



Conversion of glycerol into allyl alcohol over potassium-supported zirconia–iron oxide catalyst



Aya Konaka, Teruoki Tago*, Takuya Yoshikawa, Ayaka Nakamura, Takao Masuda

Research Group of Chemical Engineering, Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

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ABSTRACT

The catalytic conversion of glycerol was performed with iron oxide-based catalysts for production of allyl alcohol using a fixed-bed flow reactor at 623 K under atmospheric pressure. The glycerol dehydration proceeds on acid sites of catalysts while the allyl alcohol production is assumed to be catalyzed by non-acidic sites of catalysts through a hydrogen transfer mechanism. Different alkali metals, including Na, K, Rb, and Cs were supported on ZrO_2-FeO_x and all of them gave impressively higher allyl alcohol yield and suppressed glycerol dehydration due to the reduced catalyst acidic property. K-supported ZrO_2-FeO_x (K/ ZrO_2-FeO_x) was chosen for further studies, and allyl alcohol yield remarkably increased up to 27 mol% C at the K content of 3–5 mol%. Since no external hydrogen gas is supplied to the system, the hydrogen transfer mechanism should take place between the reaction of glycerol and either hydrogen atoms derived from formic acid forming during the reaction, or active hydrogen species produced from the decomposition of H_2O by ZrO_2 .

Addition of Al_2O_3 to K/ ZrO_2-FeO_x (K/ $Al_2O_3-ZrO_2-FeO_x$) was examined in order to improve structure stability during the glycerol conversion. Al_2O_3 addition to the catalyst was effective to achieve higher structure stability, leading to high glycerol conversion with stable allyl alcohol yield of above 25 mol% C. Moreover, K/ $Al_2O_3-ZrO_2-FeO_x$ can be applicable to the conversion of crude glycerol which is the waste solution obtained from biodiesel production.

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1. Introduction

Biodiesel, one of renewable and alternative fuels to fossil fuels, appears to be significant fuel due to depletion of fossil fuels and global warming problem [1–3]. Glycerol is produced as a main by-product in a biodiesel production which is a transesterification of triglycerides, such as vegetable oils and animal fats, and methanol [2,4]. Therefore, development of an effective utilization for glycerol is highly desired.

Conversion of glycerol into useful chemicals is widely studied [5–15]. Most of the works report on converting glycerol into acrolein [5–7], acetol [8], or 1,2- and 1,3-propanediol [9–11]. Acrolein and acetol are produced through gas-phase dehydration of glycerol over acidic catalysts including Nb_2O_5 , heteropolyacids, and zeolites, and copper metal catalysts, respectively. 1,2- and 1,3-Propanediol are obtained through hydrogenolysis of glycerol over supported Ru, Rh, and Pt catalysts. Additionally, some of the works have reported recently on synthesis of allyl alcohol from glycerol which is assumed to form via hydride or hydrogen

transfer mechanism [12–15]. Among these chemicals, allyl alcohol can be more useful and valuable chemical because it can be used as an important chemical intermediate in the production of resins, paints, coatings, silane coupling agents, and polymer crosslinking agents, etc. Thus, allyl alcohol is one attractive and valuable chemical that can be obtained from glycerol.

On the contrary, we have developed zirconia–iron oxide catalyst, ZrO_2-FeO_x , for the catalytic conversion of biomass resources. We have succeeded in producing phenol and ketones from tar derived from wood biomass [16–19], sewage sludge [20], and fermentation residue [21] over ZrO_2-FeO_x , in which ZrO_2 loaded on FeO_x contributes to the high catalytic performance and stability. Since ZrO_2-FeO_x works effectively on the organic compounds having hydroxyl and carboxyl groups, the catalyst is expected to be applicable to the catalytic conversion of glycerol into useful chemicals.

Using ZrO_2-FeO_x , we have succeeded in producing useful chemicals, including propylene, allyl alcohol, carboxylic acids, and ketones, from reagent glycerol [22]. These useful 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 production of carboxylic acids from acetol, followed by their ketonization (Pathway

* Corresponding author. Tel.: +81 11 706 6551; fax: +81 11 706 6552.
E-mail address: tago@eng.hokudai.ac.jp (T. Tago).

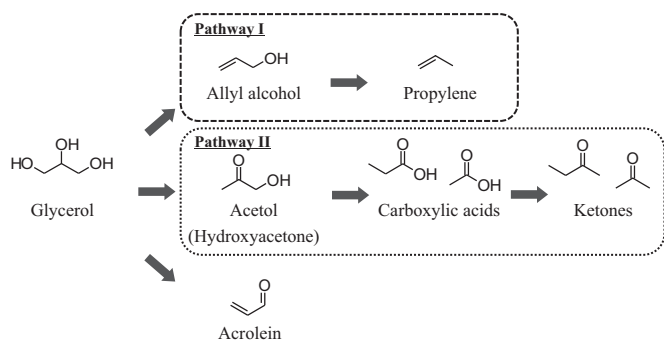


Fig. 1. Expected reaction pathways for glycerol over $\text{ZrO}_2\text{-FeO}_x$.

II), as shown in Fig. 1. We previously reported that the incorporation of ZrO_2 into FeO_x significantly improved the BET surface area of the catalysts; FeO_x has the surface area of $14 \text{ m}^2 \text{ g}^{-1}$ while $\text{ZrO}_2\text{-FeO}_x$ with ZrO_2 content of 7.0 wt% has that of $56 \text{ m}^2 \text{ g}^{-1}$ [22,23]. This increase in the catalyst surface area further improved the catalytic activity for the production of the useful chemicals shown in Fig. 1. Furthermore, it was also revealed that $\text{ZrO}_2\text{-FeO}_x$ improved the catalytic stability because ZrO_2 has an ability to produce active oxygen species from H_2O for regeneration of the consumed lattice oxygen in FeO_x [22–24]. In our previous research, $\text{ZrO}_2\text{-FeO}_x$ was considered to have acid sites which generally promote dehydration reaction [25–27]. In order to obtain higher selectivity to the Pathway I, particularly allyl alcohol, suppressing the Pathway II and the acrolein production, which are the dehydration of glycerol, appears to be a solution to our system.

In this study, different alkali metals, including Na, K, Rb, and Cs were supported on $\text{ZrO}_2\text{-FeO}_x$ to suppress glycerol dehydration that proceeded on the acid sites of the catalyst. Na-, K-, Rb-, and Cs-supported $\text{ZrO}_2\text{-FeO}_x$ were used for the catalytic conversion of glycerol. K-supported $\text{ZrO}_2\text{-FeO}_x$ was selected for the further studies and its effects of K content on the product yield and catalytic stability were investigated. Main objectives of this study are to investigate the effects of supported alkali metals on the product yield and to develop a catalyst showing high selectivity to allyl alcohol with high stability. Finally, the catalyst was applied to convert crude glycerol derived from biodiesel production to allyl alcohol.

2. Experimental

2.1. Catalyst preparation and characterization

All reagents were purchased from Wako Pure Chemical Industries (Japan). $\text{ZrO}_2\text{-FeO}_x$ was prepared by a coprecipitation method using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ aqueous solutions and ammonia solution. 10 wt% ammonia solution was added by a micropump to the aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ under continuous stirring until the pH of each solution reached pH 7 and filtered subsequently. The obtained precipitate was dried at 383 K for 24 h to obtain $\text{ZrO}_2\text{-FeO}_x$ precursor. In our previous research [22], the effect of ZrO_2 content on product yield from glycerol was examined, in which it was revealed that ZrO_2 content of 7.0 wt% in FeO_x was appropriate. In this study, $\text{ZrO}_2\text{-FeO}_x$ with ZrO_2 content of 7.0 wt% was used as a catalyst.

The $\text{ZrO}_2\text{-FeO}_x$ precursor was used to prepare alkali metal-supported $\text{ZrO}_2\text{-FeO}_x$ by an impregnation method with their content of 1.0 mol% based on the total amount of Zr and Fe. As for K, its content was varied in the range of 0–10 mol%, denoted hereafter “K[Z]/ $\text{ZrO}_2\text{-FeO}_x$ ” where Z was the K content (mol%). Aqueous solution of each alkali metal nitrates was added to the $\text{ZrO}_2\text{-FeO}_x$ precursor, stirred and dried in a vacuum at 313 K for 2 h and 333 K for 2 h. The obtained precipitate was again dried at 383 K for 24 h

and finally calcined at 773 K for 2 h in an air atmosphere. The BET surface area of the representative catalyst, K[5]/ $\text{ZrO}_2\text{-FeO}_x$, was $51 \text{ m}^2 \text{ g}^{-1}$ and its crystal phase was hematite.

K-supported $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-FeO}_x$, K/Al $_2\text{O}_3\text{-ZrO}_2\text{-FeO}_x$, was also prepared by a combination of coprecipitation and impregnation methods. $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-FeO}_x$ precursor was first obtained by a coprecipitation method similarly to the protocols for the preparation of $\text{ZrO}_2\text{-FeO}_x$ [23]. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used as the Al_2O_3 source. Al_2O_3 content was 10 mol% of the total amount of Al, Zr, and Fe. K was supported on $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-FeO}_x$ by an impregnation method. The $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-FeO}_x$ precursor and KNO_3 aqueous solution were mixed, stirred, and subsequently dried in a vacuum at 313 K for 2 h and 333 K for 2 h. The obtained precipitate was dried at 383 K for 24 h and finally calcined at 973 K for 2 h in an air atmosphere. The obtained catalyst had the BET surface area of $62 \text{ m}^2 \text{ g}^{-1}$ and the crystal phase of hematite.

The composition of the catalysts and the amount of ZrO_2 or alkali metals in the catalysts were confirmed by X-ray fluorescence analyzer (XRF Supermini; Rigaku Co. Ltd.). The surface areas of the catalysts were measured by a nitrogen adsorption and desorption method (Belsorp mini; BEL Japan, Inc.). The crystal phases of the catalysts were analyzed by an X-ray diffractometer (JDX-8020; JEOL). The acidic property of the catalysts was evaluated by the temperature-programmed desorption profile of ammonia ($\text{NH}_3\text{-TPD}$) method using the quadrupole mass spectrometer (BEL-mass; BEL Japan, Inc.) combined with the catalyst analyzer (BEL-cat; BEL Japan, Inc.). The sample was pretreated in Ar flow at 823 K. After cooling down to 373 K, NH_3 was introduced for 30 min and the sample was subsequently heated at 10 K min^{-1} in Ar flow up to 823 K.

2.2. Catalytic conversion of glycerol

The catalytic conversion of glycerol over different catalysts was carried out in a fixed-bed flow reactor for 2–6 h at the reaction temperature of 623 K under atmospheric pressure. Catalysts were pelletized and formulated into the particle size of 300–850 μm . Nitrogen gas was introduced as a carrier gas at the flow rate of $20 \text{ cm}^3/\text{min}$. The values of W/F , where W is the amount of catalyst (g) and F is the flow rate of the feedstock (g h^{-1}), were varied in the range of 1–5 h to obtain similar initial glycerol conversion between each experiment. Glycerol aqueous solution was used as a feedstock and fed to the reactor with a syringe pump. Crude glycerol solution, the waste solution obtained in the process of biodiesel fuel production, was also used as a feedstock. The main source of the crude glycerol is edible vegetable oil and methanol. Potassium hydroxide, KOH, is used as a catalyst for the transesterification reaction of them to produce biodiesel fuel and glycerol.

The liquid and the gas products were collected with an ice trap and a gas pack, respectively, for every 2 h and product yields showed the average of each 2 h. The liquid products were analyzed by a gas chromatograph equipped with a flame ionization detector (GC-2014; Shimadzu Co. Ltd.) and a gas chromatograph mass (GC-17A GCMS-QP5050) equipped with a DB-Wax capillary column. The gas products were analyzed by gas chromatographs with thermal conductivity and flame ionization detectors (GC-8A; Shimadzu Co. Ltd.) equipped with activated charcoal and Porapak Q columns, respectively. The product yields were calculated based on the amount of glycerol fed to the reactor.

3. Results and discussion

3.1. Catalytic reactions over alkali metal-supported $\text{ZrO}_2\text{-FeO}_x$

In a biodiesel fuel production process, alkali metals such as sodium (Na) or potassium (K) hydroxides are used as catalysts in

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