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Distillate Range of Hydrocarbon Production from Bio-Ethanol Dehydration Using HY, HBeta, and HZSM-5 as Supports of Phosphorus Oxide

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HZSM-5 has the potential in the dehydration of ethanol to gasoline (ETG) because of its acid property and shape selectivity. HZSM-5 had been used as the support of phosphorus oxide for ethanol dehydration, which resulted in the production of oil in the gasoline range. It can be noticed that the moderate pore size of HZSM-5 limits the production of heavier oils in the kerosene and gas oil ranges. Therefore, in this work, the large pore size zeolites, HY, and HBeta, were expected to produce larger hydrocarbon molecules. Then, bio-ethanol dehydration using HY and HBeta doped with phosphorus oxide was investigated, aiming to improve the production of distillate-range products. The reaction was carried out in an isothermal fixed-bed reactor. The temperature was controlled at 500 °C, and the LHSV was fixed at 0.5 h^{-1}. Phosphorus oxide (5 %wt) was loaded to all zeolites using incipient wetness impregnations. The characterization techniques; XRD, XPS, SAA, were used to characterize the catalysts. The products were analyzed by using GC, GC×GC-MS/TOF and SIMDIST GC. As a result, it was shown that HBeta (modified and unmodified) gave the greater selectivity to kerosene and gas oil than HZSM-5 that gave gasoline mostly. On the other hand, HY gave the LVGO, and HVGO than other supports. Moreover, Kerosene and gas oil was improved when introducing phosphorus oxide to zeolite.

1. Introduction

Depleting reserve of petroleum nowadays makes the world face with high price of the conventional fuels; that are, gasoline, kerosene, and gas oil. Bio-fuel, especially ethanol, is one of high potential, renewable petroleum substitutes to solve the problems. Corn crop, sugarcane, and other agriculture wastes and by-products can be utilized to produce bio-ethanol. Purified bio-ethanol is used to blend with gasoline to become in E10, E20, and E85 gasohol, used directly in some types of vehicles.

Moreover, ethanol can be the feedstock of some valuable petrochemical products via the catalytic dehydration process. Several research articles focused on ethylene production (Sheng et al., 2013). They studied the ethanol dehydration to ethylene by using HZSM-5 with steam treatment, and found that the ethylene was produced around 98 % yield at 250-290 °C. Propylene was also produced by using HZSM-5 with various particle sizes (Meng et al., 2012). They found that 24 % of propylene selectivity was obtained from using the 100 nm particle size of HZSM-5 with 10 h time-on-stream. Moreover, the oil product that can be separated to petroleum fractions may also contain highly valuable products. Furthermore, some large pore size zeolites, which are HY and HBeta, were reported to enhance kerosene^{+} products from ethanol transformation (Madeira et al., 2009). They found that C_5-C_{11} was yielded mostly by HZSM-5;

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however, C_{12}^+ was found mostly by using HY and HBeta at the early of the reaction. They also claimed that C_{12}^+ were almost the aromatic compounds.

Aiming to produce distillate range product, Pasomsub (2013) found that kerosene and larger hydrocarbons (kerosene$^+$) were produced by using HZSM-5 (SiO_2/Al_2O_3 = 40), a moderate pore size zeolite, doped with phosphorus oxide at 1 – 4 % loading (elemental basis). The results show that gas oil$^+$ increased with the increasing loading percentage of phosphorus oxide. Thus, in this work, the catalytic dehydration of bio-ethanol using HY and HBeta zeolites doped with phosphorus oxide were investigated on the attempt to increase the kerosene$^+$ products, and the results were also compared with using HZSM-5 as a support in order to investigate the effect of pore size of zeolites. All zeolites used had a very similar value of SiO_2/Al_2O_3 ratio (27–30) in order to avoid the effect of acid properties of zeolites.

2. Methodology

2.1 Catalyst preparation

The catalysts were prepared from a commercial H-Y zeolite (SiO_2/Al_2O_3 = 30, 360HUA grade, Zeolyst company), and NH_4-Beta zeolite (SiO_2/Al_2O_3 = 27, 930NHA grade, Tosoh company) and NH_4-HZSM-5 zeolite (SiO_2/Al_2O_3 = 30, Zeolyst International). The NH_4-Beta and NH_4-HZSM-5 zeolites were initially dried in an oven at 100 °C for 1 h, followed by calcination at 500-600 °C for 3-5 h to obtain the proton form of zeolite catalyst. Diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), was used as the source of P. A solution of this compound was loaded on the supports using the incipient wetness impregnation technique until the final loading amount of 5.0 %wt was achieved. After impregnation, a wet catalyst was dried in an oven at 100 °C for 1 h, followed by calcination at 500 °C for 3 h. Then, the calcined sample was hydraulically pressed to pellets. Subsequently, the pellets were crushed and sieved to 20 – 40 mesh particles before use in the reactor.

2.2 Catalyst characterization

The surface area (BET), pore volume (HK), and pore size (HK) were determined based on N_2 physisorption using the Thermo Finnigan/Sorptomatic 1990. Crystallographic spectra of the zeolites were determined using Rigaku SmartLab® in BB/Dtex mode with CuKα radiation. The machine collected from 5 ° – 90 ° at 10 °/min and the increment of 0.01 °. XPS was used to determine the oxidation states of metal oxides dispersed in zeolites. The scan pass energy was 160 kV for wide scan and 40 kV for narrow scan. The electron source was Al Kα that gave 10 mA of emission and 15 kV of anode HT. The neutralizer was set at 1.8 A of filament current, 2.6 V of charge balance, and 1.3 V of filament bias.

2.3 Bio-ethanol dehydration

The fuel grade bio-ethanol (99.5 % purity) was obtained from Sapthip co., ltd., Thailand. The catalytic dehydration of bio-ethanol was conducted in a U-tube fixed bed reactor (10 mm, inside diameter and 45.8 cm, length) under atmospheric pressure at 500 °C for 8 h. Helium was used as a carrier gas fed at 13.725 ml/min. Bio-ethanol was fed at 2 mL/h. 3 g of catalyst was used in the reaction. The gas product was analyzed by using a GC-TCD (Agilent 6890N) to determine the gas compositions, and a GC-FID (Agilent 6890N) was used to determine the ethanol concentration in gas stream. The liquid product was condensed in the collector immerged in an ice-salt bath, and then the oil phase was extracted from the liquid product using CS_2. The oil was next analyzed by using GC-TOFMS (Rxi-5SilMS, and RXi-17) to determine its composition. Moreover, the true boiling point curve of oil was determined by using SIMDIST GC. The range of boiling points indicates the type of petroleum products; <120 °C for gasoline, 149-232 °C for kerosene, 232-343 °C for gas oil, 343-371 °C for light vacuum gas oil, and >371 °C for high vacuum gas oil (Pasomsup, 2013).

3. Results and discussion

3.1 Catalyst characterization

The BET surface area and pore volume decrease when all zeolites are doped with phosphorus oxides as shown in Table 1. Oxidation state of phosphorus oxides on the modified zeolites is determined by using XPS, and the results are shown in Figure 1 (A). XPS spectra of phosphorus oxide-modified catalysts illustrate the P $2p_{3/2}$ binding energies at 135.8, 134.7, 133.3, and 132.4 eV that can be interpreted to P_4O_{10}, metaphosphate, pyrophosphate, and phosphate, respectively (Moulder, 1992).

The XRD spectra are shown in Figure 1(B). The characteristic peaks of HY are located at 6.34 °, 10.33 °, and 15.9 °, and those of HBeta are located at 7.74 °, 12.24 °, and 22.09 ° whereas those of HZSM-5 (HZ5) are at 7.94 °, 8.89 °, 14.77 °, and 23.96 °. The XRD patterns of pure zeolites and corresponding modified

Table 1: Physical properties of pure zeolites and phosphorus oxide-supported zeolites

Catalyst	Surface area (m^2/g) *	Pore volume (cm^3/g) **	Pore diameter (Å) **
HY	658.7	0.3333	7.975
P/HY	346.7	0.1695	7.835
HBeta	498.1	0.2501	8.154
P/HBeta	347.1	0.1675	7.087
HZ5	359.1	0.1590	8.968
P/HZ5	188.2	0.0915	6.897

*BET surface area, ** HK pore volume and average pore diameter

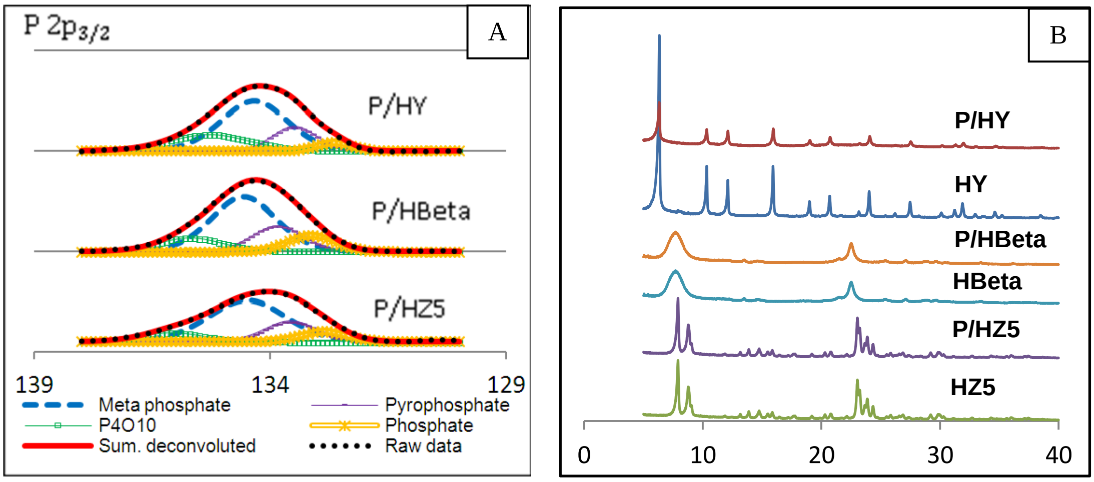

Figure 1: Phosphorus oxide forms on various zeolite supports (A) and Crystallographic spectra of pure- and modified- zeolites (B)

zeolites show the same 2θ of identity peaks. So, the modification of the zeolites did not destroy the structure of the zeolites.

3.2 Effect of zeolite type

The conversion of ethanol is in the range of 96-100 % as shown in Table 2. The oil yield is ranked as follows: HZ5>HY>HBeta. Propane and methane seem to be produced by HZ5 mostly (38.9 % and 17.9 %); but ethylene and ethane are produced by HBeta and HY. The oil of HZ5 contains 93.7 % of gasoline range as shown in Table 3, which is the common of HZ5 that is the moderate pore size zeolite (straight one of 0.53x0.56 nm and sinusoidal one of 0.51x0.55 nm). Kerosene and gas oil can be produced by HBeta that has large pore size (straight channel of 0.76x0.64 nm and intersection opening of 0.56x0.65 nm).

Table 2: Bio-ethanol conversion, product yield, and gas composition using pure zeolites and zeolites with phosphorus oxide promoter

Catalyst	HZ5	P/HZ5	HBeta	P/HBeta	HY	P/HY
% Bio-ethanol conversion	99.5	99.0	96.7	99.1	99.6	99.4
Product yield (wt %)						
Oil	7.05	3.49	1.55	4.40	3.45	3.52
Gas	74.0	70.3	82.4	77.9	83.2	86.5
Water	19.0	26.2	16.0	17.7	13.4	10.0
Gas composition (wt %)						
Methane	17.9	0.00	4.04	1.77	5.57	2.05
Ethylene	14.0	96.9	32.4	44.6	24.5	45.5
Ethane	13.3	0.66	39.8	45.9	41.8	46.3
Propylene	3.53	1.76	10.3	4.09	19.2	3.09
Propane	38.9	0.00	5.47	2.30	2.69	1.07
C4	4.45	0.68	5.77	1.04	2.15	0.97
CO_2	8.02	0.00	2.24	0.33	4.16	1.04

Table 3: Compositions and petroleum fractions in oils using pure zeolites and zeolites with phosphorus oxide promoter

Catalyst	HZ5	P/HZ5	HBeta	P/HBeta	HY	P/HY
Petroleum Fractions in oil (wt %)						
Gasoline	93.7	52.5	68.0	46.3	86.9	87.3
Kerosene	4.47	38.5	17.4	6.03	2.73	2.95
Gas oil	1.87	6.42	10.3	29.9	2.20	1.74
Light Vacuum Gas Oil (LVGO)	0.00	0.89	0.66	6.98	0.51	0.44
Heavy Vacuum Gas Oil (HVGO)	0.00	1.72	3.65	10.8	7.69	7.55
Oil composition (wt %)						
Oxygenated H.C.	0.18	18.6	1.03	3.63	0.71	7.31
Non-aromatics	10.4	5.27	0.00	0.00	3.52	1.87
Benzene	1.28	7.48	30.0	29.3	44.9	45.6
Toluene	3.70	4.98	34.8	27.4	31.3	18.0
o-Xylene	6.52	6.10	9.26	3.80	4.40	3.88
m-Xylene	9.87	2.59	10.7	5.56	5.12	4.02
p-Xylene	4.66	2.55	8.33	4.46	3.85	2.92
Ethylbenzene	1.03	1.29	1.18	1.41	1.27	1.02
C9 Aromatics	26.4	2.23	2.70	4.51	0.88	2.66
C10+ Aromatics	36.0	48.9	1.97	20.0	4.00	12.7
Aromatics in oil (wt %)	89.4	76.1	99.0	96.4	95.8	90.8
Yield of aromatics (wt %)	6.30	2.66	1.53	4.24	3.30	3.20
BTEX/Aromatics	0.30	0.33	0.95	0.75	0.95	0.83
BTEX/Oil	0.27	0.25	0.94	0.72	0.91	0.75
Xylenes/BTEX	0.78	0.45	0.30	0.19	0.15	0.14
p-Xylene/Xylenes	0.22	0.23	0.29	0.32	0.29	0.27

Moreover, HY, which is a large pore size (0.74 nm) zeolite with super cage (1.24 nm), can produce the more HVGO and LVGO than the other zeolites. It can be seen that range of petroleum cuts is increased with the pore size of zeolite. On the other hand, HZ5, which is a moderate pore size zeolite, allows a less amount of large intermediate to pass through the pore. The large active intermediate products are restricted by reactant shape selectivity of HZ5. The oil compositions from ethanol dehydration using all catalysts are shown in Table 3.

Benzene selectivity is increased along with the increasing pore size because the large pore size zeolite has less diffusion constraints that make the molecule of products pass through easily. The pore size of HZ5 is normally proper to p-xylene production (Van Vu et al., 2006), but in this case, HZ5 produced a significant amounts of C9 aromatics and C10+ aromatics together with the low selectivity of p-xylene. On the other hand, HZ5 still produces a considerable ratio of xylenes in BTEX (0.78) as seen in Table 3. Xylenes, C9, and C10$^+$ can be produced by the Diels-Alders reaction and free radicals mechanism (Cole et al., 1984). Moreover, these aromatic compounds can be converted to other forms via dealkylation, transalkylation, and disproportionation (Ali et al., 2013). HBeta zeolite also produces high selectivity to p-xylene with the low amount of C9 and C10+ aromatics. The oil product contains 94 % BTEX in oil and 95 % in total aromatics, which are the highest among the other supports. HBeta seems to be the zeolite that has proper acidity and pore size for BTEX production. HY zeolite can produce benzene and toluene abundantly because of the largest pore size. Moreover, the cage effect of HY also increases the retention time that allows the molecules can be cracked for a longer time.

3.3 Effects of phosphorus oxide promoter

In P/HBeta, the oil yield is increased from 1.55 % to 4.40 % when phosphorus oxide is introduced to HBeta as shown in Table 3. This can be described that phosphorus oxide deposits in the large pore size of HBeta, which is supported by the decrease in pore diameter. So, the modified pore sizes are much proper to produce aromatic products, which resulted in the increasing oil product. However, phosphorus oxide accompanies to strong acid sites, and decreases the overall acid strength of HZ5, causing P/HZ5 to have lower oil yields than pure HZ5. Moreover, the oil product from P/HY slightly increases. The oil yield can be

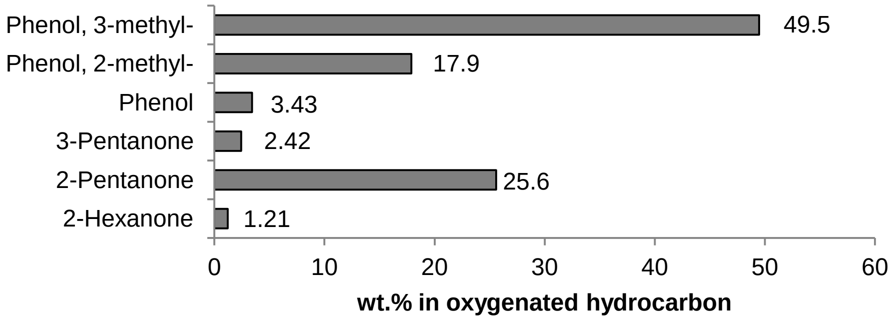

Figure 2: Major oxygenated compounds (wt %) obtained from using P/HZ5.

ranked as follows: P/HBeta>P/HY>P/HZ5. Moreover, C10+ aromatics are increased by using all zeolite supports with phosphorus oxide promoter. This occurs in accordance the increases in kerosene and gas oil. P/HZ5 gives the greatest kerosene content in the oil (38.5 %) with a low oil yield, a low production of BTEX product, and a large percentage of C10+ aromatic products as shown in Table 3. P/HZ5 yields kerosene mainly; on the other hand, P/HBeta yields gas oil the most. This is due to the pore size of modified zeolites that limit the size of product. P/HY shows the same trend as the undoped catalyst, which mainly yields gasoline with the high content of benzene and toluene. It was evident that phosphorus oxide doped on HZ5 can cause the decrease of strong acid site and the increase in weak acid site (Xue et al., 2007). With these reasons, P/HZ5 produces the great amount of ethylene as shown in Table 2, which the weak acid site and oxide participate in ethanol dehydration reaction (Inaba et al., 2006).

Moreover, the oxygenate product is produced dominantly by P/HZ5 (19.4 % in oil). It is composed of ketone, phenol, and cresol. The major oxygenate product is 3-methyl-phenol. It holds 50 % of all oxygenate compounds in oil. The total of all phenol derivatives is 71 %. The ketone product is composed of 2-pentanone, 3-pentanone, and 2-hexanone as shown in Figure 2. In addition, 2-pentanone is the main oxygenate products by using P/HBeta, and P/HY.

4. Conclusions

HBeta gave 27.7 %; but, HZSM-5 gave 6.34 % of distillate-range products (kerosene and gas oil). The production of distillate-range products were found governed by pore size of the zeolite. On the other hand, HY, which was the large pore size zeolite can gave distillate-range products only 4.93 % because their large cages and zig-zag channel structure. Moderate pore size zeolite (HZ5) tends to have the highest activity by giving 7.05 % of oil yield which is largest among other supports. Phosphorus oxide promoter also helped to yield more kerosene and gas oil range with the decrease in gasoline range, related to the increase of C10+ aromatic products. P/HBeta gave 36.9 % of distillate-range products. Moreover, 3.43 % of phenol, 67.4 % of cresol, that are high valuable oxygenate products, were produced by P/HZ5 with SiO_2/Al_2O_3 = 30.

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