Formation of hydrocarbon with C-C double bond from glycerol over iron-oxide based catalyst

Teruoki Tago*, Hirofumi Shitara, Kazuhiro Terai, Yuta Nakasaka, Takao Masuda
Hokkaido University, Sapporo, Hokkaido 060-8628 Japan
**corresponding author:tago@eng.hokudai.ac.jp*

Introduction

Glycerolis regarded as a major platform chemical in a biorefinery, and there are a large number of research works on catalytic conversion of glycerol into useful chemicals such as acrolein and propane-diol. We have succeeded in producing useful chemicals, including propylene, allyl alcohol, carboxylic acids, and ketones, from glycerol using ZrO_2-FeOx catalyst. These chemicals are expected to be produced from glycerol through two main pathways: one pathway involves the production of allyl alcohol and propylene (Pathway I), and another involves the dehydration of glycerol to produce hydroxyacetone and acrolein (Pathway II), as shown in **Figure 1** [1]. The production of hydrocarbons with C-C double bond such as allyl-alcohol and propylene (Pathway I) is characteristic in glycerol conversion using FeOx based catalyst. Dehydration of glycerol successfully progresses using hydrogen atoms, which are generated by decomposition of formic-acid produced as by-product in glycerol conversion using ZrO_2-FeOx catalyst. Moreover, we found that the potassium-supported ZrO_2-FeOx (K/ZrO_2-FeOx) was an effective catalyst to improve the allyl-alcohol yield with suppressing the production of other chemicals [2].

Main objective of this study is selective production of hydrocarbons with C-C double bond (allyl-alcohol and propylene) using FeOx-based catalyst. To increase the hydrogen concentration on the catalyst surface, the effect of formic-acid addition into reaction system on yields of allyl-alcohol and propylene was investigated. Finally, this reaction system was applied to produce 1,3-butadiene from erythritol (C4 polyol).

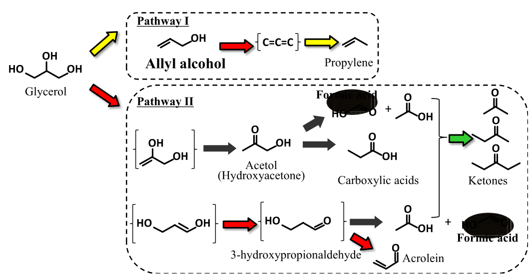

Figure 1. Expected reaction pathways for glycerol conversion over FeOx-based catalyst.

Materials and Methods

ZrO_2-FeOx and Al_2O_3-FeOx catalysts were prepared by a co-precipitation method. The catalytic reaction was carried out in a fixed-bed down flow reactor at a reaction temperature of 623 K in an atmospheric pressure. Feedstock (30 wt% glycerol-water or 30wt% erythritol-water solution) and formic acid solution were fed into the reactor and nitrogen was used as a carrier gas. The gaseous and liquid products were analyzed by GC and GC-MS. The product yield was calculated based on the amount of glycerol fed to the reactor.

Results and Discussion

In glycerol conversion to allyl-alcohol (Pathway I), hydrogen is necessary for dehydration. In contrast, there was no H_2 feed in the reaction system. Therefore, it was considered that the allyl-alcohol was produced by dehydration of glycerol using hydrogen atoms generated by decomposition of formic-acid produced as by-product. In order to increase the hydrogen concentration on the catalyst surface, formic acid addition into reaction system was examined. **Figure 2** shows the effect of formic acid addition on the allyl-alcohol yield. As the formic acid concentration increased, the allyl-alcohol yield was increased from 26 to 36 C-mol%. Because the formic acid was an intermediate in water gas shift reaction, the formic acid would convert into H_2 and CO_2. Accordingly, the concentration of hydrogen atoms on the catalyst surface was increased with the formic acid addition, which enhanced the allyl-alcohol production. In addition, the product yield related to Pathway I (allyl-alcohol and propylene) increased up to 43 mol%-C in K/Al_2O_3-FeOx catalyst. Hydrogen atoms produced by decomposition of formic-acid would be effectively appropriated for dehydration of glycerol. Finally, the K/Al_2O_3-FeOx catalyst was applied to produce butadiene from erythritol (C4 polyol). The product yield was listed in **Table 1**. Self-cyclization reaction occurred without catalyst condition and useful chemicals could not be produced. While the self-cyclization occurred, 1,3-butadiene (yield of approximately 16 mol%-C) could be obtained using K/Al_2O_3-FeOx catalyst.

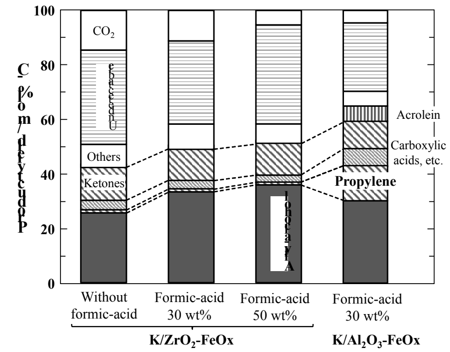

Figure 2. Effect of formic acid addition on glycerol conversion over FeOx-based catalyst.

Table 1. Product yield for erythritol conversion.

	1,3-Butadiene	Ketones	Others	Cyclic compounds
Without cat.	**0.0**	0.0	0.0	81.0
K/Al_2O_3-FeOx	**15.7**	13.6	25.1	42.0

Concentration of erythritol: 30 wt%
Concentration of formic-acid: 30 wt%

Significance

Hydrocarbons with C-C double bond such as allyl-alcohol and propylene are sucssesfully produced from glycerol using FeOx-based catalyst. While self-cyclization occurs, butadiene can be obtained from erythritol.

References

1. Konaka, A.; Tago, T.; Yoshikawa, T.; Shitara, H.; Nakasaka Y.; Masuda, T. *Ind. Eng. Chem. Res.* **2013**, *52*, 15509.
2. Konaka, A.; Tago, T.; Yoshikawa, T.; Shitara, H.; Nakasaka Y.; Masuda,T. *Appl. Catal. B, environ.* **2014**, *146*, 267.