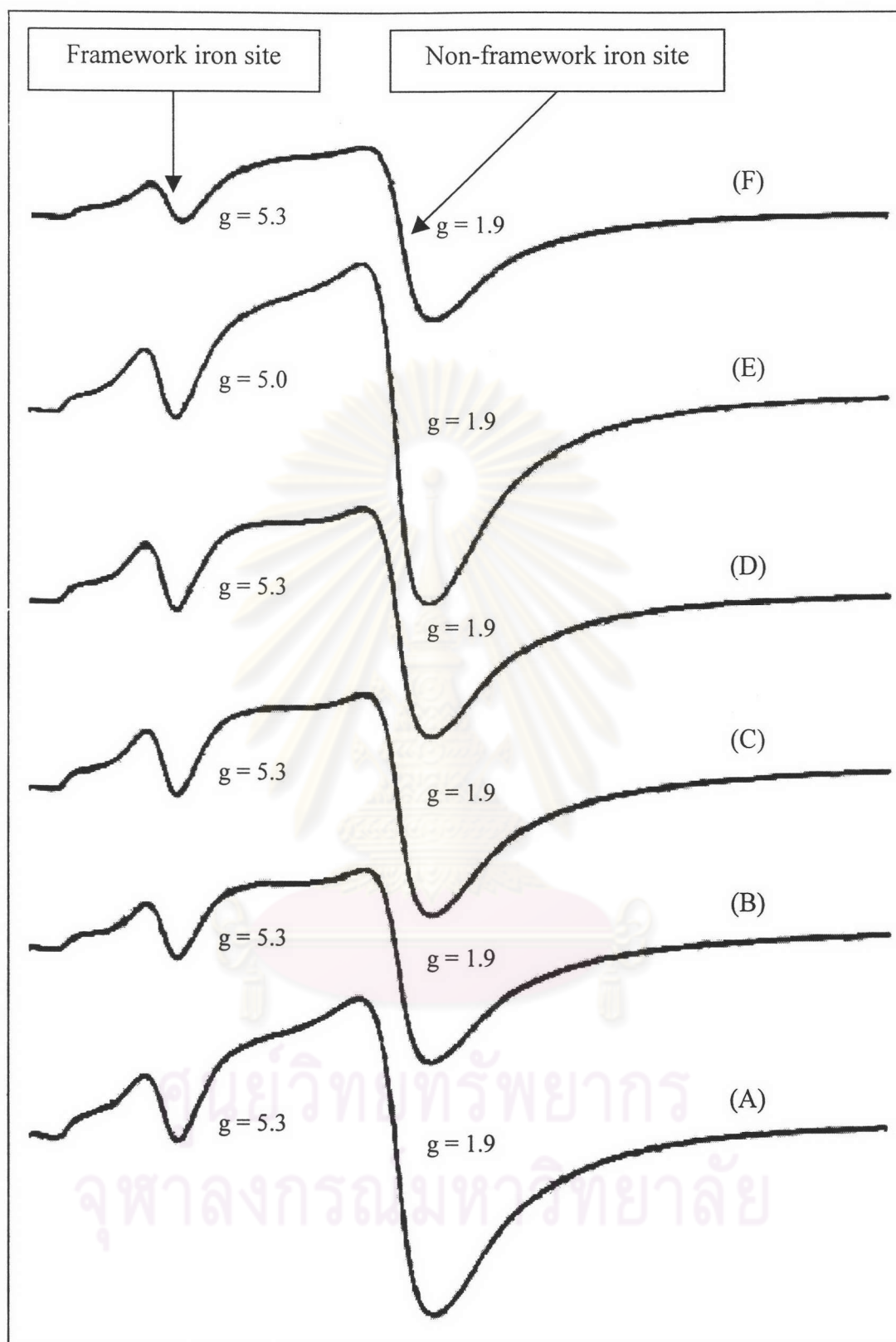
Figure 4.4 ESR spectra recorded at room temperature of calcined Fe-MFI (the Si/Fe ratio in gel of 90) prepared at the small scale and different pH gel value, (A) pH = 8.0, (B) pH = 9.0, (C) pH = 9.5, (D) pH = 10.0, (E) pH = 10.5, and (F) pH = 11.0.

Table 4.2   ESR data and Si/Fe ratio in catalyst of the Fe-MFI catalyst (the Si/Fe ratio in

gel of 90) prepared at the small scale obtained from different pH of gel

pH of gel	g_{NF} value[a]	g_F value[b]	Relative intensity of framework iron sites[c] (%)	Si/Fe ratio in catalyst
8.0	1.9	5.3	17.4	84
9.0	1.9	5.3	22.1	87
9.5	1.9	5.3	22.2	84
10.0	1.9	5.3	21.9	82
10.5	1.9	5.0	21.6	80
11.0	1.9	5.3	17.8	68

[a] *The g value of the ESR signal for non-framework iron site.*
[b] *The g value of the ESR signal for framework iron site.*
[c] *Compared to total no of iron sites* (Fe_{Td} + Fe_{Oh})

Although the crystallization is initiated from the reactants with the same Si/Fe ratio in the gel composition, the content of the framework iron in Fe-MFI is different. This is due to the different synthesis conditions employed, mainly pH of the starting gel.[73] The pH of gel need to be adjusted to give basic condition necessary to promote molecular sieve crystallization. However, the basic condition has a critical effect on the framework iron in Fe-MFI. Szostak *et al.*[41] suggested that the pH for the successful preparation by hydrothermal crystallization of ferrisilicate having iron in the framework sites was necessary to be adjusted to the range of 8 and 11.

The crystal growth of MFI structure, resulting in crystallinity and particle size, is affected by some parameters during the synthesis such as pH, gel composition, temperature, time, aging, and stirring. For the catalytic purpose, formation of small crystals is needed. Therefore, the pH value of 9.0 was selected for the synthesis of Fe-MFI at different Si/Fe ratios. Moreover, it gives rise to high crystallinity of the Fe-MFI product and rather small particle size. However, such a condition may suppress the formation of MFI structure at

the high iron content. Therefore, the synthesis at higher pH, *i.e.* 10.5 has been also attempted and they will be discussed in a different section.

4.1.2 Effect of Si/Fe Ratio on Formation of Fe-MFI at the pH Value of 9.0

4.1.2.1 XRD Results

The preparation of Fe-MFI with various Si/Fe ratios was firstly carried out at the pH value of 9.0. XRD patterns of resulting as-synthesized products with the Si/Fe ratios in gel of 90, 30 and 10 are shown in Figure 4.5. For the Si/Fe ratios of 90 and 30, XRD patterns are similar to the typical one of MFI structure. For the Si/Fe ratio of 10, the phase of MFI structure is not observed by XRD and only amorphous phase. The relative crystallinity of Fe-MFI, determined by comparing intensities of the same peak, decreases with increasing the iron content in gel, *i.e.* lowering the Si/Fe ratio. This indicates that the crystallinity of Fe-MFI is affected by the iron content in gel. The XRD pattern and crystallinity of Fe-MFI are not much affected by the scale of synthesis, comparing between 76 g and 179 g of total weight of the reactant mixture for small- and large-scale preparation, respectively. The intensities of the reflection peaks in XRD pattern of the product formed in the small-scale preparation are relatively higher than those for the large-scale preparation. This is accounted by a preferred orientation of crystal arrangement in aggregates formed in the latter as indicated by the images of SEM.

As mentioned earlier, pH is an important factor to control the crystal growth and particle size of the catalyst. At the pH value of 9.0 the crystal growth of Fe-MFI was suppressed, as a result, small crystal and particle sizes are formed. In addition, the nucleation centers are formed more difficult than at other pH that allows formation of large crystal size. This effect may be stronger with increasing iron content because heteroatom addition is known to cause less order of the zeolite crystal structure.
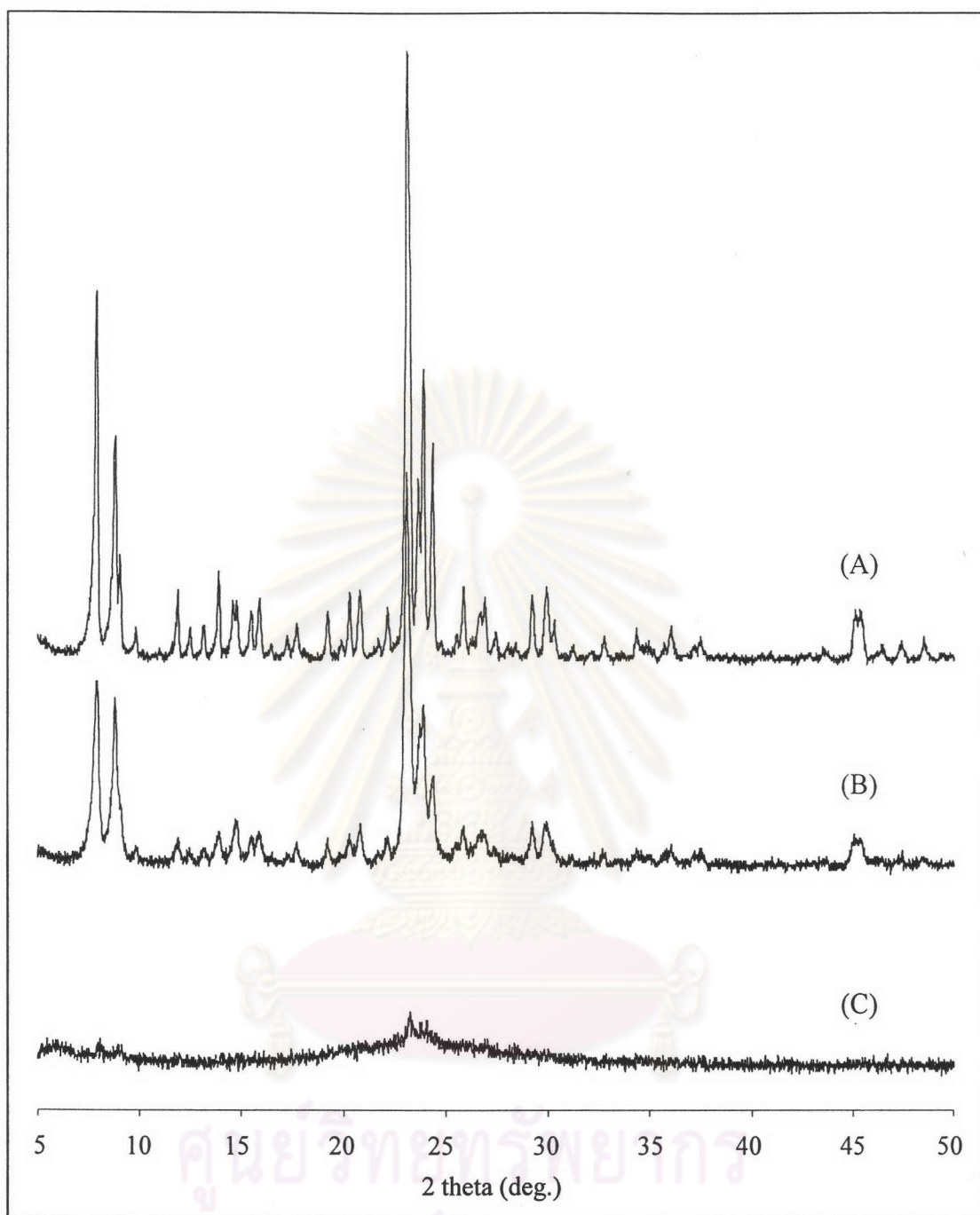
Figure 4.5 XRD patterns of as-synthesized Fe-MFI prepared at the pH of 9.0, at the large-scale preparation and with various Si/Fe ratios in gel, (A) Si/Fe = 90, (B) Si/Fe = 30, and (C) Si/Fe = 10.

4.1.2.2 SEM Images

SEM images of Fe-MFI with the Si/Fe ratios in gel of 90 and 30, prepared at small and large scales at the pH value of 9.0 are depicted in Figure 4.6 and 4.7, respectively. Iron content and scale of preparation play important roles on the particle size and morphology. The higher iron content, the smaller the particle size is. In the small-scale preparation, the uniform twinned plus-like crystals as shown in Figure 4.6(A) are formed for the Si/Fe ratio of 90. In contrast, irregular sizes of Fe-MFI are obviously found for the Si/Fe ratio in gel of 30 as shown in Figure 4.6(B). At higher magnification, it reveals that the spheres consist of small rectangular rod crystals with a 0.2 μm cross section, lying in a preferred orientation
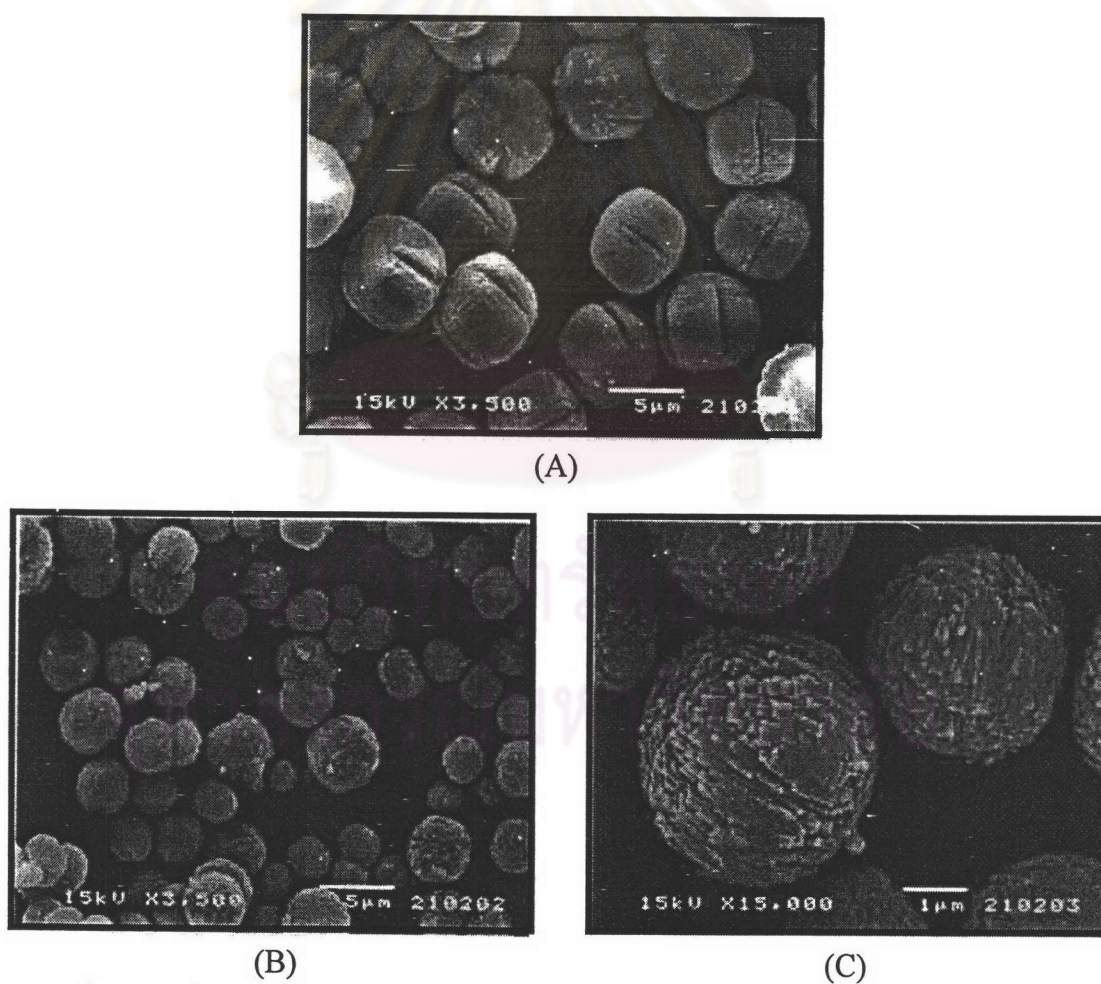
(A)

(B)   (C)

Figure 4.6   SEM images of as-synthesized Fe-MFI prepared at the small scale, at the pH of 9.0 and with different Si/Fe ratios in gel, (A) Si/Fe = 90, (B) Si/Fe = 30, and (C) Si/Fe = 30 at high magnification.

From Figure 4.7 SEM images present spherical aggregates with highly uniform size are observed in case of the Si/Fe ratio in gel of 90 as shown in Figure 4.7(A). At higher magnification, the number of intergrowth of crystals (1.4 to 3.1 μm in size), arranging in random direction are observed as noticed from Figure 4.7(B). At the Si/Fe ratio in gel of 30, quite smaller particles with random orientation in spherical aggregates are obtained as shown in Figure 4.7(C and D). The results are in agreement with those for the small-scale preparation at the same pH value of 9.0 that the aggregate size and shape depends on the iron content in gel. The large-scale preparation provides the crystal arrangement at random orientation while the small-scale preparation gives rise to the crystal arrangement at a preferred orientation. This is accounted for the relatively higher intensity of the reflection peak in the XRD pattern of the small-scale Fe-MFI sample.
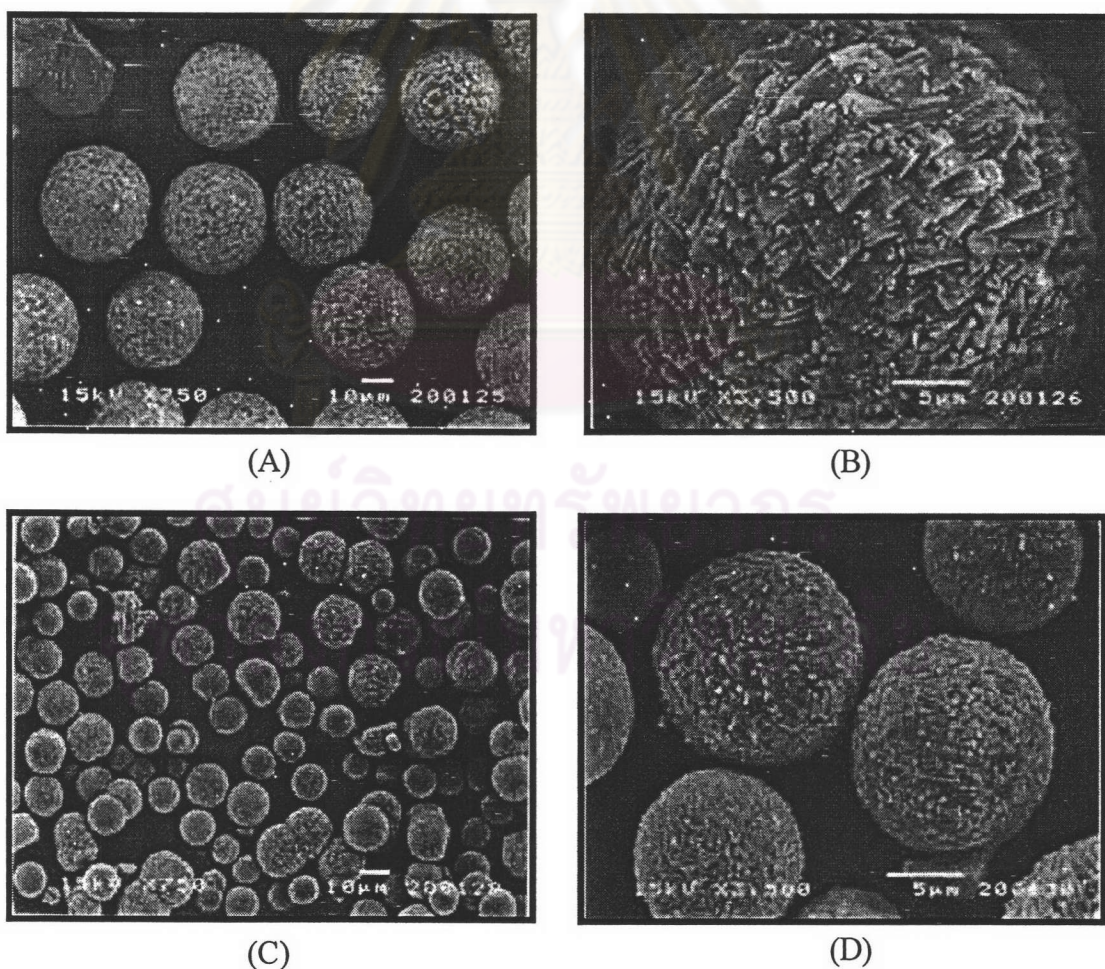

(A)   (B)

(C)   (D)

Figure 4.7   SEM images of as-synthesized Fe-MFI prepared at the large scale, at the pH
of 9.0 and with different Si/Fe ratios in gel, (A), (B) Si/Fe = 90, (C) and
(D) Si/Fe = 30 at different magnification.

The particle size, morphology and BET surface area of Fe-MFI with the Si/Fe ratios in gel of 90 and 30 prepared at the pH value of 9.0, at the small and large scale can be summarized in Table 4.3. Major part of the particle size of Fe-MFI in the small-scale is smaller than that at the large-scale preparation. In addition, the particle size also decreases with an increase in iron contents in both scale of preparation. This indicates that the iron contents and scale for preparation affect the particle size. The particle deteriorated to irregularly-shaped aggregates when the iron content increases in both scales of synthesis. These results are in agreement with observation by Smith and Handreck.[47] They found that the iron content and the preparation mode using stirred and unstirred crystallization affected the morphology and particle size of iron-containing MFI catalysts. The samples with low iron content (Si/Fe ratio of 104) were characterized by spherically particle, consisting of large number of square-ended intergrowths (0.6 μm in size). In contrast, for the high iron content (Si/Fe ratio 1.6) decreased the intergrowths became smaller (0.26 μm in size) and were less well defined. On the other hand, the static preparation showed two types of particles: the first was highly irregular, consisting mainly of poorly defined crystallites; the other type of particle was smaller in size, and more uniformly spherical in shape.

From Table 4.3 the BET specific surface area of Fe-MFI catalysts ranges from 303 to 364 m^2/g. This is in accordance with the value reported in the literature.[59,74,98-100] Moreover, the specific surface area of Fe-MFI catalysts prepared at the small scale is higher than that achieved at the large-scale preparation. The smaller particle size of Fe-MFI in the small-scale preparation leads to the higher surface area than that in the large-scale preparation. Moreover, the surface area decreases with increasing iron content in both scales. This suggests that the intra-crystal pore surface of low iron-content Fe-MFI is greater than that of high iron-content Fe-MFI.[30]

Table 4.3   Particle size, morphology and BET specific surface area of Fe-MFI with the

Si/Fe ratio in gel of 90 and 30 prepared at the pH value of 9.0 in the small and

large-scale preparation

Scale for preparation	Si/Fe ratio in gel	Particle size (μm)	Population (%)	Mean particle size (μm)	Morphology	BET specific surface area (m^2/g)
Small	90	0.42 to 0.78	4.9[a]	7.6	Twinned plus-like	364
		3.1 to 22	90[a]			
	30	2.5 to 2.9	16[b]	4.6	Spherical shape	358
		4.2 to 5.0	61[b]			
		6.2 to 7.1	22[b]			
Large	90	26 to 76	94[a]	39	Spherical shape	347
	30	1.7 to 2.3	2.7[a]	18	Spherical shape	303
		9.0 to 48	83[a]			

[a] *The particle size and population of catalysts are measured by particle size analyzer.*
[b] *The particle size and population of catalysts are estimated from SEM images.*

In general, to obtain the small and uniform crystal for the large-scale preparation of zeolite like materials, it is necessary to crystallize in a stirring mode.[97] However, in this work Fe-MFI catalysts in the large-scale preparation were crystallized in a static condition. The particle size distributions of Fe-MFI with the Si/Fe ratio in gel of 90 and 30 at the pH of 9.0 in the large-scale preparation are exhibited in Figure 4.8. The former shows a narrow particle size distribution curve, whereas a broad particle size distribution curve is observed in the latter. The low iron content the more uniform particle size appears. This indicates that the iron content plays an important role the particle size distribution.
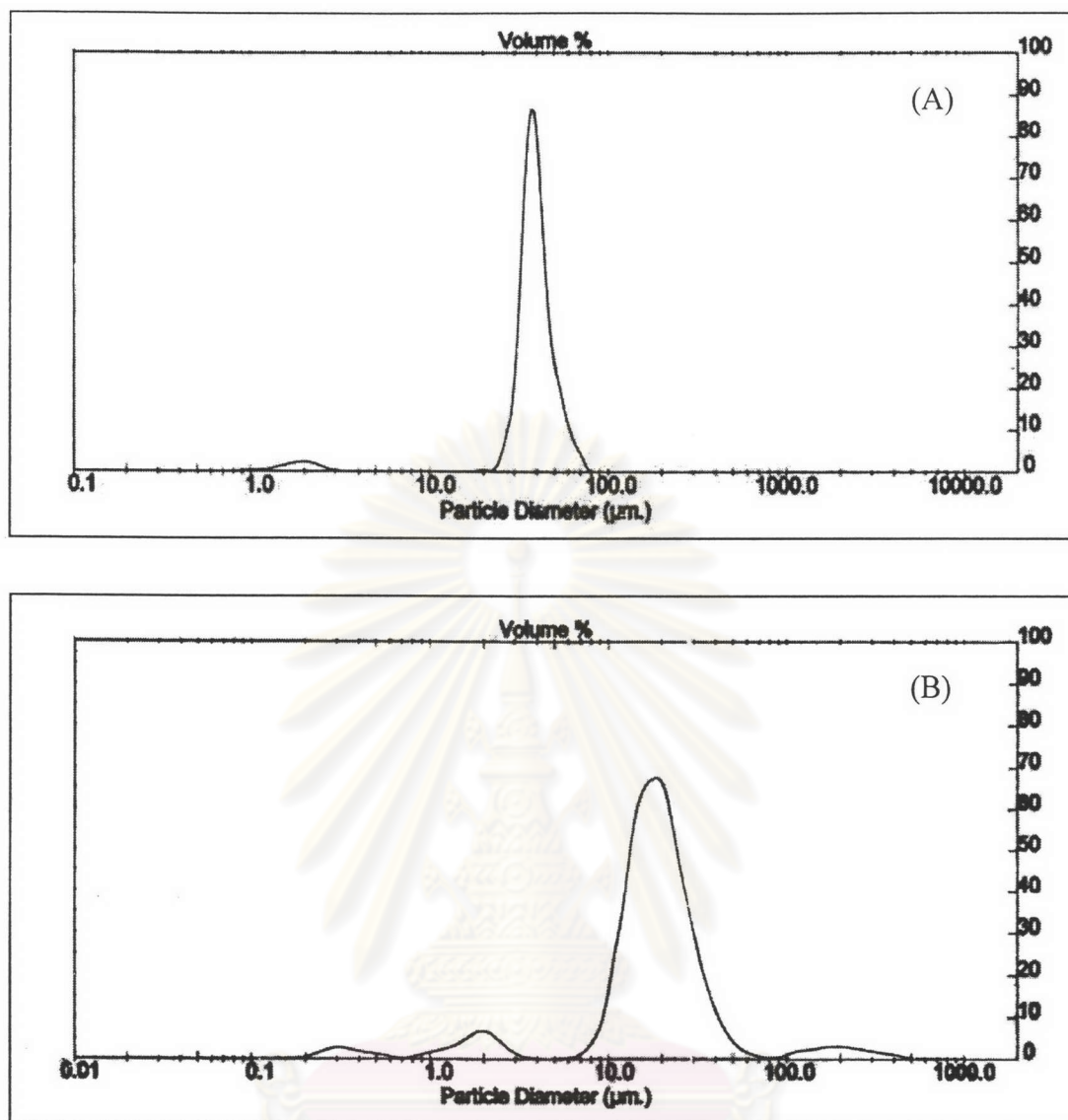
Figure 4.8   Particle size distribution of Fe-MFI prepared at the pH of 9.0, at the large

scale with Si/Fe ratios in gel of (A) 90 and (B) 30.

4.1.2.3 ESR Results and Chemical Analysis

Figure 4.9 shows ESR spectra recorded at room temperature for calcined

Fe-MFI with Si/Fe ratios in gel of 90 and 30 prepared at the pH value of 9.0, either in the

small- or large-scale preparation. Two signals appeared at g value of 1.9 and 5.3 for all

catalysts, similar to the results in section 4.1.1.3. Intensity of framework iron site decreases

with increasing the iron content at both scales, whereas intensity of non-framework irons site

increases. This indicates that high iron loading leads to non-framework iron sites. ESR data of

the Fe-MFI catalyst with different Si/Fe ratios obtained from different scales of preparation at

the pH value of 9.0 are concluded in Table 4.4. The relative intensity of framework iron site decreases when the Si/Fe ratio decreases in both preparation scale and for the Si/Fe ratio of 30 prepared at the small scale, the relative intensity is lower than that at the large scale. The Si/Fe ratios in gel are close to those in catalyst for all cases, except the Si/Fe ratio in gel of 90 prepared at the large scale.
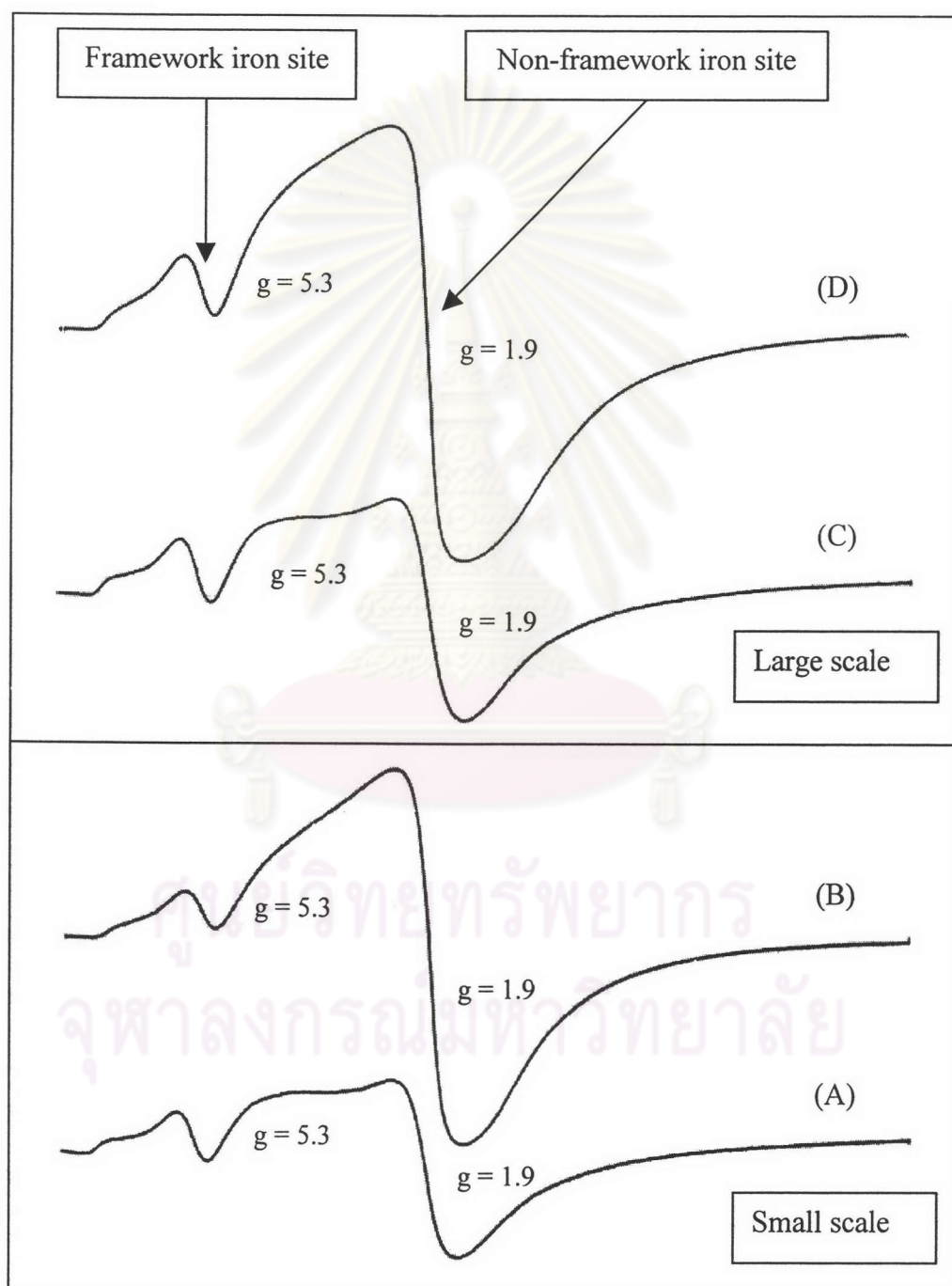

Figure 4.9 ESR spectra recorded at room temperature of calcined Fe-MFI with different Si/Fe ratios in gel, (A), (C) Si/Fe = 90, (B) and (D) Si/Fe = 30 at the pH value of 9.0 and at different scale preparations.

Table 4.4 ESR data of the Fe-MFI catalyst with different Si/Fe ratios obtained from different scales of preparation at the pH value of 9.0

Scale for preparation	Si/Fe ratio in gel	g_{NF} value[a]	g_F value[b]	Relative intensity of framework iron sites[c] (%)	Si/Fe ratio in catalyst
Small	90	1.9	5.3	22.1	87
	30	1.9	5.3	9.0	26
Large	90	1.9	5.3	22.1	76
	30	1.9	5.3	12.2	27

[a] *The g value of the ESR signal for non-framework iron site.*
[b] *The g value of the ESR signal for framework iron site.*
[c] *Compared to total no of iron sites ($Fe_{Td} + Fe_{Oh}$)*

4.1.3 Effect of Si/Fe Ratio on Formation of Fe-MFI at the pH Value of 10.5

4.1.3.1 XRD Results

Since the crystal growth was suppressed at low pH as described in Section 4.1.2.1, the preparation of Fe-MFI was also attempted at the pH value of 10.5. XRD patterns of resulting as-synthesized products with the Si/Fe ratios in gel of 90, 30 and 10 are shown in Figure 4.10. All products have characteristics of MFI structure and no impurity phase is observed. However, the crystallinity of the Fe-MFI decreases with increasing the iron content. This indicates that the iron content has influence on the crystallinity of Fe-MFI such color becomes yellow. This is in accordance with reported by Zhang *et al.*[102] They found that with the decrease of the Si/Fe ratio (the Si/Fe ratio in gel of 100 to 15), the crystallinity of zeolites decreased, the amorphous formed during the crystallization increased and solution color became yellow. Moreover, this result is similar to that in section 4.1.2.1 and there is not significantly different in the crystallinity of the catalysts at the pH gel of 9.0 and 10.5 in the small-scale preparation. The highest peak (2theta of 23.1) intensity of catalysts with the Si/Fe ratio in gel of 30 and 10, respectively, are 58 and 23% compared to that of 90 in the small-scale preparation.
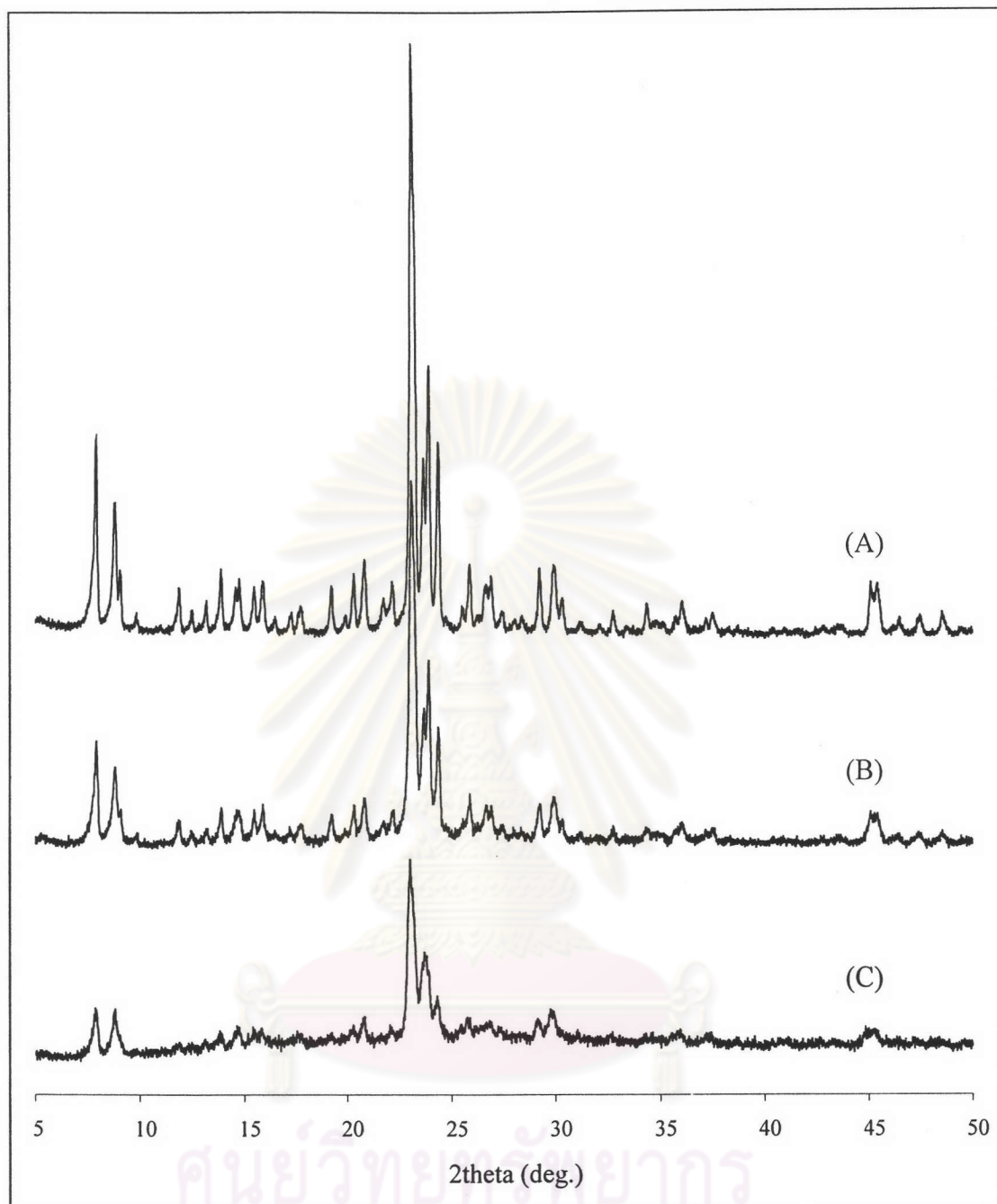
Figure 4.10 XRD patterns of as-synthesized Fe-MFI prepared at the pH of 10.5 and with various Si/Fe ratios in gel, (A) Si/Fe = 90, (B) Si/Fe = 30, and (C) Si/Fe = 10.

4.1.3.2 SEM Images

SEM images of Fe-MFI with the Si/Fe ratios in gel of 90, 30 and 10 at the pH of 10.5 prepared at the small scale are shown in Figure 4.11. The polycrystals with spherical shape are observed in all catalysts, but the particle size is different. This indicated that the particle size is affected by the iron content. In case of Fe-MFI with the Si/Fe ratio in

gel of 90, the image of rough surface of the uniformly spherical shape is obtained and amorphous matter is not found on its external surface as shown in Figure 4.11(A). Furthermore, regular square-ended intergrowth of crystals (0.88 μm in size) at preferred crystal orientation as observed in Figure 4.11(B). Nevertheless, there is the different in morphology of Fe-MFI with the Si/Fe in gel of 90 at the pH value of 9.0 twinned plus-like and 10.5 (spherical shape). It indicates that the morphology of Fe-MFI with the Si/Fe in gel of 90 depends on pH of gel. Fe-MFI with the Si/Fe ratio in gel of 30 (Figure 4.11(C)) has a smooth surface of uniformly spherical shape polycrystals and a few pieces amorphous matters are observed on the external surface as illustrated in Figure 4.11(D). The irregularly tiny square-ended intergrowth of crystals (0.15 to 0.29 μm in size) rotates the head into the outside position as exhibited in Figure 4.11(E). In addition, the spherical shape are observed in Fe-MFI with the Si/Fe ratio in gel of 30 at the pH value of 9.0, but their crystals prefer a specific direction. It notes that the pH of the gel does not affect the morphology of high iron content Fe-MFI (the Si/Fe in gel of 30). For the higher iron loading (the Si/Fe ratio in gel of 10), the rough and smooth surface of spherical shape polycrystals are observed due to the presence of the different size of the square-ended intergrowth of crystals (0.12 to 0.32 μm and 0.20 to 0.59 μm for smooth and rough surface of spherical shape, respectively) and their crystals are random in direction as shown in Figure 4.11(F) and (G). In addition, a number of amorphous matters are detected as illustrated in Figure 4.11(H) and (I). The amorphous matters in the Si/Fe ratio in gel of 10 have a similar shape to that of Fe_2O_3 as shown in Figure 4.11(J). This indicates that the higher iron contents lead to the formation of amorphous Fe_2O_3, could not detected by XRD. Particle size and morphology of Fe-MFI with the Si/Fe ratios in gel of 90, 30 and 10 are summarized in Table 4.5. The smallest particle size is observed with low iron content (the Si/Fe in gel of 90). Nonetheless, the particle size of Fe-MFI with the Si/Fe ratio in gel of 90 and 30 at the pH of 9.0 is smaller, compared to that at the pH of 10.5.
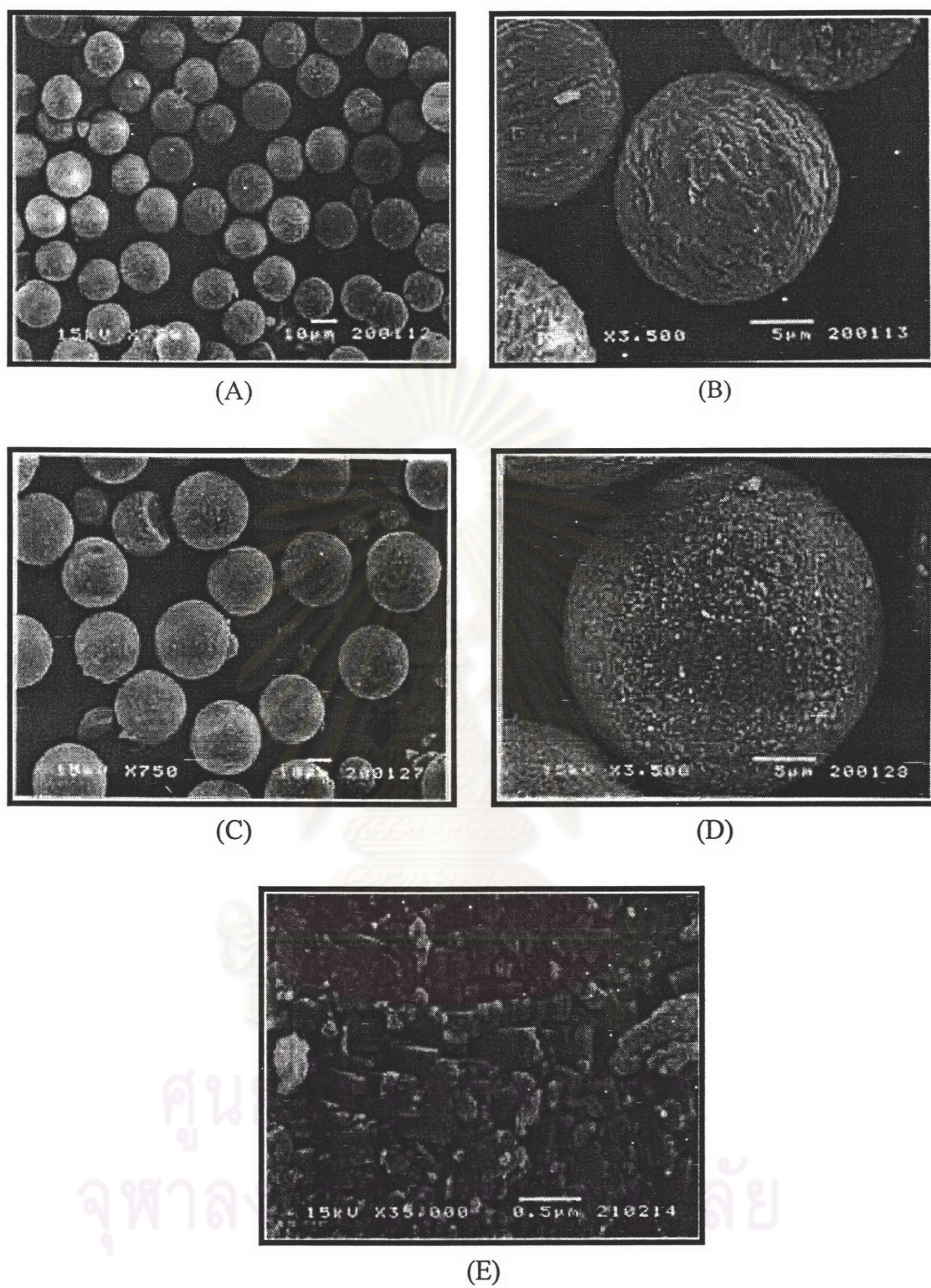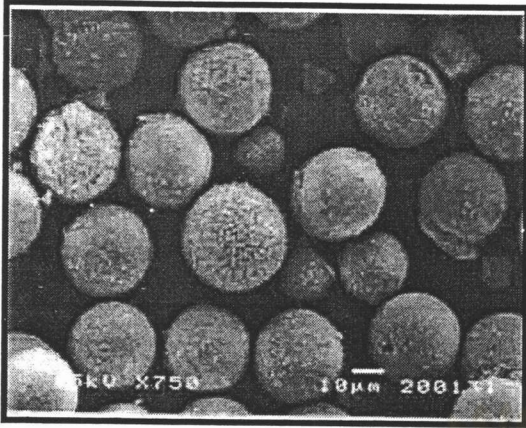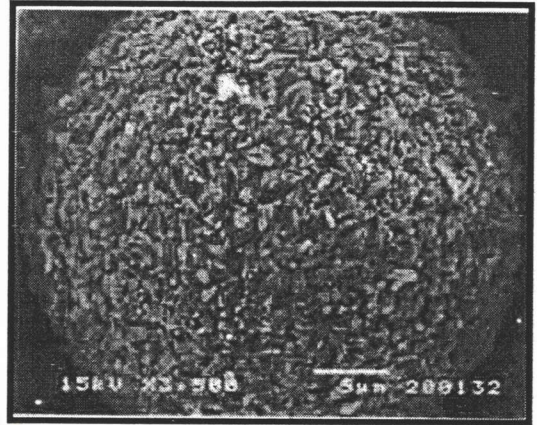
(A)

(B)

(C)

(D)

(E)

Figure 4.11   SEM images of as-synthesized Fe-MFI prepared at the small scale, at the pH of 10.5 and with different Si/Fe ratios in gel, (A), (B) Si/Fe = 90, (C), (D), (E) Si/Fe = 30, (F), (G), (H), (I)   Si/Fe = 10, and (J) Fe_2O_3 at different magnification.
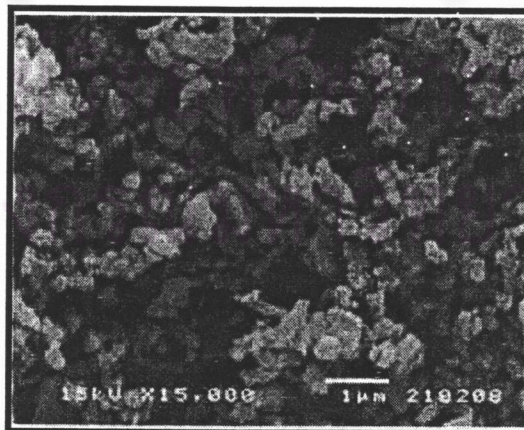
(F)

(G)

(H)

(I)

(J)

Figure 4.11   (continued).

Table 4.5 Particle size and morphology of Fe-MFI with various Si/Fe ratios in gel at the pH value 10.5 in the small-scale preparation

Si/Fe ratio in gel	Mean particle size^a (μm)	Morphology
90	16	Rough surface of spherical shape
30	28	Smooth surface of spherical shape
10	24	Smooth and rough surface of spherical shape

^{a} *The mean particle size of catalysts are estimated from SEM images.*

4.1.3.3 X-ray Mapping Images

The distributions of silicon and iron atom in the catalysts was analyzed by the X-ray mapping. X-ray mapping images of silicon and iron in Fe-MFI with the Si/Fe ratios in gel of 90, 30, and 10 at the pH value of 10.5 in the small-scale preparation are shown in Figure 4.12, which show a very good distribution of silicon and iron throughout the particles for all of catalysts. The silicon and iron distribution looks denser with increasing the element content.

4.1.3.4 ESR Results and Chemical Analysis

The relative intensity of framework iron sites in catalysts (the Si/Fe ratio in gel of 90, 30, and 10) synthesized at a pH value 10.5 were studied and compared to that at the pH value of 9.0 in section 4.1.2.3. The results are Figure 4.13 and should be compared to Figure 4.9. Two signals appear at g value at 1.9 and around 5.0 for Fe-MFI with the Si/Fe ratio in gel of 90 and 30, while a catalyst with the Si/Fe ratio in gel of 10 shows g value at 1.9 and 4.4. Intensity of framework iron decreases, while intensity of non-framework iron increases when the iron content increases. This indicates that high iron loading leads to higher non-framework iron sites. Thus, under the synthesis condition of low Si/Fe ratio, that is, high iron content, excessive amount of iron both inhabits the formation of MFI type zeolite and
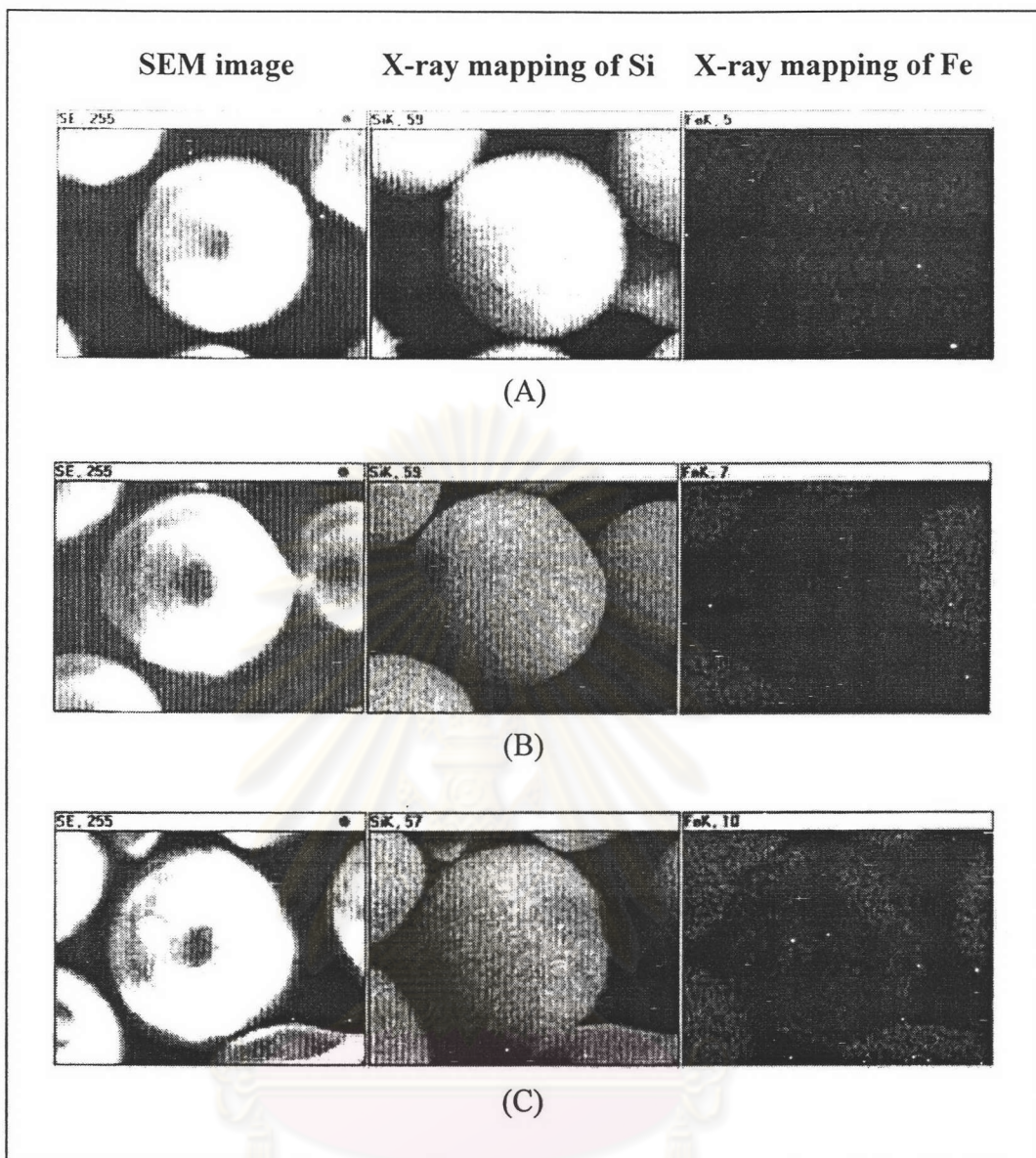
Figure 4.12 X-ray mapping images of silicon and iron distributed in calcined Fe-MFI prepared at the small scale, at pH value of 10.5 with different Si/Fe ratios in gel, (A) Si/Fe = 90, (B) Si/Fe = 30, and (C) Si/Fe = 10.

restricts the amount of iron ion that can be incorporated into the framework of MFI. This is due to the reason that the Fe species are not fully combined with the Si species during crystallization.[102] The free Fe species both influence the normal crystallization of MFI type zeolite and induce the formation the impurities such as ferric oxide amorphous at low Si/Fe ratio, which observed in ESR results and SEM images, Figure 4.11(H) and (I). Table 4.6 reveals ESR data of the Fe-MFI catalyst with different Si/Fe ratios obtained from the small-scale preparation at the pH value of 10.5. The ratio of framework to non-framework irons site decreases with increasing the iron contents. Generally, these results in accordance with the ESR results in section 4.1.2.3 in the small- and large-scale preparation. Consequently, the Si/Fe ratios in catalysts are closed to that in the gel.

4.2   Preparation of H-Fe-MFI Catalysts

The ESR spectra of H-Fe-MFI(B) and parent NaH-Fe-MFI are exhibited in Figure 4.14. There are two signals appear at g value at 1.9 and 5.3 for all catalysts, but the intensity of framework iron sites decreases for H-Fe-MFI(B) treated by Method B in Section 3.6. This indicates that some of the framework iron is transferred to non-framework iron sites during NH_4 ion exchange process, as a result of three times calcination of Fe-MFI(B). Calcination causes the breakdown of some framework Fe-O bonds and induces formation of iron oxide aggregates.[101] The framework iron is maintained for H-Fe-MFI(A) treated by Method A (not shown) because it is treated in mild condition than Method B. Table 4.7 reveals ESR data of different hydrogen content Fe-MFI with the Si/Fe ratio of 87 obtained from the small-scale preparation at the pH value of 9.0. The relative intensity of framework iron sites of H-Fe-MFI (B) is lower than the parent NaH-Fe-MFI.
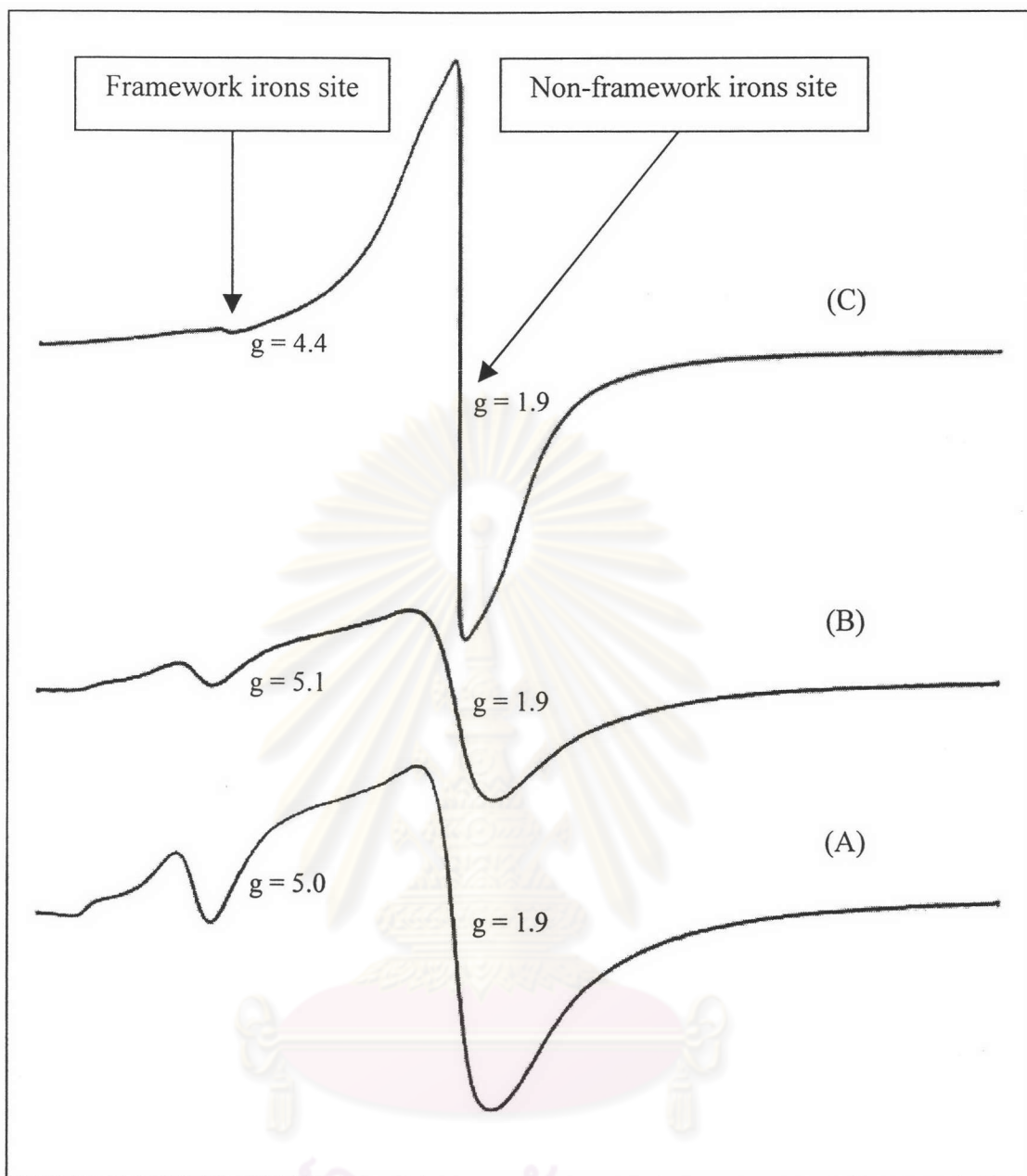
Figure 4.13 ESR spectra recorded at room temperature of calcined Fe-MFI with different Si/Fe ratios in gel, (A) Si/Fe = 90, (B) Si/Fe = 30 and (C) Si/Fe = 10 at the pH value of 10.5 in the small-scale preparations.

Table 4.6   ESR data of the Fe-MFI catalyst with different Si/Fe ratios obtained from the small-scale preparation at the pH value of 10.5

Si/Fe ratio in gel	g_{NF} value[a]	g_F value[b]	Relative intensity of framework iron sites[c] (%)	Si/Fe ratio in catalyst
90	1.9	5.0	21.6	80
30	1.9	5.1	10.5	25
10	1.9	4.4	0.44	9.9

[a] *The g value of the ESR signal for non-framework iron site.*
[b] *The g value of the ESR signal for framework iron site.*
[c] *Compared to total no of iron sites ($Fe_{Td} + Fe_{Oh}$)*
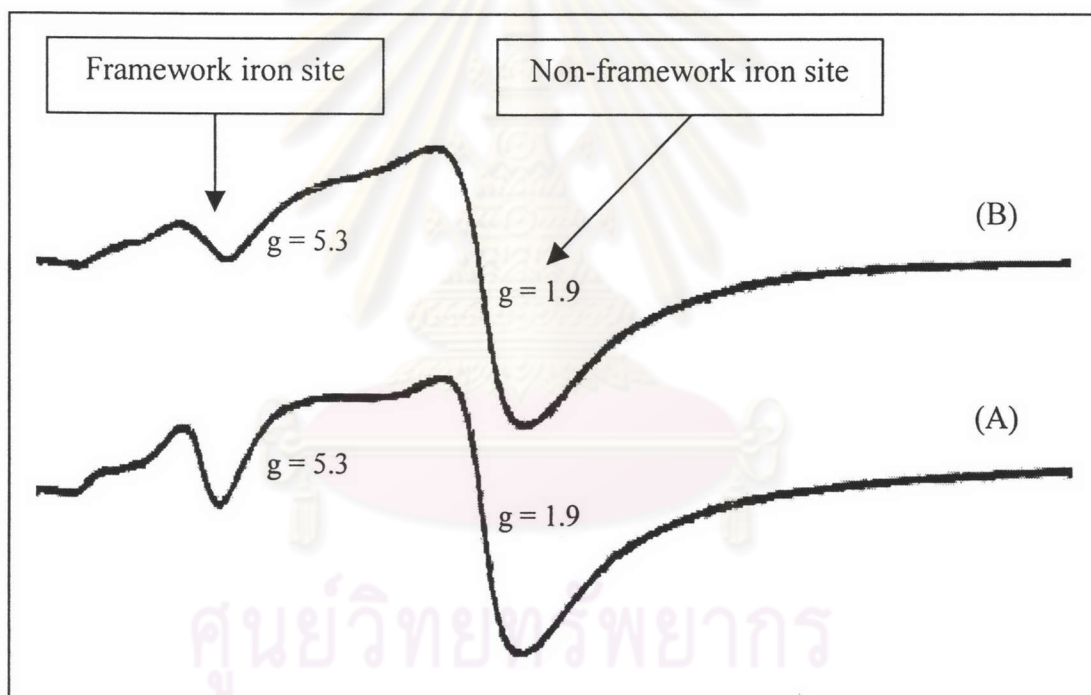

Figure 4.14   ESR spectra recorded at room temperature of calcined Fe-MFI with the Si/Fe ratio 87 and with different hydrogen content, (A) NaH-Fe-MFI and (B) H-Fe-MFI(B).

Table 4.7   ESR data of different hydrogen content Fe-MFI with Si/Fe ratio of 87

obtained from the small-scale preparation at the pH value of 9.0

Catalysts	g_{NF} value[a]	g_F value[b]	Relative intensity of framework iron sites[c] (%)
NaH-Fe-MFI	1.9	5.3	22.1
H-Fe-MFI(B)[d]	1.9	5.3	11.7

[a] *The g value of the ESR signal for non-framework iron site.*
[b] *The g value of the ESR signal for framework iron site.*
[c] *Compared to total no of iron sites (Fe_{Td} + Fe_{Oh})*
[d] *H-Fe-MFI(B) was prepared using the ammonium exchange Method B*

4.3   Test of the Fe-MFI Catalysts for MTO

According to the previous work[102] of our research group, the values of GHSV and TOS for MTO catalysis has been investigated. The activity was maximized at a GHSV of 2000 h^{-1} and TOS of 40 min. The same conditions were used through this work.

4.3.1 Effect of Na ions on MTO

4.3.1.1 The Values of %Conversion, Product Yield and Coke Deposited

The values of %conversion of methanol, yield of products and the amount of coke deposited obtained from methanol conversion over various catalysts: NaH-Fe-MFI, H-Fe-MFI(A) and H-Fe-MFI(B) with the same Si/Fe ratio in catalyst of 87 prepared at the gel pH of 9.0 in the small-scale preparation, are compiled in Table 4.8. H-Fe-MFI(A) and H-Fe-MFI(B) give nearly complete conversion of methanol, whereas conversion becomes markedly decreased using NaH-Fe-MFI as catalyst. Moreover, the highest yield of gas product and the lowest yield of liquid product are obtained in the case of H-Fe-MFI(B). The amount of coke deposited on each catalyst was found in order: NaH-Fe-MFI > H-Fe-MFI(A) > H-Fe-MFI(B). This result is in agreement with the results reported by Tsoncheva and Dimitrova[21] who studied the methanol conversion over H-MCM-41 and Na-MCM-41 (Na$^+$ exchanged H-MCM-41). They found that about two times decrease of yield of hydrocarbons

was observed using Na-MCM-41 as catalyst compared to H-MCM-41. This indicated that a part of Brønsted acid sites, which are well known as the active sites in MTO process, was blocked by Na^+ ions. Similarly, NaH-Fe-MFI has low activity than H-Fe-MFI(A) activity of which is still lower than H-Fe-MFI(B), suggesting that the number of acid sites increases as follows: NaH-Fe-MFI < H-Fe-MFI(A) < H-Fe-MFI(B). The reasons, schematically shown in Scheme 4.1, could be due to the fact that increasing a refluxing time together with calcination promotes the efficiency in ammonium ion exchange. Method B in Section 3.6 leads toward the higher amount of Na^+ ions migration out from the Fe-MFI channels. The migration of the Na ions remaining in a zeolite can be activated at a high temperature above 500ºC before repeated ammonium ion exchange. Although NaH-Fe-MFI has lower number of acid sites than H-Fe-MFI(B), the ESR results indicates that the ratio of framework to non-framework iron site for NaH-Fe-MFI is higher than that of H-Fe-MFI(B).

Table 4.8   Percentage conversion, yields of products and coke content after the methanol conversion over various Fe-MFI catalysts with the same Si/Fe ratio of 87 (Conditions: 0.3 g catalyst, GHSV = 2000 h^{-1}, $T_{catalyst}$ = 500˚C, T_{MeOH} = 30˚C, and TOS = 40 min)

	Catalyst		
	NaH-Fe-MFI	H-Fe-MFI(A)[a]	H-Fe-MFI(B)[b]
%Conversion of methanol	82	99	99
Yield of gas product (%wt.)	23	22	40
Yield of liquid product (%wt.)	55	72	58
Coke (% wt. of catalyst)	2.6	2.4	0.44

[a] *H-Fe-MFI(A) was prepared using the ammonium exchange Method A*
[b] *H-Fe-MFI(B) was prepared using the ammonium exchange Method B*
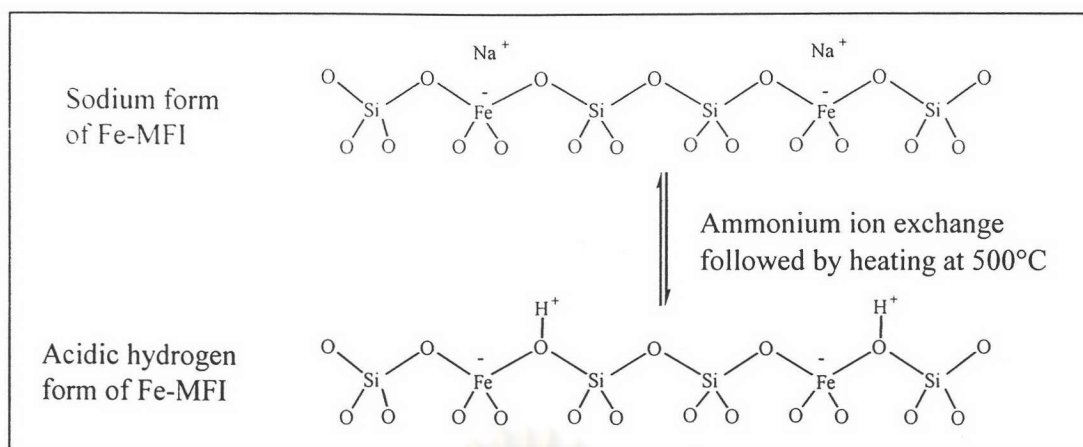
Scheme 4.1   The generation of Brønsted acid sites in Fe-MFI catalyst.

4.3.1.2 Product Distribution of the Gaseous Phase

Figure 4.15 exhibits the gaseous products distribution obtained from methanol conversion at 500°C on various Fe-MFI catalysts (the Si/Fe ratio of 87) prepared at the pH value of 9.0 in the small-scale preparation with different H^+ content. Methane content and coke formation decrease in the sequence: Na-Fe-MFI > H-Fe-MFI(A) > H-Fe-MFI(B), while propylene and C_4 olefins selectivity increase in order: Na-Fe-MFI < H-Fe-MFI(A) < H-Fe-MFI(B). Moreover, selectivity to C_2 to C_4 olefins increases in order: Na-Fe-MFI < H-Fe-MFI(A) < H-Fe-MFI(B), whereas the total selectivity to paraffins decreases.

4.3.1.3 Product Distribution of Volatile Liquid Phase

For all cases, the volatile liquid product is almost only water, determined by GC-MS. The data prove that reaction mechanism for MTO process is *via* dehydration of protonated methanol which transformed to a surface methoxy species and reacted in turn with other methanol to form a dimethyloxonium ion (DMO^+).[79] Deprotonation of the latter yielded dimethyl ether and H^+, as shown in Scheme 4.2. Product distributions of volatile liquid obtained form the MTO over Fe-MFI catalysts with various H^+ contents are exhibited in Figure 4.16. Considering the relation between the amount of unreacted methanol and %conversion of methanol, which shows that it decreases with increasing %conversion of methanol. The highest amount of C_5 alkanes is obtained from using H-Fe-MFI(A) as catalyst.
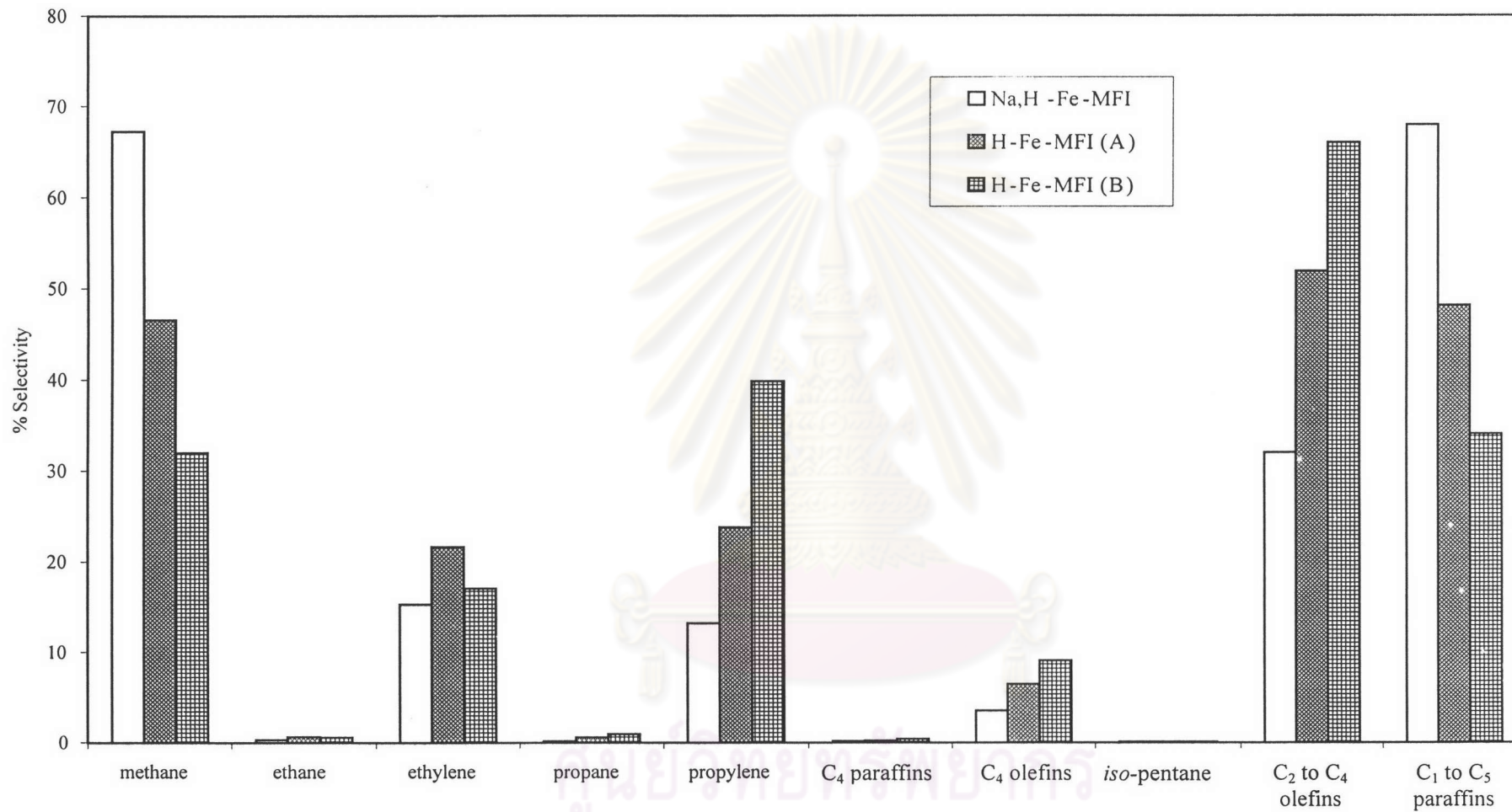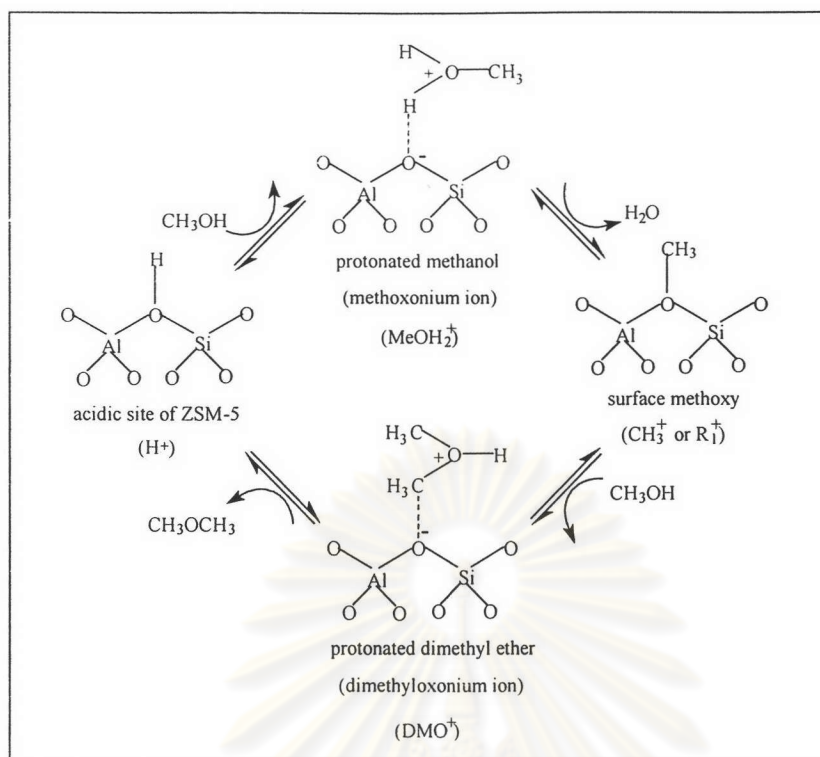
Figure 4.15 Product distribution of gas phase obtained from the methanol conversion over various Fe-MFI catalysts corresponding to the condition in Table 4.8.

Scheme 4.2 Formation of dimethyl ether during the course of MTO process.[79]
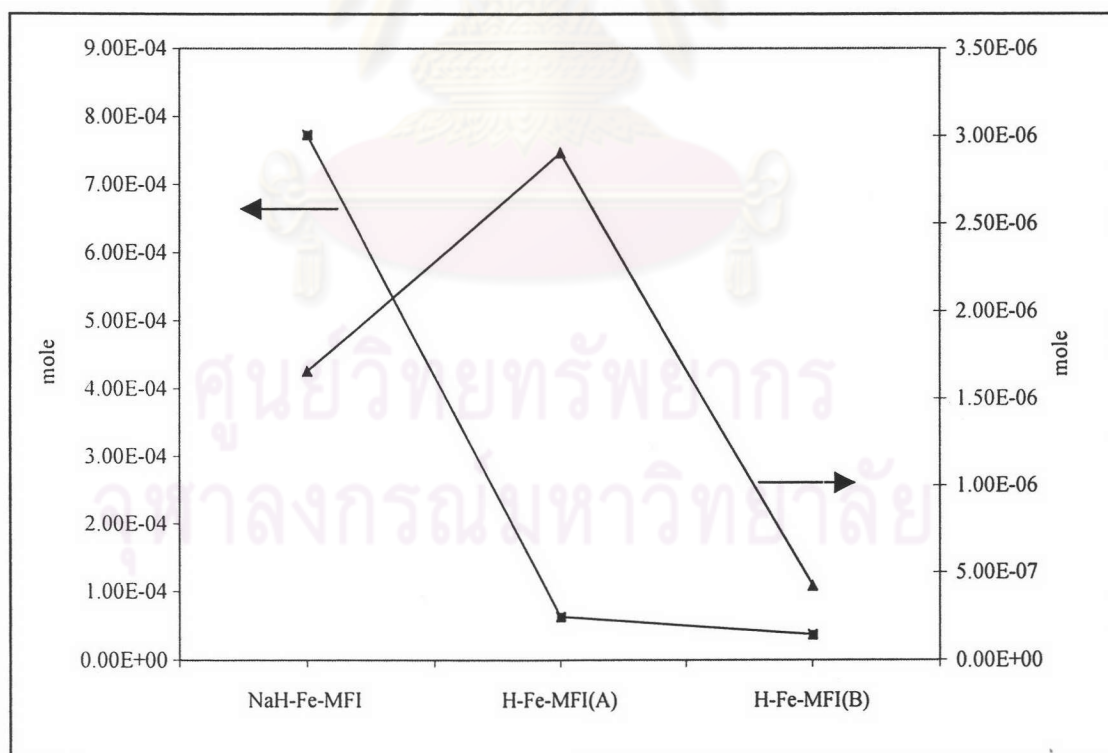

Figure 4.16 Product distribution of volatile liquid phase obtained from the methanol conversion over various Fe-MFI catalysts corresponding to the condition in Table 4.8 (■ = methanol; ▲ = C_5 alkanes).

From these results, H-Fe-MFI(B) gives not only a highest yield of gas products, a lowest amount of coke deposited and a lowest yield of liquid products, but also a highest selectivity to C_2 to C_4 olefins and the lowest total selectivity to paraffins. Although it has a lower intensity ratio of framework to non-framework iron sites compared to NaH-Fe-MFI, it gives a higher catalytic activity for methanol conversion. Therefore, Method B is chosen as the optimal method for preparing the H-Fe-MFI catalysts for methanol conversion to olefins. The notation B will be omitted.

4.3.2 Effect of Temperatures on MTO

4.3.2.1 The Values of %Conversion, Product Yield and Coke Deposited

Table 4.9 reveals the %conversion of methanol, yield of products and coke deposited obtained from using H-Fe-MFI catalyst in Section 4.3.1.2 at various temperatures (300, 350, 400, 450 and 500°C). Above the temperature of 350°C, the %conversion of methanol is nearly complete, while reducing the temperature to 300°C decreases the methanol conversion significantly. The amount of coke deposited decreases when the temperature increases, except at the temperature of 300°C. The explainable reason of the data at high temperature (> 350°C) is that when the temperature increases, thermal cracking of heavy hydrocarbons increases, resulting in a reducing of the yield of liquid products as well as the amount of coke deposited. The low catalytic activity is found at the temperature as low as 300°C as a result of lowering methanol conversion. In all cases, the liquid is the major component of the products.

Table 4.9 Percentage conversion, yields of products and coke content after the methanol conversion over H-Fe-MFI with the Si/Fe ratio in catalyst of 87 (Conditions: 0.3 g catalyst, GHSV = 2000 h^{-1}, T$_{catalyst}$ = 300-500˚C, T$_{MeOH}$ = 30˚C, and TOS = 40 min)

	Temperature (°C)				
	300	350	400	450	500
%Conversion of methanol	78	98	99	99	99
Yield of gas product (%wt.)	36	22	20	27	40
Yield of liquid product (%wt.)	41	74	78	71	58
Coke (% wt. of catalyst)	0.29	1.2	0.76	0.62	0.44

4.3.2.2 Product Distribution of the Gaseous Phase

Considering Figure 4.17, most of the products are olefins rather than paraffins, except at the temperature of 300°C. Although the highest yield of gas products is obtained at the temperature of 300 °C, its major component is methane. At low temperature, e.g. 300°C, the decomposition of methanol produces methane, while at elevated temperatures especially at the temperature of 500°C, methane is formed by the competitive cracking of hydrocarbons over the acid Fe-MFI catalyst to smaller molecules. In addition, this phenomenon results in the increase in methane at the expense of larger C$_3$ to C$_5$ paraffins and C$_3$ to C$_4$ olefins. The results are similar to that previously observed by others.[17,18,103] When the temperature is raised form 350 to 450°C, the selectivity to C$_2$ to C$_4$ olefins is almost higher, whereas the highest selectivity to propylene, 59 %, is obtained at the temperature of 450°C.

Considering the methanol conversion to olefins at the temperature of 350 and 450°C, the latter gives not only the higher yield of gas products and the lower yield of liquid products, but also the highest amount of propylene. Although the selectivity to methane slightly increases at the temperature of 450°C compared to that of 350 and 400°C, it becomes markedly decreased in comparison with that of 300 and 500°C. Therefore, the temperature of 450°C is chosen for the rest of the catalytic test.
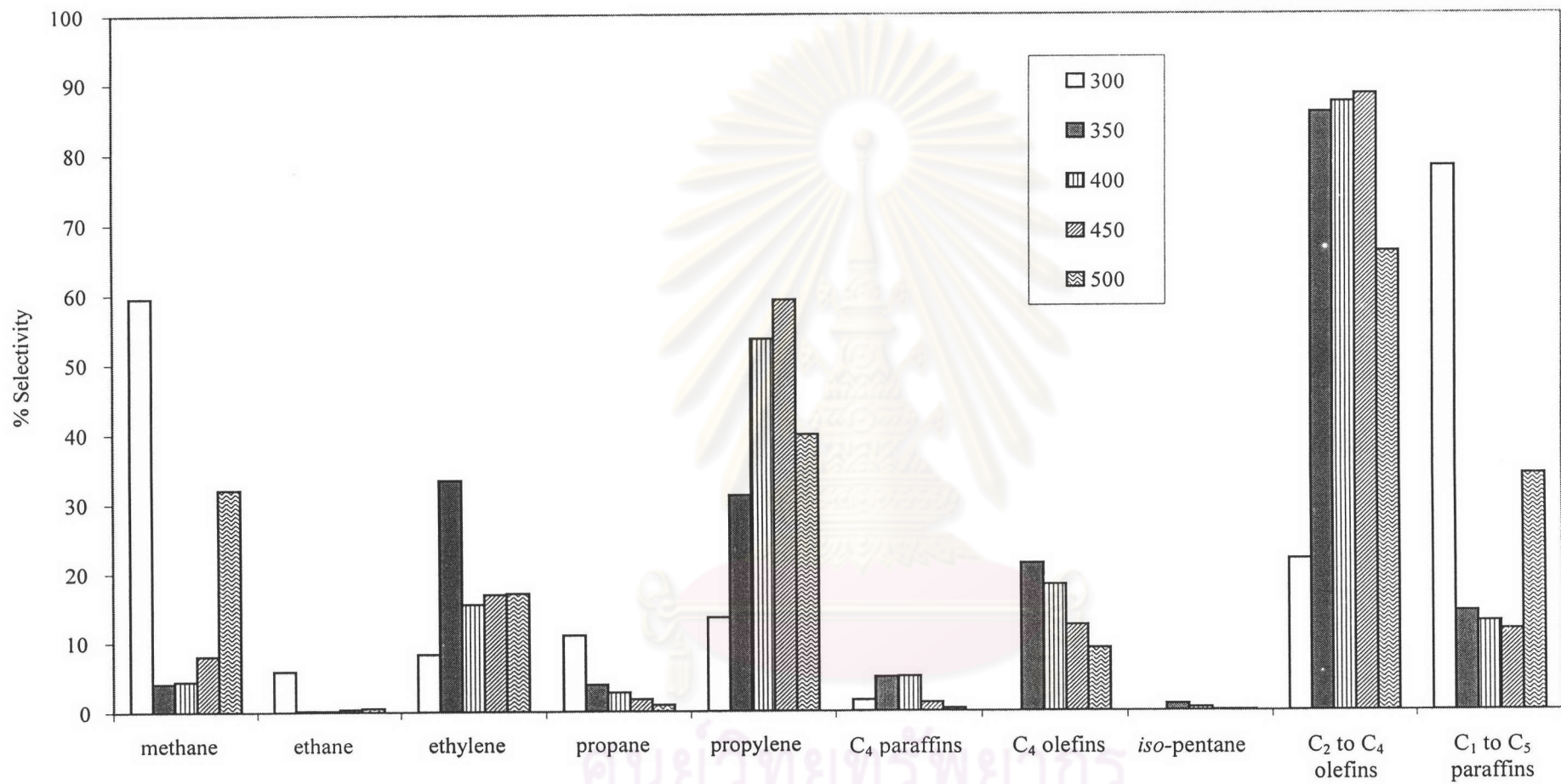
Figure 4.17 Product distribution of gas phase obtained from the methanol conversion over various Fe-MFI catalysts corresponding to the condition in Table 4.9.

4.3.2.3 Product Distribution of the Volatile Liquid Phase

Product distributions of volatile liquid obtained form MTO over H-Fe-MFI catalysts (Si/Fe = 87) at various temperatures are shown in Figure 4.18. Amount of unreacted methanol decreases with increasing %conversion of methanol. With increasing in amount of C_5 alkanes, the temperature increases from 300 to 400°C, while above 400°C it decreases.
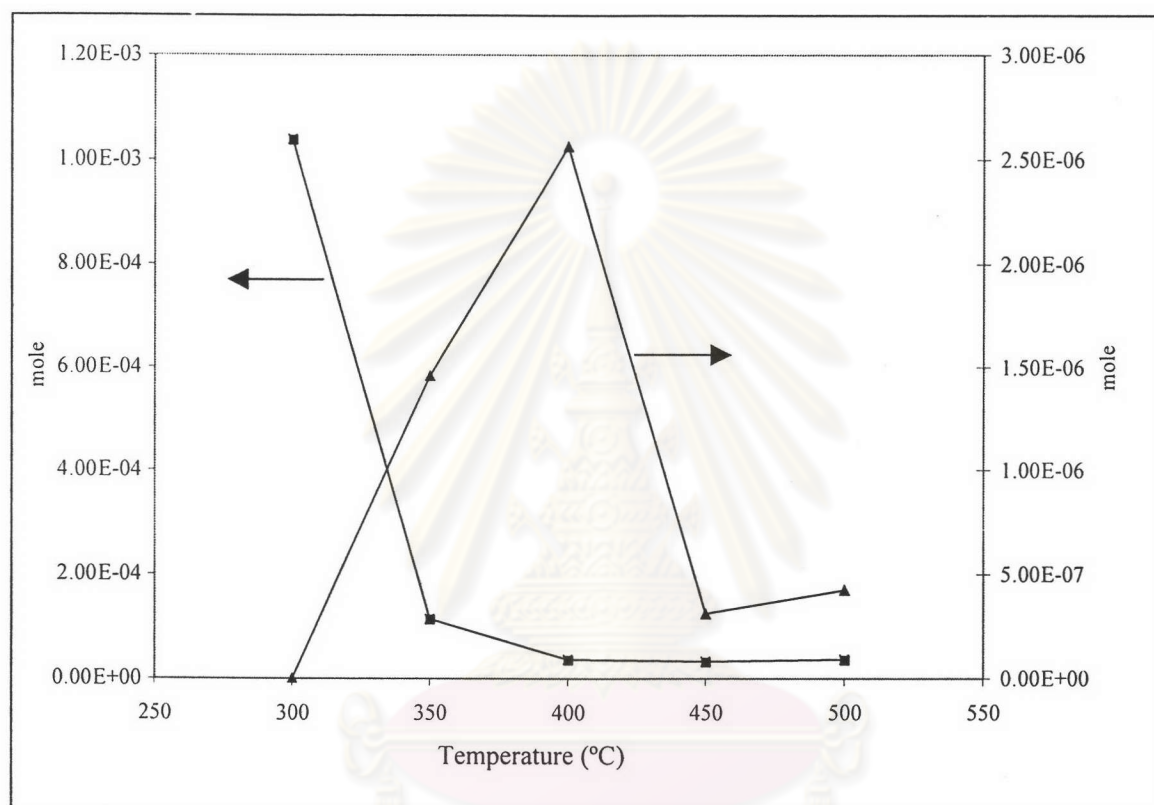

Figure 4.18 Product distribution of volatile liquid phase obtained from the methanol conversion over various Fe-MFI catalysts corresponding to the condition in Table 4.9 (■ = methanol; ▲ = C_5 alkanes).

4.3.3 Blank Test on MTO

4.3.3.1 The Values of %Conversion, Product Yield and Product Distribution of Gaseous Phase

To study the effect of thermal cracking of methanol on MTO, the blank catalytic test using only quartz wool instead of catalyst is investigated at the temperature of 300 and 450°C as shown in Table 4.10. In both cases, the lower %conversion of methanol and the higher yield of liquid products are observed compared to using H-Fe-MFI as catalyst. Only one type of gas product, methane, is detected which is formed by the decomposition of methanol. It should be note from Table 4.10 that methanol can be decomposed thermally without any catalyst. Moreover, the major part of volatile liquid is the unreacted methanol.

Table 4.10 Percentage conversion, yields of products and coke content after the methanol conversion without catalyst (Conditions: GHSV = 2000 h^{-1}, $T_{reaction}$ = 300 and 450°C, T_{MeOH} = 30°C, and TOS = 40 min)

	Temperature (°C)	
	300	450
%Conversion of methanol	29	28
Yield of gas product (%wt.)	11	9
Yield of liquid product (%wt.)	18	19
Product Distribution (%mol) Methane	100	100

4.3.4 Effect of Si/Fe Ratio on MTO

4.3.4.1 The Values of %Conversion, Product Yield and Coke Deposited

Considering Table 4.11, the conversion of methanol is nearly complete at the Si/Fe ratios in catalyst of 25 and 80. The conversion of methanol decreases with increasing iron content or decreasing the Si/Fe ratio in a catalyst. Similar results are reported by Martin *et al.*[2,3] The explainable reason of the result could be due to the fact that the number of acid sites of the high iron content catalyst, especially the Si/Fe ratio in gel of 9.9, is too high leading to a fast deactivation caused by coke deposited and higher yield of liquid products. The data is in accordance with using Al-ZSM-5[6] as the catalysts. It was found that the amount of coke deposited increases with decreasing the Si/Al ratio, or increasing Al content in the catalyst. From this study the amount of coke deposited increases by a factor of 3 when iron content gradually increase form Si/Fe ratio of 80, 2.5, and 9.9 to, respectively, 0.35, 0.97, and 2.6. The highest yield of gas product and the lowest yield of liquid product are observed at the Si/Fe ratio of 80.

Table 4.11 Percentage conversion, yields of products and coke content after the methanol conversion over H-Fe-MFI with various Si/Fe ratios in catalyst (Conditions: 0.3 g catalyst, GHSV = 2000 h^{-1}, $T_{catalyst}$ = 450˚C, T_{MeOH} = 30˚C, and TOS = 40 min)

	Si/Fe ratio		
	9.9	25	80
%Conversion of methanol	91	96	97
Yield of gas product (%wt.)	29	29	50
Yield of liquid product (%wt.)	60	66	46
Coke (% wt. of catalyst)	2.6	0.97	0.35

4.3.4.2 Product Distribution of the Gaseous Phase

Figure 4.19 shows distribution of gaseous products obtained from methanol conversion on H-Fe-MFI with various Si/Fe ratios at the pH gel of 9.0 in the small-scale preparation at 450°C. C_2 to C_4 olefins are major products distribution in comparison with the total paraffins. Methane selectivity decreases with decreasing iron content, whereas propylene and C_2 to C_4 olefins selectivities increase. The reason may be due to cracking of C_3 and C_4 olefins at high iron content, the number of acid sites is too high. These data indicates that the optimal Si/Fe ratio providing the highest selectivity to propylene and also C_2 to C_4 olefins, and the lowest selectivity to total paraffins is 80.

4.3.4.3 Product Distribution of the Volatile Liquid Phase

Figure 4.20 illustrates distribution of volatile liquid obtained form MTO using H-Fe-MFI catalysts with various Si/Fe ratios at 450°C. The amount of unreacted methanol from volatile liquid corresponds well to %conversion of methanol, *i.e.*, low amount when the conversion is high. The highest amount of C_5 alkanes is obtained from using H-Fe-MFI with the Si/Fe ratio of 25.
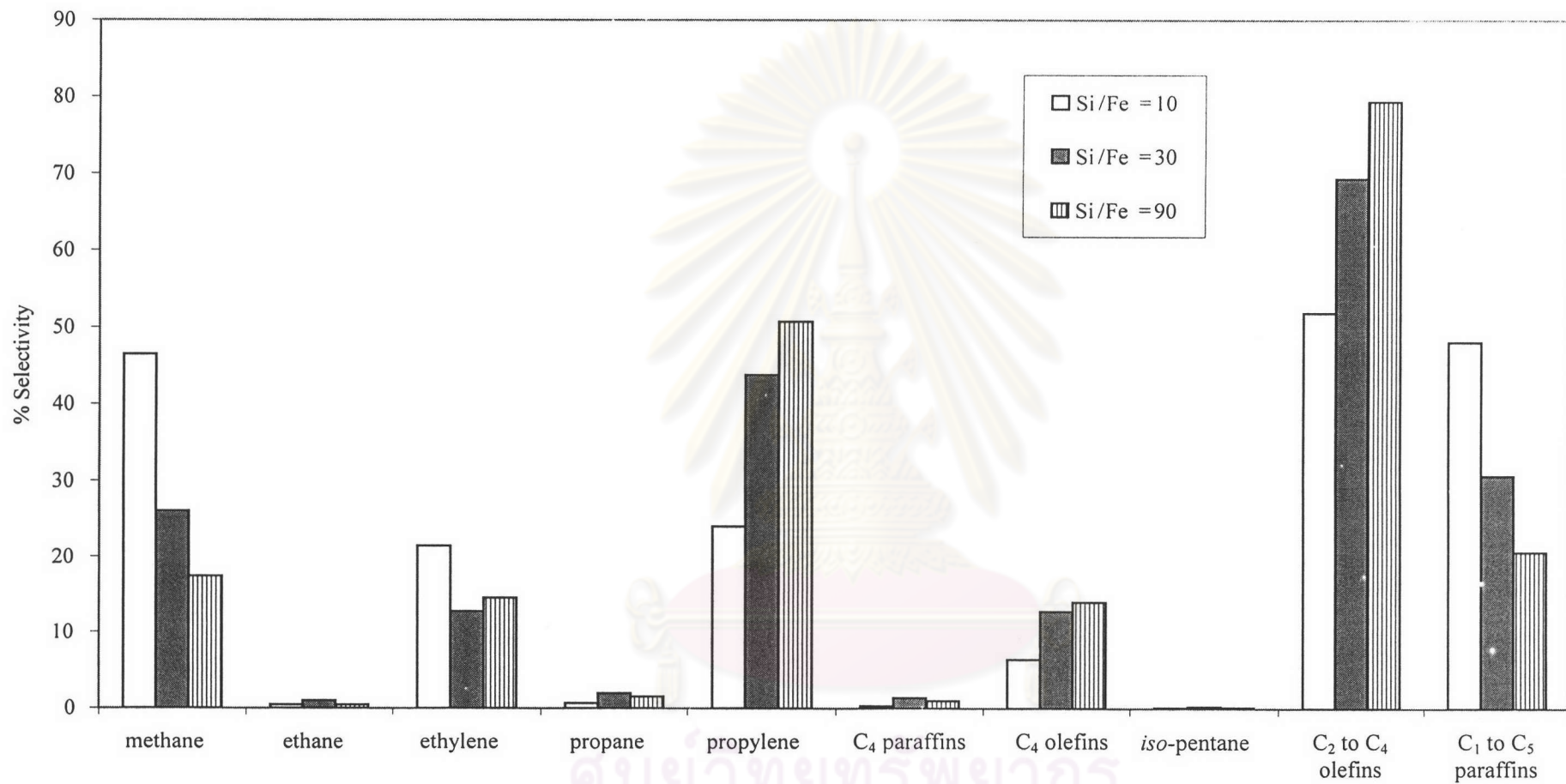
Figure 4.19 Product distribution of gas phase obtained from the methanol conversion over H-Fe-MFI with various Si/Fe ratios in catalyst corresponding to the condition in Table 4.11.
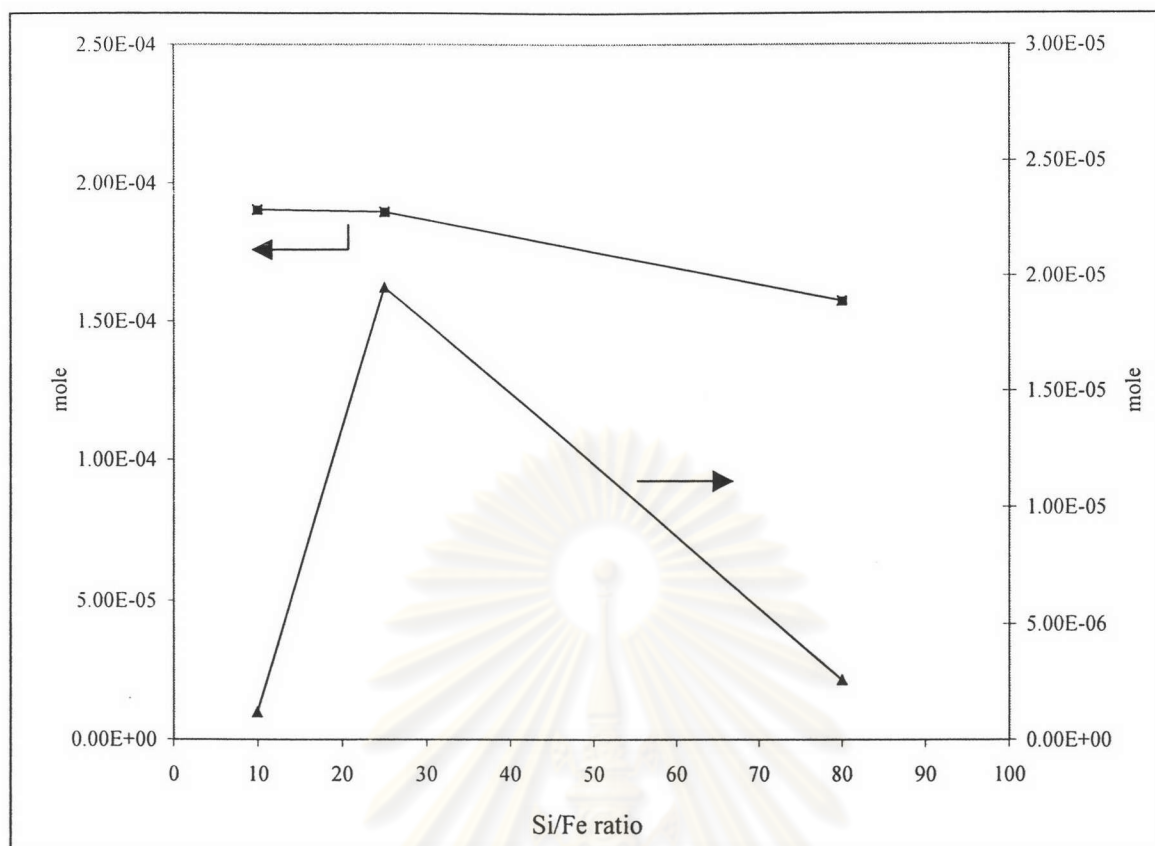
Figure 4.20 Product distribution of volatile liquid phase obtained from the methanol conversion

over H-Fe-MFI with various Si/Fe ratios in catalyst, corresponding to the condition

in Table 4.11 (■ = methanol; ▲ = C_5 alkanes).

4.3.5 Effect of Catalyst Morphology on MTO

4.3.5.1 The Values of %Conversion, Product Yield and Coke Deposition

The values of %conversion of methanol, yield of products and coke content

obtained form methanol conversion over H-Fe-MFI with various morphologies of the catalysts are

compiled in Table 4.12. For images see Figure 4.6(A), 4.11(A), and 4.7(A) for twinned plus-like

shape (gel pH value of 9.0, the small-scale preparation), spherical shape (gel pH value of 10.5, a

small-scale preparation), and spherical shape (gel pH value of 10.5 in the small-scale preparation)

Fe-MFI, respectively. There is no significant difference in either the %conversion value of methanol

or the amounts of coke deposited. Considering the relation between the conversion of methanol and

mean particle size, however, it is found that it gradually increases with decreasing the particle size.

Particle size slightly affects the catalytic activity. Nevertheless, the morphology dramatically affects

the yield of gas and liquid products. The higher yield of gas products and the lower yield of liquid products are obtained from using spherical shape compared to twinned plus-like shape of Fe-MFI catalysts. The data prove that the spherical shape provides the highest yield of gas products. Moreover, there is no significant difference in either the yields of gas or the yields of liquid products using spherical shape Fe-MFI in either the small-scale or large-scale preparation. This indicates that the product yields does not dramatically depend on the scale of preparation Fe-MFI catalyst although it depends on the morphology of the catalyst.

Table 4.12 Percentage conversion, yields of products and coke content after the methanol conversion over H-Fe-MFI with various morphologies of aggregates (Conditions: 0.3 g catalyst, GHSV = 2000 h^{-1}, $T_{catalyst}$ = 450°C, T_{MeOH} = 30°C, and TOS = 40 min)

	Particle morphology / size		
	Plus-like[a], 7.6 µm	Spherical shape[b], 18 µm	Spherical shape[c], 39 µm
%Conversion of methanol	99	97	95
Yield of gas product (%wt.)	27	50	44
Yield of liquid product (%wt.)	71	46	50
Coke (% wt. of catalyst)	0.62	0.35	0.58
BET specific surface area (m^2/g)	364	380	347

[a] *Fe-MFI with the Si/Fe ratio in gel of 90 at the gel of 9.0 in the small-scale-preparation.*
[b] *Fe-MFI with the Si/Fe ratio in gel of 90 at the gel of 10.5 in the small-scale-preparation.*
[c] *Fe-MFI with the Si/Fe ratio in gel of 90 at the gel of 9.0 in the large-scale-preparation.*

4.3.5.2 Product Distribution of the Gaseous Phase

Considering Figure 4.21, the lowest amount of methane and the highest amount of propylene are obtained from using twinned plus-like morphology. In addition, there is no significant difference in either ethylene selectivity or C$_4$ olefins selectivity among the three catalysts. This indicates that selectivity to propylene and methane depends on the morphology of

these catalysts, but that of ethylene and C_4 olefins does not. The selectivity to propylene is not dramatic (59, 53 and 51 % using twinned plus-like shape at pH gel value of 9.0 in the small-scale preparation, spherical shape at pH gel value of 10.5 in the small-scale preparation, and spherical shape at the pH value of 9.0 in the large-scale preparation, respectively). A spherical shape Fe-MFI exhibits similar activity with regardless of the scale for preparation.

4.3.5.3 Product Distribution of the Volatile Liquid Phase

Distribution of volatile liquid obtained form MTO using H-Fe-MFI catalysts with various Si/Fe ratios at 450°C are illustrated in Figure 4.22. Considering the relation between amount of unreacted methanol and C_5 alkanes, the latter increases when the amount of unreacted methanol decreases. The amount of C_5 alkanes depends on the particle size of these catalysts. It increases when the particle size increases.
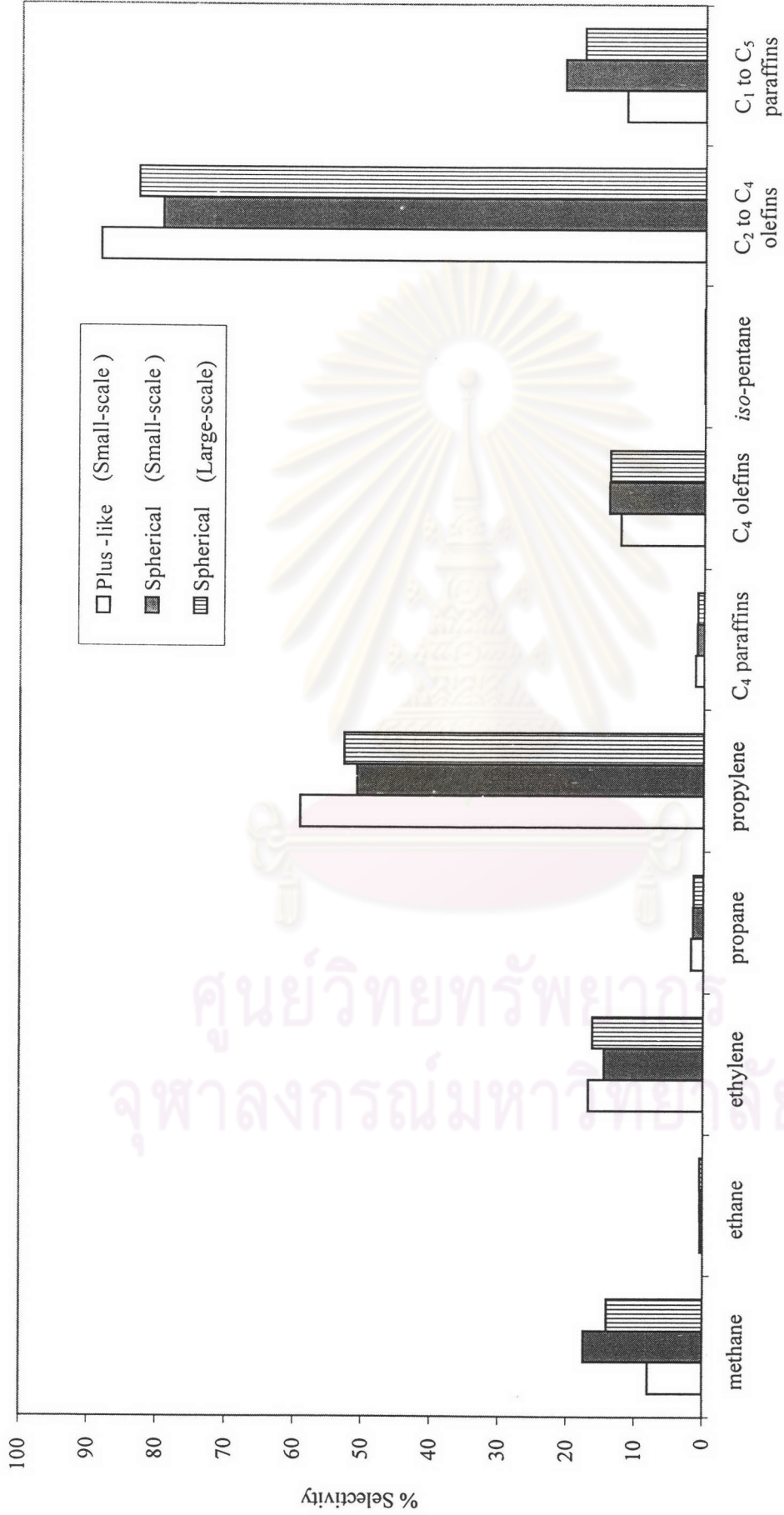
Figure 4.21 Product distribution of gas phase obtained from the methanol conversion over H-Fe-MFI with various morphologies of aggregates corresponding to the condition in Table 4.12.
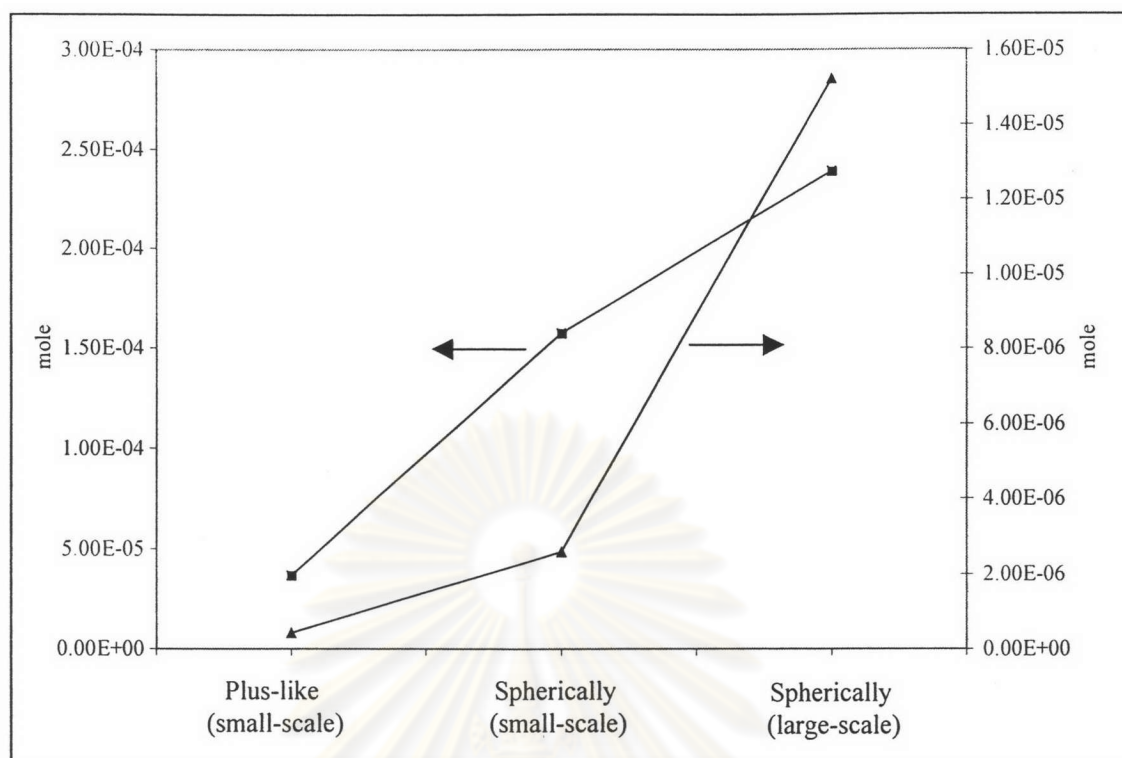
Figure 4.22   Product distribution of volatile liquid phase obtained from the methanol conversion over H-Fe-MFI with various morphologies of aggregates, corresponding to the condition in Table 4.12 (■ = methanol; ▲ = C₅ alkanes).