

# PRODUCTION OF VALUABLE CHEMICALS FROM GLYCEROL OVER ZIRCONIA-IRON OXIDE COMPOSITE CATALYST

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## Summary

Conversion reaction of low-grade glycerol to useful chemicals was examined using  $\text{ZrO}_2\text{-FeO}_x$  catalyst. Glycerol water solution was used as the feedstock, and the catalytic reaction was carried out in a fixed-bed reactor at 623 K in an atmospheric pressure. Useful chemicals such as allyl alcohol, propylene, and ketones were obtained from the glycerol water solution. It was found that the reaction was consecutive reactions where allyl alcohol and acetic acids were the intermediates, and the product yields can be easily controlled by the W/F values.

## Keywords

Biomass processing technologies, Reaction Path Analysis, Environmental Reaction Engineering

## Introduction

From the viewpoint of depletion of fossil fuel and global warming, renewable and alternative fuels such as biodiesel are attracting much attention worldwide. Biodiesel is generally synthesized by trans-esterification of vegetable oils with methanol, and glycerol is generated as a main by-product. Accordingly, the market for low-grade glycerol derived from vegetable oils as well as petrochemical has saturated because of the increase in global production of biodiesel, leading to decline in the commercial price of low-grade glycerol. Therefore, the effective utilization method of glycerol is required.

For the catalytic conversion of biomass resources, we have developed iron oxide composite catalysts (abbreviated as  $\text{ZrO}_2\text{-FeO}_x$ ), and succeeded in selective production of phenol and ketones from oil palm waste and sewage sludge<sup>1-3</sup>). Because this catalyst has an effective activity on alcoholic hydroxyl groups in organic compounds, it is considered that the catalyst can be adapted to produce useful chemicals from glycerol. In this study, catalytic conversion of glycerol into valuable chemicals over  $\text{ZrO}_2\text{-FeO}_x$  was investigated. Moreover, catalytic reactions using model compounds were also examined in order to clarify the reaction path.

## Experimental

$\text{ZrO}_2\text{-FeO}_x$  was prepared by a co-precipitation method. The structure of the catalyst was analyzed with an X-ray diffractometer. The catalytic reaction was carried out in a fixed-bed down flow reactor at a reaction temperature of 623 K in an atmospheric pressure. A schematic of the

reactor is shown in Fig. 1. The aqueous solution of glycerol or model compounds was fed into the reactor as a reactant. W/F (W: catalyst amount /g, F: feed rate /g h<sup>-1</sup>) varied in the range of 0-11 h. The gas and liquid products were analyzed by gas chromatography and gas chromatograph mass spectrometry.

## Results and Discussion

Fig. 2 shows the effect of W/F on the product yields after the reaction of glycerol solution over  $\text{ZrO}_2\text{-FeO}_x$ . In these reactions, allyl alcohol, ketones and carboxylic acids were produced as liquid products, and propylene and CO<sub>2</sub> were produced as gaseous products. Main components of carboxylic acids and ketones were acetic acid and propionic acid, and acetone and 2-butanone, respectively. The yield of other components was very low. The yield of

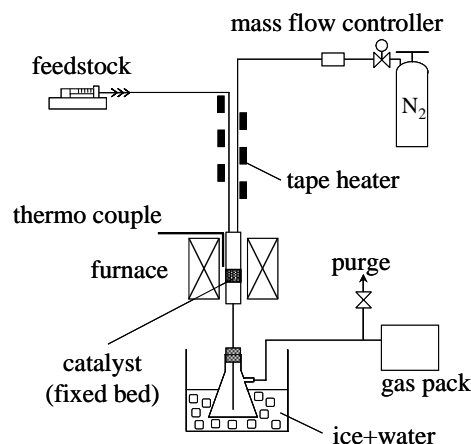


Fig.1 Schematic of experimental apparatus of the fixed bed flow reactor.

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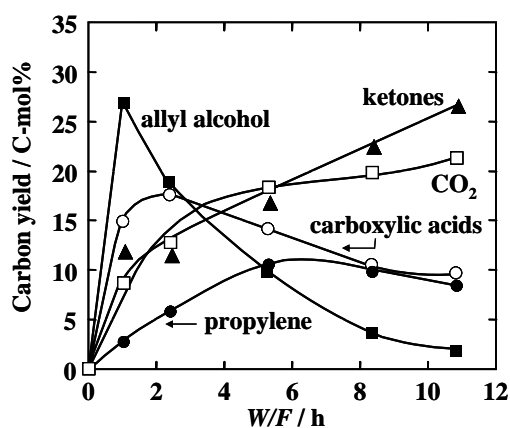


Fig. 2 The effect of W/F on the product yields after the reaction of glycerol over  $\text{ZrO}_2\text{-FeO}_x$  catalyst. Reaction condition:  $T=623\text{ K}$ ,  $P=0.1\text{ MPa}$ ,  $F=10\text{ wt\%}$  of glycerol aqueous solution,  $0.2\text{ g-glycerol h}^{-1}$ .

Table. 1 Main product yields from reaction using model compounds.

Reactant	Main product	Yield/C-mol%
<b>(a) Products at lower W/F<sup>a</sup></b>		
acetic acid	acetone	61.1
allyl alcohol	propylene	62.0
<b>(b) Glycerol-like compounds<sup>b</sup></b>		
ethylene glycol	ethylene	46.2
1,2-propanediol	propylene	22.3
1,3-propanediol	1-propanol	19.3
<b>(c) Dehydration compounds<sup>c</sup></b>		
hydroxyacetone <sup>c1</sup>	carboxylic acids	22.3
	ketones	14.5
acrolein <sup>c2</sup>	—	—

Reaction conditions:  $T=623\text{ K}$ ,  $P=0.1\text{ MPa}$ ,  
 $F = ^{a,b} 5$ ,  $^{c} 10\text{ wt\%}$  aqueous solution of reactant,  
 $W/F = ^{a,b} 10$ ,  $^{c1} 1.0$ ,  $^{c2} 1.7\text{ h}$

allyl alcohol and carboxylic acids were the highest at low value of the W/F ( $W/F=1\text{-}2\text{ h}$ ). On the other hand, their yield decreased and the yield of propylene and ketones increased as the W/F increased. Accordingly, it is suggested that propylene and ketones were produced via consecutive reactions, and W/F can control the product composition.

In order to clarify the reaction path, the catalytic reactions using model compounds were carried out. Table 1 shows the model compounds and yields of main products after each reaction. Acetic acid and allyl alcohol were selectively converted into acetone and propylene, respectively (Table 1(a)), which is in good agreement with the result shown in Fig. 2. Moreover, Table 1(b) shows that carbon-carbon double bond was only formed by the reaction of model compounds with neighboring hydroxyl groups. In addition, Table 1(c) shows that hydroxyacetone

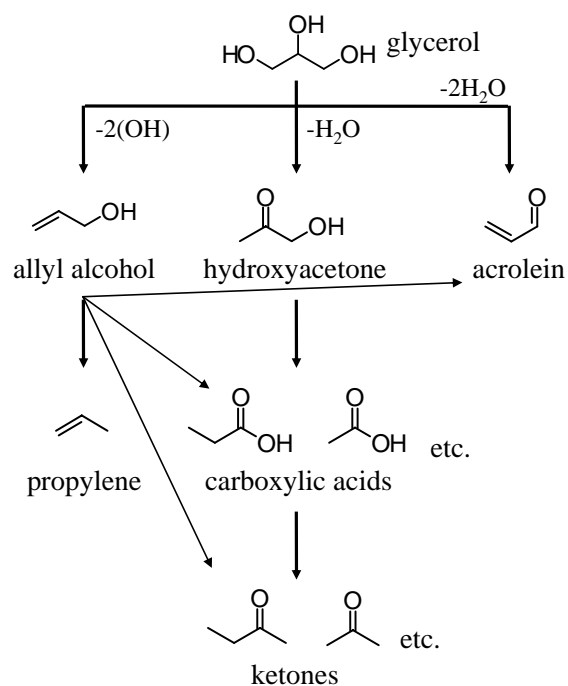


Fig. 3 Scheme of glycerol reaction over  $\text{ZrO}_2\text{-FeO}_x$ .

was easily converted into carboxylic acids and ketones, and acrolein hardly reacted. From the results shown in Fig. 2 and Table 1, the anticipated reaction scheme of glycerol over  $\text{ZrO}_2\text{-FeO}_x$  was shown in Fig. 3. It is considered that two main reaction paths exist, one is the production of carboxylic acid, followed by their ketonization, and the other is dehydration and/or dehydrogenation to produce allyl alcohol and propylene.

As a result, useful chemicals could be obtained from low-grade glycerol over  $\text{ZrO}_2\text{-FeO}_x$  catalyst, where the consecutive reaction proceeded to produce propylene and ketones from glycerol.

## Acknowledgments

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