

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the catalyst characterization results are discussed in Section 4.1, and the influences of (a) the two consecutive layers of catalytic systems, and (b) the HZSM-5 catalysts modified with oxides of group VA elements on liquid hydrocarbons production from bio-ethanol, are analyzed and discussed in Sections 4.2 and 4.3, respectively. The catalytic reaction was performed in a continuous U-tube fixed-bed reactor at 500 °C under atmospheric pressure. The catalysts and experimental design are shown in Table 4.1. Runs #1 to #4 are designed for studying the effect of the consecutive layers of Ga₂O₃-modified HZSM-5 (the first layer) and one of H-X, H-Y, and H-Beta catalysts having different pore sizes (the second layer). Runs #5 to #17 are designed for studying the effect of acidic oxides of phosphorus (P), antimony (Sb), and bismuth (Bi) supported on HZSM-5.

4.1 Characterization of Catalysts

This section discusses about the characterization of catalysts by using several techniques to examine the element content and the difference on their characteristics and properties. The oxide form of each element was analyzed by Raman spectroscopy. The element content of the modified zeolites was determined by X-Ray Fluorescence (XRF). The physical properties of catalysts, including surface area, pore volume, and pore diameter of the parent and the modified zeolites were determined by using the Surface Area Analyzer (SAA) with the Brunauer-Emmett-Teller (BET) technique.

Table 4.1 Catalysts and experimental design for the bio-ethanol dehydration to liquid hydrocarbons

# of run	Experimental Set	Catalyst in the first layer (@ 500 °C)	Catalyst in the second layer (@ 500 °C)	Abbreviation
Two consecutive layers catalytic systems				
1	2% Ga ₂ O ₃ /HZSM-5	2% Ga ₂ O ₃ /HZSM-5	-	2GaHZ5
2	2% Ga ₂ O ₃ /HZSM-5:X	2% Ga ₂ O ₃ /HZSM-5	H-X	2GaHZ5:X
3	2% Ga ₂ O ₃ /HZSM-5:Y	2% Ga ₂ O ₃ /HZSM-5	H-Y	2GaHZ5:Y
4	2% Ga ₂ O ₃ /HZSM-5:Beta	2% Ga ₂ O ₃ /HZSM-5	H-Beta	2GaHZ5:β
HZSM-5 modified with oxides of Group 5A elements				
5	HZSM5	-	-	HZ5
6	1% P ₂ O ₅ /HZSM-5	-	-	1PHZ5
7	2% P ₂ O ₅ /HZSM-5	-	-	2PHZ5
8	3% P ₂ O ₅ /HZSM-5	-	-	3PHZ5
9	4% P ₂ O ₅ /HZSM-5	-	-	4PHZ5
10	1% Sb ₂ O ₅ /HZSM-5	-	-	1SbHZ5
11	2% Sb ₂ O ₅ /HZSM-5	-	-	2SbHZ5
12	3% Sb ₂ O ₅ /HZSM-5	-	-	3SbHZ5
13	4% Sb ₂ O ₅ /HZSM-5	-	-	4SbHZ5
14	1% Bi ₂ O ₅ /HZSM-5	-	-	1BiHZ5
15	2% Bi ₂ O ₅ /HZSM-5	-	-	2BiHZ5
16	3% Bi ₂ O ₅ /HZSM-5	-	-	3BiHZ5
17	4% Bi ₂ O ₅ /HZSM-5	-	-	4BiHZ5

The Raman spectra of catalysts are displayed in Figure 4.1. The Raman bands at 551 and 737 cm^{-1} verify the formation of P_2O_5 (Tan and Chan, 2011). The Raman bands at 253 and 763 cm^{-1} verify the formation of Sb_2O_5 (Tan and Chan, 2011). The Raman bands at 446 and 563 cm^{-1} verify the formation of Bi_2O_5 (Tan and Chan, 2011). All of these oxides are acidic oxides. The content of each element loaded on the catalysts, the surface area, pore volume, and pore diameter of the parent and the modified zeolites are listed in Table 4.2. It can be noticed that the introduction of acidic oxides over HZSM-5 zeolite caused a clear decrease in the BET surface area, pore volume, and pore diameter. The pore volume and the pore diameter of the catalysts were not changed prominently, but there is a distinctive decrease in surface area. At the same element content, the larger element size leads to the lower surface area, pore volume, and pore diameter. For example, Bi, that has the largest size, causes the lowest surface area, pore volume, and pore diameter, followed by Sb, Ga, and P, which are smaller size than Bi. A higher content of element on HZSM-5 support may reduce the surface area and partially block the pore in the modified catalysts. Bi_2O_5 has the highest acid strength, followed by Sb_2O_5 and P_2O_5 . The SEM images of HZSM-5 and each oxide-modified HZSM-5 catalysts are shown in Appendix A.

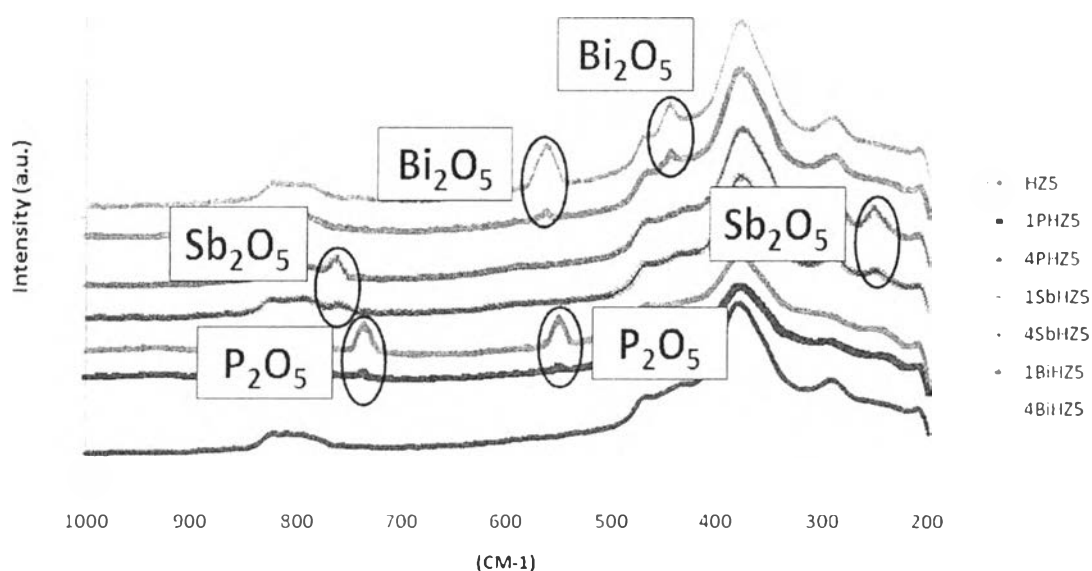


Figure 4.1 Raman spectra of catalysts in the 200-1000 cm^{-1} .

Table 4.2 Element loading content and physical properties of catalysts

Catalyst	Element loading (wt %) ^a	Surface area (m ² /g) ^b	Pore volume (cm ³ /g) ^c	Pore diameter (Å) ^c
H-Y	-	565.0	0.196	7.651
H-X	-	564.4	0.195	7.649
H-Beta	-	532.5	0.191	6.606
HZ5	-	494.8	0.185	5.596
1PHZ5	0.95	457.2	0.173	5.307
2PHZ5	2.01	450.0	0.171	5.256
3PHZ5	3.14	443.2	0.170	5.158
4PHZ5	4.20	432.4	0.166	5.049
1SbHZ5	1.03	450.7	0.172	5.270
2SbHZ5	2.13	440.2	0.170	5.256
3SbHZ5	2.98	437.5	0.168	5.223
4SbHZ5	4.05	430.5	0.164	5.217
1BiHZ5	1.14	445.4	0.170	5.264
2BiHZ5	2.10	431.9	0.169	5.247
3BiHZ5	3.11	429.7	0.167	5.220
4BiHZ5	4.08	425.9	0.163	5.205
2GaHZ5	1.98	440.7	0.176	5.272

^a determined using XRF

^b determined using BET method

^c determined using BJH method

4.2 Influence of the Two Consecutive Layers of Catalysts

This section discusses about the investigation of the two consecutive layers of catalysts for converting bio-ethanol and producing aromatic hydrocarbons. For this system, 2% Ga₂O₃/HZSM-5 (2GaHZ5) catalyst was packed as the first layer, and a catalytic layer of one of these zeolites; H-X, H-Y, or H-Beta was consecutively packed as the second layer. These reaction runs were conducted at 500 °C under atmospheric pressure for 8 hours for collecting the liquid products along time-on-stream.

4.2.1 Catalytic Performance of the first layer catalyst (2GaHZ5)

Prior to use the 2GaHZ5 as the first layer catalyst, its activity and selectivity must be examined and verified; therefore, this section discussed about the catalytic performance of the 2GaHZ5 catalyst on conversion of bio-ethanol to liquid hydrocarbons.

It can be noted that the introduction of Ga₂O₃ leads to a decrease in surface area, pore volume, and pore diameter, as shown in Table 4.2, which are tentatively attributed to covering and filling of parts of the zeolite pores with Ga₂O₃. The differences in the physical properties of HZ5 and 2GaHZ5 affect to the conversion of bio-ethanol and the distribution of each product, as shown in Table 4.3. The conversion of bio-ethanol obtained from 2GaHZ5 is approximately 96.5 % that is not significantly different from that of HZ5. The Ga₂O₃ also affects to the product distribution as shown in Figures 4.2 and 4.3, which the yield and the composition of oil and gas are specifically presented. It can be clearly seen that when Ga₂O₃ is added into the parent HZ5 catalyst, the oil yield is slightly increased from approximately 6.13 % to 6.95 %, which is improved by 13.4 %.

In addition, the obtained oil highly consists of aromatic hydrocarbons, especially toluene and m-xylene. It can be noticed that the higher the oil yield, the higher aromatics yield is also obtained. However, the HZ5 support favors the formation of toluene and ethylbenzene while 2GaHZ5 favors the formation of benzene, m- and p-xylenes, C₉ and C₁₀+ aromatics. It is evident that Ga₂O₃ is able to enhance the aromatics production from bio-ethanol, especially m- and p-xylenes.

Saha *et al.* (1992) reported that a Ga_2O_3 -doped HZSM-5 catalyst had higher activity for the conversion of ethanol to aromatic compounds than HZSM-5. 77.0 % of BTEX in oil was observed over the 2GaHZ5 catalyst. The results also showed that approximately 52.0 % of xylenes was obtained in the BTEX fraction, and the mixed xylenes were composed of 29.0 % p-xylene. With the introduction of Ga_2O_3 , toluene decreased with the increases of benzene, m- and p-xylenes, C9, and C10+ aromatics. This can be attributed to the converting of surplus toluene to benzene, m- and p-xylenes via toluene disproportionation reaction, which is one of the major practical processes for converting two moles of toluene to one mole each of benzene and xylenes as previously shown in Figure 2.2. Moreover, the mixed xylenes that are formed from toluene disproportionation can be further converted to C9 or/and C10+ aromatics via xylene disproportionation, which hence results in the high amount of C9 or/and C10+ aromatics.

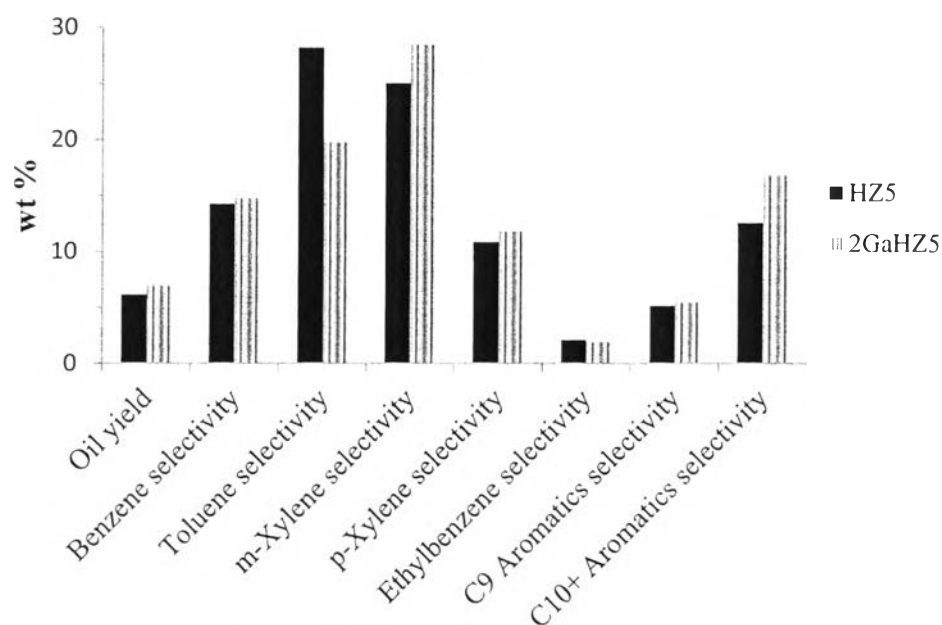


Figure 4.2 Effect of Ga_2O_3 on the yield and the selectivity of liquid products.

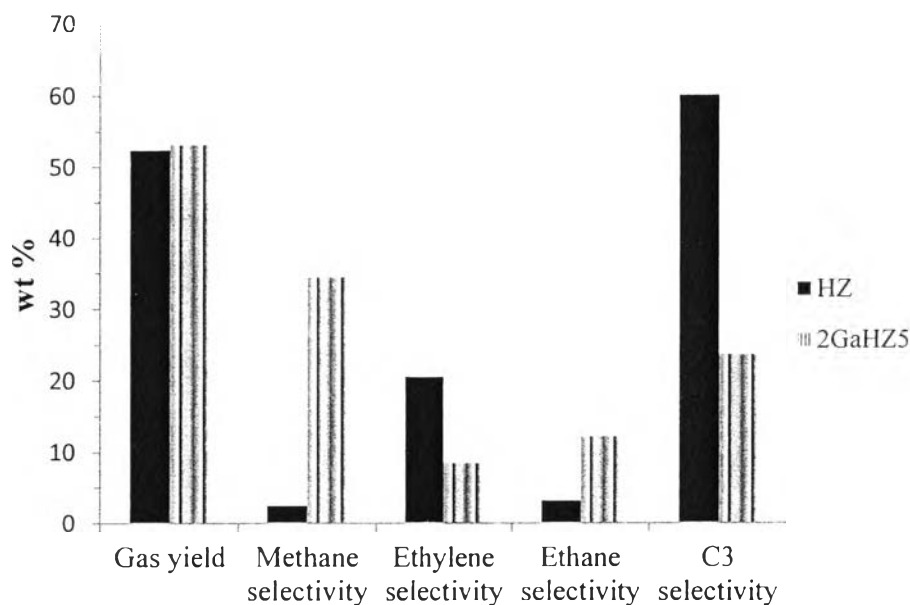


Figure 4.3 Effect of Ga_2O_3 on the yield and the selectivity of gas products.

In case of the gaseous product, the results show that approximately 52.4 % and 53.2 % total gas yields are obtained from HZ5 and 2GaHZ5, respectively as shown in Figure 4.3, which the gas yield is slightly increased around 1.53 % when Ga oxides were added. Mixed C3 hydrocarbons and ethylene are the two main compositions of the gaseous product derived from HZ5 while methane and mixed C3 hydrocarbons are the two main compositions of gaseous product derived from 2GaHZ5. With the addition of Ga_2O_3 dopant, C3 hydrocarbons appear to polymerize to larger hydrocarbons, which some are cracked into C1 or/and C2 hydrocarbons while the rest cyclizes and aromatizes.

Table 4.3 Product distribution over HZ5 and 2GaHZ5 catalysts

Catalyst	HZ5	2GaHZ5
% Bio-ethanol conversion	97.0	96.5
Product yield (wt %)		
Oil	6.10	6.90
Gas	52.4	53.2
Water	41.5	39.9
Gas composition (wt %)		
Methane	2.48	34.5
Ethylene	20.5	8.49
Ethane	3.16	12.2
C3	60.1	23.6
C4	12.5	0.00
CO ₂	1.32	21.2
	100	100
Oil composition (wt %)		
Non-aromatics	1.92	0.94
Benzene	14.3	14.8
Toluene	28.2	19.8
o-Xylene	0.00	0.00
m-Xylene	25.0	28.5
p-Xylene	10.8	11.8
Ethylbenzene	2.11	1.92
C9 Aromatics	5.15	5.45
C10+ Aromatics	12.5	16.8
	100	100
Aromatics in oil (wt %)	98.1	99.1
Yield of aromatics (wt %)	6.01	6.88
BTEX/Aromatics	0.82	0.78
BTEX/Oil	0.80	0.77
Xylenes/BTEX	0.45	0.52
p-Xylene/Xylenes	0.30	0.29
Petroleum Fractions in oil (wt %)		
Gasoline	84.1	80.0
Kerosene	11.3	10.4
Gas oil	1.73	4.60
Light Vacuum Gas Oil (LVGO)	0.44	2.03
Heavy Vacuum Gas Oil (HVGO)	2.44	2.91

Data were taken at the eighth hour of time-on-stream

4.2.2 Performance of the Two Consecutive Layers of Catalysts

From Section 4.2.1, it was verified that 2GaHZ5 was able to convert bio-ethanol to aromatics that are highly composed of m-xylene and toluene. So, using 2GaHZ as the catalyst, m-xylene and toluene are highly produced from the first layer. Aimed at to further converting m-xylene and toluene to more valuable aromatics, especially p-xylene, each of some large-pore size zeolites; H-X, H-Y, or H-Beta, was consecutively loaded as the second layer.

As shown in Table 4.2, H-Y has the highest surface area, pore volume, and pore diameter followed by H-X and H-Beta. As a results, the yield and the composition of oil and gas are presented in Table 4.4. The bio-ethanol conversion obtained from 2GaHZ5:X, 2GaHZ5:Y, and 2GaHZ5:β catalysts is approximately in the range of 96.0 – 96.1 %, which is not significantly different from that from 2GaHZ5 catalyst. It can be summarized that whether or not the second layer was packed with H-X, H-Y, or H-Beta zeolite, the bio-ethanol conversion is not significantly affected. However, the addition of H-X, H-Y, or H-Beta zeolite in the second layer instead affects to the yield and the composition of oil and gas as shown in Figures 4.6 and 4.7, respectively. The oil yield and the aromatics yield are suppressed when H-X, H-Y, or H-Beta zeolite was added to the catalytic bed as the second layer. The oil yield and aromatics yield are ranked as follows; 2GaHZ5 > 2GaHZ5:Y > 2GaHZ5:X > 2GaHZ5:β.

For the oil composition, the addition of the second layer catalyst (H-X, H-Y or H-Beta zeolites) brings about the reduction of light aromatic hydrocarbons (benzene, toluene, and m-xylene) selectivities and the enhancement of heavy aromatic hydrocarbons (C₉, and especially C₁₀₊ aromatics) selectivities. The highest selectivities of C₉ and C₁₀₊ aromatics are obtained when H-X zeolite was employed. The selectivities of C₉ aromatics is ranked as follows; 2GaHZ5:X > 2GaHZ5:Y > 2GaHZ5:β > 2GaHZ5. The selectivities of C₁₀₊ aromatics is ranked as follows; 2GaHZ5:X > 2GaHZ5:β > 2GaHZ5:Y > 2GaHZ5. The results also show that mixed xylenes in the BTEX fraction are slightly enhanced when H-Y or H-Beta was added. So is p-xylene that also enhanced in xylenes fraction when the second layer was modified by H-X, H-Y, or H-Beta zeolite. It is evident that the second layer catalysts promote the transformation of benzene, toluene, and m-xylene to

aromatics hydrocarbons, like C9 and C10+ aromatics. It can be attributed to the lowest Si/Al ratio of H-X that leads to the highest acid density which promotes the disproportionation and transalkylation reactions of toluene to xylenes as shown in Figure 4.4. Moreover, the occurred xylenes can be further transformed to C9 and C10+ aromatics via the disproportionation and transalkylation reactions of xylenes because the acid density is high enough as shown in Figure 4.5. Similarly, H-Beta that has the highest Si/Al ratio and the highest acid strength can also promote the disproportionation and transalkylation of toluene, and can further promote the disproportionation and transalkylation of xylenes because the acid strength is high enough.

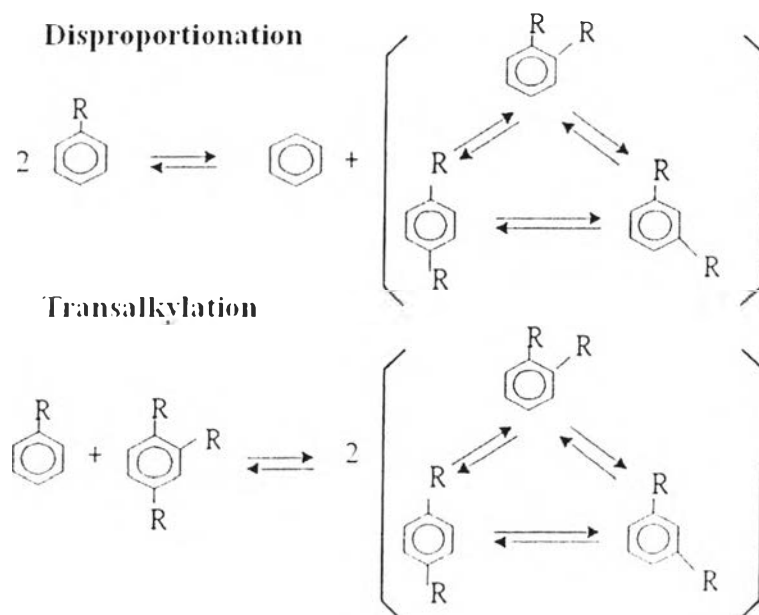
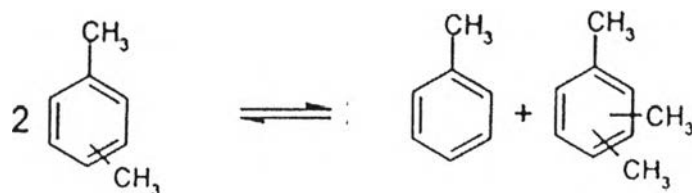


Figure 4.4 Disproportionation and transalkylation reactions of toluene.

Disproportionation



Transalkylation

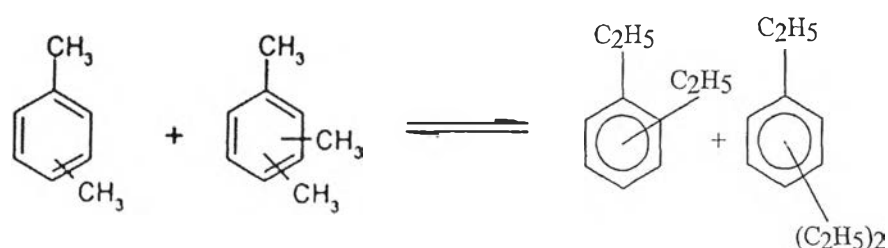


Figure 4.5 Disproportionation and transalkylation reactions of xylenes.

H-X, H-Y, and H-Beta zeolites are acid catalysts that have three dimensional 12-membered rings pore system with pore size 7.649 Å, 7.651 Å and 7.606 Å, respectively. These zeolites have high activity and selectivity for the disproportionation and transalkylation of xylenes because of their high acid density or/and strength and large-pore size that can absorb bulky molecules like toluene, xylenes, ethylbenzene from the first layer. Over acid catalysts, disproportion and transalkylation of both toluene and xylenes generally occur through a bimolecular mechanism involving transformation of methyl group to form heavier aromatic hydrocarbons like C₉ and C₁₀⁺. So, an acidic zeolite having high acid density like H-X or high acid strength like H-Beta can promote the transformation of BTX to C₉ and especially 10⁺ aromatics.

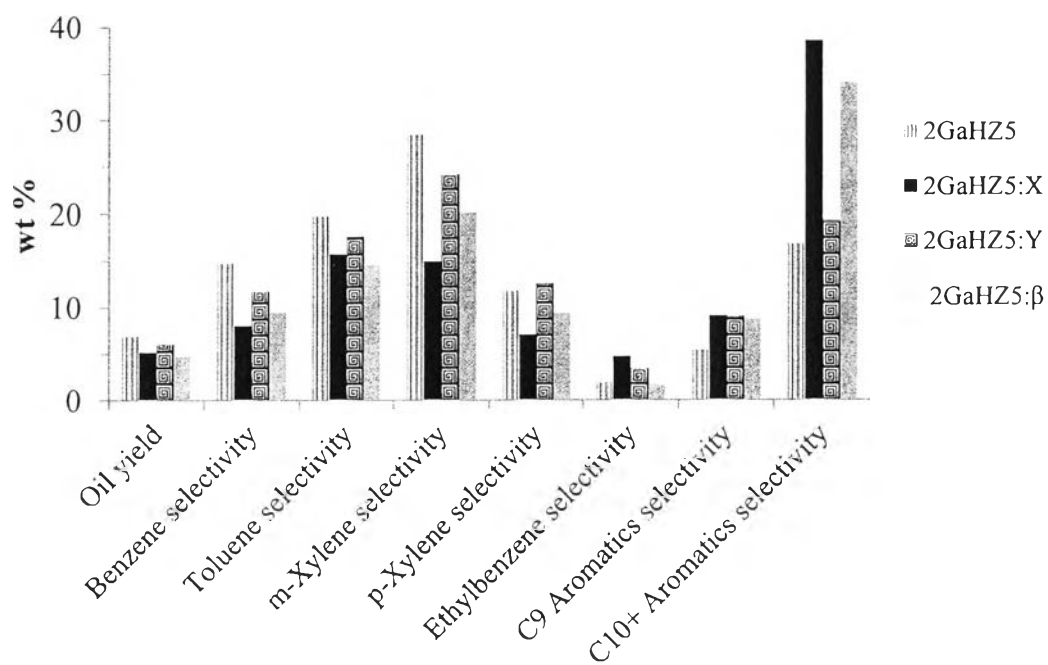


Figure 4.6 Effect of the two consecutive layers of catalysts on the yield and the selectivity of liquid products.

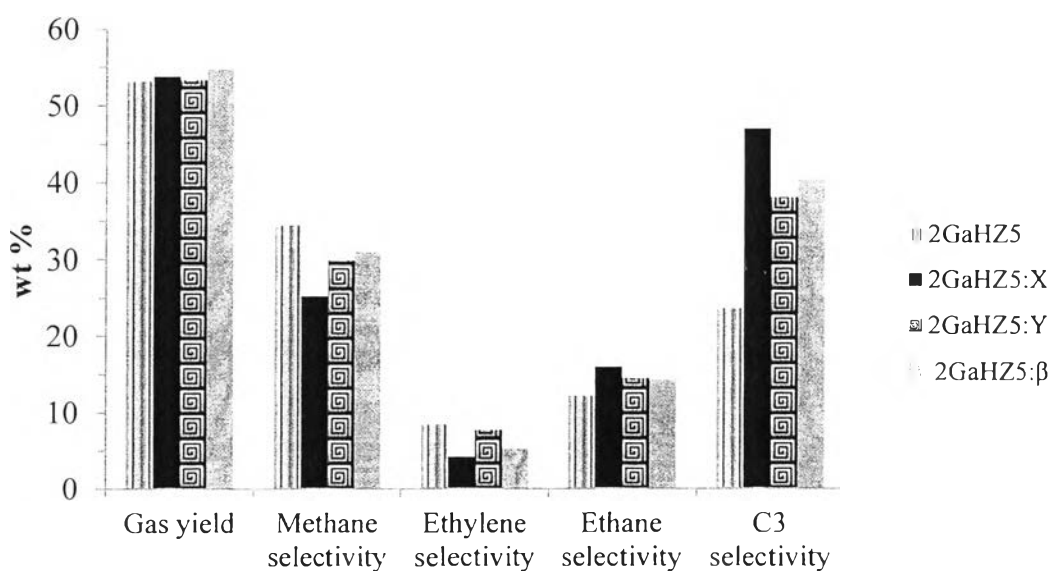


Figure 4.7 Effect of the two consecutive layers of catalysts on the gas yield and the selectivity of gas products.

Table 4.4 Product distribution over 2GaHZ5, 2GaHZ5:X, 2GaHZ5:Y, and 2GaHZ5:β catalysts

Catalyst	2GaHZ5	2GaHZ5:X	2GaHZ5:Y	2GaHZ5:β
% Bio-ethanol conversion	96.5	96.0	96.1	96.1
Product yield (wt %)				
Oil	6.90	5.20	6.10	4.70
Gas	53.2	53.8	53.3	54.8
Water	39.9	41.0	40.6	40.5
Gas composition (wt %)				
Methane	34.5	25.2	29.9	31.0
Ethylene	8.49	4.21	7.73	5.29
Ethane	12.2	15.9	14.5	14.3
C3	23.6	47.0	38.0	40.4
C4	0.00	0.00	0.00	0.00
CO ₂	21.2	7.65	9.87	9.08
	100	100	100	100
Oil composition (wt %)				
Non-aromatics	0.94	1.97	2.08	2.01
Benzene	14.8	8.04	11.7	9.49
Toluene	19.8	15.7	17.7	14.6
o-Xylene	0.00	0.00	0.00	0.00
m-Xylene	28.5	14.9	24.2	20.1
p-Xylene	11.8	7.07	12.6	9.35
Ethylbenzene	1.92	4.73	3.44	1.70
C9 Aromatics	5.45	9.08	9.07	8.73
C10+ Aromatics	16.8	38.5	19.2	34.0
	100	100	100	100
Aromatics in oil (wt %)	99.1	98.0	97.9	98.0
Yield of aromatics (wt %)	6.88	5.09	5.96	4.66
BTEX/Aromatics	0.78	0.51	0.71	0.56
BTEX/Oil	0.77	0.50	0.70	0.55
Xylenes/BTEX	0.52	0.44	0.53	0.53
p-Xylene/Xylenes	0.29	0.32	0.34	0.32
Petroleum Fractions in oil (wt %)				
Gasoline	80.0	75.2	75.9	71.7
Kerosene	10.4	19.9	18.9	18.1
Gas oil	4.60	3.43	4.20	8.66
LVGO	2.03	0.87	1.01	1.30
HVGO	2.91	0.60	0.05	0.29

Data were taken at the eighth hour of time-on-stream

For the gaseous product, the gas yield is increased when the second layer of H-X, H-Y, or H-Beta zeolite is added to the catalytic bed as shown in Figure 4.7. According to the composition, the highest formations of ethane and mixed C3 hydrocarbons are obtained when H-X zeolite was employed. However, the formations of methane and ethylene are suppressed when the second layer was added. The addition of H-X, H-Y, or H-Beta as the second layer results in the significant increase of C3 hydrocarbons. This can be attributed to an acidic zeolite having large pore size, like H-X, H-Y, or H-Beta, is able to crack some heavier hydrocarbons (C5+ and aromatics) into lighter hydrocarbons (C1-C3) and some of C3 hydrocarbons may be further cracked into C1 or/and C2 hydrocarbons. Besides the oil-producing reactions, the dealkylation of alkylbenzenes producing light gas is a set of some side reactions which can be simultaneously occurred and hence results in a high amount of C3 hydrocarbons.

The TBP curves of oils derived from the two consecutive layers of catalysts were cut into petroleum fractions, according to boiling point ranges, as shown in Table 4.5.

Table 4.5 Boiling point range of petroleum fractions (Ding *et al.*, 2009)

Fractions	Boiling point (°C)
Gasoline	<149
Kerosene	149-232
Gas oil	232-343
Light vacuum gas oil (LVGO)	343-371
Heavy vacuum gas oil (HVGO)	>371

The petroleum fractions derived from the two consecutive layers of catalysts are shown in Figure 4.8. The oils from all catalysts are highly composed of gasoline, which is the range of 71.7 – 80.0 wt %. The results show that when the second layer of H-X, H-Y, or H-BETA zeolite was employed, gasoline, LVGO, and HVGO slightly decrease. However, kerosene significantly increases from 10.4 wt % to around 19.0 wt %. It means that the addition of the second layer catalyst, right

after the layer of Ga₂O₃-modified HZSM-5, can slightly retard the formation of gasoline but improve the formation of kerosene.

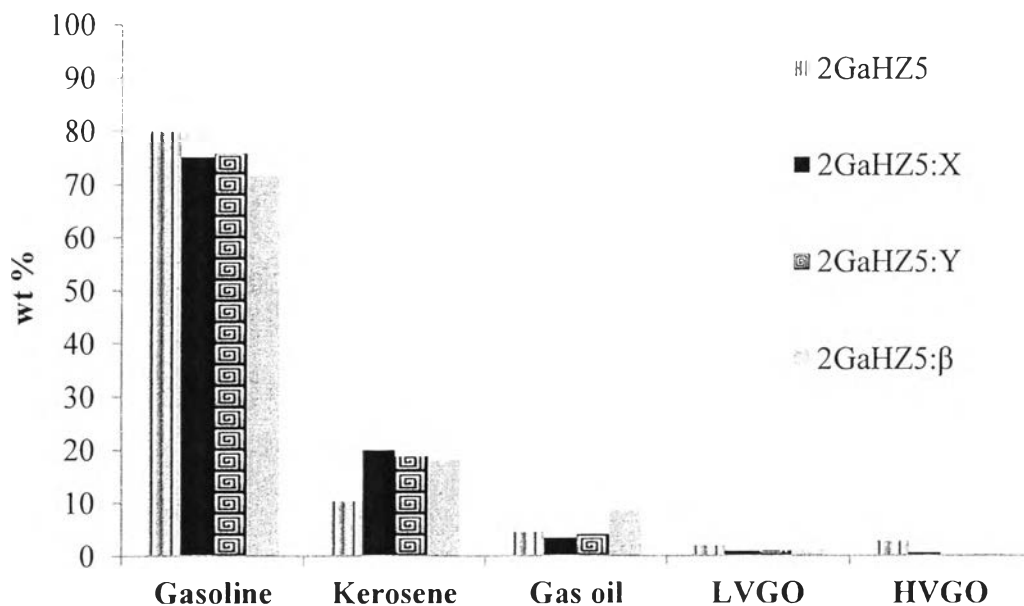


Figure 4.8 Petroleum fractions in oils derived from the two consecutive layers of catalysts.

4.3 Performance of HZSM-5 Modified with Oxides of Group VA Elements

In this section, P₂O₅, Sb₂O₅, and Bi₂O₅ were also investigated for their activity on the enhancement of aromatics production. P, Sb, and Bi are elements in Group VA in the periodical table that gives an acidic property. Due to the fact that elements in the same group have similar properties but different sizes, so, this section discusses the effect of promoter size on bio-ethanol dehydration to liquid hydrocarbons over the HZSM-5 support. The reaction conditions were the same as the case of the two consecutive layers of catalysts. HZ5 was loaded with various loading amounts of 1.0 wt %, 2.0 wt %, 3.0 wt %, and 4.0 wt % of each promoter.

4.3.1 Effect of P₂O₅ Loaded on HZSM-5

The diffusion resistance in the pore of HZSM-5 appears to be more intense with loading with P₂O₅ in the zeolite due to the blocking of the pores of the zeolite, and then partial covering of a part of the acid sites inside and outside the pores. As shown in Table 4.2, the surface area, the pore volume, and the pore diameter decrease gradually with the increase of P content. The conversion of bio-ethanol and the distribution of each product over all P₂O₅-modified catalysts are shown in Table 4.6. According to the results, the conversions of bio-ethanol derived from pure HZ5 and PHZ5 at various P₂O₅ loadings are not significantly different. For all catalyst testings, the bio-ethanol conversion is approximately 97.0 %. It can be seen that whether or not the HZ5 was modified by P₂O₅, the bio-ethanol conversion is not significantly affected. In contrast, the P₂O₅ loading affects to the product distribution, which can be seen in Figures 4.11 and 4.12. The results reveal that approximately 6.13% of oil yield is acquired from the HZ5 catalyst. In case of the modified catalysts, the oil yield is enhanced to 7.07 %, which is improved around 15.3 % when 1.0 wt % P was added. However, the oil yield decreases gradually with the increase of P content above 1.0 wt %. The aromatics yield follows the same trend as the oil yield.

Aromatic hydrocarbons are the main composition of derived oil that highly consists of toluene, m-and p-xylenes, and C₁₀+ aromatics. It can be clearly seen that when P₂O₅ was added into the HZ5, the p-xylene selectivity was increased significantly. The HZ5 support favors the formation of benzene, toluene and m-xylene, but suppresses the formation of ethylbenzene, C₉ and C₁₀+ aromatics. However, the formations of p-xylene, ethylbenzene, C₉ and C₁₀+ aromatics increase, but that of benzene, toluene, and m-xylene decreases when P₂O₅ was added. The formation of ethylbenzene decreases gradually with the increase of P loading. As P content increases, the selectivity of p-xylene increases first, passing through a maximal value at 3.0 wt % P (3PHZ5). However, the selectivity of toluene and m-xylene decreases significantly when the P₂O₅ was added. Further increase of the P loading over 3.0 wt % brings about a slight decrease in the selectivity of toluene and m-xylene. Moreover, P₂O₅ causes the reduction of BTEX in oil, and the enhancement of mixed xylenes in the BTEX fraction, and p-xylene in mixed xylenes. Among all

catalysts, the 1PHZ5 catalyst presents the best performance in the p-xylene selectivity in mixed xylenes, indicating that 1 % P is the most selective loading for p-xylene. According to the results, benzene and toluene decrease, but p-xylenes, ethylbenzene, C9, and C10+ aromatics increase with P loading. It can be attributed to the disproportionation of toluene to m- and p-xylenes, and benzene, which may be further reacted with ethylene to form heavier aromatics as shown in Figure 4.9. Moreover, m-xylene may be transformed to p-xylene via xylene isomerization as shown in Figure 4.10, which may simultaneously occur with xylene disproportionation and transalkylation in which xylene is converted to C9 or/and C10+ aromatics as shown in Figure 4.5.

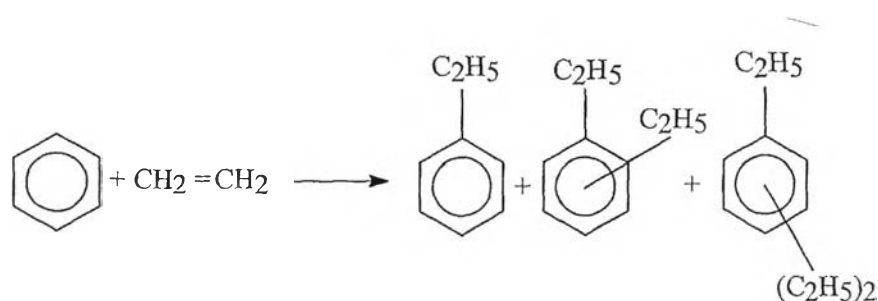


Figure 4.9 Transformation of benzene to heavier aromatics.

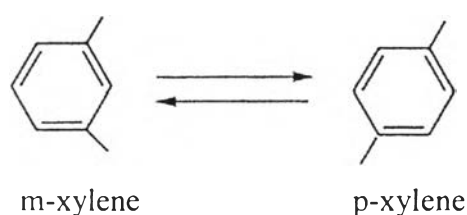


Figure 4.10 m-Xylene isomerization reaction.

Furthermore, it is observed that the yield of gaseous product decreases with the decrease in % P loading as shown in Figure 4.12. Of all the catalysts, the gas products mainly consist of mixed C3 hydrocarbons and ethylene. However, the mixed C3 hydrocarbons formation decreased gradually with the increase of P_2O_5 loading. In contrast, the ethylene formation tends to increase gradually over 1.0 wt % P_2O_5 loading. With the addition of P_2O_5 , C3 hydrocarbons further polymerize to larger hydrocarbons, some of which are cracked into C1 or/and C2 hydrocarbons

while others cyclize and aromatize. Due to the high amount (20 – 50 % in the gas products), some of ethylene may react with benzene, resulted in aromatics formation.

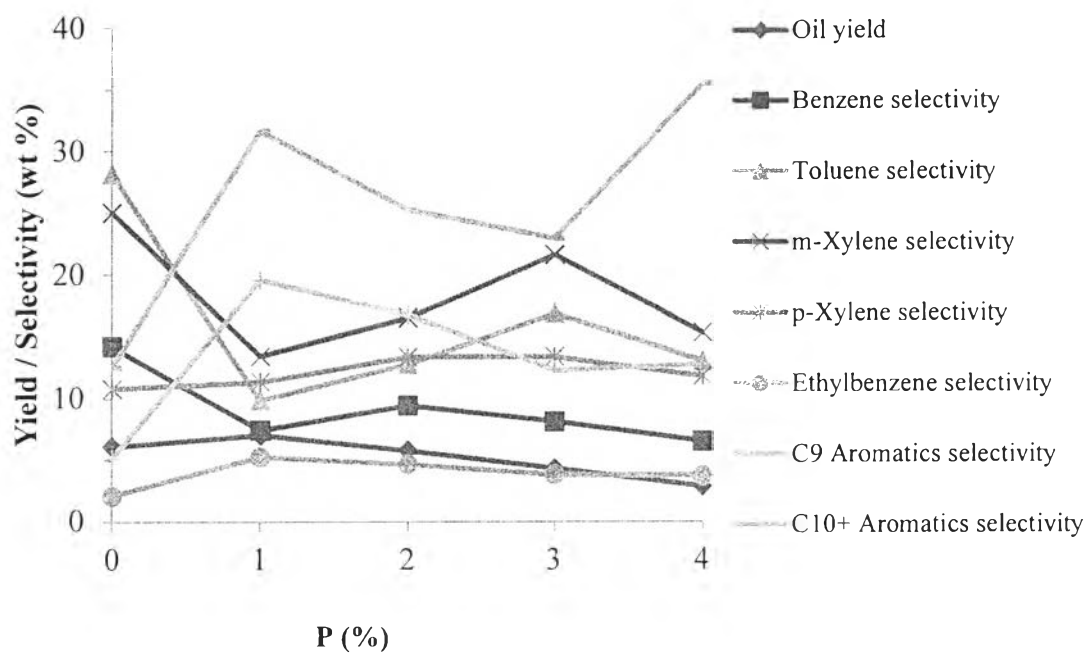


Figure 4.11 Effect of P_2O_5 on the oil yield and the selectivity of liquid products.

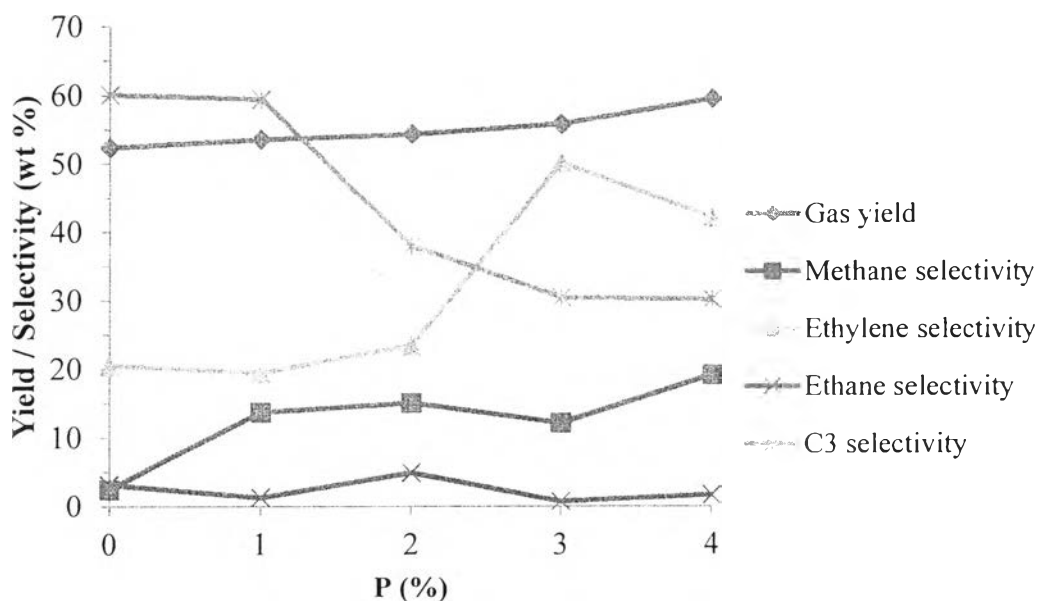


Figure 4.12 Effect of P_2O_5 on the gas yield and the selectivity of gas products.

Table 4.6 Product distribution over all P₂O₅-modified catalysts

Catalyst	HZ5	1PHZ5	2PHZ5	3PHZ5	4PHZ5
% Bio-ethanol conversion	97.0	97.0	97.0	96.9	96.9
Product yield (wt %)					
Oil	6.10	7.10	5.80	4.30	2.80
Gas	52.4	53.5	54.3	55.8	59.5
Water	41.5	39.4	39.9	39.9	37.7
Gas composition (wt %)					
Methane	2.48	13.7	15.1	12.1	19.1
Ethylene	20.5	19.4	23.4	50.1	42.0
Ethane	3.16	1.27	4.90	0.71	1.69
C3	60.1	59.4	38.0	30.4	30.1
C4	12.5	1.97	9.00	3.88	0.00
CO ₂	1.32	4.33	9.67	2.71	7.00
	100	100	100	100	100
Oil composition (wt %)					
Non-aromatics	1.92	1.37	1.15	0.96	1.22
Benzene	14.3	7.46	9.46	8.15	6.55
Toluene	28.2	9.87	12.8	16.9	13.0
o-Xylene	0.00	0.00	0.00	0.00	0.00
m-Xylene	25.0	13.5	16.5	21.6	15.3
p-Xylene	10.8	11.4	13.4	13.4	11.8
Ethylbenzene	2.11	5.27	4.68	3.84	3.77
C9 Aromatics	5.15	19.6	16.8	12.3	12.8
C10+ Aromatics	12.5	31.6	25.2	22.9	35.5
	100	100	100	100	100
Aromatics in oil (wt %)	98.1	98.6	98.8	99.0	98.8
Yield of aromatics (wt %)	6.01	6.97	5.74	4.31	2.84
BTEX/Aromatics	0.82	0.48	0.58	0.64	0.51
BTEX/Oil	0.80	0.47	0.57	0.64	0.51
Xylenes/BTEX	0.45	0.52	0.53	0.55	0.54
p-Xylene/Xylenes	0.30	0.46	0.45	0.38	0.44
Petroleum Fractions in oil (wt %)					
Gasoline	84.1	81.5	85.0	85.1	86.8
Kerosene	11.3	13.6	5.61	4.95	4.00
Gas oil	1.73	1.99	3.61	4.45	1.60
LVGO	0.44	0.50	0.90	0.92	0.40
HVGO	2.44	2.41	4.86	4.60	7.20

Data were taken at the eighth hour of time-on-stream

Another way to consider the composition of the oils derived from catalysts modified with P_2O_5 is that the true boiling curve of oils is cut into petroleum fractions, shown in Figure 4.13. The derived oils from all catalysts highly consist of gasoline, which is higher than 80.0 wt % observed. The results show that the gasoline and HVGO increase, but kerosene decrease with P_2O_5 loading. Moreover, gas oil and LVGO increase gradually with the increase of P_2O_5 content, but decrease when P_2O_5 loading is over 3.0 wt %. It can be seen that the increase of P_2O_5 content over 1.0 wt % can slightly improve gasoline production but suppresses kerosene production.

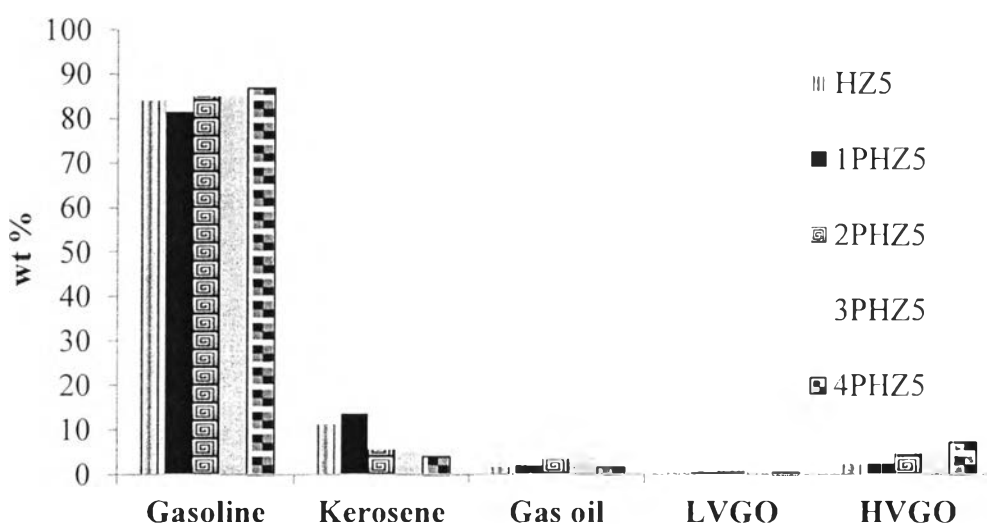


Figure 4.13 Petroleum fractions in oils derived from using P_2O_5 -modified catalysts.

4.3.2 Effect of Sb_2O_5 Loaded on HZSM-5

The results reveal that when Sb_2O_5 was loaded on HZ5, the conversion of bio-ethanol is not considerably affected, it decreases slightly from 97.0 % to 96.0 %. In contrast, the Sb_2O_5 affects to the product distribution, as shown in Table 4.7, Figures 4.14 and 4.15, which the yield and the compositions of oil and gas are also reported. From the results, as the Sb_2O_5 content increases, the oil yield increases first from 6.13 %, passing through a maximum value over 2.0 wt %. However, the oil yield and aromatics yield gradually decrease when Sb reaches over

2.0 wt %. The 2.0 wt % of Sb loading gives the highest oil yield and aromatics yield, which are around 7.87 % and 7.79 %, respectively.

Additionally, the derived oils highly consist of aromatic hydrocarbons, which toluene, m-xylene and C10+ aromatics are predominantly formed, and the formations of benzene and toluene decrease with Sb loading. When the formations of ethylbenzene, C9, and C10+ aromatics are compared, it is found that the Sb₂O₅ promoter can predominantly enhance the formation of these aromatics. It is evident that the Sb₂O₅ can promote the formation of heavy aromatics like C10+.

However, the selectivity of p-xylene slightly decreases when the content of Sb loading is over 2.0 wt%. Moreover, the obtained aromatics mainly consist of BTEX, especially xylenes. About 45.0 %, 52.0 %, 50.0 %, 55.0 %, and 53.0 % of xylenes in BTEX fraction were observed whereas the concentration of p-xylene in mixed xylenes is about 30.0 %, 23.0 %, 39.0 %, 35.0 %, and 36.0 % over HZ5, 1SbHZ5, 2SbHZ5, 3SbHZ5, and 4SbHZ5, respectively. It can be summarized that the Sb oxide can help to enhance the selectivity of p-xylene in mixed xylenes when the loading was over 1.0 wt %. Of all the catalysts, the 2SbHZ5 catalyst presents a considerable performance in p-xylene selectivity in xylenes, indicating that 2SbHZ5 catalyst is the most selective for p-xylene. According to the results, benzene, toluene, m- and p-xylenes decrease, but ethylbenzene, C9, and C10+ aromatics increase when Sb₂O₅ is added. It can be attributed to the disproportionation of toluene to m- and p-xylenes, and benzene that may be further reacted with ethylene to form heavier aromatics. Moreover, the m- and p-xylenes may be transformed to C9 or/and C10+ aromatics via xylene disproportionation and transalkylation reactions as shown in Figure 4.5.

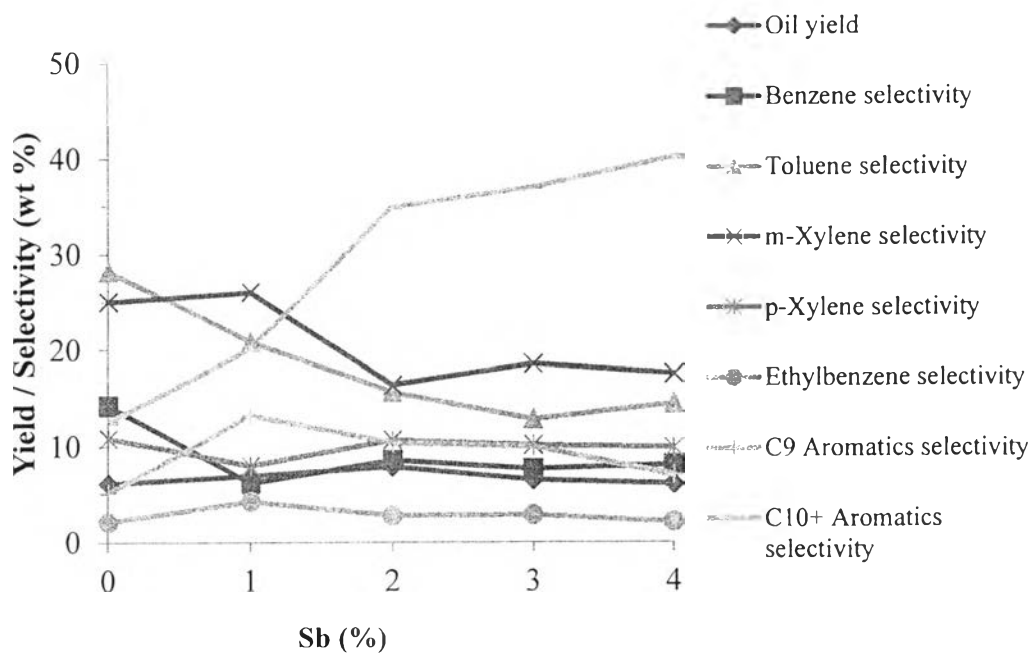


Figure 4.14 Effect of Sb_2O_5 on the oil yield and the selectivity of liquid products.

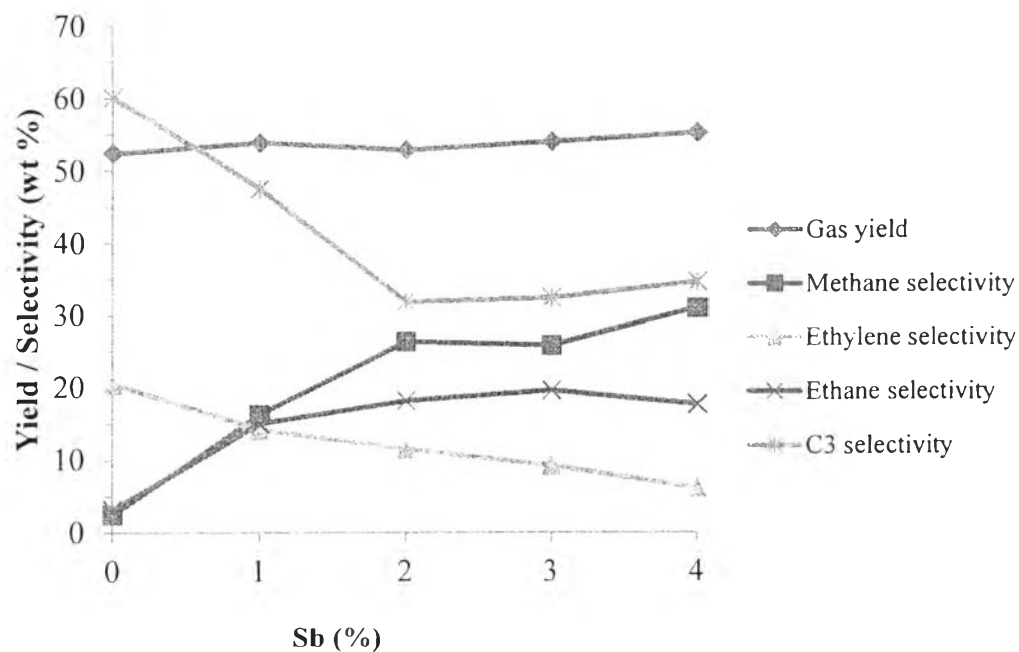


Figure 4.15 Effect of Sb_2O_5 on the gas yield and the selectivity of gas products.

Table 4.7 Product distribution over all Sb₂O₅ catalysts

Catalyst	HZ5	1SbHZ5	2SbHZ5	3SbHZ5	4SbHZ5
% Bio-ethanol conversion	97.0	96.2	96.2	96.1	96.2
Product yield (wt %)					
Oil	6.10	6.90	7.90	6.40	6.10
Gas	52.4	53.9	52.8	54.0	55.2
Water	41.5	39.2	39.3	39.6	38.7
Gas composition (wt %)					
Methane	2.48	16.3	26.4	25.8	31.0
Ethylene	20.5	14.2	11.5	9.24	6.16
Ethane	3.16	15.1	18.2	19.6	17.7
C3	60.1	47.5	31.8	32.4	34.6
C4	12.5	0.00	0.00	0.00	0.00
CO ₂	1.32	6.94	12.1	13.0	10.6
	100	100	100	100	100
Oil composition (wt %)					
Non-aromatics	1.92	1.44	0.93	1.17	0.97
Benzene	14.3	6.16	8.54	7.63	8.08
Toluene	28.2	20.9	15.6	12.8	14.4
o-Xylene	0.00	0.00	0.00	0.00	0.00
m-Xylene	25.0	26.0	16.3	18.5	17.5
p-Xylene	10.8	7.96	10.6	10.1	9.85
Ethylbenzene	2.11	4.25	2.75	2.84	2.09
C9 Aromatics	5.15	13.2	10.3	9.95	6.99
C10+ Aromatics	12.5	20.1	34.8	36.9	40.1
	100	100	100	100	100
Aromatics in oil (wt %)	98.1	98.6	99.1	98.8	99.0
Yield of aromatics (wt %)	6.01	6.84	7.79	6.40	6.00
BTEX/Aromatics	0.82	0.66	0.54	0.53	0.52
BTEX/Oil	0.80	0.65	0.54	0.52	0.52
Xylenes/BTEX	0.45	0.52	0.50	0.55	0.53
p-Xylene/Xylenes	0.30	0.23	0.39	0.35	0.36
Petroleum Fractions in oil (wt %)					
Gasoline	84.1	83.3	83.8	79.1	75.0
Kerosene	11.3	11.9	11.5	16.1	19.5
Gas oil	1.73	1.95	1.93	1.78	2.49
LVGO	0.44	0.49	0.49	0.45	0.50
HVGO	2.44	2.30	2.28	2.55	2.54

Data were taken at the eighth hour of time-on-stream

For gaseous products, the results in Figure 4.16 reveal that when Sb_2O_5 was loaded on to the parent HZ5 catalyst, methane and ethane increase significantly, but ethylene and mixed C3 hydrocarbons are suppressed. However, ethylene decreases gradually with the increase of Sb_2O_5 loading. When the Sb_2O_5 loading reaches 4.0 wt %, the amount of ethylene is less than 7.0 %. So, further increase of Sb_2O_5 loading brings about a decrease in the formation of ethylene. As the introduction of Sb_2O_5 , C3 hydrocarbons may further polymerize to larger hydrocarbons; some of which are cracked into C1 or/and C2 hydrocarbons while the others cyclize and aromatize.

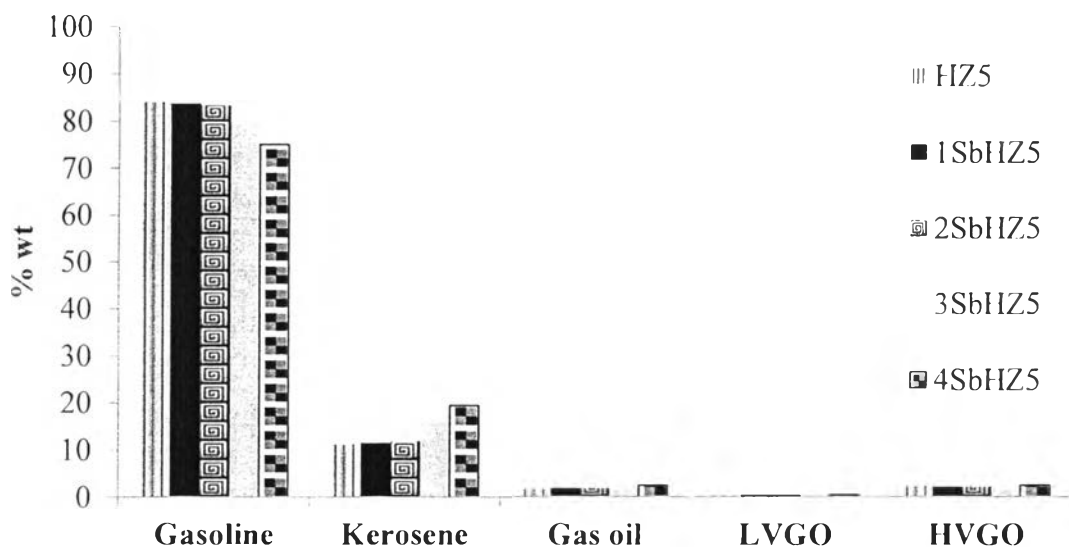


Figure 4.16 Petroleum fractions in oils derived from using Sb_2O_5 -modified catalysts.

The true boiling point curves of oils derived from the catalysts modified with Sb_2O_5 were cut into petroleum fractions in the oils, and the results are shown in Figure 4.16. The derived oils from all catalysts highly consist of gasoline, which is in the range of 75.0 – 84.0 wt %. The quantity of gasoline decreases and that of kerosene increases gradually with the increase of Sb_2O_5 content. Moreover, the distributions of gas oil, LVGO, and HVGO obtained from SbHZ5 are not

significantly different from that obtained from HZ5. It can be seen that the increase of Sb_2O_5 content slightly enhances to kerosene production from bio-ethanol.

4.3.3 Effect of Bi_2O_5 Loaded on HZSM-5

The conversions of bio-ethanol acquired from HZ5 and BiHZ5 at various loadings are shown in Table 4.8. The results indicate that the conversion decreases to around 96.2 % when Bi_2O_5 was loaded. The Bi_2O_5 loading does not only affect to the bio-ethanol conversion but also the product distribution. The product distribution and the composition of oil and gas are also presented in Figures 4.17 and 4.18. For all modified HZ5 catalysts, the oil yield is improved at least 1.63 % and then 8.65 % when 2.0 wt % Bi were added.

In addition, the oils highly consist of aromatic hydrocarbons, especially toluene, m-xylene and C10+ aromatics. It can be noticed that the highest oil yield in conjunction with the highest aromatics yield are obtained from 2BiHZ5. 5 % Bi loading favors the formation of C9 and C10+ aromatics, but suppresses the formation of benzene, toluene, m- and p-xylenes. The formations of m- and p-xylenes decrease gradually with the increase of Bi loading. However, the formations of m- and p-xylenes tend to increase whereas the formation of benzene tends to decrease when Bi content is over 3.0 wt %. Further increase of Bi loading leads to a slight increase in the formation of m- and p-xylenes and a decrease in the formation of benzene. Moreover, Bi loading results in the reduction of BTEX in oil and the enhancement of xylenes in BTEX fraction.

The concentration of p-xylene in mixed xylenes is about 30.0 %, 29.0 %, 31.0 %, 28.0 %, and 26.0 % over HZ5, 1BiHZ5, 2BiHZ5, 3BiHZ5, and 4BiHZ5, respectively, indicating that 2.0 wt % Bi_2O_5 can slightly increase the selectivity of p-xylene in xylenes. According to the results, benzene, toluene, m- and p-xylenes decrease, but ethylbenzene, C9, and C10+ aromatics increase when Bi_2O_5 was added. It can be attributed to the same reasons as explained in the case of modification with Sb_2O_5 .

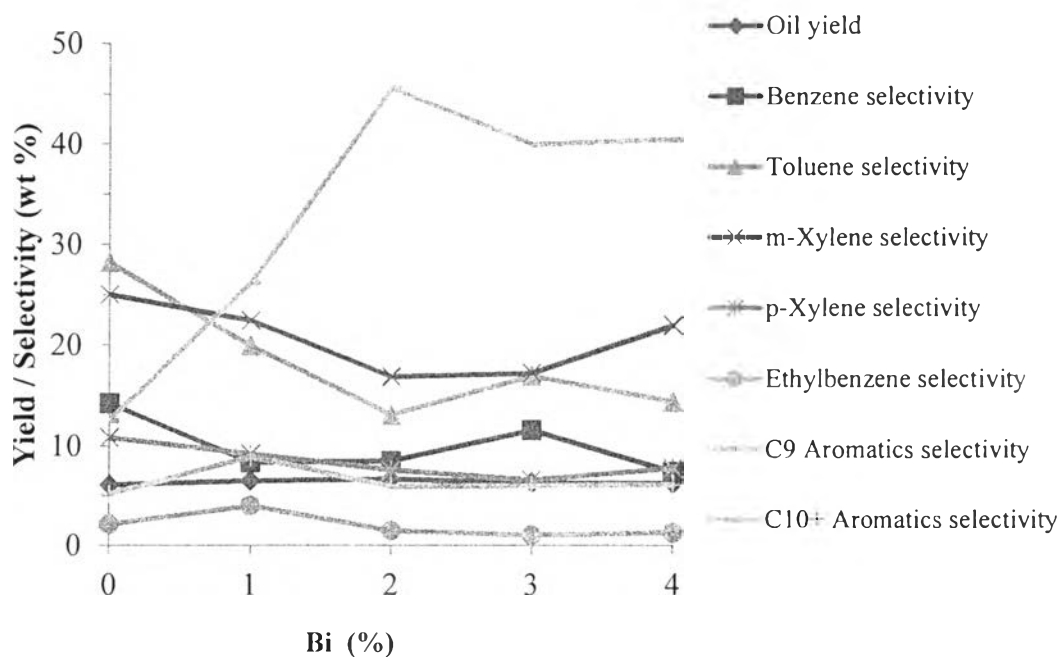


Figure 4.17 Effect of Bi_2O_5 on the oil yield and the selectivity of liquid products.

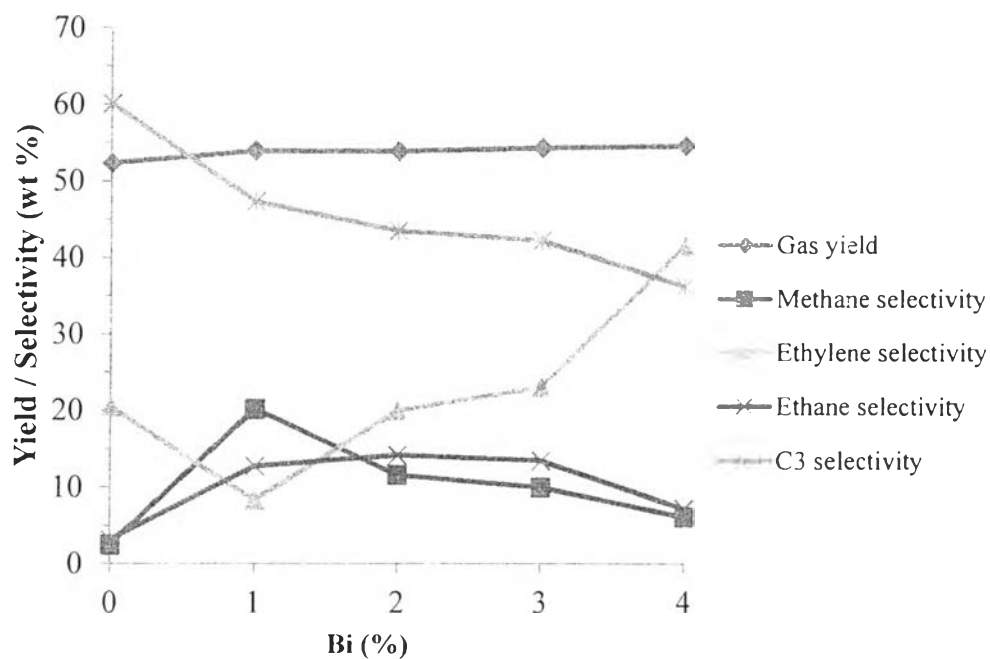


Figure 4.18 Effect of Bi_2O_5 on the gas yield and the selectivity of gas products.

Table 4.8 Product distribution over all Bi₂O₅ -modified catalysts

Catalyst	HZ5	1BiHZ5	2BiHZ5	3BiHZ5	4BiHZ5
% Bio-ethanol conversion	97.0	96.2	96.1	96.2	96.2
Product yield (wt %)					
Oil	6.10	6.50	6.70	6.30	6.20
Gas	52.4	54.0	53.9	54.3	54.6
Water	41.5	39.5	39.4	39.4	39.2
Gas composition (wt %)					
Methane	2.48	20.2	11.6	9.99	6.13
Ethylene	20.5	8.39	20.0	23.1	41.6
Ethane	3.16	12.8	14.2	13.5	7.19
C3	60.1	47.3	43.5	42.2	36.2
C4	12.5	0.95	4.76	5.01	2.92
CO ₂	1.32	10.4	5.92	6.19	5.99
	100	100	100	100	100
Oil composition (wt %)					
Non-aromatics	1.92	0.98	1.12	0.86	0.94
Benzene	14.3	8.38	8.46	11.6	7.36
Toluene	28.2	19.9	13.1	16.9	14.3
o-Xylene	0.00	0.00	0.00	0.00	0.00
m-Xylene	25.0	22.4	16.9	17.2	21.9
p-Xylene	10.8	9.20	7.56	6.57	7.75
Ethylbenzene	2.11	4.00	1.49	1.04	1.29
C9 Aromatics	5.15	8.92	5.90	6.00	6.08
C10+ Aromatics	12.5	26.2	45.5	39.9	40.4
	100	100	100	100	100
Aromatics in oil (wt %)	98.1	99.0	98.9	99.1	99.1
Yield of aromatics (wt %)	6.01	6.44	6.58	6.23	6.17
BTEX/Aromatics	0.82	0.65	0.48	0.54	0.53
BTEX/Oil	0.80	0.64	0.47	0.53	0.53
Xylenes/BTEX	0.45	0.49	0.51	0.45	0.56
p-Xylene/Xylenes	0.30	0.29	0.31	0.28	0.26
Petroleum Fractions in oil (wt %)					
Gasoline	84.1	69.0	69.8	69.9	73.3
Kerosene	11.3	23.3	24.5	22.7	22.0
Gas oil	1.73	5.46	3.28	4.87	2.38
LVGO	0.44	0.79	0.68	0.70	0.60
HVGO	2.44	1.49	1.68	1.84	1.66

Data were taken at the eighth hour of time-on-stream

The results also show that around 53.9 – 54.6 % of gas yield is obtained from BiHZ5 at various loadings as shown in Figure 4.18. Mixed C3 hydrocarbons and ethylene are the main composition of gaseous products derived from HZ5 and BiHZ5 at various loadings. However, the formation of ethylene firstly decreases and then increases over 2.0 wt % Bi. Mixed C3 hydrocarbons decrease gradually with the increase of Bi loading. When the Bi loading reaches 4.0 wt %, the amount of ethylene is more than 41.6 % whereas that of mixed C3 hydrocarbons is less than 36.2 %. So, further increase of Bi loading brings about an increase in the formation of ethylene and a decrease in mixed C3 hydrocarbons. It can be attributed to the same reasons as in the case of zeolite catalysts modified with P_2O_5 and Sb_2O_5 .

The petroleum fractions in the oils derived from HZ5 modified with Bi_2O_5 catalysts are shown in Figure 4.19. The derived oils from all catalysts highly consist of gasoline, which decreases with Bi_2O_5 loading. However, the addition of Bi_2O_5 causes the reduction of kerosene and gas oil. In addition, the distribution of LVGO and HVGO obtained from BiHZ5 is not significantly different from that of HZ5. It can be summarized that the addition of Bi_2O_5 suppresses the production of gasoline but enhances the production of kerosene.

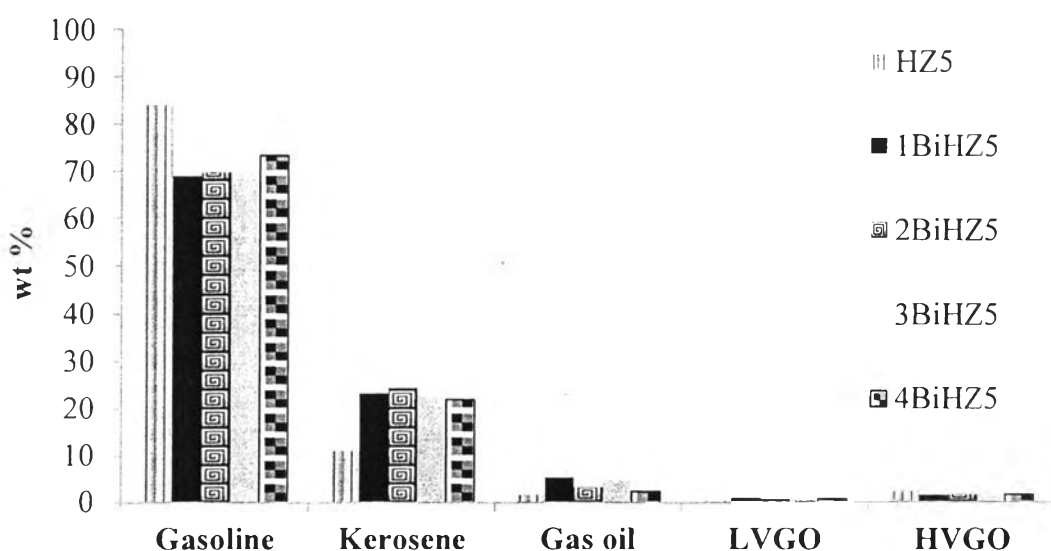


Figure 4.19 Petroleum fractions in oils derived from using Bi_2O_5 -modified catalysts.

4.3.4 Effect of Oxide Species

In order to investigate the effect of the different type of acidic oxides on liquid hydrocarbons production from bio-ethanol, all catalysts with 2 % loading are compared under the following aspects; the bio-ethanol conversion, the yields of oil and gas, and the distributions of oil and gas.

It can be clearly seen that the introduction of acidic oxides leads to a decrease in surface area, pore volume, and pore diameter as shown in Table 4.2. The results also show that the biggest size of Bi_2O_5 leads to the lowest surface area, pore volume, and pore diameter, followed by those of Sb_2O_5 and P_2O_5 that have a smaller size than Bi_2O_5 , respectively. The differences in the physical properties of catalysts results in the difference in the conversion of bio-ethanol and the distribution of products over all catalysts as shown in Table 4.9. According to the results, the conversions of bio-ethanol derived from four catalysts are not considerably different, which is approximately in the range of 96.0 – 97.0 %. It can be seen that the different type of acidic oxides does not significantly affect to the conversion of bio-ethanol. Nevertheless, the type of acidic oxides has the influences on the yield and the compositions of oil and gas, which can be noticed in Figures 4.20 and 4.21. The yield of oil and aromatics are improved when Sb_2O_5 and Bi_2O_5 species were added. The yields of oil and aromatics can be ranked as follows; $2\text{SbHZ5} > 2\text{BiHZ5} > \text{HZ5} > 2\text{PHZ5}$.

For the oil composition, the formation of p-xylene is enhanced when P_2O_5 species was added. The formation of p-xylene can be ranked as follows; $2\text{PHZ5} > \text{HZ5} > 2\text{SbHZ5} > 2\text{BiHZ5}$. The formation of ethylbenzene is enhanced when P_2O_5 or Sb_2O_5 species was added. The formation of ethylbenzene can be ranked as follows; $2\text{PHZ5} > 2\text{SbHZ5} > \text{HZ5} > 2\text{BiHZ5}$. The formation of C9 and C10+ aromatics are enhanced when each oxide species was added. The formation of C9 aromatics can be ranked as follows; $2\text{PHZ5} > 2\text{SbHZ5} > 2\text{BiHZ5} > \text{HZ5}$. The formation of C10+ aromatics can be ranked as follows; $2\text{BiHZ5} > 2\text{SbHZ5} > 2\text{PHZ5} > \text{HZ5}$. However, the fraction of BTEX in the oil and the formation of non-aromatics, benzene, toluene, and m-xylene are suppressed when all oxide species were added. In addition, P_2O_5 species also give the highest ratio of xylenes to BTEX fraction and p-xylene to mixed xylenes. The ratio of xylenes to BTEX fraction can be

ranked as follows; 2PHZ5 > 2BiHZ5 > 2SbHZ5 > HZ5. And the ratio of p-xylene to mixed xylenes can be ranked as follows; 2PHZ5 > 2SbHZ5 > 2BiHZ5 > HZ5. According to the results, ethylbenzene, C9 and C10+ aromatics tend to increase when each metal oxides was added. This can be attributed to the same reasons as the case of zeolite catalysts modified with P₂O₅, Sb₂O₅, or Bi₂O₅.

For the gas composition, the formation of ethylene is enhanced when P₂O₅ species was added as shown in Figure 4.21. The formation of ethylene is ranked as follows; 2PHZ5 > HZ5 > 2BiHZ5 > 2SbHZ5. The formation of mixed C3 and C4 hydrocarbons are suppressed when each oxide species was added. The formation of mixed C3 hydrocarbons is ranked as follows; HZ5 > 2BiHZ5 > 2PHZ5 > 2SbHZ5. Moreover, the formation of mixed C4 hydrocarbons is ranked as follows; HZ5 > 2PHZ5 > 2BiHZ5 > 2SbHZ5.

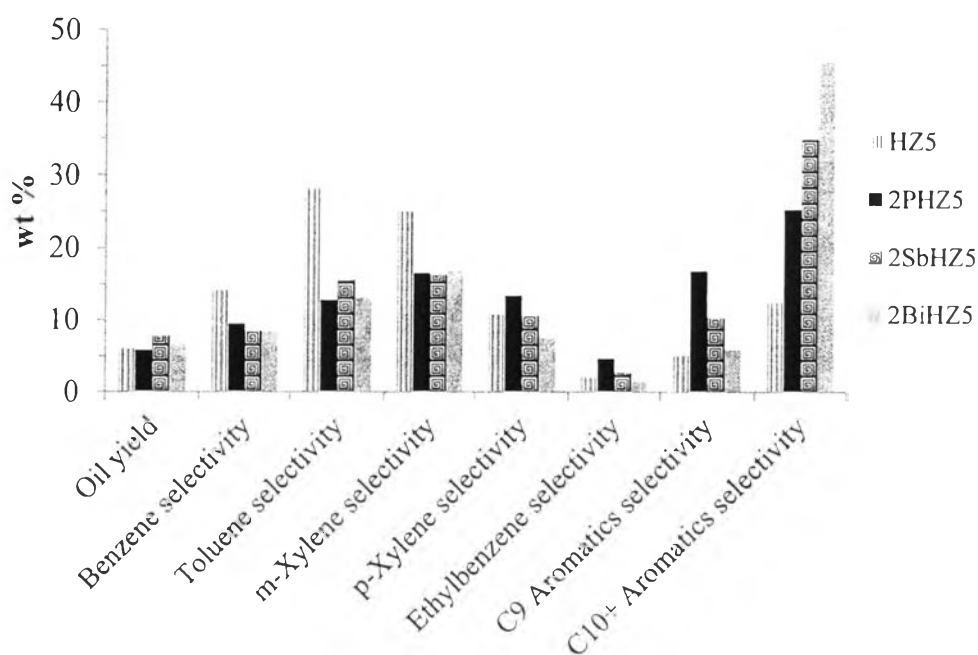


Figure 4.20 Effect of acidic oxide type on the oil yield and the selectivity of liquid products.

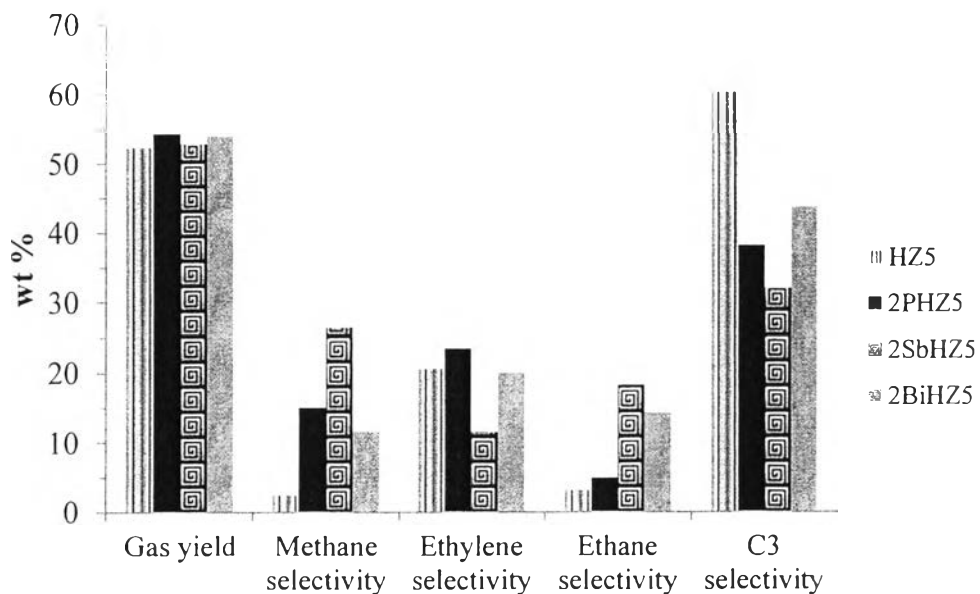


Figure 4.21 Effect of acidic oxide type on the gas yield and the selectivity of gas products.

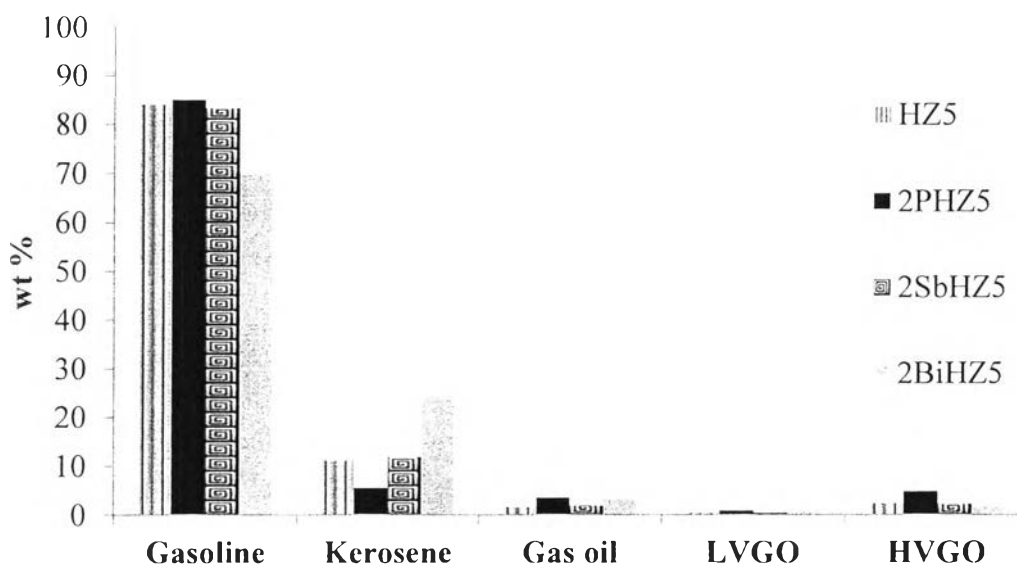


Figure 4.22 Petroleum fractions in oils derived from HZ5, 2PHZ5, 2SbHZ5, and 2BiHZ5 catalysts.

Table 4.9 Product distribution over HZ5, 2PHZ5, 2SbHZ5, and 2BiHZ5 catalysts

Catalyst	HZ5	2PHZ5	2SbHZ5	2BiHZ5
% Bio-ethanol conversion	97.0	97.0	96.2	96.1
Product yield (wt %)				
Oil	6.10	5.80	7.90	6.70
Gas	52.4	54.3	52.8	53.9
Water	41.5	39.9	39.3	39.4
Gas composition (wt %)				
Methane	2.48	15.1	26.4	11.6
Ethylene	20.5	23.4	11.5	20.0
Ethane	3.16	4.90	18.2	14.2
C3	60.1	38.0	31.8	43.5
C4	12.5	9.00	0.00	4.76
CO ₂	1.32	9.67	12.1	5.92
	100	100	100	100
Oil composition (wt %)				
Non-aromatics	1.92	1.15	0.93	1.12
Benzene	14.3	9.46	8.54	8.46
Toluene	28.2	12.8	15.6	13.1
o-Xylene	0.00	0.00	0.00	0.00
m-Xylene	25.0	16.5	16.3	16.9
p-Xylene	10.8	13.4	10.6	7.56
Ethylbenzene	2.11	4.68	2.75	1.49
C9 Aromatics	5.15	16.8	10.3	5.90
C10+ Aromatics	12.5	25.2	34.8	45.5
	100	100	100	100
Aromatics in oil (wt %)	98.1	98.8	99.1	98.9
Yield of aromatics (wt %)	6.01	5.74	7.79	6.58
BTEX/Aromatics	0.82	0.58	0.54	0.48
BTEX/Oil	0.80	0.57	0.54	0.47
Xylenes/BTEX	0.45	0.53	0.50	0.51
p-Xylene/Xylenes	0.30	0.45	0.39	0.31
Petroleum Fractions in oil (wt %)				
Gasoline	84.1	85.0	83.8	69.8
Kerosene	11.3	5.61	11.5	24.5
Gas oil	1.73	3.61	1.93	3.28
LVGO	0.44	0.90	0.49	0.68
HVGO	2.44	4.86	2.28	1.68

Data were taken at the eighth hour of time-on-stream

The petroleum fractions derived from HZ5, 2PHZ5, 2SbHZ5, and 2BiHZ5 catalysts are shown in Figure 4.22. The results showed that the addition of P_2O_5 species slightly increases gasoline, gas oil, LVGO, and HVGO but suppresses kerosene. On the other hand, the addition of Sb_2O_5 species slightly decreases gasoline, but slightly increases kerosene. Moreover, the addition of Bi_2O_5 species significantly decreases gasoline, but significantly enhances kerosene.

From the results, it can be explained that $Bi_2O_5/HZSM-5$ has the highest acid strength that can easily protonate a hydrocarbon molecule and then promote the generation of carbenium ions, which can further undergo desired protonation of a small molecule to a large molecule, as shown in Figure 4.23 as an example, and hence results in the decline of lighter hydrocarbons (BTX) and the enhancement of larger hydrocarbons (C9 and C10+ aromatics). On the other hand, the $P_2O_5/HZSM-5$ catalyst favors the formation of p-xylene, ethylbenzene, and C9+ aromatics because of its moderate acid strength that is not high enough to further protonate these aromatics to heavy aromatics like C10+ aromatics.

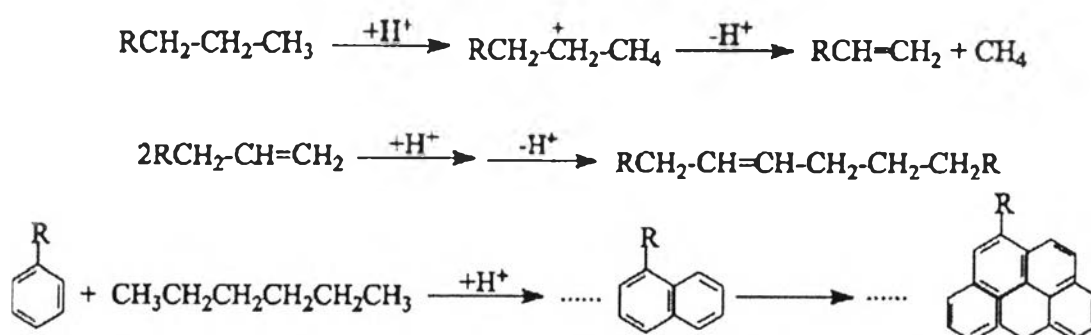


Figure 4.23 Example of protonation of a small hydrocarbon molecule to a larger molecule via carbenium ion mechanism.

Normally, the catalysis of bio-ethanol dehydration to aromatic hydrocarbons over the catalyst can be separated into two main steps. First, bio-ethanol is initially activated on the acid site of HZ5 catalyst via dehydration reaction. Thus, the primary products are ethylene and water as shown in Figure 4.24. Then, the ethylene can be further catalyzed by the acid site of HZ5 and new acidic center of acidic oxide through a carbenium ion mechanism to form carbenium ion.

Subsequently, H-transfer, oligomerization, isomerization, cyclization, aromatization and/or cracking are rapidly simultaneously occurred.

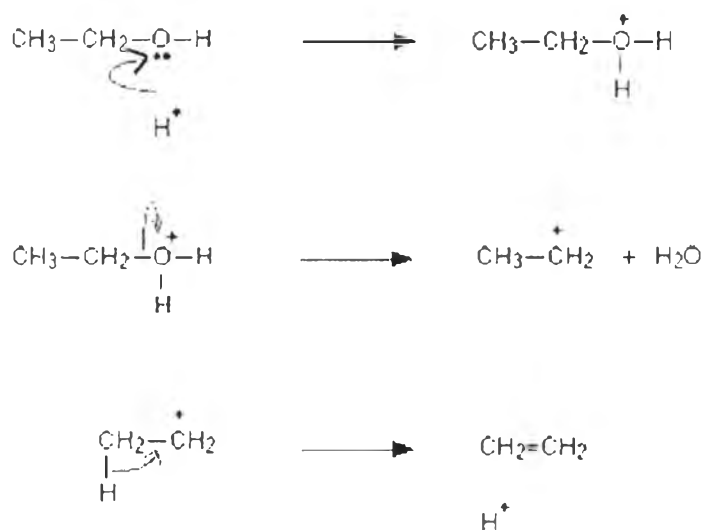


Figure 4.24 Simple mechanism of ethanol conversion to ethylene over an acid catalyst (<http://www.chemguide.co.uk/mechanisms/elim/dhethanol.html>).

The higher catalytic activity of oxide-modified HZSM-5 catalysts towards aromatic hydrocarbons may be attributed to the synergistic effect between the promoters and the support. The HZSM-5 zeolite alone is an acidic solid catalyst that is effective for cracking, dehydrogenation, isomerization, and oligomerization reactions, which are catalyzed by acidic catalysts, to form aromatic hydrocarbons. However, the ability of aromatics formation over the HZSM-5 alone has limitations, and hence the zeolite requires an increase in acid strength by modification with various acidic oxides. Therefore, the addition of suitable oxide to HZSM-5 can help to improve some activity of the catalyst. An oxide, like Ga_2O_3 , P_2O_5 , Sb_2O_5 , and Bi_2O_5 , can enhance dehydrocyclization, disproportionation, and transalkylation reactions, which require both oxide and acidic functions. Since the oxide alone does not catalyze the branching reaction, it requires an acidic function to initially generate carbenium ions which further undergo desired protonation. Sometimes, some acidic sites of zeolite are not sufficiently strong enough to generate some carbenium ion because it is too weak to protonate bio-ethanol, so an appropriate oxide is needed to catalyze the dehydration of bio-ethanol to give olefins that are easily further protonated.