

Production of gasoline from bioethanol over solid acid catalysts

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ABSTRACT

Production of bioethanol from biomass resources is getting enhanced for last several years, which leads to many studies for valorization of bioethanol. For example, ethylene, 1-butanol, useful olefins and oxygenates can be produced from bioethanol in catalytic systems. Among them, catalytic conversion of bioethanol to gasoline is presented in this work. In the reaction, strong solid acid catalysts, such as HZSM-5, have been used, however, the strong acidity of HZSM-5 and its intrinsic pore structures cause significant coke formation and dealumination, followed by catalyst deactivation. To overcome the critical problems of HZSM-5, we impregnated transition metals, such as Ni, Cu, and Zn, on HZSM-5. In addition, we synthesized mixed metal oxides exhibiting strong Brønsted acid sites and applied the prepared catalysts into the bioethanol conversion to gasoline.

1. INTRODUCTION

Ethanol is one of the most important chemical obtained from renewable resources via fermentation of lignocellulosic biomass, such as wood and grasses, without competing with food production (Centi 2011). Ethanol has been utilized as a fuel-additive for transport fuels. However, the blending amount of ethanol in transport fuels is limited, and the blending of ethanol can induce the phase separation between ethanol and fuels at cold atmosphere. By the way, there is a way to directly use ethanol as a transport fuel. Ethanol can be transformed to hydrocarbons through catalytic conversion processes (Tret'yakov 2010, Sun 2014). For example, hydrocarbons like gasoline can be selectively produced from the ethanol conversion over zeolites such as HZSM-5 (Maderia 2009, Inaba 2006). However, in spite of the high selectivity of HZSM-5, its high acidity causes coke formation, leading to deactivation of the acid catalyst. Thus, many researchers have vigorously investigated the catalytic conversion of ethanol to hydrocarbons over heterogeneous catalysts, in order to find new catalysts showing better catalytic activity and lower deactivation (Ramasamy 2014, Gayubo 2010).

2. CATALYTIC CONVERSION OF ETHANOL TO HYDROCARBONS

Ethanol was reacted at 350 °C for 4 h over different acid catalysts in a SUS316 batch reactor. As listed in Table 1, the initial atmospheric pressure significantly

increased depending on the kind of catalyst. For instance, the pressure inside the batch reactor reached to 4.3 bar after the reaction finished in the absence of catalyst. This increase of pressure can be explained by generation of hydrogen in the catalyst-free reaction, as displayed in Fig. 1. At 350 °C, ethanol exists in supercritical state and thus dehydration of ethanol occurs vigorously. However, the produced hydrogen seemed to barely participate in the ethanol conversion to hydrocarbons without any catalysts, since a considerable amount of water is produced by dehydration reaction of ethanol for production of ethylene, a precursor of hydrocarbons.

Table 1. Distribution of product phase over different catalysts.

Reaction condition	T=350 °C, t=4 h, EtOH(99.5%)=50 g, Catalyst=1 g, Stirring=200 rpm, Initial gas loading=H ₂ (1 atm)			
Catalyst	Blank	γ -Al ₂ O ₃	HZSM-5	Ni/H-ZSM5
P _{T=350 °C} (bar)	152.9	159.7	225.8	306.9
P _{RT} (bar)	4.3	10.3	19.4	21.0
Liquid product-upper phase (g)	46.0	24.8	11.9	14.4
Liquid product-lower phase (g)			15.9	19.8
Water content-upper phase (wt%)	1.6	18.4	0.1	0.1
Water content-lower phase (wt%)			68.3	62.3

The employment of acid catalysts, such as γ -Al₂O₃, HZSM-5 and Ni/HZSM-5, promoted the conversion of ethanol to hydrocarbons though consuming hydrogen produced from ethanol. As an evidence, the amount of hydrogen decreased about seven times when γ -Al₂O₃ was used as a catalyst. In addition, the production of ethylene and water were significantly accelerated, confirming the hydration reaction of ethanol. In cases of zeolite catalysts, much higher pressure, ethylene yield and water content in products were observed comparing with γ -Al₂O₃, indicates the better catalytic performance of zeolite catalysts than γ -Al₂O₃.

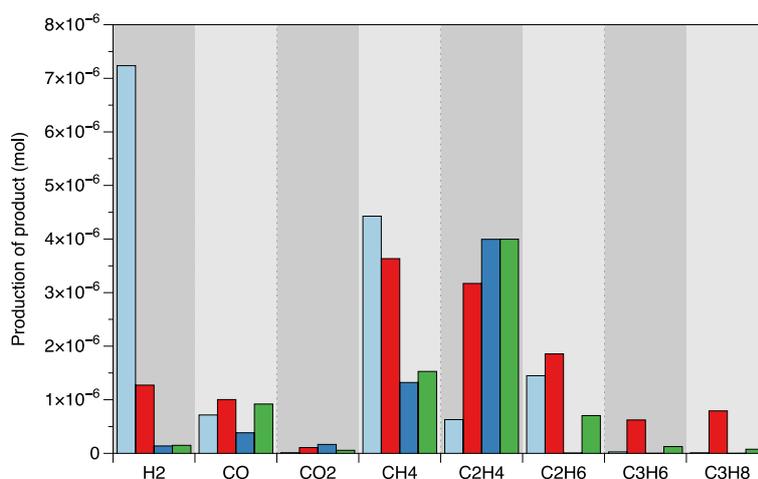


Fig. 1. Gas product distribution over different catalysts.

Ethylene is a major platform chemical for production of hydrocarbons, such as aromatics, olefins and paraffins. The large amount of water produced by dehydration of ethanol to ethylene demonstrates the production of hydrocarbons. As shown in Fig. 2, phase separation between aqueous and oily phases was observed when ethanol was reacted over zeolite catalyst, HZSM-5 and Ni/HZSM-5, at 350 °C. Upper phase was composed of long-chain hydrocarbons with extremely small water content less than 0.1 wt%. On the other hand, lower phase contained large quantity of water over 60 wt%. As a result, the two phases were naturally separated due to difference in density. On the other hand, γ -Al₂O₃ also catalyzed the production of long-chain hydrocarbons during the reaction, however, the quantity was small. In the catalyst-free reaction, there was not hydrocarbons after the reaction.

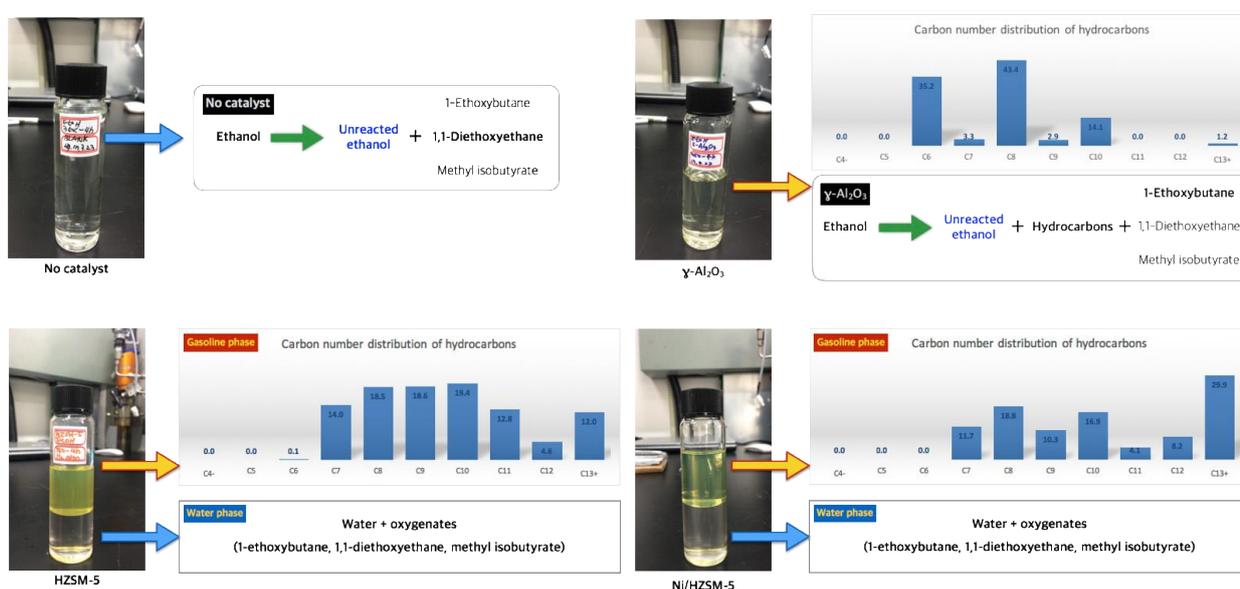


Fig. 2. Carbon number distribution of liquid products.

The fuel properties of liquid products obtained from catalytic ethanol conversion are listed in Table 2. All products have higher HHV comparing with ethanol (29.7 MJ/kg), suggesting that the ethanol conversion over acid catalysts induces the upgrading of fuel properties of ethanol. In particular, zeolite catalysts remarkably improved the upgrading, and the hydrocarbon parts (upper phase) of products exhibited gasoline-like properties.

Table 2. Atomic composition and water content of liquid products.

Catalyst	Water content (wt%)	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Sulfur (wt%)	Oxygen ^a (wt%)	HHV ^b (MJ/kg)
γ -Al ₂ O ₃	1.7	74.3	7.9	0.3	0.0	17.6	33.4
HZSM-5 (upper phase)	< 0.1	84.3	13.9	0.0	0.0	1.8	45.7
Ni/HZSM-5 (upper phase)	< 0.1	83.0	14.2	0.0	0.0	2.8	45.6
Gasoline	< 0.1	85.4	14.1	0.0	0.0	2.1	43.9

a) O is balanced.

b) HHV(KJ/kg) for bio-oil = [(34*C)+(124.3*H)+(6.3*N)+(19.3*S)-(9.8*O)]/100 (DIN 51900)

By the way, the addition of nickel into HZSM-5 influenced the product distribution of hydrocarbon phases in liquid products as shown in Table 3. Ni/HZSM-5 produced long-chain aliphatic hydrocarbons with alkyl groups, whereas pure HZSM-5 promoted the production of aromatic hydrocarbons with alkyl groups. Based on the result, nickel has an important role of controlling the chain structure of hydrocarbons. In a case of γ -Al₂O₃, cyclohexane was dominantly produced after the reaction, although the yield of hydrocarbon products was quite low.

Table 3. Product distribution of liquid products obtained from ethanol conversion over , γ -Al₂O₃, HZSM-5 and Ni/ZSM-5.

γ -Al ₂ O ₃		HZSM-5		Ni/HZSM-5	
Compound name	GC-MS area percentage (%)	Compound name	GC-MS area percentage (%)	Compound name	GC-MS area percentage (%)
Cyclohexene	27.7	Benzene, 1-ethyl-2-methyl-	6.1	Heptane, 3-methyl-	4.4
Heptane, 3-methyl-	8.0	Heptane, 3-methyl-	4.1	Heptane	2.0
Octane	7.1	Benzene, 1,4-diethyl-	3.9	Pentane, 3-ethyl-3-methyl-	1.9
Cyclohexene, 1-ethyl-	5.1	Benzene, 1-ethyl-3-methyl-	3.7	Pentane, 3-ethyl-	1.9
Cyclohexane, ethyl-	2.6	Benzene, 1,2-diethyl-	3.6	Hexane, 2-methyl-	1.8
Decane	2.6	p-Xylene	3.6	Decane	1.8

Cyclohexene, 1-ethyl-	2.1	Ethane, 1,1-diethoxy-	2.5	Heptane, 2-methyl-	1.8
3-Ethyl-3-methylheptane	1.6	Hexane, 2-methyl-	2.3	Hexane, 3-methyl-	1.7
4-Octene, (E)-	1.5	Benzene, methyl-	2.2	Nonane	1.7
Nonane, 3-methyl-	1.4	Hexane, 3-methyl-	2.2	Heptane, 3-ethyl-	1.6
Heptane, 4, 4-dimethyl-	1.4	Benzene, 4-ethyl-1,2-dimethyl-	2.2	2-Hexene, 2-methyl-	1.5
Nonane, 3-methyl-	1.4	Undecane, 2,7-dimethyl-	2.2	Benzene, 1-ethyl-4-methyl-	1.5
2-Octene, (E)-	1.4	Heptane	2.1	Dodecane	1.4
Octane, 4-ethyl-	1.3	Benzene, 1,4-diethyl-2-methyl-	1.9	Decane, 3,8-dimethyl-	1.4
4-Decene	1.2	3-ethyl-(3H)-isobenzofuran-1-one	1.6	Nonane, 3-methyl-	1.4
2-Octene, (E)-	1.1	Decane	1.5	Benzene, 1,4-diethyl-	1.3
2-Hexene, 2-methyl-	0.9	Nonane	1.5	Heptane, 4-methyl-	1.3
Bicyclo(3.2.1)oct-2-ene	0.9	Pentane, 3-ethyl-3-methyl-	1.5	Octane, 4-methyl-	1.3
Nonane	0.9	Benzene, 1-methyl-4-(1-methylpropyl)-	1.5	Dodecane	1.2
4-Tetradecene (E)-	0.9	Benzene, ethyl-	1.4	Tridecane	1.1

3. CONCLUSIONS

Gasoline-like hydrocarbon products were synthesized by catalytic conversion of ethanol over acid catalysts. HZSM-5-based catalysts having higher acidity than $\gamma\text{-Al}_2\text{O}_3$ showed the excellent catalytic activity for the ethanol conversion to hydrocarbons. When nickel was added into HZSM-5, aliphatic hydrocarbon compounds were mainly produced while aromatic hydrocarbon compounds were dominantly produced over HZSM-5. $\gamma\text{-Al}_2\text{O}_3$ catalyst exhibited considerably high selectivity to hydrocarbons, however, the conversion of ethanol was significantly low in comparison with HZSM-5 and Ni/HZSM-5. The hydrocarbon phase produced over HZSM-5-based catalysts had 45 MJ/kg of HHV, comparable with commercial gasoline (43.9 MJ/kg). The catalytic conversion of ethanol to hydrocarbons is a promising process for producing bio-fuels, and the composition of final products can be controlled by catalyst design.

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