

SELECTIVE PRODUCTION OF ALLYL-ALCOHOL FROM GLYCEROL OVER IRON OXIDE CATALYST

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Abstract

The catalytic conversion of glycerol was examined using iron oxide-based catalysts for the production of allyl alcohol in a fixed-bed flow reactor at 623 K under atmospheric pressure. Useful chemicals such as allyl-alcohol, propylene and ketones were obtained. It was found that the Brønsted acid site on magnetite (Fe_3O_4) structure was effective to produce allyl alcohol from glycerol over FeOx-based catalyst. Moreover, the catalyst was applied to produce butadiene from erythritol (C4 polyol). While the self-cyclization occurred, 1,3-butadiene (yield of approximately 16 mol%-C) could be obtained.

Keywords

Glycerol, Allyl alcohol, Iron oxide catalyst

Introduction

Glycerol 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, acetol, acrolein and ketones from glycerol using FeOx-based catalyst (Yoshikawa, 2111). 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 (Konaka, 2013), 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.

The oxidation number of Fe ion in as-prepared catalyst is (III) with hematite structure ($\alpha\text{-Fe}_2\text{O}_3$). When glycerol

conversion progressed over $\alpha\text{-Fe}_2\text{O}_3$ catalyst, the reduction of Fe ions occurred to form magnetite structure (Fe_3O_4) due to hydrogen atoms which are generated by decomposition of formic-acid produced as by-product in glycerol conversion. Moreover, we found that addition of formic acid into the reaction system enhanced the allyl alcohol yields (Konaka 2014).

Because the dehydration of glycerol proceeds over the acid sites on the FeOx surface, the change in crystal structure from hematite to magnetite would induce the changes in acidic properties, which affects the product

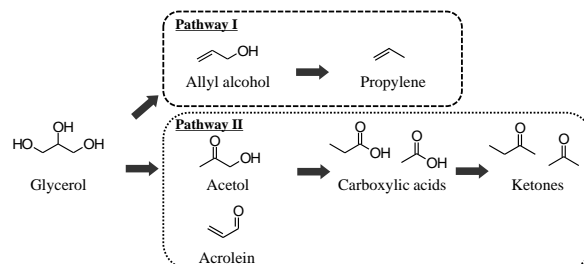


Fig. 1 Expected reaction pathways for glycerol over FeOx.

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yield during the glycerol conversion over the FeOx-based catalyst. Moreover, the addition of formic acid into the reaction system could accelerate the change in crystal structure and contribute to the stability of magnetite structure during the glycerol conversion. Main objective of this study is selective production of allyl alcohol using FeOx-based catalyst. In order to clarify an appropriate oxidation state of FeOx-based catalyst, several types of iron oxide such as FeO (II), Fe₃O₄ (II & III) and Fe₂O₃ (III) were employed as catalysts, and the effects of oxidation states on the acidic properties and the allyl alcohol yield were examined. Next, to increase the hydrogen concentration on the catalyst surface, the effect of formic-acid addition into reaction system on yields of allyl-alcohol was investigated.

Experimental

FeOx-based catalyst was 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 by syringe pump 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

Effect of oxidation state and crystal structure of FeOx on the product yields were examined. Although the glycerol conversion was less than 10 C-mol% in FeO catalyst, the conversions in Fe₃O₄ and α -Fe₂O₃ catalysts reached to approximately 100 C-mol%. Moreover, while α -Fe₂O₃ catalyst showed the comparable product yields corresponding to the reaction pathways I and II, Fe₃O₄ exhibited the high yield of allyl alcohol of approximately 25 C-mol% (pathway I in Fig. 1).

In order to elucidate the reason for the difference in the product yields between α -Fe₂O₃ and Fe₃O₄, the acidic properties of these catalysts were investigated using pyridine-IR method (Fig. 2). As shown in the figure, Lewis acid sites existed on α -Fe₂O₃ catalyst, on which the dehydration of glycerol to produce acetol, ketones and acrolein (Pathway II) proceeded (Garbey, 2011).

In order to inhibit the reaction pathway II, potassium (K) ion was loaded on the catalyst to remove the Lewis acid sites. As shown in the figure, the peaks corresponding to Lewis acid sites were completely disappeared (Fig.2). Next, K-loading FeOx catalyst was used as catalyst and effect of formic acid addition on the allyl-alcohol yield was investigated (Fig. 3). As the formic acid concentration increased, the allyl-alcohol yield was increased from 25 to 40 C-mol%. Moreover, as shown in Fig. 2, it was found that the Brønsted acid site newly formed after the glycerol conversion using K/FeOx catalyst. From the X-ray diffraction analysis, the crystallinity of FeOx changed from hematite to magnetite after the glycerol conversion. Since the magnetite is

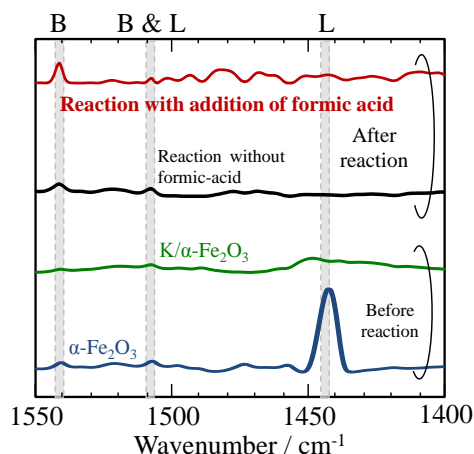


Fig. 2 IR spectra of adsorbed pyridine over FeOx-based catalyst.

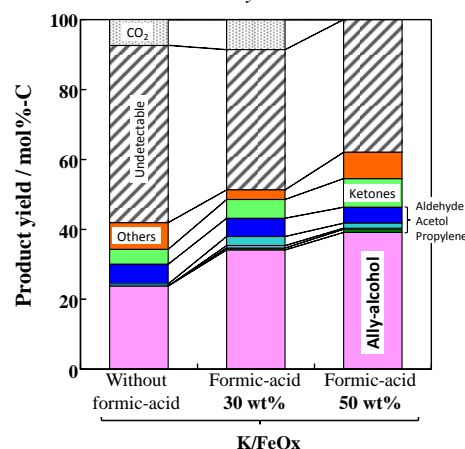


Fig. 3 Effect of formic acid addition on product yields in glycerol conversion over K/FeOx catalyst.

composed of mixed iron oxides of Fe(II) and Fe(III) ions, Fe-OH exhibiting the Brønsted acidity would be formed at the Fe₃O₄ surface. Accordingly, it was concluded that the Brønsted acid sites which were newly formed on K/FeOx catalyst during the reaction were effective to produce allyl-alcohol from glycerol, and that the change in crystal structure from hematite to magnetite would be accelerated and stabilize the active site (Brønsted acid site) by addition of formic acid.

Conclusion

Glycerol conversion to produce allyl-alcohol was conducted using K/FeOx catalyst. The change in crystal structure occurs from hematite to magnetite and K/FeOx catalyst showed the Brønsted acidity, which was the appropriate active site to produce allyl-alcohol. Moreover, the addition of formic-acid into the reaction system is effective to accelerate the crystal structure change from hematite to magnetite and increase the allyl-alcohol yield.

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