CHAPTER V

RESULTS AND DISCUSSIONS

This chapter is divided into two sections. The first section contains the effect of reaction temperature and Si/Al ratio on methanol to light olefins reaction. This section used to select the suitable Si/Al ratio and temperature reaction to use in the second section. The second section focused on the effect of cobalt loading and particle size of catalysts. In each section consisted of the catalyst characterization and catalytic reaction.

5.1 The effect of Si/Al ratio of ZSM-5 catalyst and reaction temperature

5.1.1 Characterization of catalyst

The commercial catalysts used in this work were first characterized in order to overview the differences of their characteristics and properties. The structure and crystallinity of MFI catalyst were measured by XRD. The specific surface area and amount of Si and Al in catalyst were measured to investigate their physical properties. The acidity of catalyst was measured by NH_3- TPD.

5.1.1.1 *X-Ray diffraction*

The X-Ray diffraction patterns for the commercial H/ZSM-5 of catalyst are shown in Figure 5.1. The X-Ray diffraction patterns for the catalysts prepared with various Si/Al ratios are illustrated in Figure 5.2. The patterns of catalysts prepared by the rapid crystallization method, were similar to those of H/ZSM-5. This indicated that all the prepared catalysts had the similar pentasil pore opening structure as H/ZSM-5.

5.1.1.2 Physical properties

The physical properties for all catalysts are summarized in Table 5.1. The specific surface area estimated by BET and composition of catalyst in this study measured by XRF technique are also listed. The crystallinity was calculated based on the area of main peak of XRD compared with that of H/ZSM-5 as a reference. No significant loss of crystallinity was observed for all catalysts.

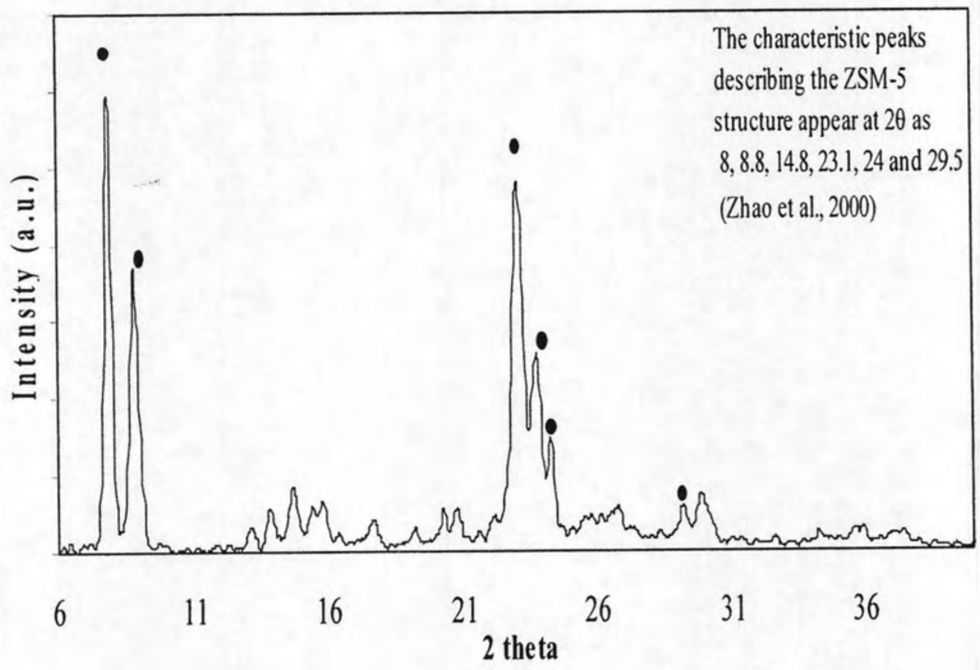

Figure 5.1 X-Ray diffraction patterns of commercial MFI zeolite.

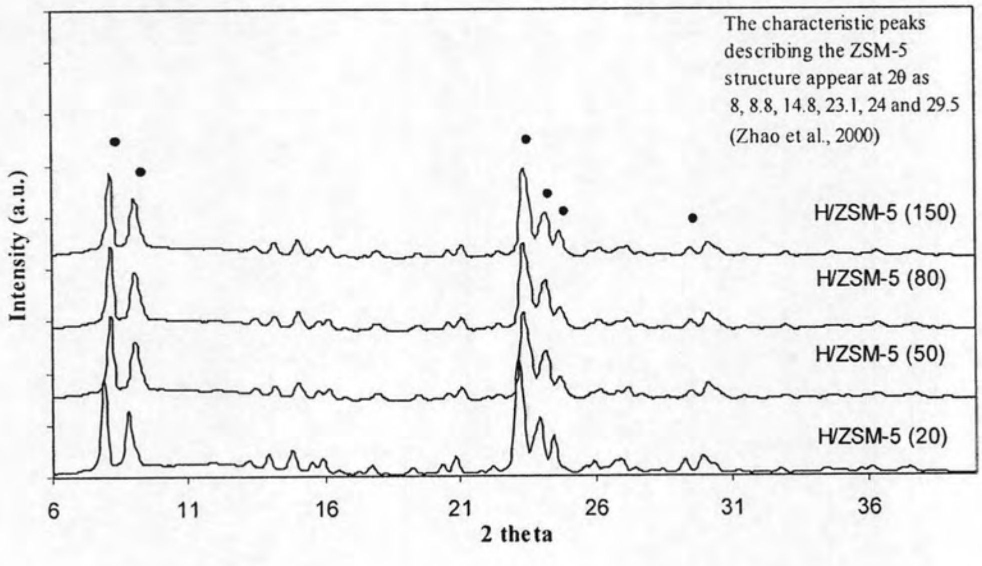

Figure 5.2 X-Ray diffraction patterns of H/ZSM-5 with various Si/Al ratios .

Table 5.1 Physical properties of various Si/Al ratio of H/ZSM-5

Catalyst	Si/Al ratio	Si/Al ratio [a] observed	BET surface area [b] (m^2/g)	% Crystallinity [c]
H/ZSM-5	20	44.22	364	75.2
	50	72.28	359	70.2
	80	91.12	347	68.5
	150	156.26	341	71.2

a measured by XRF

b based on N_2 physisorption

c based on XRD measurement

5.1.1.3 The acidity of catalyst

The NH_3- TPD profiles for all catalysts with various Si/Al ratios are shown Table 5.2. The profiles are composed of two peaks, i.e. a high temperature peak represents strong acid sites and a low temperature peak refers to weak acid sites. It was found that high Si/Al ratio resulted in lower acidity than the low Si/Al ratio.

Table 5.2 Acidity of various Si/Al ratios of H/ZSM-5

Catalyst	Adsorbed volume of ammonia (ml)	Total acid site (μmol H^+/g)
H/ZSM-5 (20)	2.29	937
H/ZSM-5 (50)	1.39	570
H/ZSM-5 (80)	0.87	355
H/ZSM-5 (150)	0.60	246

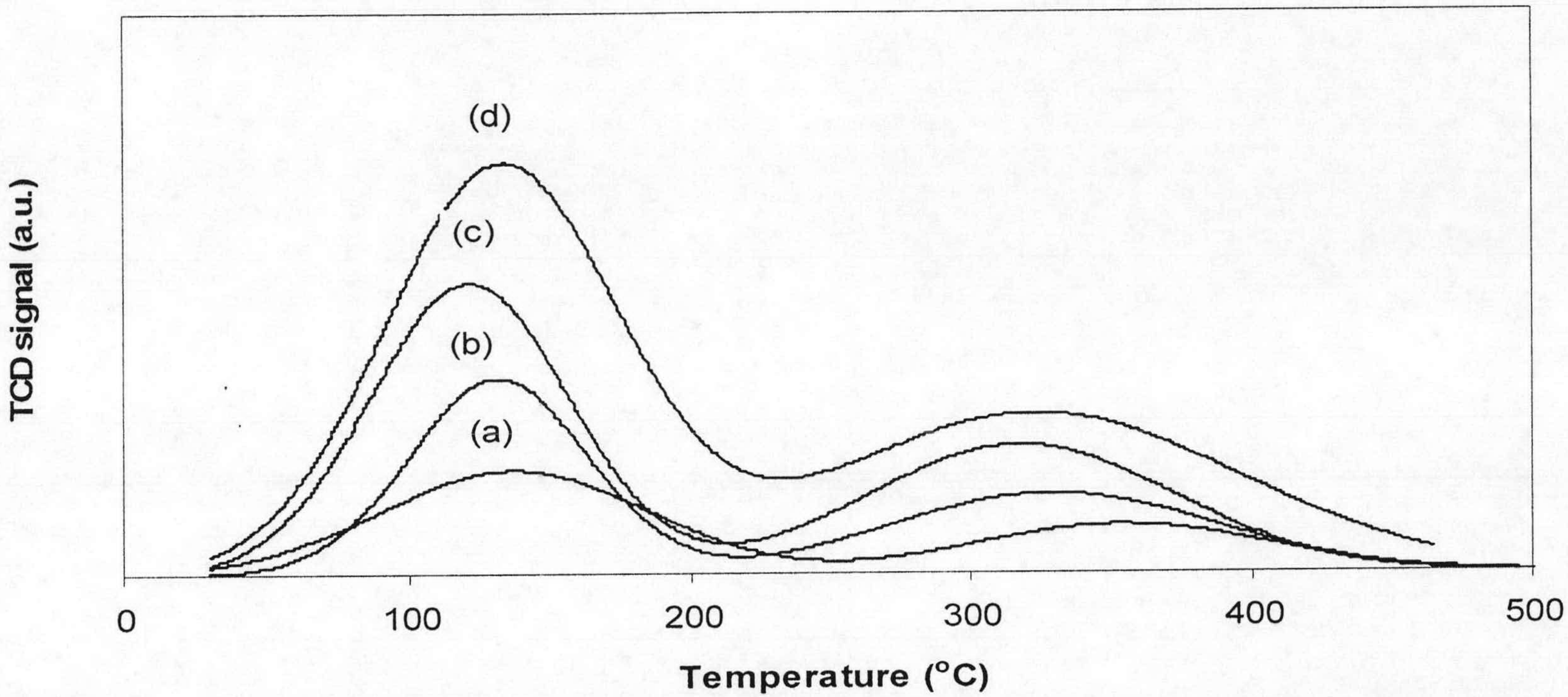

Figure 5.3 The NH_3-TPD Profile of various Si/Al ratios of H/ZSM-5 catalysts
(a) Si/Al =150, (b) Si/Al = 80, (c) Si/Al = 50, (d) Si/Al = 20.

5.1.2 Catalytic Reaction

Effects of reaction temperature and Si/Al ratio of H/ZSM-5 are shown in Figure 5.4 -5.6. The various reaction temperatures raged between 200-500 °C were studied. The reaction temperature apparently affected to methanol conversion and light olefins selectivity. The methanol conversion increased with increased reaction temperature. It revealed that at 200 ^{0}C, the light olefins did not occur, thus the main product at this temperature was dimethyl ether (DME). Light olefins appeared at 300-500 ^{0}C. It was found that at 300 ^{0}C was a suitable temperature to convert methanol into light olefins. In addition, the main products at high temperature were aromatic and paraffin.

The various Si/Al ratios of H/ZSM-5 catalysts were also studied. The Si/Al ratios of 20, 50 and 80 possessed adjoining methanol conversion. However at Si/Al ratio of 150 low methanol conversions was evident, because the catalyst having Si/Al of 150 had lower acidity than the other Si/Al ratios. The light olefin selectivity of Si/Al at 150 was higher than other Si/Al ratios. The light olefin selectivity for Si/Al of 20, 50, 80 was detected that obtained from for all reaction temperatures used in this study.

The results showed that the Si/Al ratio of H/ZSM-5 catalyst affected to both methanol conversion and light olefin selectivity where high acidity responded for the high methanol conversion, but low light olefins selectivity was found.

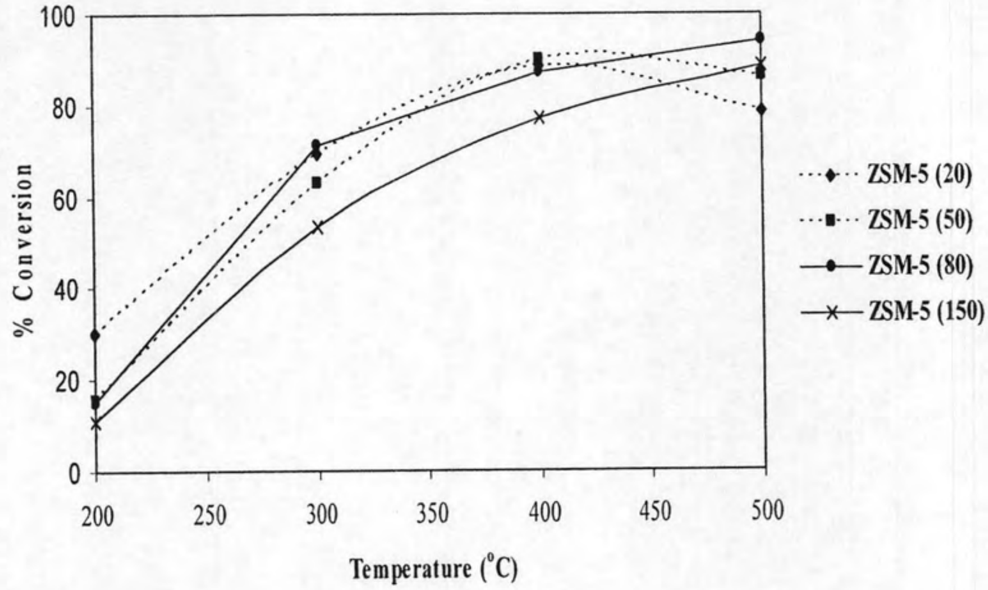

Figure 5.4 The effect of reaction temperature and Si/Al ratio of ZSM-5 on the methanol conversion.

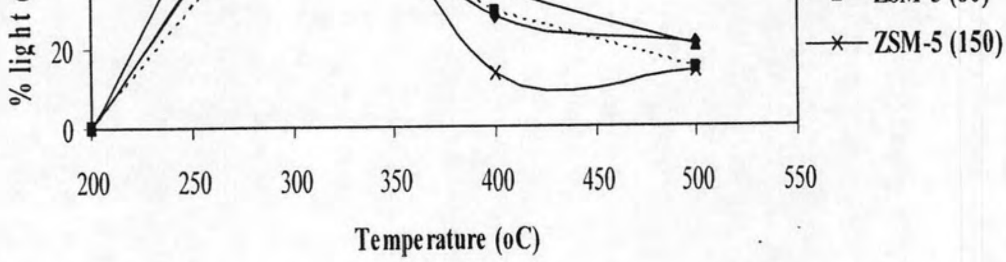

Figure 5.5 The effect of reaction temperature and Si/Al ratio of ZSM-5 on the light olefin selectivity.

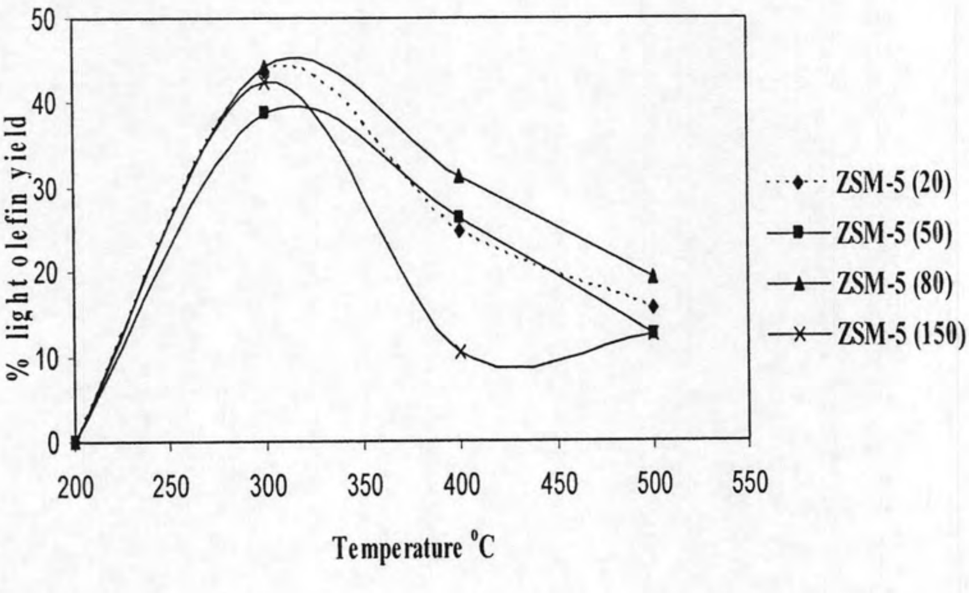

Figure 5.6 The effect of reaction temperature and Si/Al ratio of ZSM-5 on the light olefin yield.

Based on the light olefin yield obtained, it was found that the H/ZSM-5 at Si/Al ratio of 80 was the suitable catalyst at 300 ^{0}C that should be used for methanol conversion to light olefins. Therefore, the Si/Al ratio of 80 and reaction temperature at 300 ^{0}C were selected for studying the effect of cobalt loading and particle size in next part.

5.2 The effect of cobalt loading and particle size of catalyst

5.2.1 Characterization of the catalysts

The commercial catalyst used in this work was first characterized to overview the differences of their characteristics and properties. The structure and crystallinity of MFI catalyst were measured by XRD. The specific area and amount of Si and Al, and Co catalyst were measured to investigate their physical properties. The morphology was determined by SEM. The acidity of catalyst was measured by NH_3-TPD. Finally, XPS was used to measure the binding energy and the composition on the surface layer of the catalysts.

5.2.1.1 X-Ray diffraction pattern

The structure and crystallinity of ZSM-5 and Co/ZSM-5 catalysts with various particle sizes were analyzed by X-ray diffraction (XRD). The XRD patterns of all 1.8 , 3.4 , 4.7 μm of ZSM-5 catalysts and Co/ZSM-5 catalyst were similar as expected because all catalysts used in this study were prepared from the same MFI zeolite structure. Hence, the MFI catalyst structure should not be affected by particle size. The X-ray diffraction patterns of 1.8, 3.4, 4.7 μm for ZSM-5 and Co/ZSM-5 at different Co loading are depicted in Figure 5.7 - 5.10. No significant change of MFI structure was observed for various particle sizes.

5.2.1.2 Morphology

Images for the Scanning electron microscopy (SEM) of the prepared catalysts are shown in Figures 5.10-5.12. The shapes of all catalyst are roughly crystallize having spherical particles, which are composed of many small regular plates. The particle sizes of the zeolite samples were measured from SEM by average the diameter of particle. Particle size values estimated from SEM images of the catalyst have been reported in many researches. Considerating the SEM micrographs depicted in Figure 5.11-5.13, it indicated that the diameters of H/ZSM-5 zeolite samples were 1.8, 3.4, and 4.7. The SEM micrographs depicted in Figure 5.14-5.16 indicated that the morphologies of Co/ZSM-5 zeolite samples having Co loading of 1, 5, and 10 %wt, respectively.

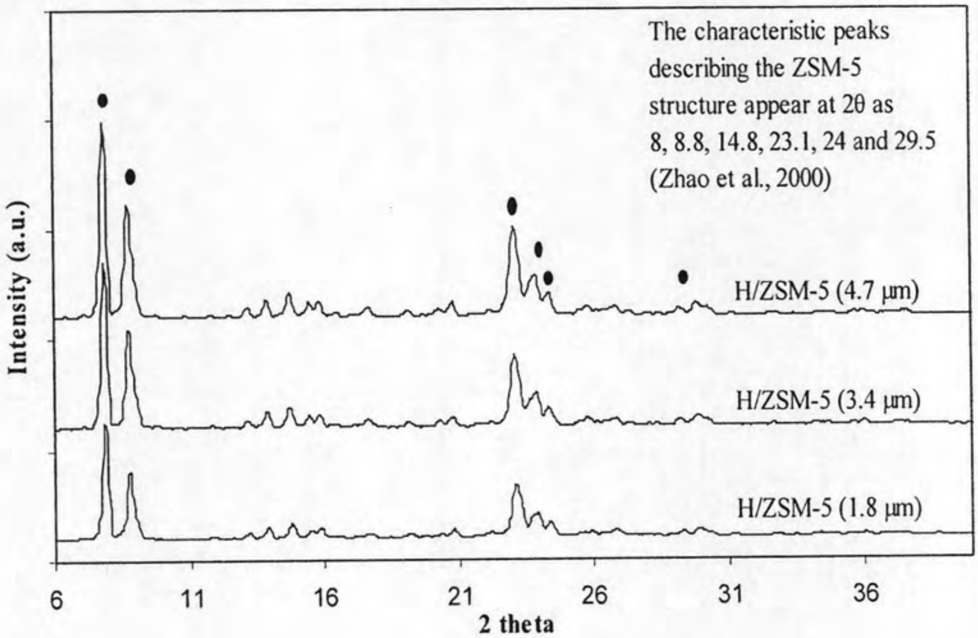

Figure 5.7 X-ray diffraction patterns of H/ZSM-5 catalysts

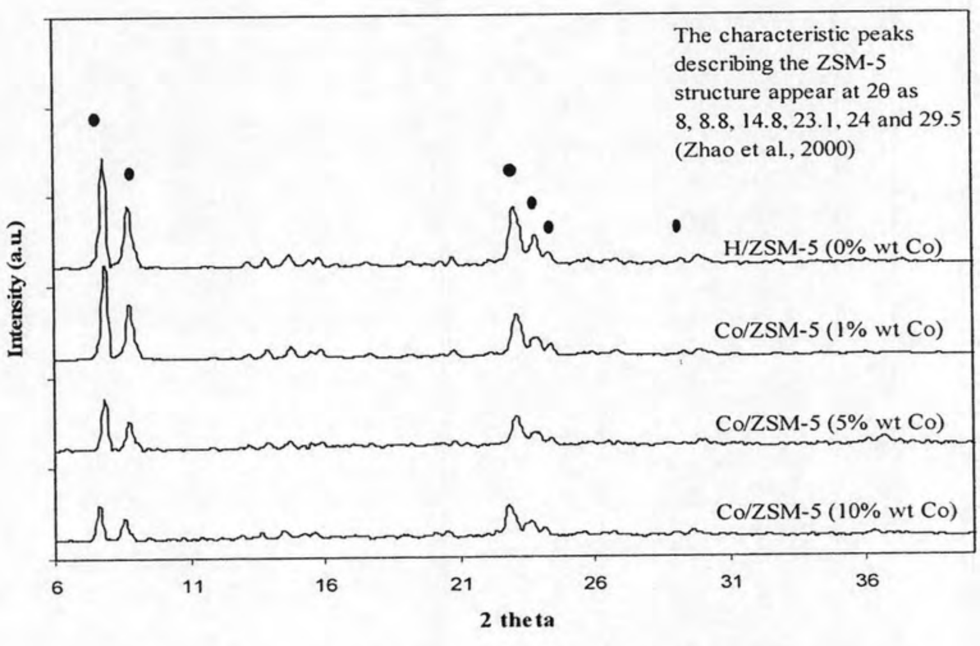

Figure 5.8 X-ray diffraction patterns of Co/ZSM-5(1.8µm) catalysts

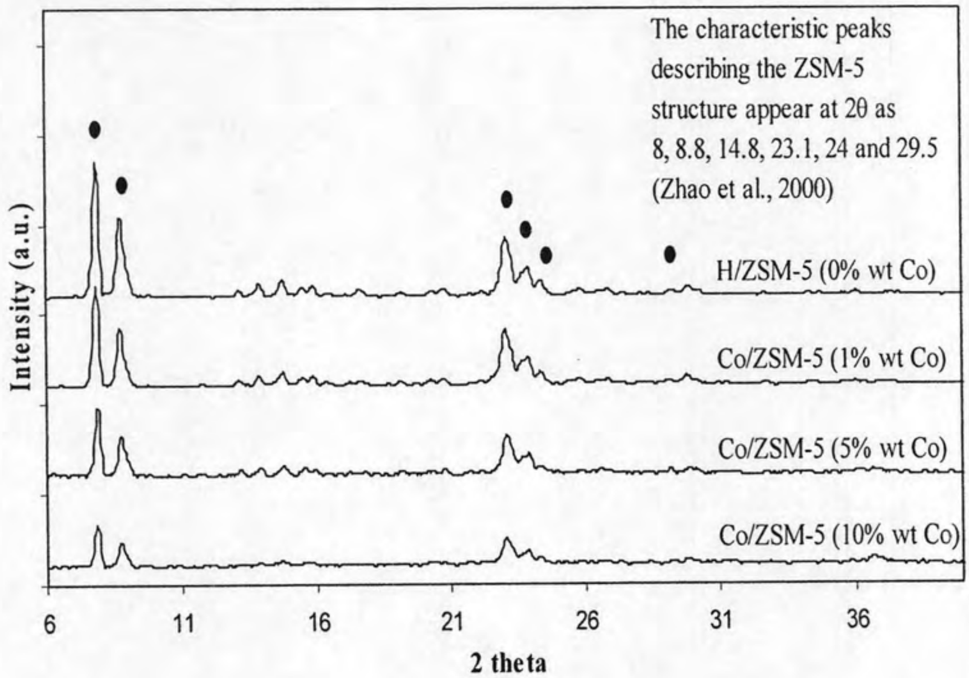

Figure 5.9 X-ray diffraction patterns of Co/ZSM-5(3.4μm) catalysts

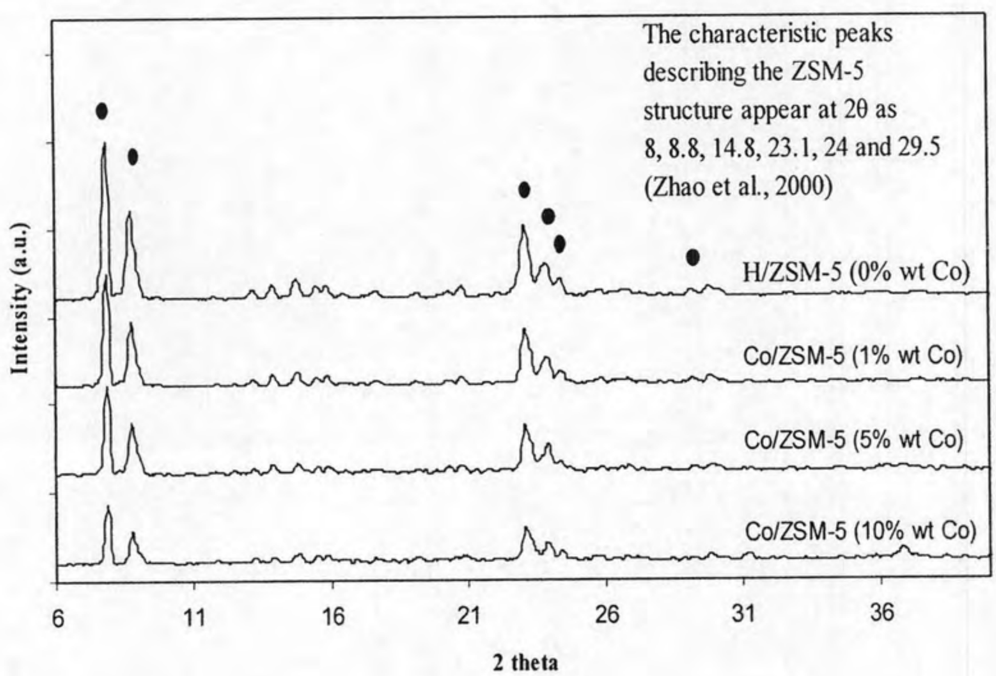

Figure 5.10 X-ray diffraction patterns of Co/ZSM-5(4.7μm) catalysts

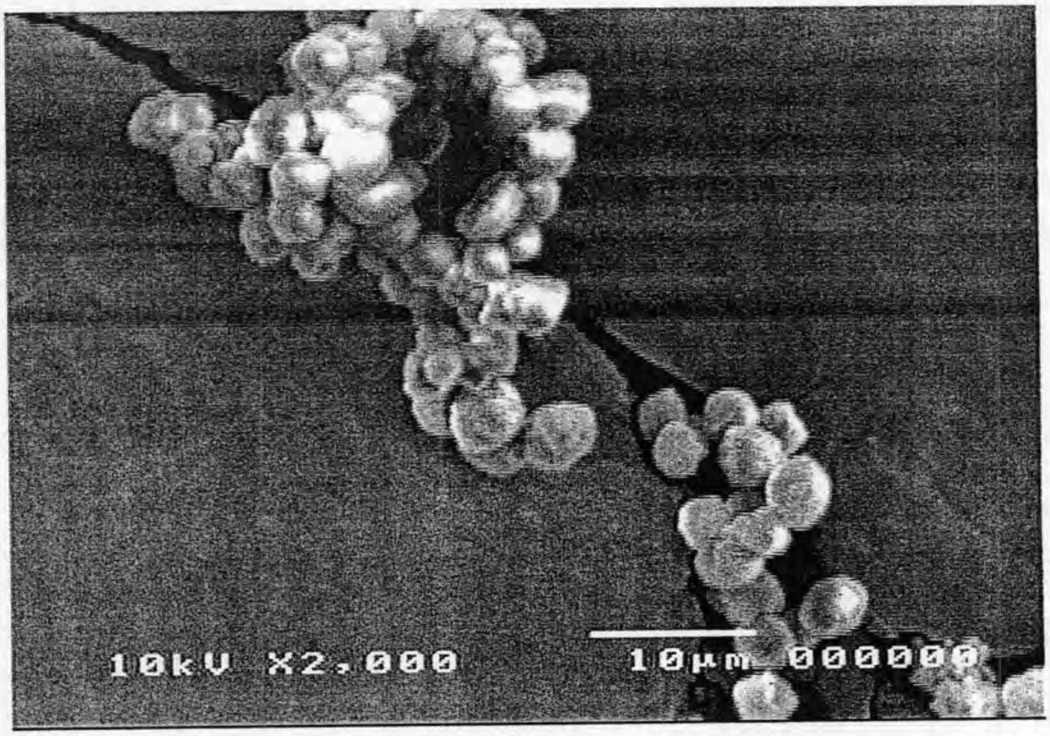

Figure 5.11 Scanning electron micrograph of H ZSM-5 (1.8µm)

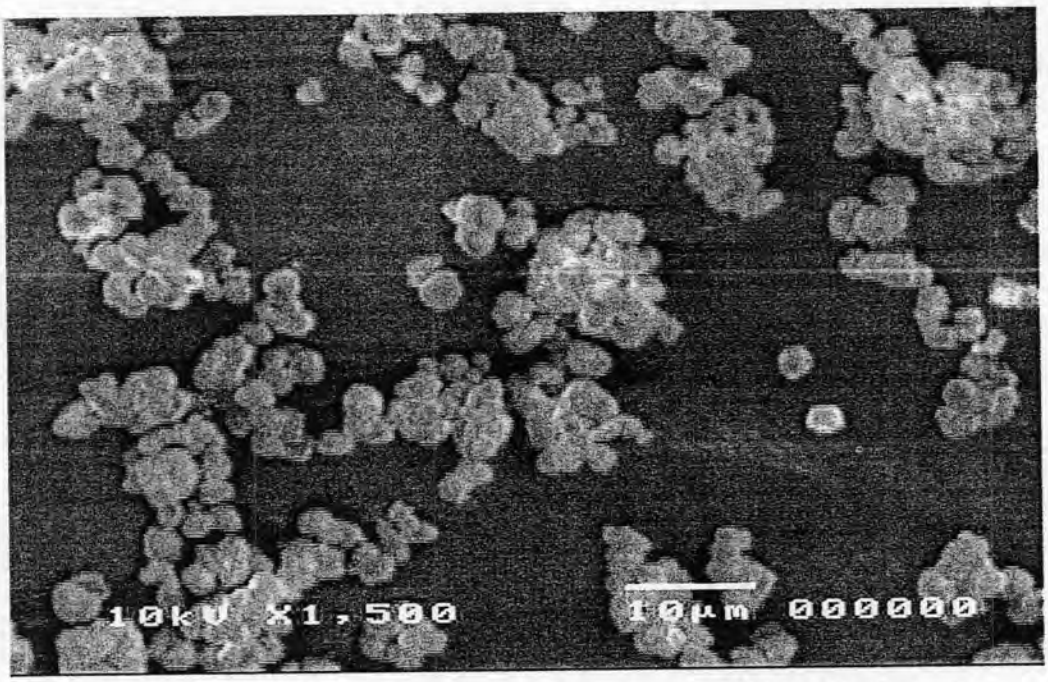

Figure 5.12 Scanning electron micrograph of H ZSM-5 (3.4µm)

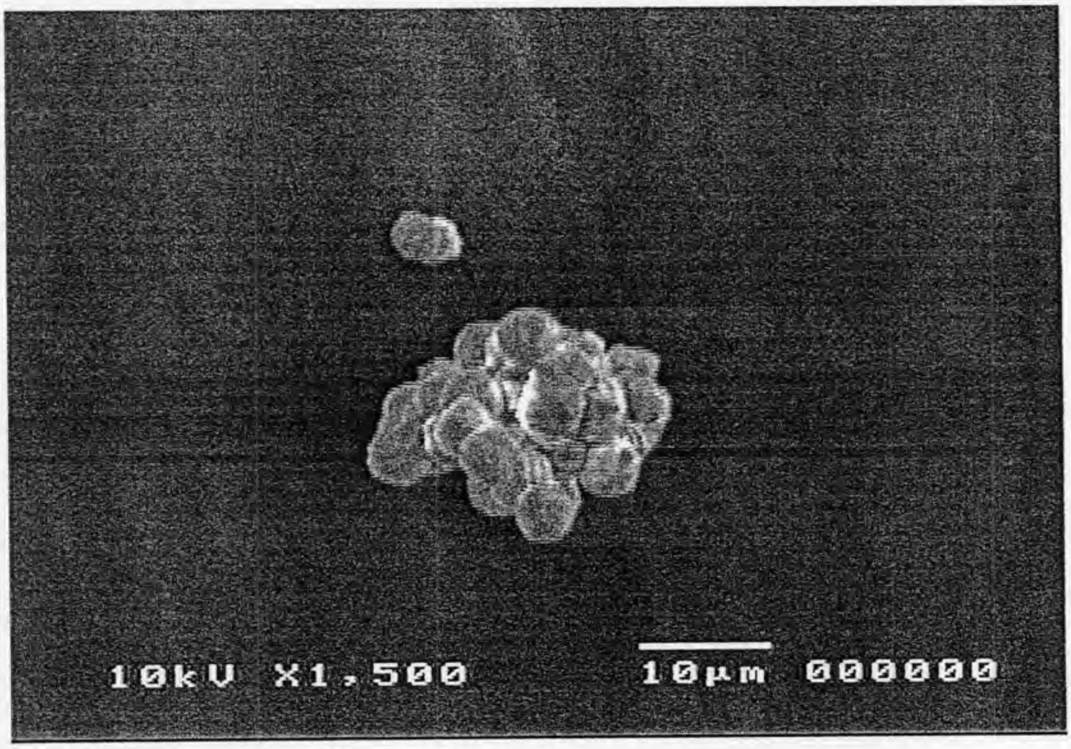

Figure 5.13 Scanning electron micrograph of H ZSM-5 (4.7µm)

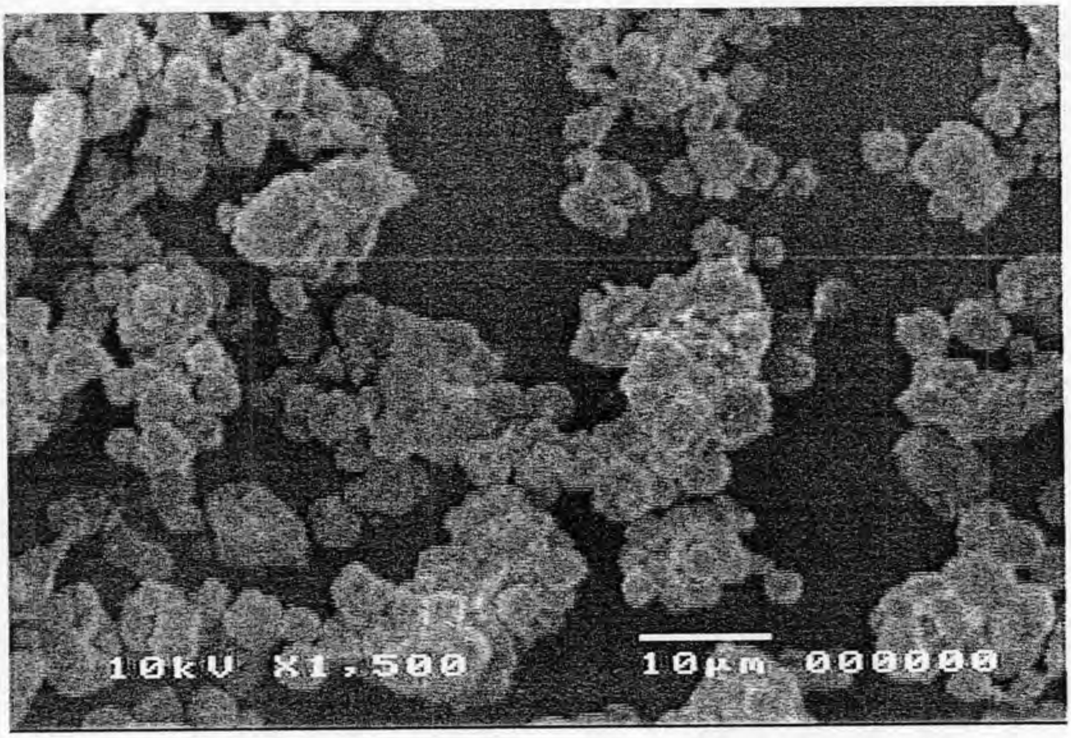

Figure 5.14 Scanning electron micrograph of Co/ZSM-5 (1%wt Co,4.7µm)

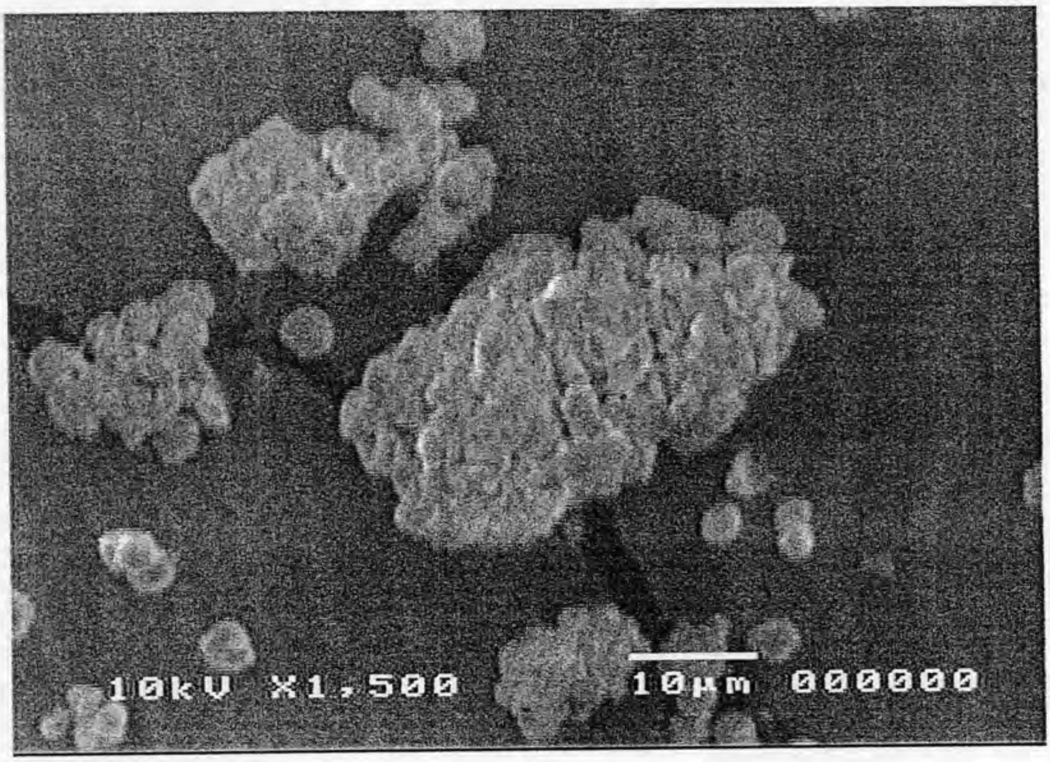

Figure 5.15 Scanning electron micrograph of Co/ZSM-5 (5%wt Co, 4.7µm)

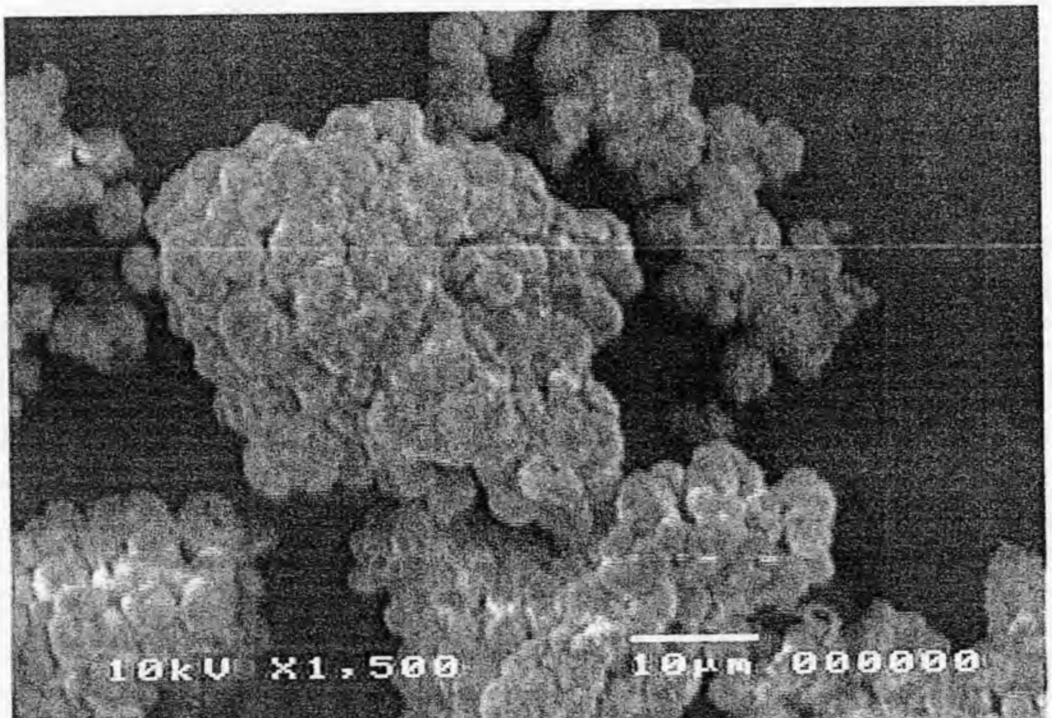

Figure 5.16 Scanning electron micrograph of Co/ZSM-5 (10%wt Co, 4.7µm)

5.2.1.3 Physical Properties

The physical properties of ZSM-5 and Co/ZSM-5 catalysts were summarized in Table 5.3. BET surface area decreased after the introduction of the cobalt in ZSM-5 indicating a textural attention of the parent zeolite, probably because of pore blocking by cobalt species either dispersed in the channels or deposited at the other surface of the zeolite. Table 5.3 shows the zeolite catalysts with Si/Al ratio of 80 varying with particle size and cobalt content. Crystallinity, as determined by XRD, was calculated based on the area of main peak compared with the MFI as a reference. The crystallinity decreased when cobalt was loaded into ZSM-5 catalyst. The large particle size exhibited high crystallinity than small particle.

Table 5.3 Physical properties of various particle sizes of Co/ZSM-5 catalysts

Catalyst	Particle diameter diameter by SEM	BET surface area (m^2/g)	% Crystallinity
ZSM-5	1.8	379	68.5
Co 1%	1.8	362	53.1
Co 5%	1.8	330	36.4
Co 10%	1.8	311	29.5
ZSM-5	3.4	359	76.3
Co 1%	3.4	333	55.5
Co 5%	3.4	328	48.4
Co 10%	3.4	308	30.6
ZSM-5	4.7	343	97.2
Co 1%	4.7	339	56.4
Co 5%	4.7	332	50.4
Co 10%	4.7	312	40.5

5.2.1.4 Acidity

The NH_3-TPD profiles of ZSM-5 and Co/ZSM-5 catalysts are shown in Table 5.4. The profiles are composed of two peaks, i.e., a high temperature peak represents strong acid sites and a low temperature peak refers to weak acid sites (Inui, T., 1984)

Table 5.4 The peak concentration of acid site of the various particle sizes

Catalyst	Adsorbed volume of NH_3 (ml)	Total acid site (μmol H^+/g)
ZSM-5 (4.7μm)	0.871	356.4
ZSM-5 (3.4μm)	0.849	347.3
ZSM-5 (1.8μm)	0.879	359.5
Co-ZSM-5 (1%,4.7μm)	0.834	341.2
Co-ZSM-5 (1%,3.4μm)	0.820	335.4
Co-ZSM-5 (1%,1.8μm)	0.825	337.4
Co-ZSM-5 (5%,4.7μm)	0.783	320.6
Co-ZSM-5 (5%,3.4μm)	0.755	308.7
Co-ZSM-5 (5%,1.8μm)	0.812	332.0
Co-ZSM-5 (10%,4.7μm)	0.809	331.0
Co-ZSM-5 (10%,3.4μm)	0.801	327.5
Co-ZSM-5 (10%,1.8μm)	0.819	335.2

From the Figures 5.17 -5.20, they show NH_3-TPD profiles of various %wt cobalt loading and particle sizes. The NH_3-TPD indicated that the particle size had no significant effect on the acidity of catalyst. On the other hand, %wt cobalt loading affected the acidity of catalyst. After loading cobalt, the NH_3-TPD profiles revealed loss of strong acid site. The acidity of catalyst affected on types of main product. Where light olefin was obtained from the low acidity catalyst, whereas aromatic was obtained from the high acidity catalyst.

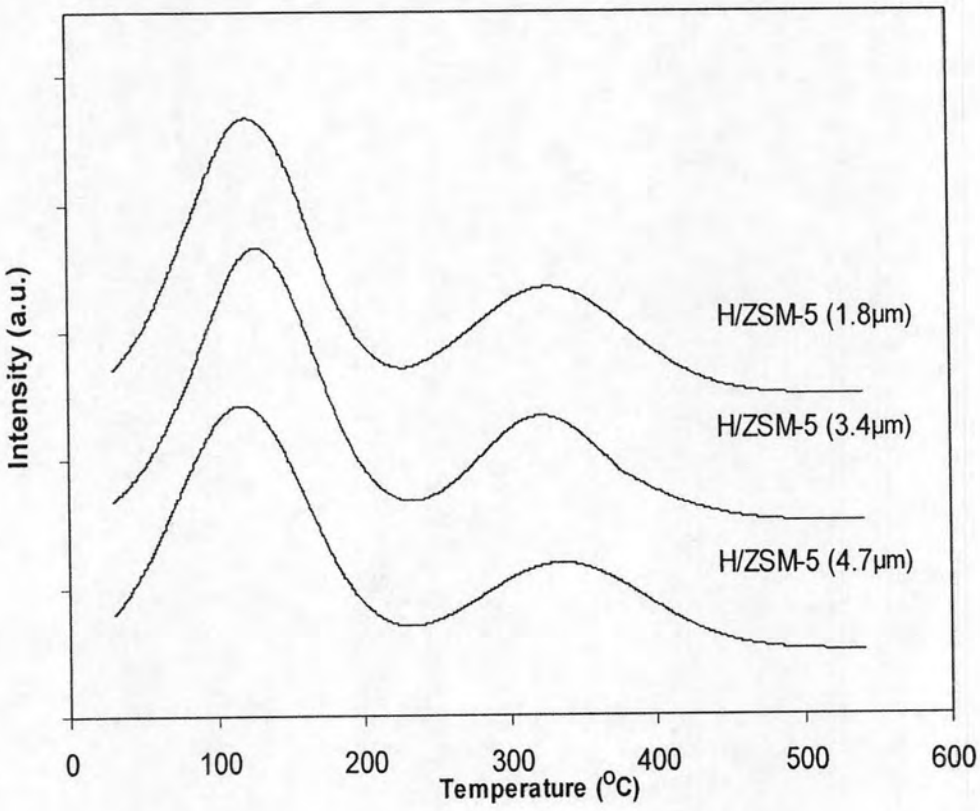

Figure 5.17 The NH_3-TPD profile of H/ZSM-5 catalyst of various particle sizes

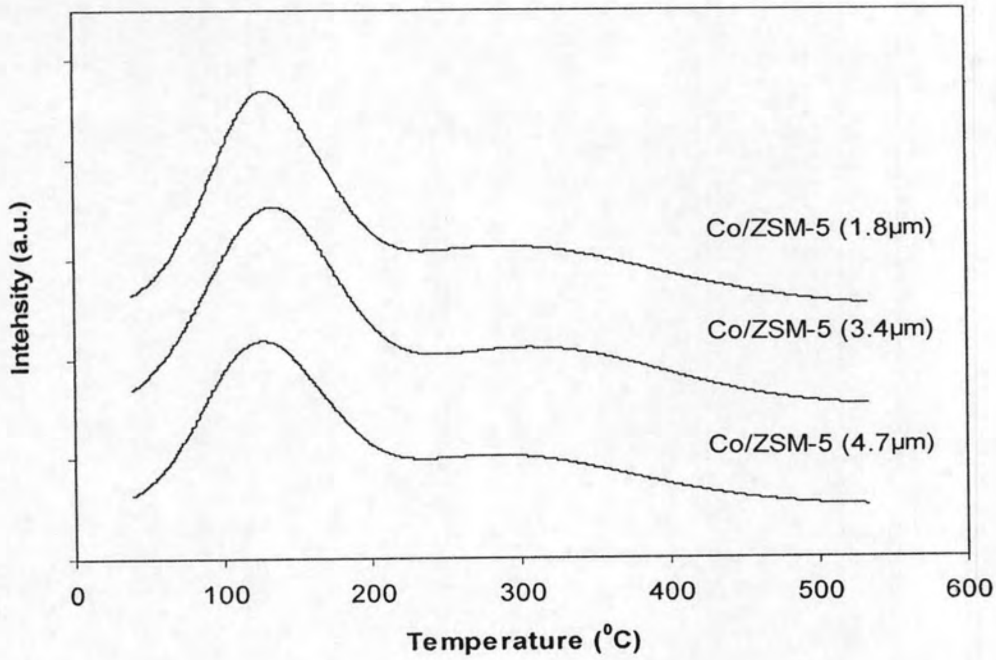

Figure 5.18 The NH_3-TPD profile of Co/ZSM-5 catalyst having 1%wt of cobalt loading on various particle sizes

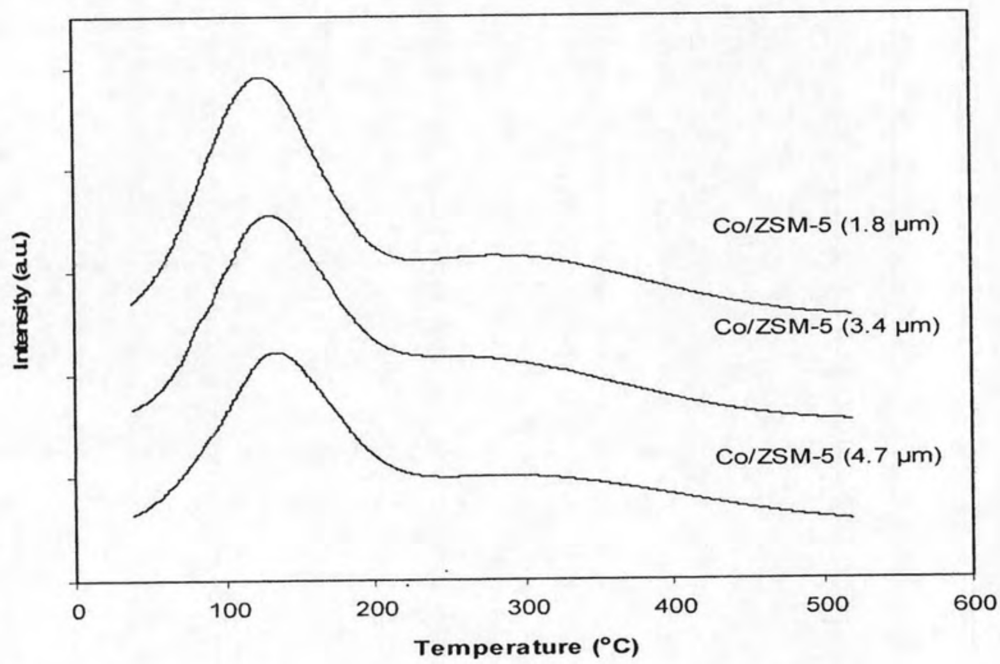

Figure 5.19 The NH_3-TPD profile of Co/ZSM-5 catalyst having 5%wt of cobalt loading on various particle sizes

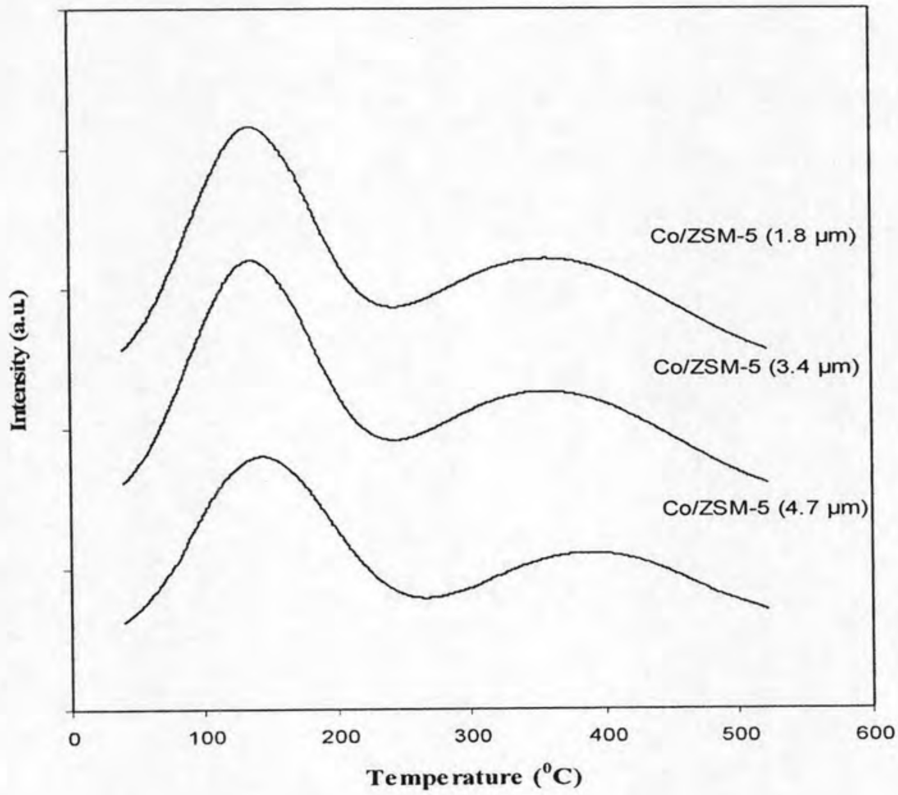

Figure 5.20 The NH_3-TPD profile of Co/ZSM-5 catalyst having 10%wt of cobalt loading of various particle sizes

5.2.1.5 Surface Composition

This section is, therefore aimed to study the surface composition of the metal catalyst having various particle sizes and different percent cobalt loading using X-ray photoelectron spectroscopy (XPS). Figure 5.21 illustrates the XPS spectrum of Co/ZSM-5 prepared from incipient-wetness impregnation samples. The Co/ZSM-5 with 1% did not have cobalt species indicating that all cobalt species dispersed in the channel. The effect of particle size of Co/ZSM-5 was also studied. For the large particle size it was found that cobalt species deposited at the outer surface of catalyst, which were higher than those of the small particle size, as shown in Figure 5.22. Product selectivity was also affected by the quantity of cobalt species dispersed in the channel of catalyst because this caused changes in the resident times and shape selectivity of catalyst.

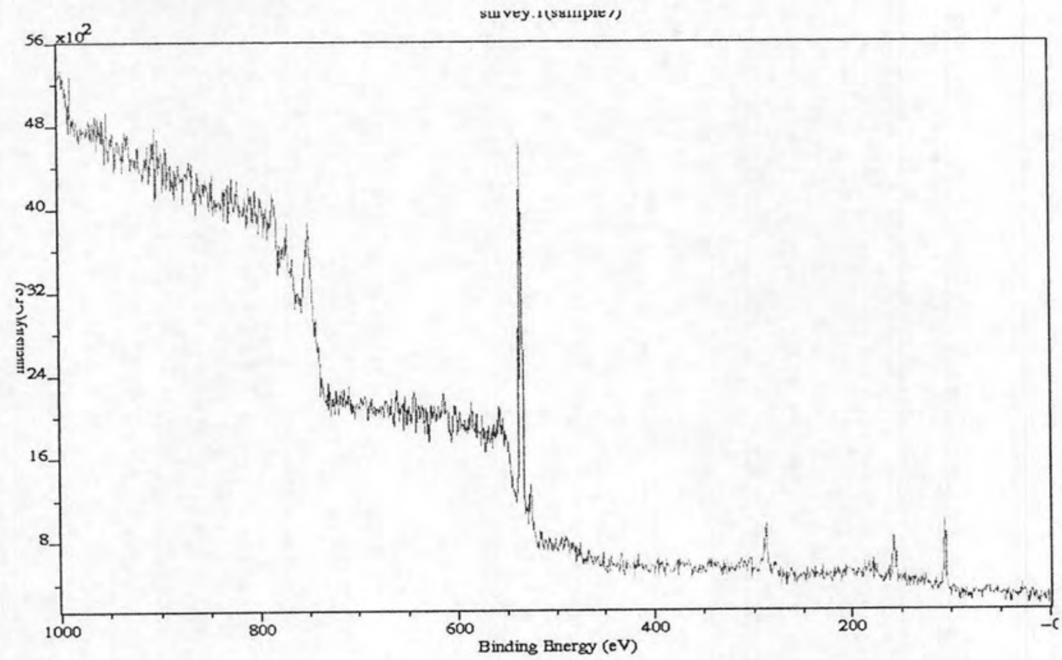

Figure 5.21 XPS survey spectrum for Co/ZSM-5 (10 %wt Co) catalysts

Table 5.5 XPS binding energies of Co/ZSM-5 simulated catalyst

Crystal size (μm)	% Cobalt loading	Co 2p		Co Atomic concentration (%)
		Peak position (ev)	FWHM	
1.8	1	-	-	-
1.8	5	781.7	1.412	0.3
1.8	10	781.5	2.166	0.78
3.4	1	-	-	-
3.4	5	781.7	1.065	0.3
3.4	10	780.7	1.874	1.46
4.7	1	-	-	-
4.7	5	781.2	1.889	0.7
4.7	10	781.2	2.588	2.28

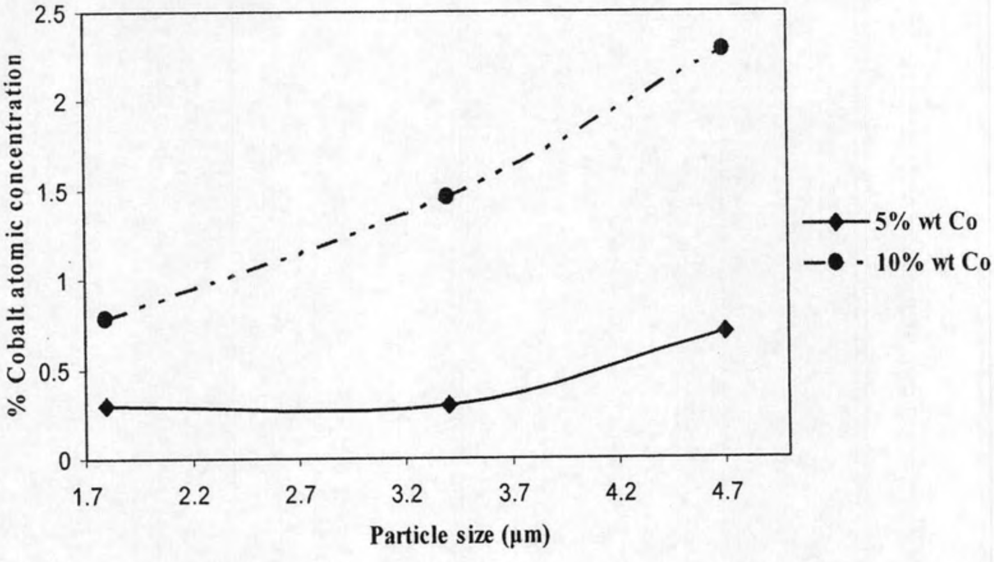

Figure 5.22 The cobalt atomic concentration of Co/ZSM-5 catalyst at 5%, 10% wt cobalt loading for various particle sizes

5.2.2 Catalytic Reaction

In this section, the catalytic properties of the catalyst prepared in this study were tested for methanol conversion into light olefins (using 20% wt methanol)

The effect of cobalt loading and particle sizes on the methanol conversion.

The effect of cobalt loading on methanol conversion was compared. The methanol conversion decreased with the introduction of cobalt to H/ZSM-5 catalyst indicating a textural alternation of the parent zeolite, probably because of pore blocking by cobalt species either dispersed in the channels or deposited at the outer surface of zeolite.

The effect of particle size of Co/ZSM-5 on methanol conversion was also studied. The small particle size (1.8µm) showed higher methanol conversion than the large particle size (3.4, 4.7 µm). The small particle size also exhibited higher stability than large particle size, as shown in Figure 5.23

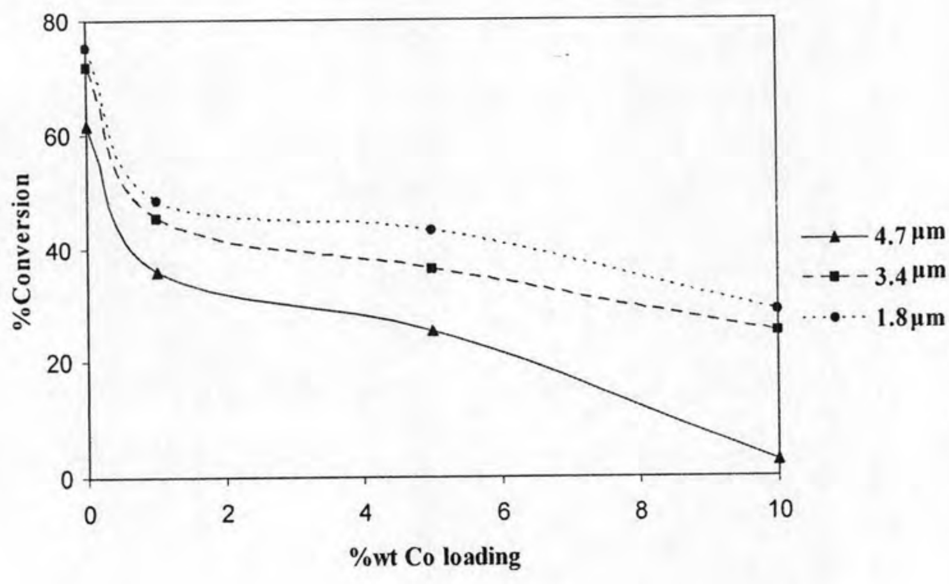

Figure 5.23 The effect of cobalt loading and particle size of ZSM-5 on the methanol conversion

The effect of cobalt loading and particle size on the light olefin selectivity

The effect of cobalt loading to light olefin selectivity was compared. The light olefin selectivity of 1% and 5% wt cobalt loading increased with cobalt loading. On the other hand, at 10% wt cobalt loading the light olefins selectivity decreased due to increased acidity of catalyst as shown in Figure 5.24

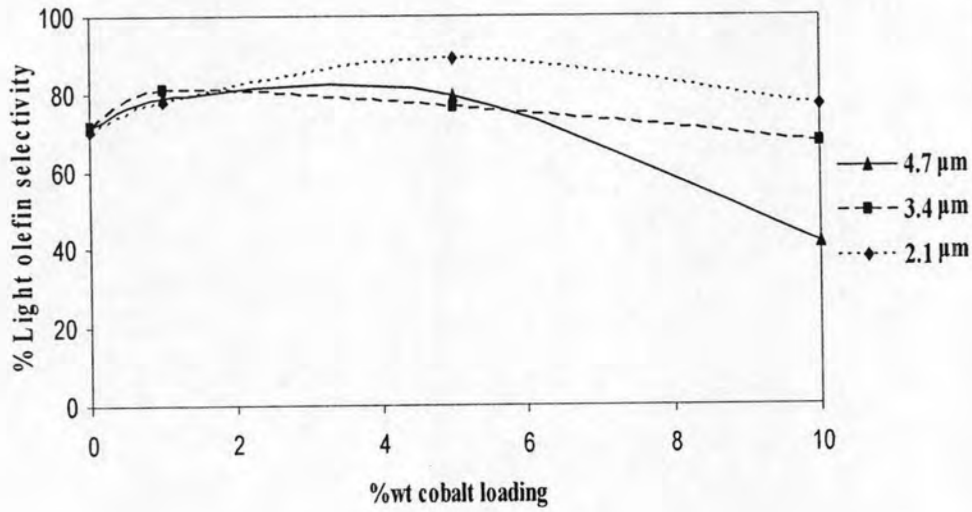

Figure 5.24 The effect of cobalt loading and particle size of ZSM-5 on the light olefin selectivity

The effect of particle size of Co/ZSM-5 on the light olefin selectivity was also studied. The H/ZSM-5 catalyst, Co/ZSM-5 with 1%wt Co and 5% wt Co did not have significant change in light olefin selectivity. On the other hand, the various particle sizes of 10% wt Co/ZSM-5 affected the light olefins selectivity as shown in Figure 5.25. The small particle size of Co/ZSM-5 (1.8 µm) showed the greater light olefins selectivity than large Co/ZSM-5 particle sizes (3.4, 4.7) because cobalt species dispersed in the channel of small size higher than large Co/ZSM-5 particle sizes. The cobalt species dispersed in the channel effected the changes in the resident time and product selectivity as shown in Figure 5.26.

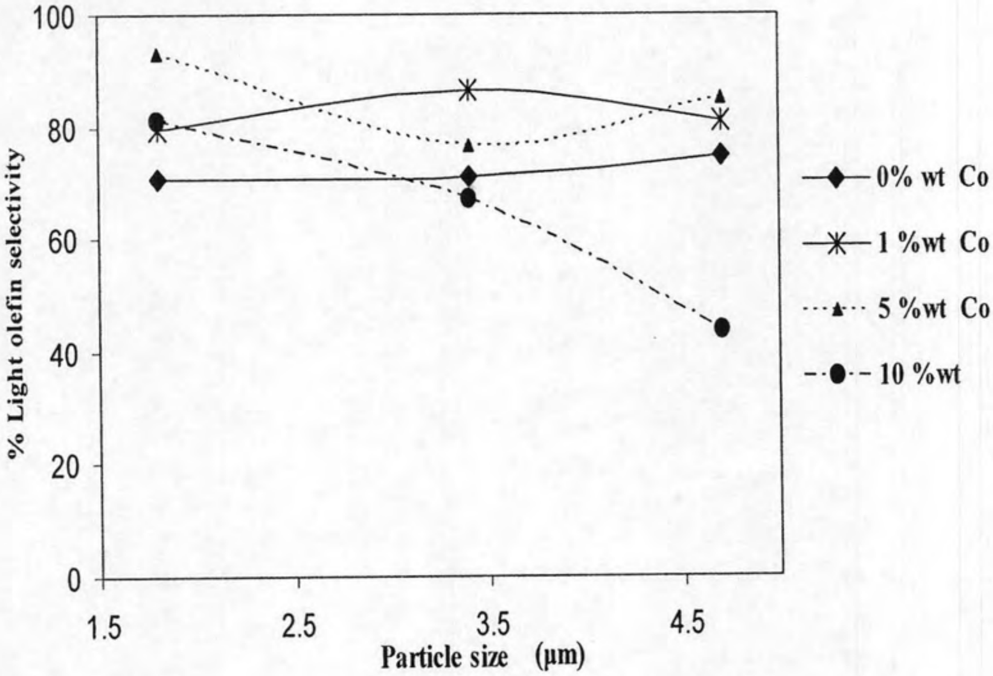

Figure 5.25 The effect of particle size of ZSM-5 on the light olefin selectivity

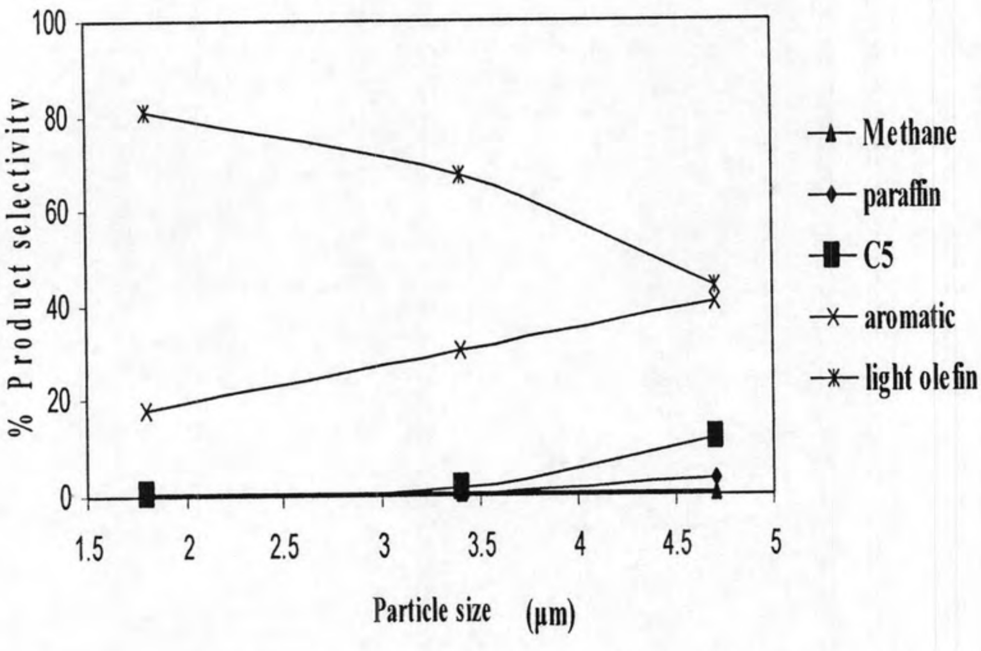

Figure 5.26 The product selectivity of 10%wt Co/ZSM-5 of various particle sizes