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Aromatization of glycerol/alcohol mixtures over zeolite H-ZSM-5

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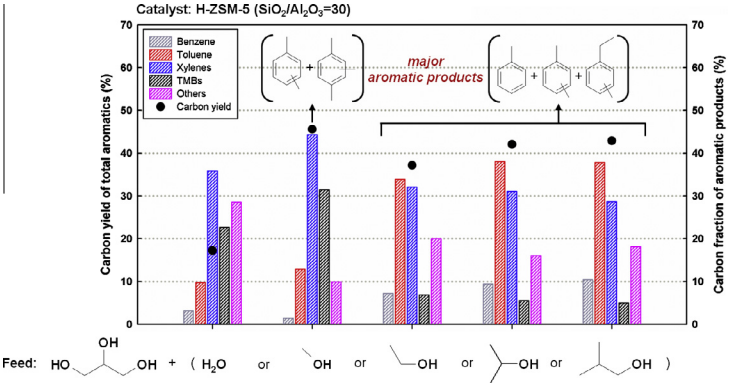
HIGHLIGHTS

- Low yield of total aromatics in the aromatization of glycerol/water mixture.
- Production of aromatics in higher amounts using glycerol/alcohol mixtures as a feed.
- Formation of xylenes and trimethylbenzenes from the glycerol/methanol mixture.
- Initial formation of toluene and xylenes from the glycerol/C_{2-4} alcohol mixtures.
- Promoted toluene alkylation with ethylene formed via dehydration of C_{2-4} alcohols.

GRAPHICAL ABSTRACT



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ABSTRACT

The aromatization of glycerol is conducted over zeolite H-ZSM-5 for glycerol valorization. Due to its high viscosity, glycerol is diluted with water, methanol, ethanol, isopropanol or isobutanol. With the aqueous glycerol feed, the total aromatics yield is low and catalyst deactivation is fast. The mixture of glycerol with each alcohol is thus used as a feed, resulting in higher aromatics yields. Furthermore, the carbon fraction of aromatic products depends upon the alcohol mixed with glycerol. In case of the glycerol/methanol feed, the formation of trimethylbenzenes along with xylenes is pronounced, since both reactant constituents can be transformed into heavy C_9 aromatics and then dealkylated to xylenes (major) and toluene (minor). In contrast, the use of higher alcohols for glycerol dilution leads to the preferential production of ethylbenzene and ethylmethylbenzenes, though xylenes and trimethylbenzenes are produced, due to alkylation of ethylene formed via dehydration (ethanol) or dehydration/cracking (isopropanol and isobutanol).

1. Introduction

Biodiesel is one of the most important biofuels successfully supplied in the transportation sector. In Republic of Korea, the government law currently mandates diesel products sold in the country to contain 2% biodiesel and, if the Renewable Fuel Standard (RFS) program starts up in 2015, the biodiesel blend rate will be gradually increased even if there is a controversy. Therefore, glycerol, which is a byproduct in the biodiesel production process via transesterification (100 kg of glycerol per ton of biodiesel produced), would be abundant in the chemical market. In this regard, glycerol is a potential starting material for further chemical derivatization. A great deal of studies in science and technology has been thus conducted to valorize the surplus of glycerol. Among various glycerol transformations, hydrogenolysis to propanediols

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[1,2], aqueous reforming to synthesis gas [3], dehydration to acrolein [4], and etherification to polyglycerols [5] have been extensively investigated.

However, few works have been reported on the catalytic conversion of glycerol into aromatic compounds. Hoang et al. [6] reported that the pore structure of the zeolite plays a significant role on the final product distribution obtained from glycerol at 400 °C; among a series of zeolites, the high yield of aromatics was obtained over three-dimensional medium-pore H-ZSM-5. Also, the aromatics yield could be enhanced using a two-bed configuration with Pd/ZnO as the first bed (partial deoxygenation and hydrogenation) and H-ZSM-5 as the second bed (aromatization). Unfortunately, such a high yield could not be maintained after the time-on-stream of 2–3 h.

When compounds with an effective H/C ratio below 2 (e.g., 0.67 in glycerol) are used as a feed, this deactivation behavior is generally observed due to coking of the catalyst [7]. The ratio is defined as $(H - 2O)/C$, where H, C, and O are the number of hydrogen, carbon, and oxygen atoms in the specific compound. Therefore, the dilution of glycerol with the solvent having an effective H/C ratio of 2 will lead to the increase in the combined H/C ratio of the feed and, consequently, improve catalyst stability. For conversion of biomass-derived compounds, a typical dilution medium is methanol with the effective H/C ratio of 2 [8–10]. Very recently, the conversion of methanol and glycerol to gasoline (MGTG) over H-ZSM-5 has been reported [11]. When compared to the methanol-to-gasoline (MTG) process, the MGTG process showed a similar gasoline composition at 500 °C, and increasing the content of glycerol in methanol from 10% to 40% did not favor the formation of aromatics but improved the yield of oxygenate compounds. However, more detailed explanation was not made on the effect of glycerol addition on distributions of aromatic compounds.

In the present work, the glycerol-to-aromatics (GTA) conversion over H-ZSM-5 is carried out using the mixture of glycerol with different dilution media, due to its high viscosity. As a preliminary test, the glycerol/water mixture is fed for aromatics production. In order to prevent several drawbacks noticed in the GTA process using an aqueous glycerol solution, four alcohol solvents such as methanol, ethanol, isopropanol, and isobutanol are chosen for glycerol dilution, where their effective H/C ratio is all 2. Since higher alcohols are able to be converted into gasoline-range molecules like the MTG process [12–15], our attention has been paid to examining the difference in product distributions of aromatics obtained with each glycerol/alcohol mixture as feedstock. Particularly, changes in the fractions of aromatic compounds as a function of time-on-stream are investigated in catalytic runs with each feed.

2. Experimental

The zeolite catalyst used in this work was a commercially available zeolite ZSM-5 with a SiO_2/Al_2O_3 ratio of 30 (CBV3024E), purchased from Zeolyst International. The ammonium form of ZSM-5 was transformed into proton form (H-ZSM-5) by calcination at 600 °C for 3 h with a heating ramp of 5 °C/min. Characterization by XRD, N_2 physisorption, ammonia temperature-programmed desorption, and pyridine-adsorbed infrared spectroscopy is conducted and presented in Fig. S1.

Catalytic experiments were performed in a gas phase, fixed-bed reactor system (stainless steel, 10 mm i.d., and 370 mm in length) at atmospheric pressure, where the catalyst (2.5 g) was mixed with silica bead (6.4 mL) and packed in the middle between two beds of silica beads. The reaction temperature was controlled with the thermocouple located in the external wall of the reactor, in which the bed temperature was monitored. The overall reaction system includes a feed pump (Younglin Instrument, SP930D), a mass flow controller (Bronkhorst EL-Flow), a preheating section before reactor entrance (usually 310–320 °C inside), a cooling zone maintained at 0 °C, and a gas–liquid separator (0 °C) to collect liquid products (Fig. S2). Once the catalyst bed was heated from room temperature to 400 °C in N_2 flow and stabilized, a liquid-phase reactant (ca. 0.04 cc/min) was fed to acquire the weight-hourly space velocity (WHSV) of 0.8 h^{-1} and the reactant partial pressure of 45 kPa. Since the effluent taken at a certain time consists of two phases (organic at top and aqueous at bottom), *n*-heptane was added for complete phase separation. Then, the extracted organic phase was mixed with cyclohexane as a GC standard and analyzed on a Younglin YL6100 GC equipped with an FID detector and an HP-Innowax (50 m × 0.2 mm × 0.40 μm). Assignment of GC peaks is conducted with individual authentic aromatic samples. In the aromatization of glycerol-containing mixture, liquid-phase products obtained through the gas–liquid separator typically consist of benzene, toluene, ethylbenzene, xylenes, ethylmethylbenzene, trimethylbenzenes, 1,3-propanediol, indene, naphthalene, and methylnaphthalenes, while alkane (methane, ethane and propane), alkene (ethylene, propylene, and trans-2-butene), and oxygenated compounds with low boiling point (dimethyl ether, diethyl ether, and crotonaldehyde) are detected, which is presented in Fig. S3. Since the focus in the present work is on the variation of liquid-phase aromatic products distribution obtained from different glycerol/alcohol mixtures, the detailed discussion on the formation of the other products is not made.

Through quantitative measurement of aromatic compounds, the carbon yield (Y_i) and carbon fraction (F_i) of species *i* are calculated as follows:

$$\text{Carbon yield of species } i\ (Y_i) = \frac{(\text{mole of species } i) \times (\text{number of carbon atom in species } i)}{(\text{mole} \times \text{number of carbon atom}) \text{ of feed}} \times 100\%$$

$$\text{Carbon fraction of species } i\ (F_i) = \frac{(\text{carbon yield of species } i)}{(\text{carbon yield of total aromatics})} \times 100\%$$

Since the GC peak corresponding to glycerol was hardly detected in the experiments, the conversion of glycerol is always close to 100% (>99.99%). Therefore, the carbon yield is approximately equivalent to the carbon selectivity of species *i*.

3. Results and discussion

3.1. Aromatization of glycerol/water mixture

As a glycerol dilution medium, H_2O is first selected. Thus, the glycerol/water mixtures with different glycerol concentrations of 25, 30, 36, 46, and 70 wt.% are tested at 440 °C and atmospheric pressure. Fig. 1a shows that higher glycerol concentrations lead to fast catalyst deactivation. With the aqueous glycerol solutions of 30–70 wt.%, the carbon yield of total aromatics reaches maximum around 25% at time-on-stream of ca. 5 h and then decreases as the reaction proceeds, where the rate of activity decay depends upon the glycerol concentration. Such an activity trend is in good agreement with the results reported in Hoang et al. [6,16]. Though the experiment with 25 wt.% glycerol/water mixture also follows the similar time-dependent behavior, the catalyst shows the carbon yield of total aromatics higher than 30% and then deactivates to a lesser extent than with other glycerol concentrations. This originates from feeding the lower amounts of glycerol for the conversion. On the other hand, the experiments conducted at 400–500 °C with 30 wt.% glycerol/water mixture indicate the decrease in the carbon yield of total aromatics after about 10 h