

CHAPTER IV

RESULTS AND DISCUSSION

The catalytic dehydration of bio-ethanol to ethylene process is a set of simultaneous parallel endothermic reactions involving direct bio-ethanol conversion (dehydration of bio-ethanol into ethylene directly) and by the consecutive reactions (the dehydration of bio-ethanol into diethyl ether (DEE) and dehydration of DEE into ethylene). Apart from ethylene, other hydrocarbons involving olefins (propylene and butylene), paraffins (ethane, propane, and butane), and aromatics can be produced via the catalytic dehydration of bio-ethanol as well (Gayubo *et al.*, 2010). These products strongly depend on the type of the catalyst used via different reactions including oligomerization, cracking, dehydrogenation, and aromatization as shown in Figure 4.1.

The aim of this research is to attain a catalyst under the suitable conditions for the production of light olefins (ethylene and propylene). Thus, this chapter is divided into two main parts. First, the catalytic activity of acidic oxides of germanium, gallium, tin, and antimony doped with SAPO-34 catalyst on the catalytic dehydration reaction of bio-ethanol to light olefins, are analyzed and discussed in Section 4.1. Second, the catalytic performance of HZSM-5 treated with KOH solutions at various concentrations is discussed in Section 4.2. To ease the discussion, the catalyst nomenclatures are summarized in Table 4.1.

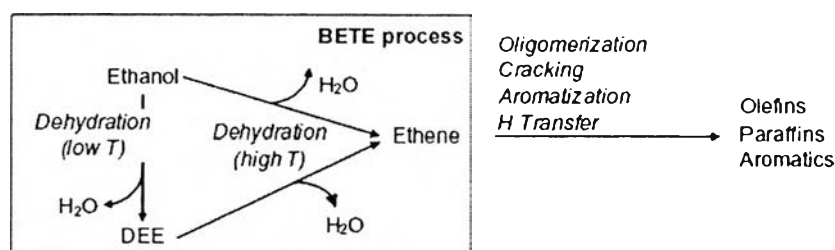


Figure 4.1 Transformation of bio-ethanol into ethylene, olefins (propylene and butylene), paraffins (ethane, propane, and butane), and aromatics on acid catalysts (Gayubo *et al.*, 2010).

Table 4.1 Catalysts and their nomenclatures

No.	Catalyst	Abbreviation	No.	Catalyst	Abbreviation
<i>The first scope</i>			<i>The second scope</i>		
1	SAPO-34	SA34	10	HZSM-5	HZ5
2	3%GeO ₂ /SAPO-34	3GeSA34	11	0.1M KOH/HZSM-5	0.1M KOH/HZ5
3	5%GeO ₂ /SAPO-34	5GeSA34	12	0.5M KOH/HZSM-5	0.5M KOH/HZ5
4	3%Ga ₂ O ₃ /SAPO-34	3GaSA34	13	0.9M KOH/HZSM-5	0.9M KOH/HZ5
5	5%Ga ₂ O ₃ /SAPO-34	5GaSA34			
6	3%SnO ₂ /SAPO-34	3SnSA34			
7	5%SnO ₂ /SAPO-34	5SnSA34			
8	3%Sb ₂ O ₃ /SAPO-34	3SbSA34			
9	5%Sb ₂ O ₃ /SAPO-34	5SbSA34			

4.1 Effect of Oxides Loaded on SAPO-34 Catalyst

This section discusses about the influence of oxides mixed with the SAPO-34 catalyst. Nine catalysts were investigated in this part; that are, pure SAPO-34, germanium oxide, gallium oxide, tin oxide, and antimony oxide mixed with the SAPO-34 catalyst with various loading percentages: 3%, and 5%. Each catalyst testing was carried out at 400 °C under atmospheric pressure. The liquid hourly space velocity (LHSV) was fixed at 0.5 h⁻¹. Three grams of a catalyst was packed in the isothermal fixed bed reactor, and the reaction time was held for 480 minutes.

The conversion of bio-ethanol obtained from the pure SAPO-34 and the modified SAPO-34 catalyst is not significantly different according to the results reported in Tables 4.2 to 4.5. For all catalysts testing, the bio-ethanol conversion is approximately in the range of 93-97%. It can be seen that whether or not the SAPO-34 was modified by oxides, the bio-ethanol conversion is not essentially affected. On the other hand, the modified SAPO-34 catalysts also affect to the product distribution, which can be discussed as follows.

4.1.1 Characterization of catalysts

This part discusses the characterization of catalysts by using several techniques to overview the differences on their characteristic and properties. The Brunauer-Emmett-Teller (BET) technique was employed to determine the physical properties of catalysts, including BET surface area, pore volume, and Horvath Kawazoe (HK) pore diameter by using a Thermo Finnigan/Sorptomatic 1990 surface area analyzer, which are revealed in Table 4.2. The modification of SAPO-34 catalyst with 5% of germanium oxide, tin oxide, gallium oxide, and antimony oxide results in the reduction of BET surface area and pore volume. However, the HK pore diameter of all modified catalysts is slightly higher than that of pure SAPO-34 catalyst. Probably, germanium oxide, gallium oxide, tin oxide, and antimony oxide loading by physical mixing with SAPO-34 cause pore blocking, especially in a narrow pore of the zeolite.

Moreover, the X-ray diffraction (XRD) patterns of SAPO-34 and the modified SAPO-34 catalysts are shown in Figure 4.2. As a result, SAPO-34 catalyst gives the peaks at 9.5°, 20.5°, and 30.4°. Moreover, 5SnSA34 gives a peak at 26.6° that belongs to SnO₂. The peak of GeO₂ is found at 25.9°, the peak of Ga₂O₃ is shown at 30.1°, and the peak of Sb₂O₃ is revealed at 28.0°. From their XRD patterns, it can be confirmed that the position in the diffraction peaks of modified catalysts were well matched and identified the oxide form with the reference to JCPDS files (Joint Committee on Powder Diffraction Standards).

Table 4.2 Physical properties of modified SAPO-34 catalysts

Catalyst	BET Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)
SA34	368.2	0.3494	4.495
5GeSA34	307.0	0.2710	4.704
5SnSA34	306.2	0.2294	4.650
5GaSA34	308.9	0.1225	4.622
5SbSA34	307.6	0.1854	4.719

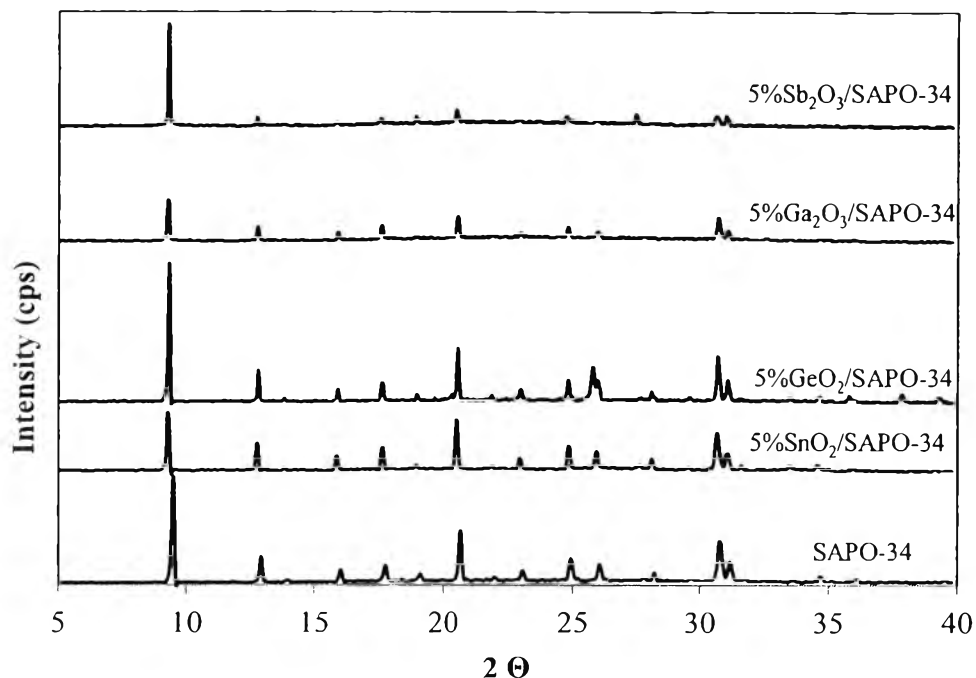


Figure 4.2 XRD patterns of SnO₂, GeO₂, Ga₂O₃, and Sb₂O₃ loading (5% elemental basis) on SAPO-34 and pure SAPO-34 catalyst.

4.1.2 Germanium oxide-doped SAPO-34 catalysts

In order to investigate the influence loading amount of germanium oxide for the catalytic dehydration of bio-ethanol to light olefins. According to the results, the product distribution of germanium oxide mixed with SAPO-34 catalysts is presented in Table 4.3. It reveals that approximately 69.2% of total gas yield and 0% of total extracted oil yield are acquired from the SAPO-34 catalyst without modification. For the gaseous product analysis, it is observed that approximately 88.7% and 85.8% of the gas yields were obtained from 3GeSA34 and 5GeSA34, respectively. However, the yield of extracted oil increases with the loading percentage of germanium, which is the opposite trend to the gas yield as shown in Figure 4.3. In addition, the gaseous products mainly consist of ethylene, whereas propylene and propane are coproduced as traces. The results are reported in Tables A2 and A3. As can be seen, the unmodified SAPO-34 catalyst produces 0.20 wt% propylene in the gas, while the highest content of propylene

in the gaseous product (9.21 wt%) is observed at 240 minutes of time-on-stream using the 5GeSA34 catalyst. However, the cooking gases (propane and butane) are significantly increased (15.94 wt% at 120 minutes time-on-stream) when 3GeSA34 is employed. As the result, the concentration of ethylene decreases whereas the propylene significantly increases with the loading percentage of Ge. This is an evidence indicating that GeO₂-modified SAPO-34 catalyst can help to enhance the gas production yield, and the composition of extracted oil (3GeSA34) mainly consists of oxygenate compounds.

The oil yield from 3% and 5% Ge on GeO₂-modified SAPO-34 catalysts increases from 3.32% to 4.14%. Additionally, all extracted oils were analyzed for true boiling point curves (TBPs). Moreover, the TBPs of oils were cut into the petroleum fractions, according to true boiling point (°C); gasoline: <149 °C, kerosene: 149-232 °C, gas oil: 232-343 °C, light vacuum gas oil: 343-371 °C, and heavy vacuum gas oil: >371 °C. The petroleum fractions of obtained oils mainly consist of gasoline, which is higher than 70 wt% as shown in Figure 4.4. However, increasing the weight percentage of germanium results in the increase of kerosene and gas oil. In addition, the extracted oils product from the catalytic dehydration were analyzed for their compositions using a gas chromatography equipped with a mass spectrometry of time of flight type (GC-TOF) as shown in Figure 4.5. It is observed that the oxygenate compounds are the major constituent of the oil obtained from 3GeSA34 catalyst, whereas BTEX, and aromatics (C₉ and C₁₀₊) are present at a low amount. The modification of germanium oxide with SAPO-34 can lead to the increase in acidity of the zeolite. It can be clearly seen that aromatic hydrocarbons (heavy hydrocarbons) are the main component in obtained oil (5GeSA34), which increases up to 50%, and only a small concentration of benzene, toluene, xylenes, and ethylbenzene is observed.

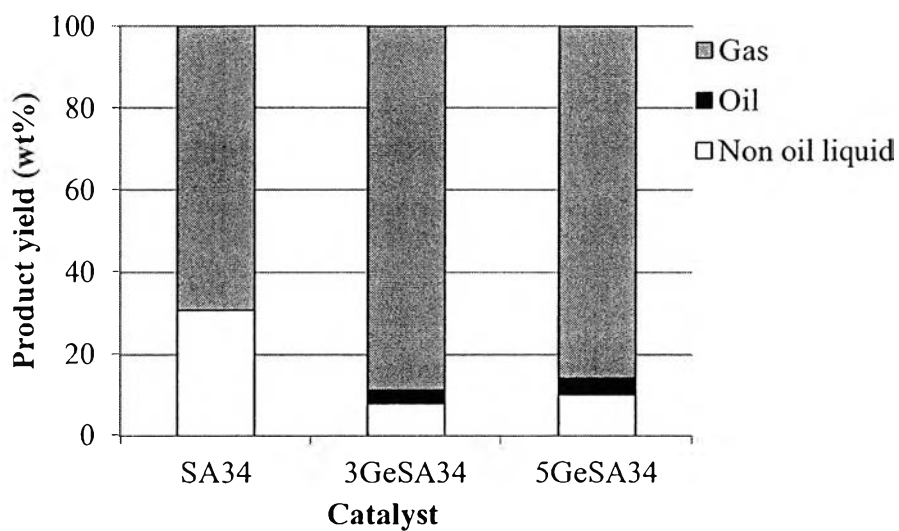


Figure 4.3 Product distribution from using GeO₂-doped SAPO-34 catalysts.

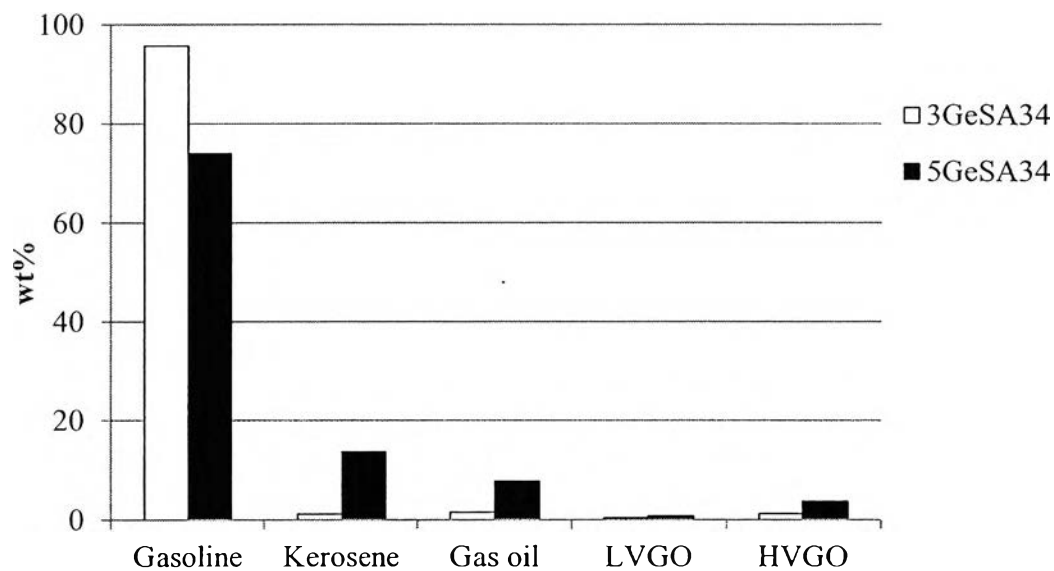


Figure 4.4 Petroleum fractions in oils from using GeO₂-doped SAPO-34 catalysts.

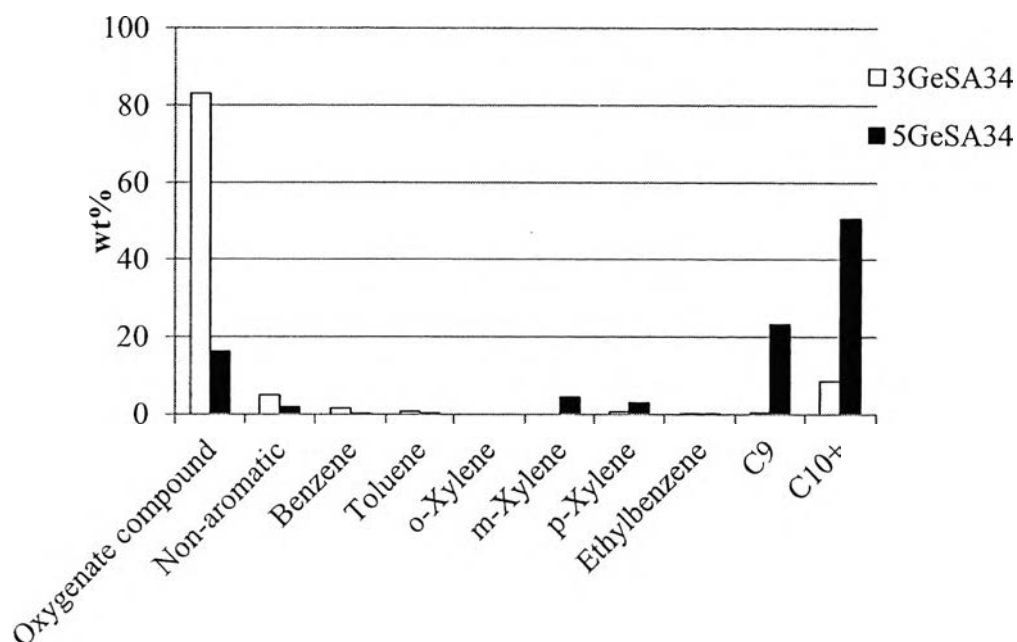


Figure 4.5 Composition of extracted oils from using GeO₂-doped SAPO-34 catalysts.

Table 4.3 Product distribution from using GeO₂-doped SAPO-34 catalysts

Catalyst	SA34	3GeSA34	5GeSA34
Ethanol conversion (%)			
	93.7	96.8	96.7
Product distribution (wt%)			
Gas yield	69.2	88.7	85.8
Extracted oil yield	0	3.32	4.14
Non oil liquid yield	30.7	8.00	10.1
Gas composition (wt%)			
Methane	0.04	0.32	0.44
Ethylene	98.7	93.0	81.5
Ethane	0.45	1.29	2.05
Propylene	0.20	3.78	9.21
Propane	0.01	1.39	6.14
Butylene	0.22	0.05	0.13
Butane	0.34	0.16	0.51
Oil composition (wt%)			

Oxygenate compound	0	83.1	16.2
Non-aromatic	0	4.94	1.91
Benzene	0	1.57	0.11
Toluene	0	0.71	0.33
o-Xylene	0	0	0
m-Xylene	0	0	4.44
p-Xylene	0	0.67	3.05
Ethylbenzene	0	0.17	0.15
C₉ Aromatic	0	0.41	23.2
C₁₀₊ Aromatic	0	8.48	50.6
Petroleum fraction (wt%)			
Gasoline	0	95.7	74.0
Kerosene	0	1.16	13.7
Gas oil	0	1.55	7.78
LVGO	0	0.39	0.81
HVGO	0	1.22	3.73

Gas samples were taken at 240 minutes of time-on-stream

4.1.3 Gallium oxide-doped SAPO-34 catalysts

This section focuses on the loading of gallium oxide (Ga_2O_3) in order to improve the acidic property of SAPO-34 catalyst. The gallium oxide loading also affects to the product distribution, which can be reported in Table 4.4. As can be seen in Figure 4.6, using the Ga_2O_3 -doped SAPO-34 catalysts, the yield of extracted oil was increased to 8.79% when 5% Ga was loaded on SAPO-34. However, the gas yield slightly decreases with the increasing weight percentage of gallium in Ga_2O_3 . At the operating conditions, the bio-ethanol was almost converted into ethylene, propylene, butylenes, and cooking gas (propane and butane). The bio-ethanol conversion of all catalysts is approximately in the range of 96.9-97.1 %. It can be seen that whether or not the SAPO-34 catalysts were modified with Ga_2O_3 , the conversion of bio-ethanol is not significantly affected.

Apart from the gas composition of ethylene, propylene, butylene, and cooking gas reported in Table 4.4, the weight percentages of ethylene, propylene, butylenes, and cooking gas on the gas products from both modified catalysts are plotted

with time on stream as shown in Figure 4.9. As can be seen, the gas composition of ethylene from unmodified SAPO-34 catalyst is the highest among that of the other products at all loading percentages. Ethylene formed from the catalytic dehydration of bio-ethanol can be further converted to other hydrocarbons, leading to the gradual decrease of ethylene and then the significant increase of propylene, butylenes, and cooking gas in the gas product by using 5GaSA34.

Additionally, the TBP curves of the extracted oils obtained from Ga_2O_3 -doped SAPO-34 catalysts were cut into the petroleum fractions, as presented in Figure 4.7. As can be seen, the obtained oils from both catalysts highly consist of gasoline of greater than 96 %. It can be clearly seen that when Ga_2O_3 was loaded to the SAPO-34 catalyst, the catalytic activity slightly increases. The results reveal that approximately 3.29 % and 8.79 % of extracted oil yield are obtained from 3GaSA34 and 5GaSA34, respectively. In addition, the obtained oils from both catalysts highly consist of aromatic hydrocarbons, especially C_{10+} aromatics.

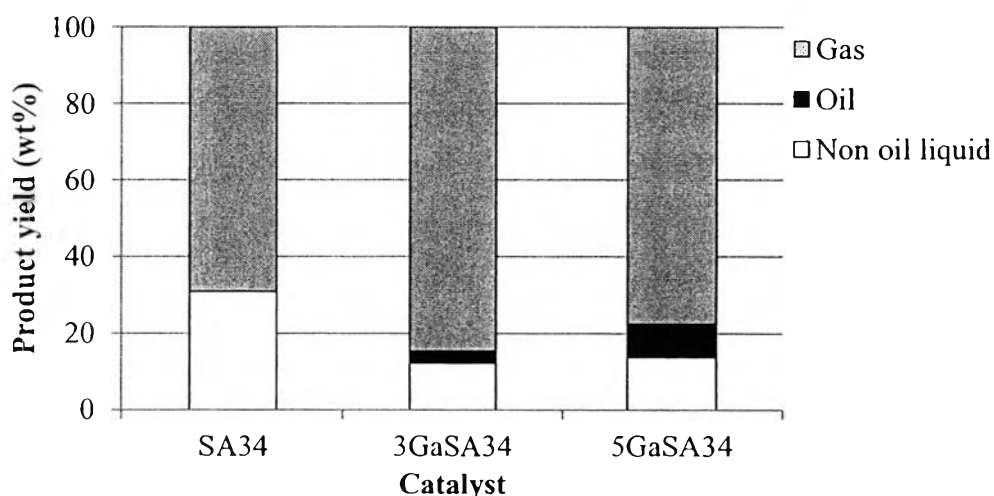


Figure 4.6 Product distribution from using Ga_2O_3 -doped SAPO-34 catalysts.

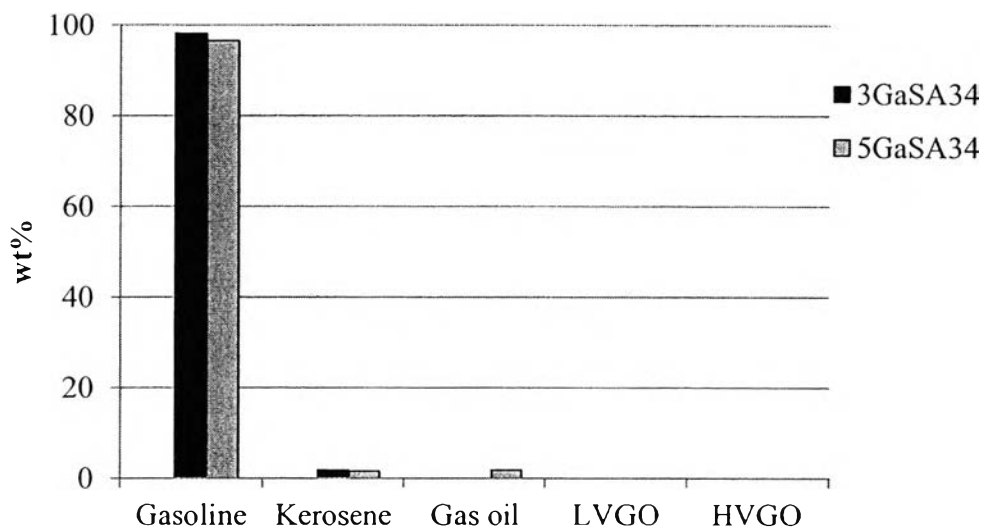


Figure 4.7 Petroleum fractions in oils from using Ga₂O₃-doped SAPO-34 catalysts.

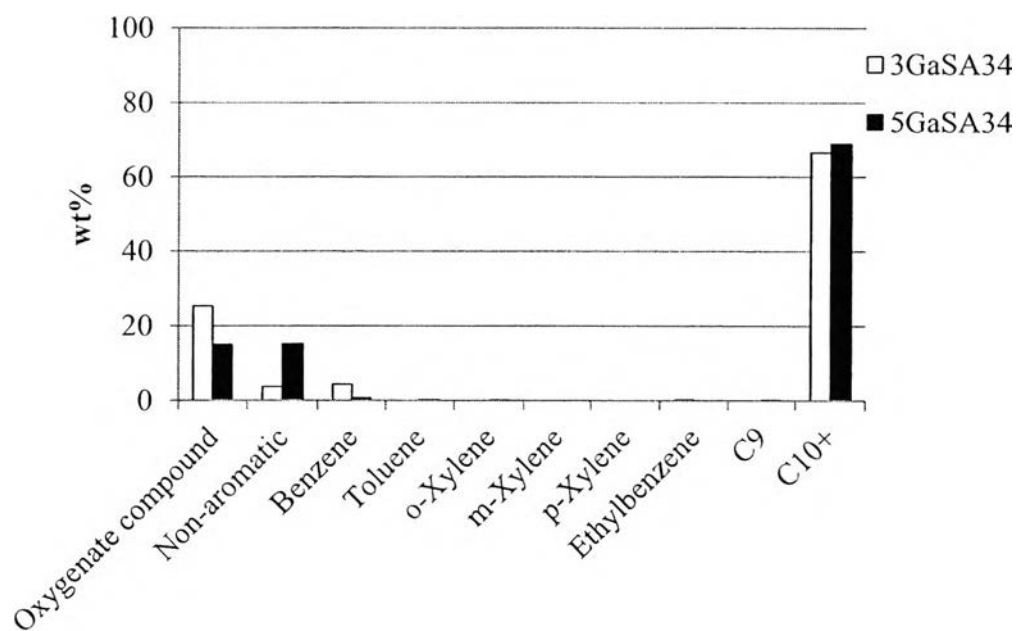


Figure 4.8 Composition of extracted oils from using Ga₂O₃-doped SAPO-34 catalysts.

Table 4.4 Product distribution from using Ga₂O₃-doped SAPO-34 catalysts

Catalyst	SA34	3GaSA34	5GaSA34
Ethanol conversion (%)			
	93.7	97.1	96.9
Product distribution (wt%)			
Gas yield	69.2	84.5	77.5
Extracted oil yield	0	3.29	8.79
Non oil liquid yield	30.7	12.2	13.8
Gas composition (wt%)			
Methane	0.04	0.22	0.43
Ethylene	98.7	90.8	78.2
Ethane	0.45	0.98	1.74
Propylene	0.20	1.66	7.54
Propane	0.01	0.42	0.12
Butylene	0.22	2.65	6.12
Butane	0.34	3.24	5.87
Oil composition (wt%)			
Oxygenate compound	0	25.2	15.0
Non-aromatic	0	3.71	15.1
Benzene	0	4.38	0.73
Toluene	0	0	0.14
o-Xylene	0	0	0.06
m-Xylene	0	0	0
p-Xylene	0	0	0
Ethylbenzene	0	0.18	0
C ₉ Aromatic	0	0	0.03
C ₁₀₊ Aromatic	0	66.5	68.9
Petroleum fraction (wt%)			
Gasoline	0	98.2	96.5
Kerosene	0	1.85	1.62
Gas oil	0	0	1.85
LVGO	0	0	0
HVGO	0	0	0

Gas samples were taken at 240 minutes of time-on-stream

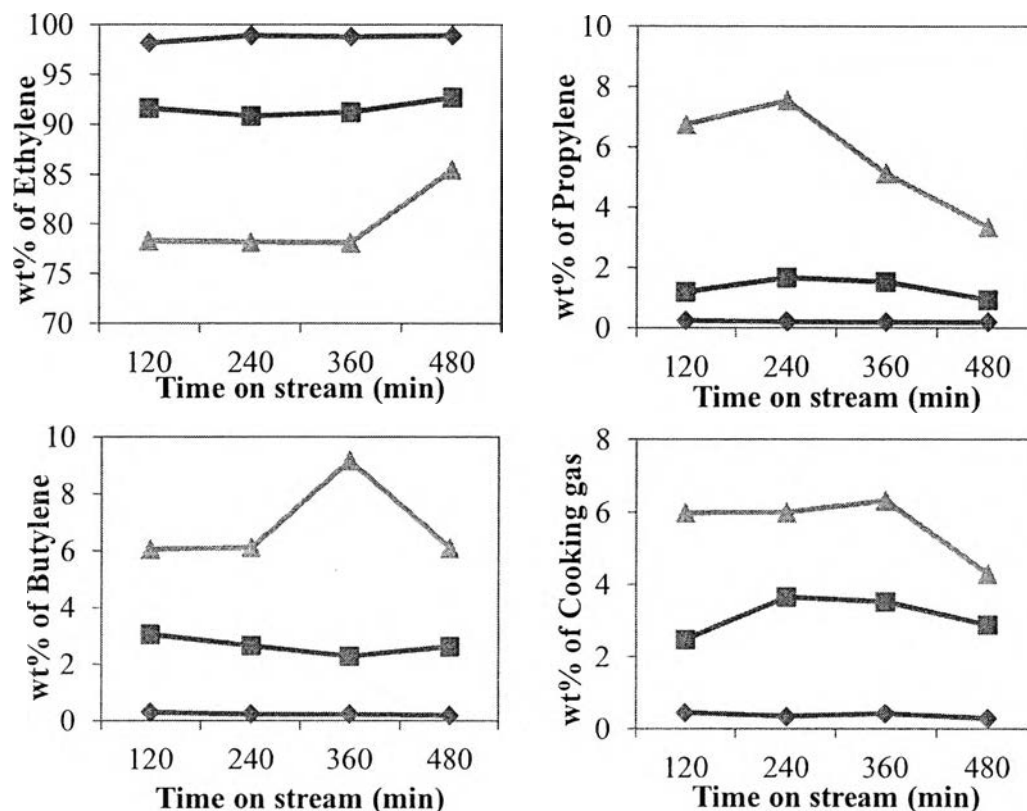


Figure 4.9 Weight percentages of ethylene, propylene, butylenes, and cooking gas (propane and butane) in the gas products from using 3% (■), 5% (▲) of Ga in $\text{Ga}_2\text{O}_3/\text{SAPO-34}$, and pure SAPO-34 (◆).

4.1.4 Tin oxide-doped SAPO-34 catalysts

Apart from germanium oxide and gallium oxide doped on SAPO-34 catalysts discussed in the previous sections, no study to date has been focused on tin oxide-doped SAPO-34 catalysts for the catalytic dehydration of bio-ethanol to light olefins. For this part, the Sn loading on SAPO-34 was varied as 3% and 5%. As a result, the product distribution of SnO_2 -doped SAPO-34 catalysts is reported in Table 4.5. The results show that for 3SnSA34 and 5SnSA34, the yield of extracted oils is slightly increased from 1.72 to 2.74 wt%, and the gas yield is increased to 85.3 and 77.3 wt%, respectively, which is improved from that of pure SAPO-34 catalyst as shown in Figure 4.10. Additionally, the TBPs of extracted oils was cut into the petroleum fractions, and

the result is shown in Figure 4.11. The derived oils from both catalysts are highly composed of gasoline, which is in the range of 95.8 – 96.7 wt %. The composition of the oils was analyzed by GC-TOF, which can be seen in Figure 4.12. The oxygenate compounds (especially, diethyl ether) are the main component of derived oils from both catalysts.

For the gaseous product analysis, it is observed that the gaseous products obtained from SnO₂-doped SAPO-34 catalysts consist of ethylene, ethane, propylene, and cooking gas (propane and butane). The weight percentages of ethane, ethylene, propylene, and cooking gas in the gas products are shown in Figure 4.13. As can be seen, the product distribution depends strongly on the SnO₂ content. The 5SnSA34 catalyst produces high amount of the propylene (15.26 wt%), ethane (4.51 wt%), and cooking gas (17.41 wt%) at 240 minutes time-on-stream. Moreover, the increase in the SnO₂ loading results in the high production of ethylene.

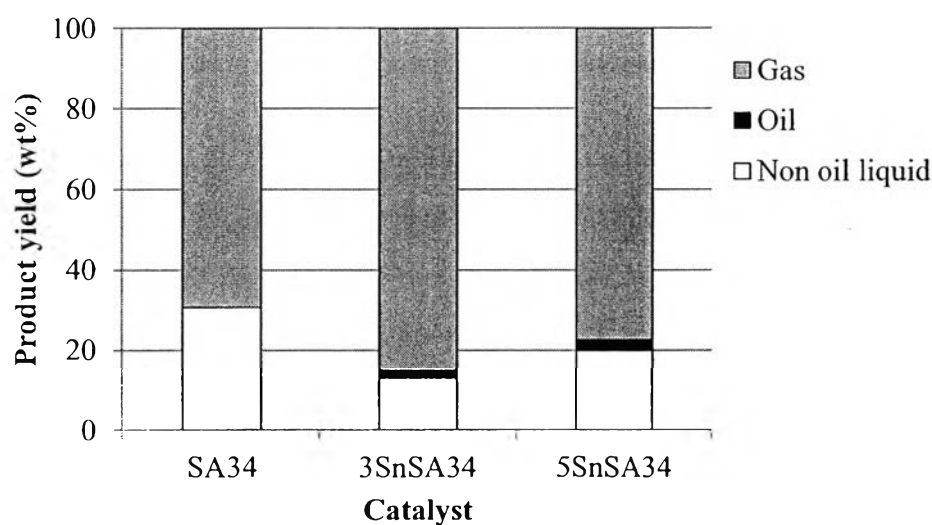


Figure 4.10 Product distribution from using SnO₂-doped SAPO-34 catalysts.

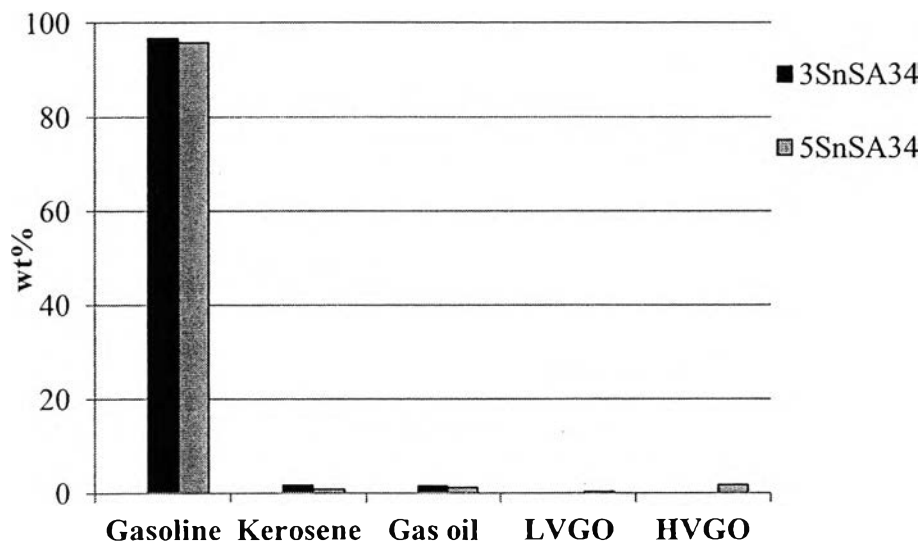


Figure 4.11 Petroleum fractions in oils from using SnO₂-doped SAPO-34 catalysts.

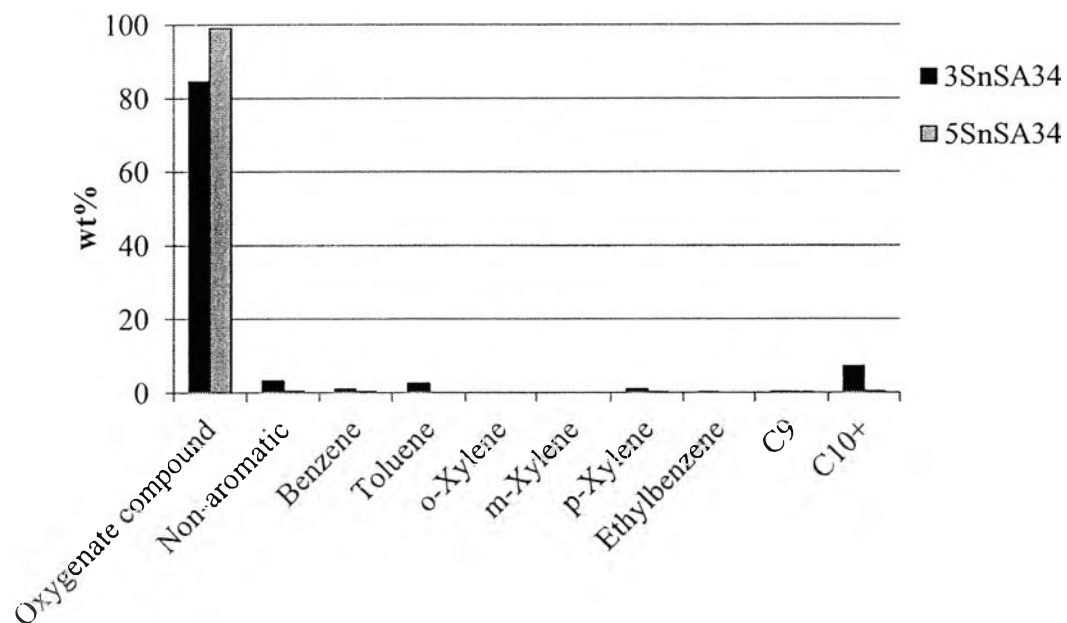


Figure 4.12 Composition of extracted oils from using SnO₂-doped SAPO-34 catalysts.

Table 4.5 Product distribution from using SnO₂-doped SAPO-34 catalysts

Catalyst	SA34	3SnSA34	5SnSA34
Ethanol conversion (%)			
	93.7	96.8	96.9
Product distribution (wt%)			
Gas yield	69.2	85.3	77.3
Extracted oil yield	0	1.72	2.74
Non oil liquid yield	30.7	12.9	19.9
Gas composition (wt%)			
Methane	0.04	1.47	1.52
Ethylene	98.7	81.3	60.6
Ethane	0.45	4.78	4.51
Propylene	0.20	10.8	15.3
Propane	0.01	1.06	15.0
Butylene	0.22	0.13	0.58
Butane	0.34	0.41	2.41
Oil composition (wt%)			
Oxygenate compound	0	84.6	99.1
Non-aromatic	0	3.28	0.33
Benzene	0	1.05	0.18
Toluene	0	2.61	0
o-Xylene	0	0	0
m-Xylene	0	0	0
p-Xylene	0	1.01	0.08
Ethylbenzene	0	0.03	0.00
C ₉ Aromatic	0	0.15	0.05
C ₁₀₊ Aromatic	0	7.27	0.28
Petroleum fraction (wt%)			
Gasoline	0	96.7	95.8
Kerosene	0	1.78	0.90
Gas oil	0	1.53	1.21
LVGO	0	0	0.31
HVGO	0	0	1.77

Gas samples were taken at 240 minutes of time-on-stream

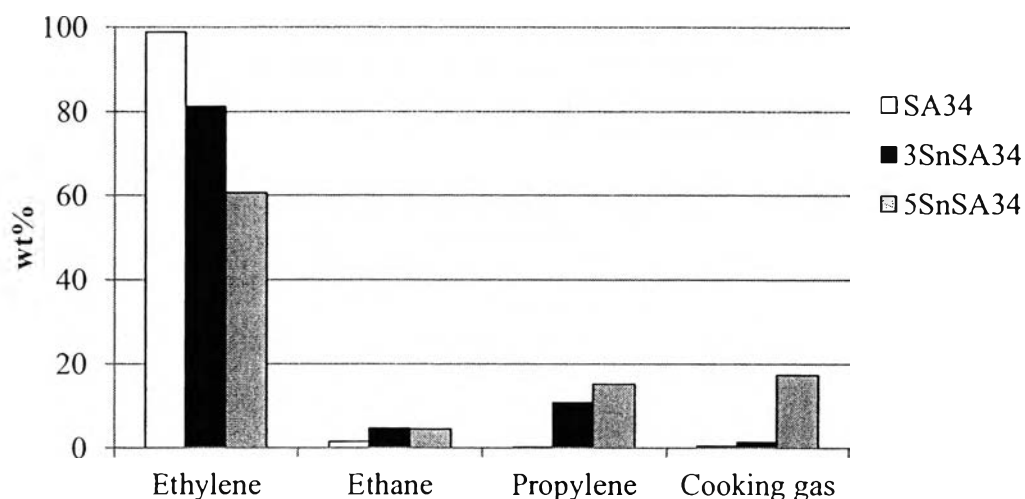


Figure 4.13 Weight percentages of ethylene, ethane, propylene, and cooking gas (propane and butane) at 240 minutes time-on-stream in the gas products from using $\text{SnO}_2/\text{SAPO-34}$, and pure SAPO-34 catalyst.

4.1.5 Antimony oxide-doped SAPO-34 catalysts

This section discusses about the effect of antimony oxide-doped SAPO-34 zeolite catalysts. The several oxides mixed with SAPO-34 catalysts were described in the previous part. It has been well-known that bio-ethanol can be converted into hydrocarbons over modified SAPO-34 catalysts. The antimony oxide loading also affects to the product distribution, which is reported in Table 4.5. According to the results shown in Figure 4.14, the gas yield is increased to 88.1 wt% using 3.0 wt% of Sb doping. However, the gas yield slightly decreases with the increase of Sb to 5.0 wt%. Additionally, as can be seen in Figure 4.15, the derived oils from all catalysts highly consist of gasoline, which is higher than 97.0 wt % observed. However, the aromatics yield is also presented in the same trend as oil yield as can be shown in Figure 4.16. Aromatic hydrocarbons are the major components in derived oil from 5SbSA34 that highly consists of C_{10+} aromatics. It can be clearly seen that when Sb_2O_3 was doped to SAPO-34 catalyst, the catalytic activity increases significantly.

Considering the gaseous products, the concentration of ethylene, propylene, ethane, and cooking gas is shown in Figure 4.16. The results reveal that when Sb_2O_3 were loaded to SAPO-34 catalyst, the formation of propylene increases significantly to 3.40 wt%, but the productions of ethane and cooking gas are suppressed.

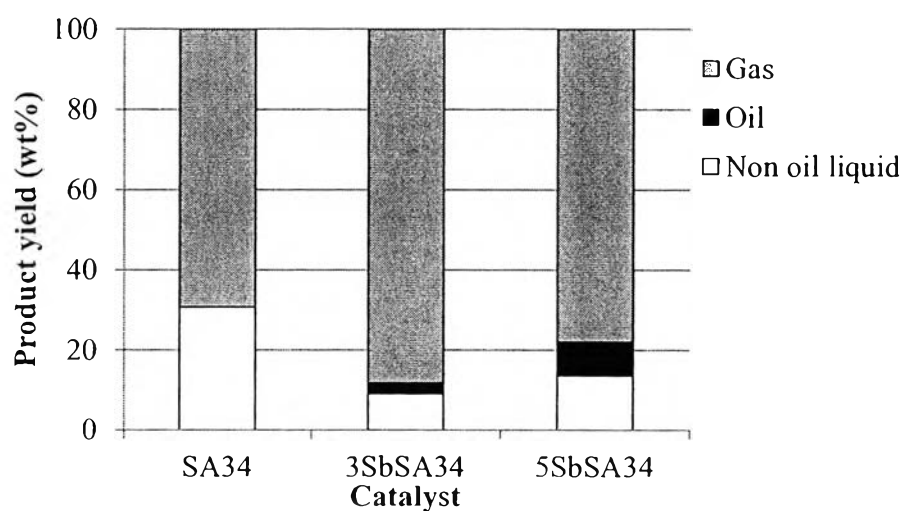


Figure 4.14 Product distribution from using Sb_2O_3 -doped SAPO-34 catalysts.

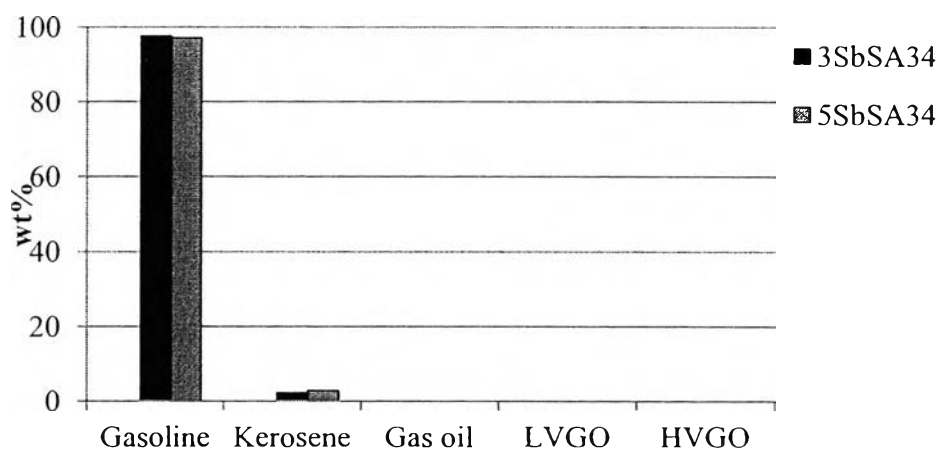


Figure 4.15 Petroleum fractions in oils from using Sb_2O_3 -doped SAPO-34 catalysts.

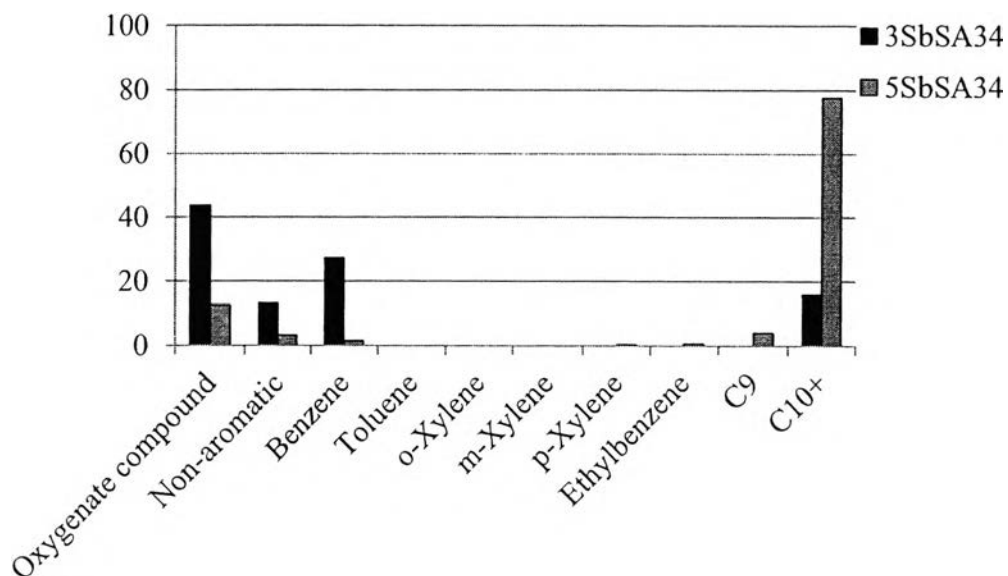


Figure 4.16 Composition of extracted oils from using Sb_2O_3 -doped SAPO-34 catalysts.

Table 4.6 Product distribution from using Sb_2O_3 -doped SAPO-34 catalysts

Catalyst	SA34	3SbSA34	5SbSA34
Ethanol conversion (%)			
	93.7	96.9	97.3
Product distribution (wt%)			
Gas yield	69.2	88.1	77.8
Extracted oil yield	0	2.79	8.51
Non oil liquid yield	30.7	9.06	13.6
Gas composition (wt%)			
Methane	0.04	1.43	0.37
Ethylene	98.7	82.4	93.2
Ethane	0.45	8.57	1.57
Propylene	0.20	2.64	3.40
Propane	0.01	0.85	0.06
Butylene	0.22	1.83	0.48
Butane	0.34	2.25	0.84
Oil composition (wt%)			
Oxygenate compound	0	43.7	12.6
Non-aromatic	0	13.1	3.24

Benzene	0	27.3	1.47
Toluene	0	0	0
o-Xylene	0	0	0
m-Xylene	0	0	0
p-Xylene	0	0	0.37
Ethylbenzene	0	0	0.67
C₉ Aromatic	0	0	4.12
C₁₀₊ Aromatic	0	15.9	77.5
Petroleum fraction (wt%)			
Gasoline	0	97.7	97.1
Kerosene	0	2.33	2.87
Gas oil	0	0	0
LVGO	0	0	0
HVGO	0	0	0

Gas samples were taken at 240 minutes of time-on-stream

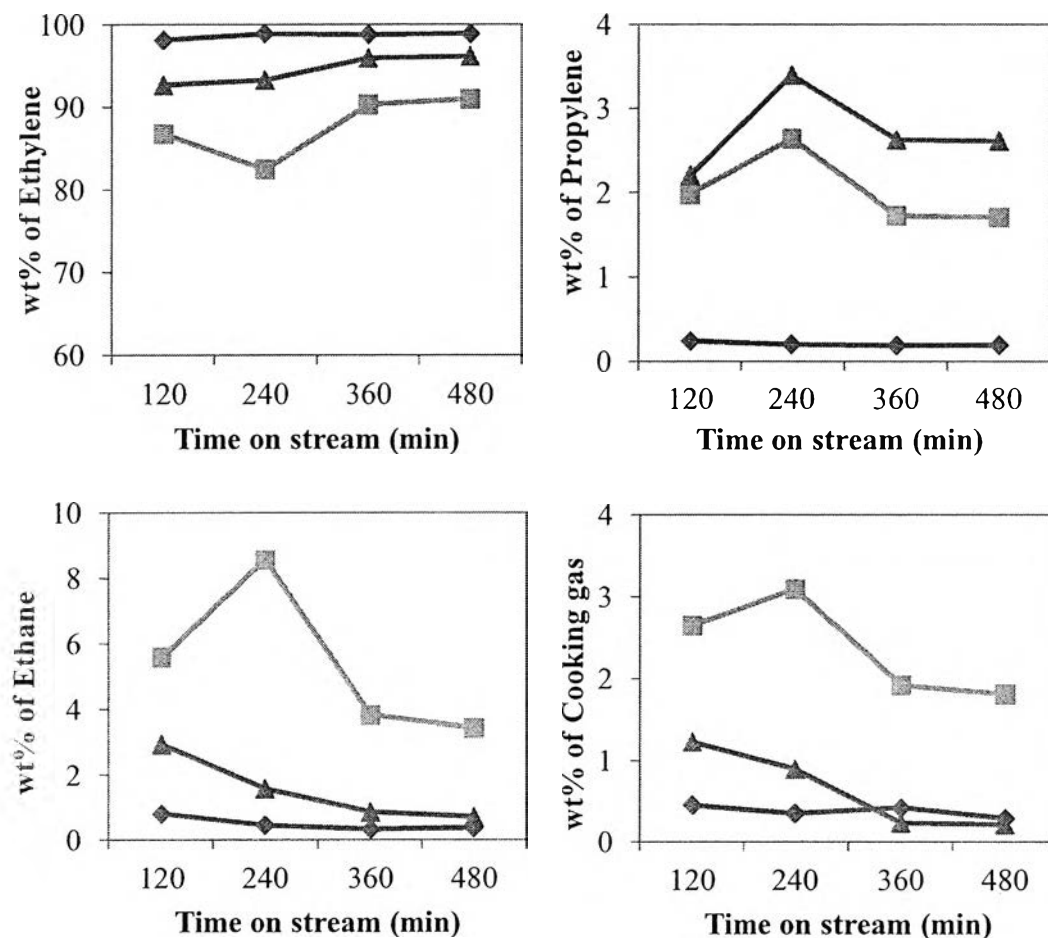


Figure 4.17 Weight percentages of ethylene, propylene, ethane, and cooking gas (propane and butane) in the gas products from using 3% (■), 5% (▲) of Sb loading on SAPO-34, and pure SAPO-34 (◆).

4.1.6 Comparison of modified SAPO-34 catalysts

This section compares and discusses the influence of the type of acidic oxides doped to SAPO-34 on the conversion of bio-ethanol and the distribution of each product. 5GeSA34, 5GaSA34, 5SnSA34, and 5SbSA34 catalysts were used for comparison. According to the results, the conversions of bio-ethanol are approximately in the range of 93.0 – 97.0 %. It can be seen that whether or not the SAPO-34 was modified by acidic oxides, the bio-ethanol conversion is not significantly affected.

However, the type of oxides affects to the product distribution, which can be summarized in Table 4.7. Apart from gas, the yields of extracted oil, and liquid (water and chemicals dissolved in water) are reported in Figure 4.17. As can be seen, the gas yield of 69.2 wt% and the 0 wt% of oil yield are acquired from SAPO-34 catalyst without modification. In case of modified SAPO-34 catalysts; that are, germanium oxide, gallium oxide, tin oxide, and antimony oxide, the yield of gaseous product is increased in the order of SA34 (69.2%) < 5SnSA34 (77.3%) < 5GaSA34 (77.5%) < 5SbSA34 (77.8%) < 5GeSA34 (85.8%), which means the acidic oxide species also affect to the gas production.

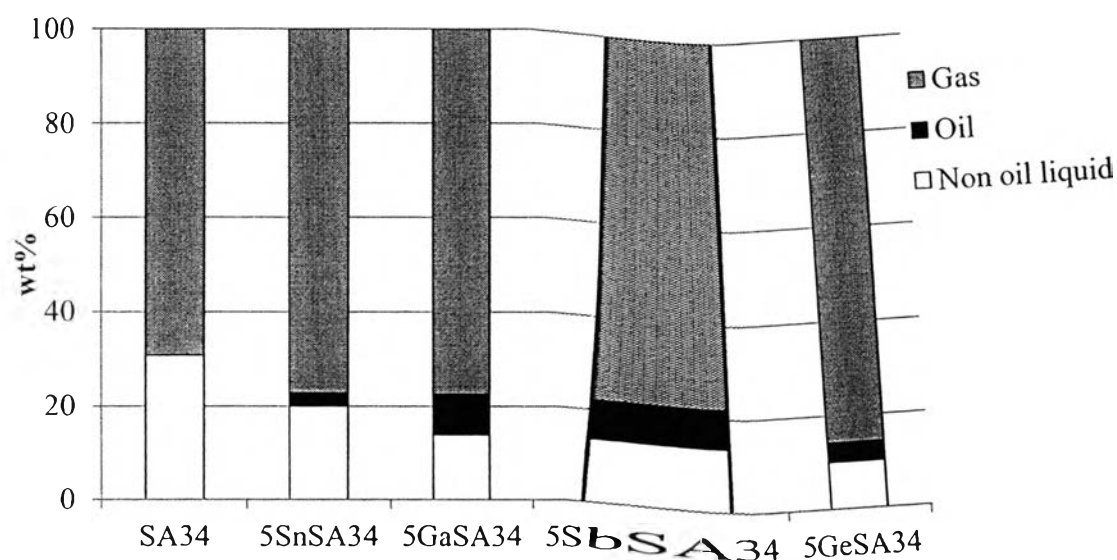


Figure 4.18 Effect of oxide species on product distribution.

The concentrations of ethylene, propylene, and cooking gas (propane and butane) in the gas products from using 5SbSA34, 5GaSA34, 5GeSA34, 5SnSA34, and SA34 catalysts are shown for comparison in Figure 4.19. The results reveal that the formation of ethylene over the doped SAPO-34 catalysts decreases from pure SAPO-34 whereas the formation of propylene is enhanced when all tested oxides were loaded. These results show that the modified SAPO-34 catalysts with moderate acid strength provide a high selectivity for propylene. The carbenium ion mechanism for the

conversion of ethylene into propylene over solid acid catalysts was proposed by Oikawa *et al.* (2006) as shown in Figure 4.20. For this proposed carbenium ion mechanism for the conversion of ethylene into propylene, the fission of a carbon-carbon bond at the β -position of the hexyl carbenium ion (2) and the 4-methyl-2-pentyl carbenium ion (4) is an important reaction in the selective production of propylene. It is expected that both the acid strength of Brønsted acid sites and the pore size of solid acid catalysts govern the formation of propylene in the conversion of ethylene.

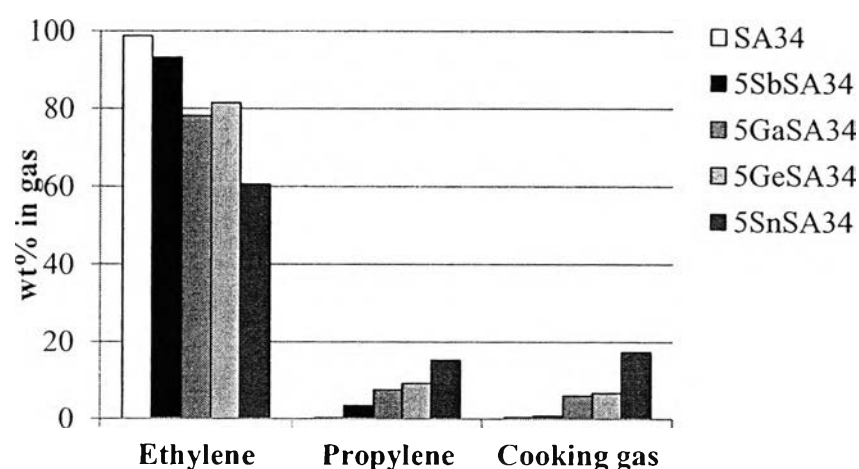


Figure 4.19 Effect of type of oxides on ethylene, propylene, and cooking gas.

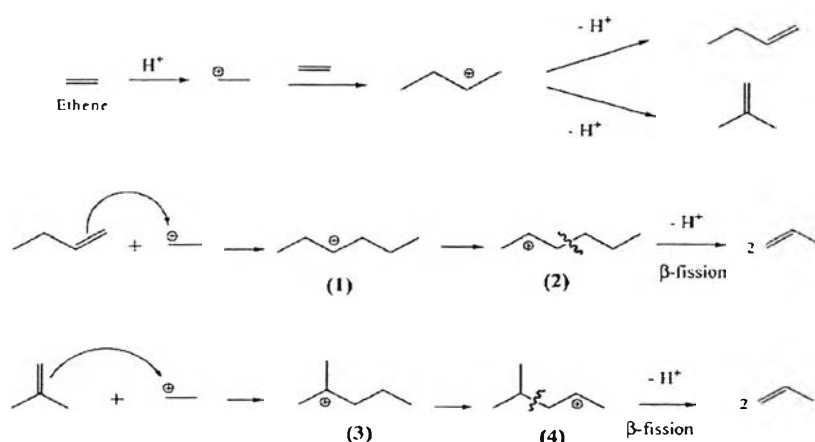


Figure 4.20 Reaction schemes for the conversion of ethylene into propylene over solid acid catalysts (Oikawa *et al.*, 2006).

The formation of propylene increases as follow; SA34 (0.20 wt%) < 5SbSA34 (3.40 wt%) < 5GaSA34 (7.54 wt%) < 5GeSA34 (9.21 wt%) < 5SnSA34 (15.3 wt%). Furthermore, the modification of SAPO-34 catalyst using acidic oxides is found to produce a high composition of cooking gases (propane and butane). The production of cooking gas is improved in the order of SA34 (0.35 wt%) < 5SbSA34 (0.9 wt%) < 5GaSA34 (5.99 wt%) < 5GeSA34 (6.65 wt%) < 5SnSA34 (17.4 wt%). The formation of ethane is enhanced when SnO₂ and GeO₂ were loaded. As can be seen in Figure 4.21, the formation of aromatics comprises the sequential steps of bio-ethanol dehydration to ethylene, oligomerization, cracking and/or cyclization and hydrogen transfer reactions. Thus, the formation of lighter hydrocarbons (C₂–C₄) is considered to occur from an initial dehydration of ethanol, dimerization of ethylene and its cracking. From the result, the SnO₂-doped catalyst produces a high amount of ethylene, propylene, and cooking gas, which means the reaction is controlled at the initial dehydration step to form olefins, but no effective oligomerization and aromatization occurred due to the presence of low acid strength. Moreover, other three catalysts (5GeSA34, 5GaSA34, and 5SbSA34) have higher acid strength than 5SnSA34 catalyst, leading easier generation of carbenium ions, which undergo further reaction according to the carbenium ion mechanism to form a large molecule.

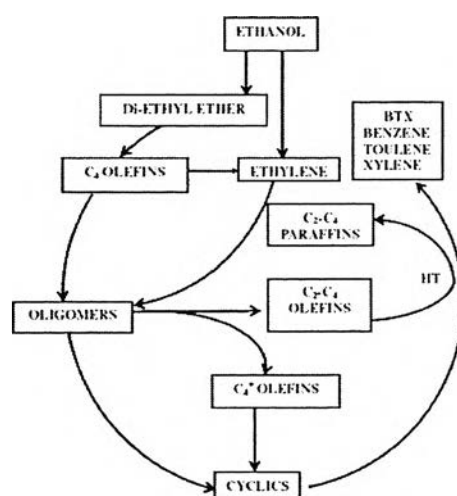


Figure 4.21 Reaction pathways of ethanol to aromatics reaction (Viswanadham *et al.*, 2012).

Moreover, the TBPs of oils obtained from the modified SAPO-34 catalysts was cut into the petroleum fractions, and it is found that the derived oils from all catalysts are mainly distributed in the range of gasoline. However, the doping 5%Ge on SAPO-34 catalyst decreases gasoline, but slightly increases kerosene. For the oil composition, the SnO₂-doped catalyst produces a remarkably high amount of oxygenate compounds. On the other hand, the GeO₂-, Ga₂O₃-, and Sb₂O₃-doped catalysts lead to the increases in the heavy hydrocarbons (C₁₀₊) instead, which is illustrated in Figure 4.22.

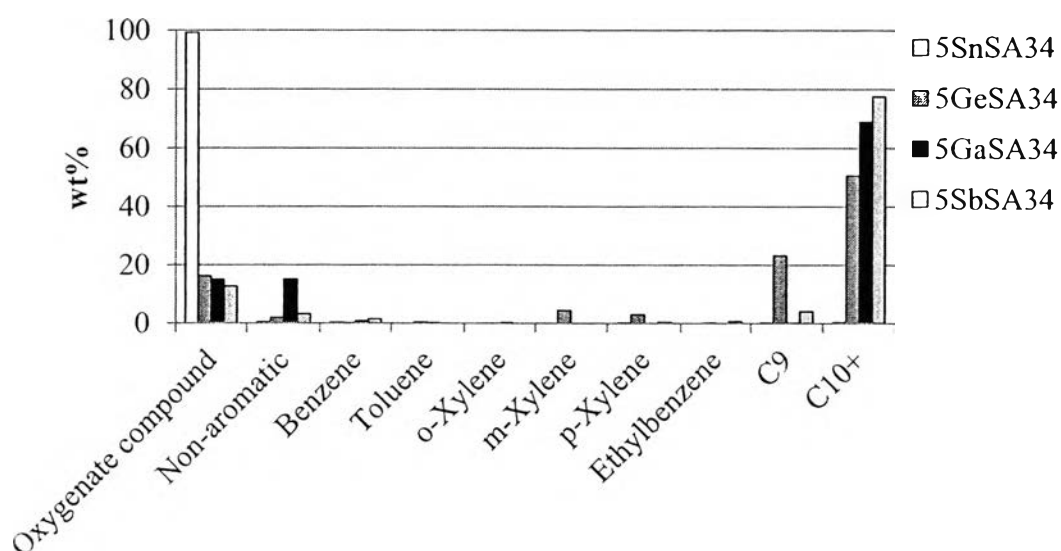


Figure 4.22 Effect of type of oxides on the composition of extracted oils.

Table 4.7 Product distribution over 5GeSA34, 5GaSA34, 5SnSA34, 5SbSA34, and SA34 catalysts

Catalyst	SA34	5GeSA34	5GaSA34	5SnSA34	5SbSA34
Ethanol conversion (%)					
	93.7	96.7	96.9	96.9	97.3
Product distribution (wt%)					
Gas yield	69.2	85.8	77.5	77.3	77.8
Extracted oil yield	0	4.14	8.79	2.74	8.51

Non oil liquid yield	30.7	10.1	13.8	19.9	13.6
Gas composition (wt%)					
Methane	0.04	0.44	0.43	1.52	0.37
Ethylene	98.7	81.5	78.2	60.6	93.2
Ethane	0.45	2.05	1.74	4.51	1.57
Propylene	0.20	9.21	7.54	15.3	3.40
Propane	0.01	6.14	0.12	15.0	0.06
Butylene	0.22	0.13	6.12	0.58	0.48
Butane	0.34	0.51	5.87	2.41	0.84
Oil composition (wt%)					
Oxygenate compound	0	16.2	15.0	99.1	12.6
Non-aromatic	0	1.91	15.1	0.33	3.24
Benzene	0	0.11	0.73	0.18	1.47
Toluene	0	0.33	0.14	0	0
o-Xylene	0	0	0.06	0	0
m-Xylene	0	4.44	0	0	0
p-Xylene	0	3.05	0	0.08	0.37
Ethylbenzene	0	0.15	0	0.00	0.67
C ₉ Aromatic	0	23.2	0.03	0.05	4.12
C ₁₀₊ Aromatic	0	50.6	68.9	0.28	77.5
Petroleum fraction (wt%)					
Gasoline	0	74.0	96.5	95.8	97.1
Kerosene	0	13.7	1.62	0.90	2.87
Gas oil	0	7.78	1.85	1.21	0
LVGO	0	0.81	0	0.31	0
HVGO	0	3.73	0	1.77	0

Gas samples were taken at 240 minutes of time-on-stream

4.2 Effect of HZSM-5 Catalysts Treated with KOH Solutions

In order to investigate the catalytic performance of treated HZSM-5 catalysts with different concentrations of KOH solutions (0.1 M, 0.5 M, and 0.9 M) and untreated HZSM-5 catalyst for the dehydration of bio-ethanol to produce light olefins. Each catalyst testing was carried out at 400 °C under atmospheric pressure. The liquid hourly

space velocity (LHSV) was fixed at 0.5 h^{-1} . Three grams of a catalyst was packed in the isothermal fixed bed reactor, and the reaction time was held for 420 minutes.

The conversions of bio-ethanol obtained from the untreated HZSM-5 and the treated HZSM-5 are in the range of 93-96%. It can be seen that the conversion of KOH-treated HZSM-5 catalysts are slightly higher than that of untreated HZSM-5 catalyst. As can be seen in Table 4.8 and Figure 4.23, the gas yields of all treated HZSM-5 catalysts are extremely less than the untreated HZSM-5 catalyst. The oil yield obtained from the 0.1 M KOH-treated catalyst is slightly higher than that of the untreated HZSM-5 catalyst. However, the liquid yields (aqueous solutions) of treated HZSM-5 catalysts are significantly high.

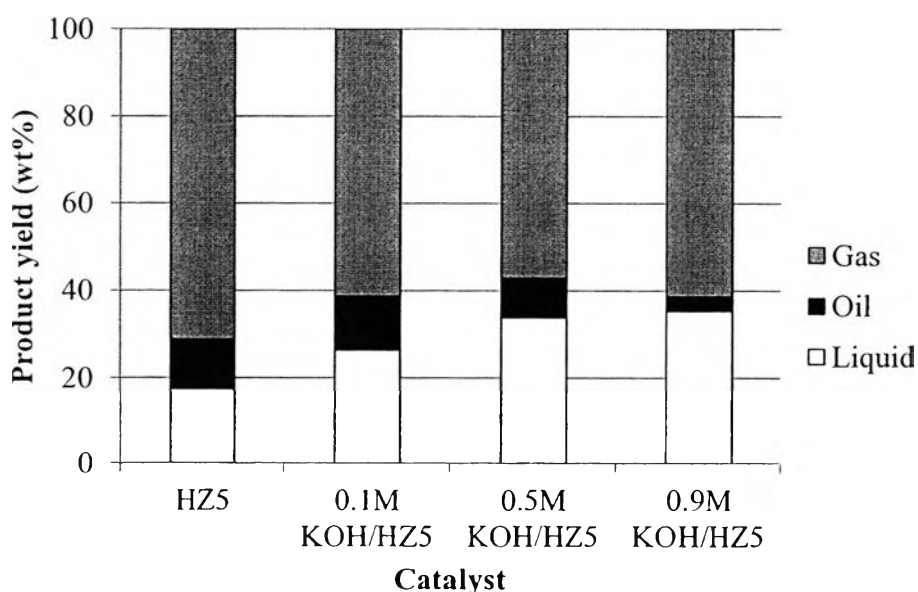


Figure 4.23 Product distribution of treated and untreated HZSM-5 catalyst.

Table 4.8 Product distribution from using KOH treated with HZSM-5 catalysts

Catalyst	HZ5	0.1M KOH/HZ5	0.5M KOH/HZ5	0.9M KOH/HZ5
Ethanol conversion (%)				

	93.9	96.3	96.7	96.9
Product distribution (wt%)				
Gas yield	71.1	61.3	57.0	61.4
Oil yield	11.5	12.3	9.11	3.30
Non oil liquid yield	17.4	26.4	33.8	35.3
Gas composition (wt%)				
Methane	2.68	2.74	3.49	0.50
Ethylene	81.7	73.3	63.1	94.3
Ethane	5.37	15.7	29.0	3.71
Propylene	0.60	3.49	2.18	0.83
Propane	6.00	1.71	0.34	0.15
Butylene	0.16	0.83	0.41	0.19
Butane	3.45	2.18	1.53	0.35
Oil composition (wt%)				
Oxygenate compound	25.3	42.8	45.2	35.9
Non-aromatic	0.25	14.9	33.6	29.7
Benzene	0.92	0.84	1.04	4.14
Toluene	0	3.21	0.71	3.73
o-Xylene	0	0	0	0
m-Xylene	0	9.73	0	4.42
p-Xylene	0.48	4.33	0.78	0
Ethylbenzene	0.05	0.83	0.08	3.42
C ₉ Aromatic	0.06	9.79	0.35	16.4
C ₁₀₊ Aromatic	73.0	13.5	18.1	2.32
Petroleum fraction (wt%)				
Gasoline	88.6	62.9	70.3	92.8
Kerosene	11.2	31.9	17.3	3.25
Gas oil	0.28	3.82	5.35	3.92
LVGO	0.00	0.91	0.88	0
HVGO	0.00	0.52	6.19	0

Data were taken at 240 minutes of time-on-stream

In addition, the gas compositions (ethylene, propylene, ethane, and cooking gas) are somewhat different when the catalyst was treated with KOH with various concentrations. As can be seen in Figure 4.24, at 0.9 M of KOH treatment, the ethylene concentration is very high, whereas the treatments with the other KOH concentrations

give high contents of ethane in the gaseous products. Moreover, the highest concentration of propylene is observed at the treatment with 0.1 M KOH. Furthermore, the untreated HZSM-5 produces more cooking gas than the treated catalysts in general.

The extracted oils obtained from untreated and treated HZSM-5 catalysts were cut into petroleum fractions, according to true boiling point obtained from SIMDIST-GC analysis, as exhibited in Table 4.8. As can be seen in Figure 4.25 shows the petroleum fractions obtained from pure HZSM-5 catalyst and treated HZSM-5 with KOH solution at 0.1, 0.5, and 0.9 M, respectively. The derived oils from all catalyst are mainly distributed in the range of gasoline. In addition, at 0.1 M KOH/HZSM-5 and 0.5 M KOH/HZSM-5 give the higher kerosene than untreated zeolite.

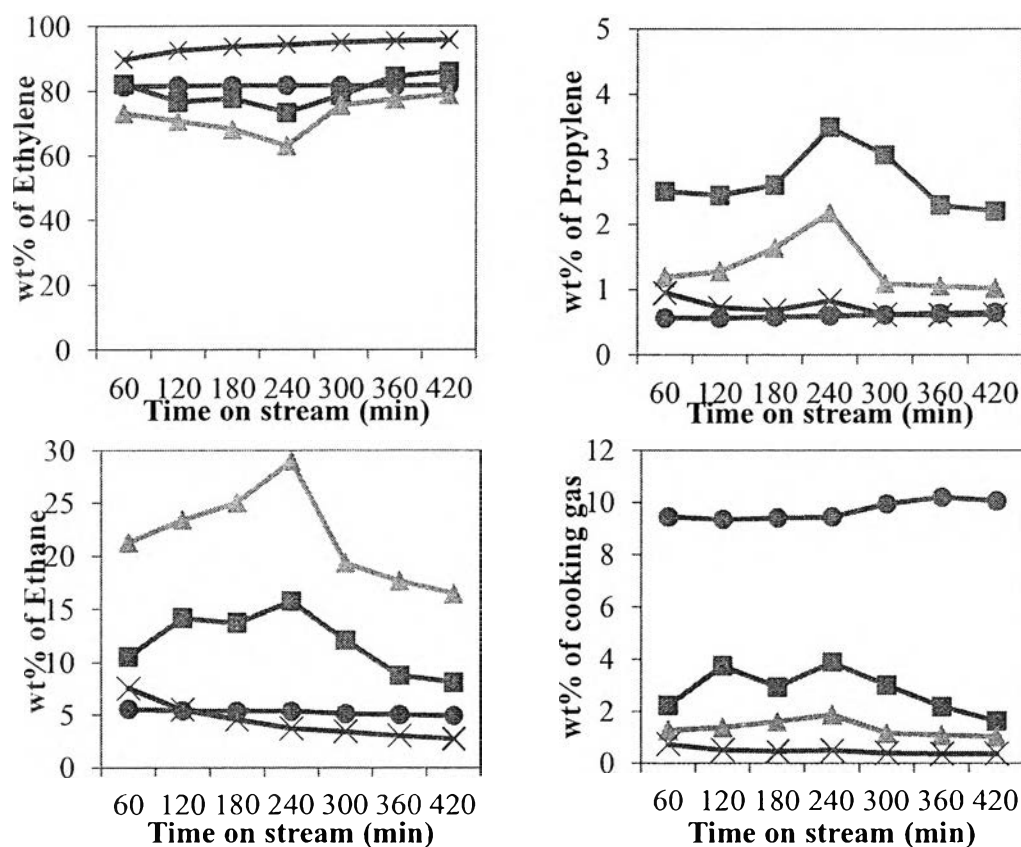


Figure 4.24 Concentrations of ethylene, propylene, ethane, and cooking gas (propane and butane) on the gas products from using 0.1 M (■), 0.5 M (▲), and 0.9 M (×) of KOH treated HZSM-5 catalysts and untreated HZSM-5 catalyst (●).

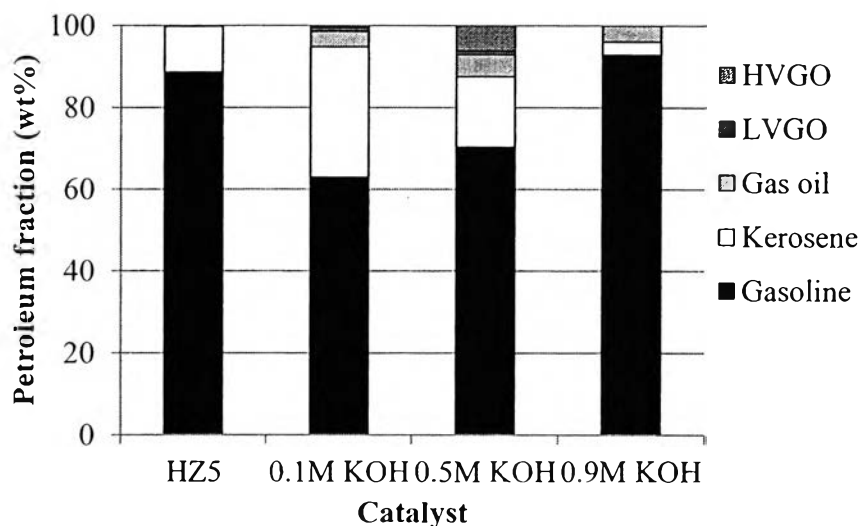


Figure 4.25 Petroleum fraction in oils obtain from treated and untreated HZSM-5 catalysts.

This part discusses the characterization of catalysts by using several techniques to overview the difference on their characteristic and properties. The physical properties of catalysts, including BET surface area, BET pore volume, HK pore volume, and HK mean pore width, and the content of potassium in catalysts determined by XRF analysis are reported in Table 4.9. As observed, the treatment with KOH solutions with different concentrations results in the reduction of BET surface area and HK pore volume. Moreover, the BET pore volume of 0.1 M KOH/HZSM-5 is significantly smaller than that of HZSM-5 catalyst. However, the treatments at higher concentrations slightly increase the BET pore volume of the zeolite. The SEM images of treated HZSM-5 catalysts are shown in Figure 4.26. The treatment at the low KOH concentration of 0.1 M still preserves the cubic structure of HZSM-5. However, the cubic structure partially collapses and breaks down when treated with 0.5 M of KOH solutions (7.56 %wt of K loading). When treated with 0.9 M KOH, the catalyst contains 16.7% K; therefore, the SEM image shows the mixture of potassium oxides and the cubic structure of HZSM-5.

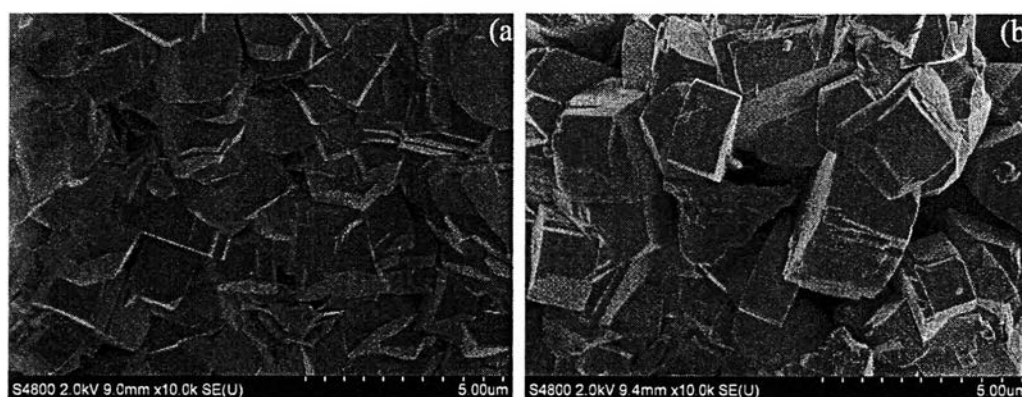
As mentioned above, the aim of ion-exchange with various concentrations of the KOH solutions was to suppress the acidity of HZSM-5 as well as to modulate the

pore size of HZSM-5 catalyst. The highest propylene production was observed at the treatment with 0.1 M KOH solution that resulted in 3.6% K loading on HZSM-5. Moreover, the loading decreased the pore of catalysts from 5.596 Å to 5.435 Å. The exchange of potassium ion in the zeolite pore is believed to adjust the pore size of HZSM-5 and enhance propylene production.

Table 4.9 Physical properties of HZSM-5 based catalysts

Properties	HZ5	0.1M KOH/HZ5	0.5M KOH/HZ5	0.9M KOH/HZ5
%K (wt%)	0.000	3.601	7.561	16.7
BET Surface area (m²/g)	494.8	285.6	137.9	61.85
BET Pore volume (cm³/g)	0.185	0.174	0.190	0.197
HK Pore volume (cm³/g)	0.161	0.144	0.068	0.026
HK Pore diameter (Å)	5.596	5.435	5.401	5.349

The typical SEM images of various concentrations treated HZSM-5 catalysts are also shown in Figure 4.19



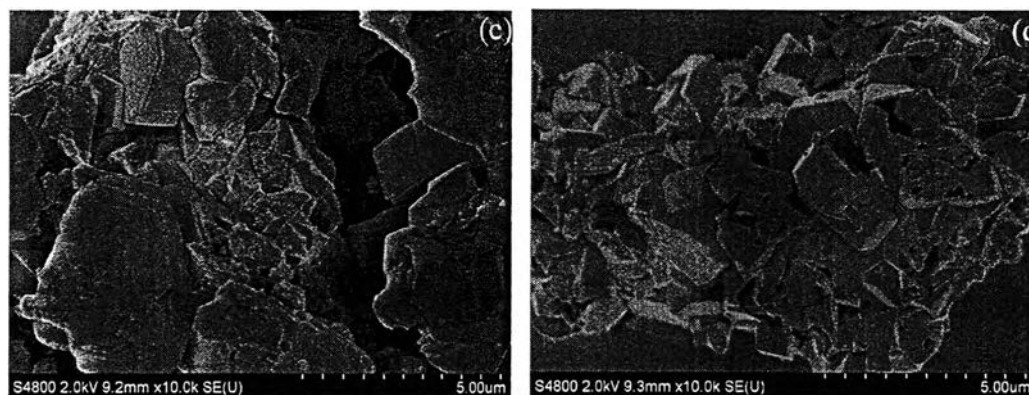


Figure 4.26 SEM images of untreated HZSM-5 (a), and treated HZSM-5 catalysts with 0.1 M (b), 0.5 M (c), and 0.9 M (d) of KOH solutions.

In conclusion, the alkali-treatment of zeolite with various KOH solutions under the same conditions influenced the crystal structure and physical properties of the zeolite. The highest concentrations of ethylene (94.3 wt%) and propylene (3.49 wt%) in the gas products were observed at the treatment with 0.9 M and 0.1 M of KOH solution, respectively. In addition, the derived oils from all catalysts were mainly distributed in the range of gasoline and kerosene.