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Investigation of reaction routes for direct conversion of glycerol over zirconia–iron oxide catalyst

Takuya Yoshikawa · Teruoki Tago ·
Ayaka Nakamura · Aya Konaka ·
Mitsushi Mukaida · Takao Masuda

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Abstract Conversion of glycerol to useful chemicals was examined using a zirconia–iron oxide catalyst. An aqueous glycerol solution was used as feedstock, and the catalytic reaction was carried out in a fixed-bed flow reactor at 623 K under atmospheric pressure. Useful chemicals, for example propylene, allyl alcohol, carboxylic acids, and ketones, were obtained from the aqueous glycerol solution. The reaction was found to involve a series of consecutive reactions, with allyl alcohol and carboxylic acids as reaction intermediates which were converted to propylene and ketones, respectively. Moreover, the catalyst had high and stable activity in the reaction of a 50 wt% glycerol solution.

Keywords Biomass utilization · Glycerol conversion · Iron oxide catalyst · Consecutive reactions

Introduction

From the perspective of fossil fuel depletion and global warming, renewable and alternative fuels, for example biodiesel, are becoming increasingly important [1–3]. Biodiesel is usually produced by transesterification of triglycerides, for example vegetable oils and animal fats, with an alcohol, for example methanol, the stoichiometrically of which requires three moles of alcohol per mole triglyceride to yield three moles of a fatty acid alkyl ester, i.e. biodiesel, and one mole of glycerol. Because an aqueous solution of glycerol is generated as a major by-product, methods for effectively utilizing the glycerol are required. Glycerol has recently

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T. Yoshikawa · T. Tago (✉) · A. Nakamura · A. Konaka · M. Mukaida · T. Masuda
Research Group of Chemical Engineering, Division of Chemical Process Engineering,
Faculty of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo,
Hokkaido 060-8628, Japan
e-mail: tago@eng.hokudai.ac.jp

attracted much attention because it is one of the most important biomass resources for production of useful chemicals, for example 1,2-propanediol [4], 1,3-propanediol [5], and acrolein [6].

For catalytic conversion of biomass resources, we have developed an iron oxide catalyst containing zirconia (abbreviated as ZrO_2–FeO_X) and have succeeded in achieving selective production of phenol and ketones from tar derived from wood biomass [7–10], sewage sludge [11], and fermentation residue [12], in which the ZrO_2 loaded on to the FeO_X effectively accelerated the reactions and contributed to high catalytic stability. Because this catalyst has effective activity for hydroxyl and carboxyl groups in organic compounds, it is believed it could be adapted to produce useful chemicals from glycerol. In this study, catalytic conversion of glycerol into useful chemicals over ZrO_2–FeO_X was examined. Moreover, catalytic reactions using model compounds were also carried out in order to investigate the reaction routes.

Experimental

Catalyst preparation and characterization

The ZrO_2–FeO_X catalyst was prepared by co-precipitation of $Fe(NO_3)_3 \cdot 9H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ aqueous solutions by addition of ammonia solution. All reagents were purchased from Wako Pure Chemical Industries (Japan) and were used without further purification. The catalysts obtained were calcined at 773 K for 2 h in an air atmosphere. The ZrO_2 content in the catalyst was analyzed by X–ray fluorescence analysis (XRF Supermini; Rigaku) and was found to vary in the range 7–66 wt%. The catalysts are denoted hereafter as $ZrO_2(Y)$–FeO_X, where Y is the weight percentage of the supporting ZrO_2 (Table 1). FeO_X and ZrO_2 were also prepared by the same method for comparison. The crystallinity of the catalyst was analyzed with an X–ray diffractometer (JDX–8020; Jeol). The surface areas of the catalysts were evaluated by an N_2 adsorption and desorption method (Belsorp mini; BEL Japan), and the acidity of ZrO_2–FeO_X was evaluated by the ac–NH_3–TPD method [13]. In the TPD experiment, carrier gas was 1.0% NH_3 with He balance, the heating rate was 5 K min^{-1} and the temperature range was from 373 to 950 K.

Catalytic reactions over ZrO_2–FeO_X

Catalytic reactions using the ZrO_2–FeO_X catalyst were conducted in a fixed-bed flow reactor for 2 h at a reaction temperature of 623 K under atmospheric pressure. To examine catalyst stability, reaction for 6 h was also conducted, and the liquid and gas products were collected every 2 h. Nitrogen gas was introduced as a carrier gas at a flow rate of 20 cm^3/min. W/F was varied in the range of 0–11 h, where W is the amount of catalyst and F is the flow rate of the feedstock. Aqueous solutions of the glycerol reagent and model compounds listed in Table 2 were used as feedstocks and fed to the reactor with a syringe pump. The liquid and gaseous products were collected with an ice trap and a gas pack, respectively. The liquid products were analyzed by gas chromatography with flame ionization detection (GC-2014;

Table 1 The surface areas of FeO_X, ZrO_2 and ZrO_2–FeO_X catalysts

ZrO_2 content/wt%	0 (FeO_X)	7	14	27	50	66	100 (ZrO_2)
SBET/m^2 g^{-1}	14	56	116	124	143	149	88

Shimadzu) and gas chromatography–mass spectrometry (GC-17A GCMS-QP5050; Shimadzu) with a DB-Wax capillary column. The gaseous products were analyzed by gas chromatography with thermal conductivity and flame ionization detection (GC-8A; Shimadzu) with activated charcoal and Porapak Q columns, respectively.

Results and discussion

Catalytic reactions over FeO_X and ZrO_2–FeO_X

Catalytic reactions of a 30 wt% aqueous glycerol solution were carried out over FeO_X and ZrO_2(7)–FeO_X catalysts at $W/F = 1.0$ h for 6 h. A reaction was also conducted without catalyst for the same concentration solution for 2 h. Figure 1 shows the product yields after each reaction after the initial 0–2 h. Without the catalyst, conversion of glycerol was low, and the product, undetectable by GC, was considered to be formed by polymerization of glycerol. On the other hand, with the FeO_X and ZrO_2(7)–FeO_X catalysts, the conversion increased and useful chemicals were obtained, including allyl alcohol, carboxylic acids, and ketones as liquid products, and propylene as gaseous product. The yield of these chemicals and conversion of glycerol were markedly improved over ZrO_2(7)–FeO_X compared with those obtained over FeO_X. Among these chemicals, allyl alcohol and ketones are regarded as more useful because they are important industrial chemicals. Allyl alcohol is used as starting

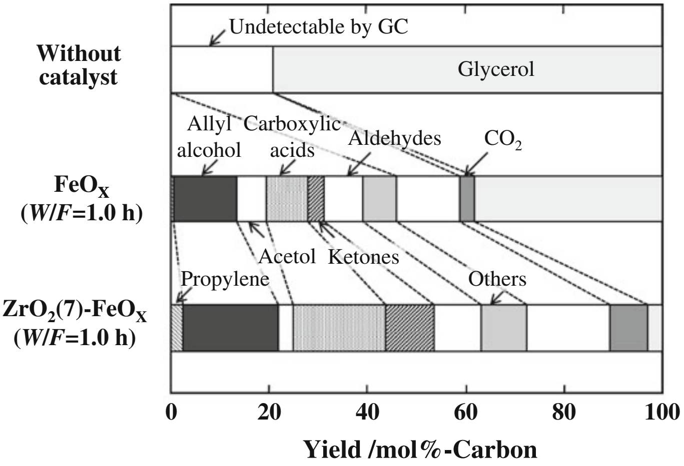

Fig. 1 Product yield after reaction of 30 wt% glycerol solution with ZrO_2(7)–FeO_X and FeO_X catalysts and without catalyst. Reaction conditions: reaction time = 2 h

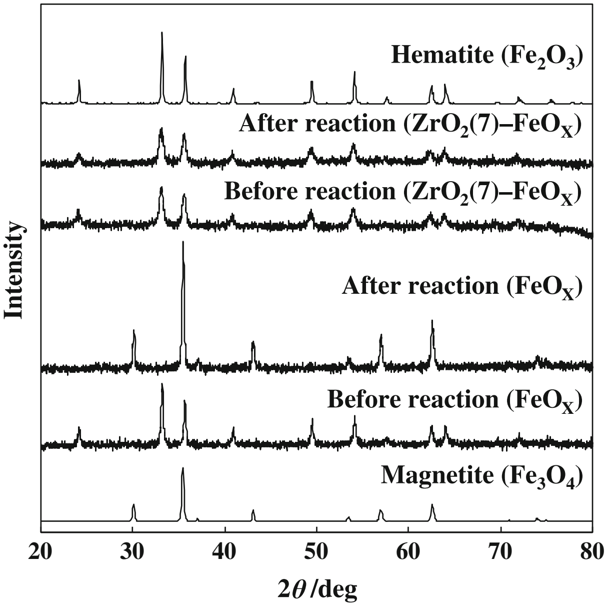

Fig. 2 XRD patterns of the catalysts before and after the reaction using ZrO_2(7)–FeO_X and FeO_X catalysts. Reaction conditions: 30 wt% glycerol solution, $W/F = 1.0$ h, reaction time = 6 h

material in the manufacture of pharmaceutical intermediates, fragrances, allyl ester resin, etc., and ketones are used as solvent, precursors of plastics, etc. The carboxylic acids comprised acetic acid and propionic acid as major products and 2-methyl propionic acid and butyric acid as minor products. The ketones included acetone and 2-butanone as the major products and 3-pentanone as a minor product. Small amounts the aldehydes acetaldehyde and acrolein were also formed.

Figure 2 shows the XRD patterns of the FeO_X and ZrO_2(7)–FeO_X catalysts before and after the glycerol reactions. We previously reported that organics adsorbed on the ZrO_2–FeO_X were oxidatively decomposed by the lattice oxygen of FeO_X, which can be regenerated by an active oxygen species produced from H_2O over ZrO_2 [14, 15]. Also the degree of catalyst deactivation corresponded to transformation of the crystallinity of the ZrO_2–FeO_X structure from hematite to magnetite. As shown in Fig. 2, the FeO_X structure after reaction was found to include magnetite whereas for ZrO_2(7)–FeO_X the initial hematite structure was retained. Therefore, addition of ZrO_2 to FeO_X improves the catalytic stability because of the regeneration mechanism described above. From Figs. 1 and 2, it can be seen that the activity and stability of ZrO_2(7)–FeO_X were greater than those of FeO_X for conversion of glycerol into useful chemicals.

Table 1 shows the BET surface area (hereafter S_{BET}) of the FeO_X, ZrO_2 and ZrO_2–FeO_X catalysts. As shown in Table 1, addition of small amount of ZrO_2 to FeO_X contributed to the great increase in S_{BET} of ZrO_2–FeO_X catalysts, so this led to improvement of the catalytic activity of ZrO_2(7)–FeO_X.

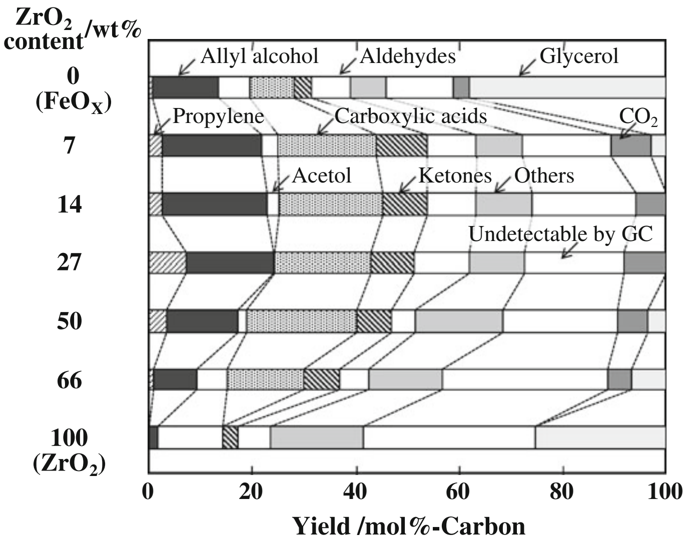

Fig. 3 Effect of the ZrO_2 content of the ZrO_2–FeO_X catalyst on product yields. Reaction conditions: 30 wt% glycerol solution, $W/F = 1.0$ h, reaction time = 2 h

Effect of ZrO_2 content on catalytic activity

Figure 3 shows the effect of the composition of the ZrO_2–FeO_X catalyst on product yield after reaction of 30 wt% glycerol solution at $W/F = 1.0$ h for 2 h. Whereas conversion of glycerol was approximately 60% using FeO_X, conversion reached nearly 100%, and the total yield of useful chemicals increased to approximately 50 mol%-carbon for amounts of ZrO_2 from 7 to 27 wt%. It is believed that this improvement of the catalytic activity of ZrO_2–FeO_X containing 7–27 wt% ZrO_2 is caused by the regeneration mechanism mentioned in the section "Catalytic reactions over FeO_X and ZrO_2–FeO_X", and the increase in the surface area of the catalysts, shown in Table 1. On the other hand, further increases in ZrO_2 from 50 to 100 wt% led to a decrease in the total yield of useful chemicals and an increase in the yield of products undetectable by GC. In addition, ally alcohol and propylene were hardly produced over ZrO_2 alone as catalyst. This indicates that the main active catalytic surface for production of useful chemicals from glycerol, especially for allyl alcohol, propylene, and ketones, is over FeO_X, and that including excessive amounts of ZrO_2 in ZrO_2–FeO_X is ineffective for glycerol conversion. Accordingly, the appropriate ZrO_2 content was found to be 7–27 wt%.

Effect of the *W*/*F* value on catalytic activity

Figure 4 shows the effect of *W*/*F* (weight of catalyst/feed rate) on product yields for the reaction of a 10 wt% glycerol solution over $ZrO_2(7)$–FeO_X for 2 h. The yields of allyl alcohol and carboxylic acids were the highest at the lowest *W*/*F* values

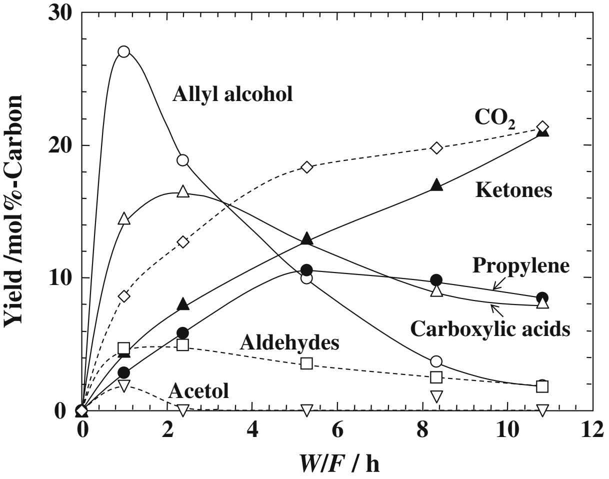

Fig. 4 Effect of the *W*/*F* value on the yields of main products. Reaction conditions: $ZrO_2(7)–FeO_X$, 10 wt% glycerol solution, *W*/*F* = 1.0 h, reaction time = 2 h

(*W*/*F* = 1–2 h). As the *W*/*F* value increased these yields decreased and the yields of propylene and ketones increased.

To clarify the reaction paths, catalytic reactions using model compounds were carried out. Table 2 lists the model compounds and yields of the main products after each reaction over $ZrO_2(7)–FeO_X$. Acetol (hydroxyacetone) was mainly converted into carboxylic acids and ketones, and it has previously been reported that carboxylic acids are selectively converted into ketones over $ZrO_2–FeO_X$ [10, 12], where bimolecular reaction proceeds and two molecules of carboxylic acid are converted into one molecule of CO_2 and one molecule of ketone. Therefore, carboxylic acids and ketones were considered to be produced consecutively from acetol over the catalyst. Allyl alcohol was selectively converted into propylene; conversion of acrolein was relatively low compared with those of acetol and allyl alcohol. These results are in good agreement with the results shown in Fig. 4 and Table 2. On the basis of these results, the expected reaction routes of glycerol over $ZrO_2–FeO_X$ are outlined in Fig. 5. It is believed that two major reaction paths exist: one is the production of carboxylic acids from acetol, followed by their ketonization, and the other is production of allyl alcohol and propylene.

In the former reaction route, acetol was produced by dehydration of glycerol. Because the dehydration reaction is generally promoted over acid sites of catalyst, the acidity of $ZrO_2(7)–FeO_X$ was evaluated by the ac–NH_3–TPD method. Because no peaks of NH_3 desorption were observed, it was concluded that the acidity of $ZrO_2(7)–FeO_X$ was very weak. Therefore, it was concluded that production of acetol by dehydration of glycerol occurred over OH groups with very weak acidity on the surface of $ZrO_2–FeO_X$. With regard to the latter reaction route, it has been reported that production of allyl alcohol from glycerol is enhanced by addition of formic acid [16]. Because carboxylic acids are produced from glycerol over $ZrO_2–FeO_X$,

Table 2 Yields of main products and conversion for the reactions of model compounds. Reaction conditions: $ZrO_2(7)–FeO_X$, reaction time = 2 h

Model compound (reaction conditions)	Conversion/ %	Propylene	Allyl alcohol	Acetol	Carboxylic acids			Ketones			Aldehydes		Others	Undetectable by GC	CO_2
					Acetic acid	Propionic acid	Other acids	Acetone	2-Butanone	3-Pentanone	Acetaldehyde	Acrolein			
Allyl alcohol (10wt%, $W/F = 10$ h)	99.1	**59.7**	0.90	0.00	0.60	0.26	0.04	2.45	1.50	0.24	1.73	2.80	2.61	13.6	13.6
Acetol (10 wt%, $W/F = 1.0$ h)	79.5	0.03	0.00	20.5	**4.15**	**16.8**	**1.06**	**10.0**	**1.25**	**1.68**	0.54	0.00	10.1	30.4	3.41
Acrolein (10wt%, $W/F = 1.7$ h)	57.5	0.06	0.00	0.00	0.00	0.00	0.00	0.21	0.05	0.00	1.47	**42.5**	1.62	**52.9**	1.21

The main products after each reaction are shown in bold. Thus, propylene was the main product after reaction of allyl alcohol, and carboxylic acids and ketones ware the main products after reaction of acetol. In the reaction of acrolein, because its conversion was low, unreacted acrolein is shown in bold

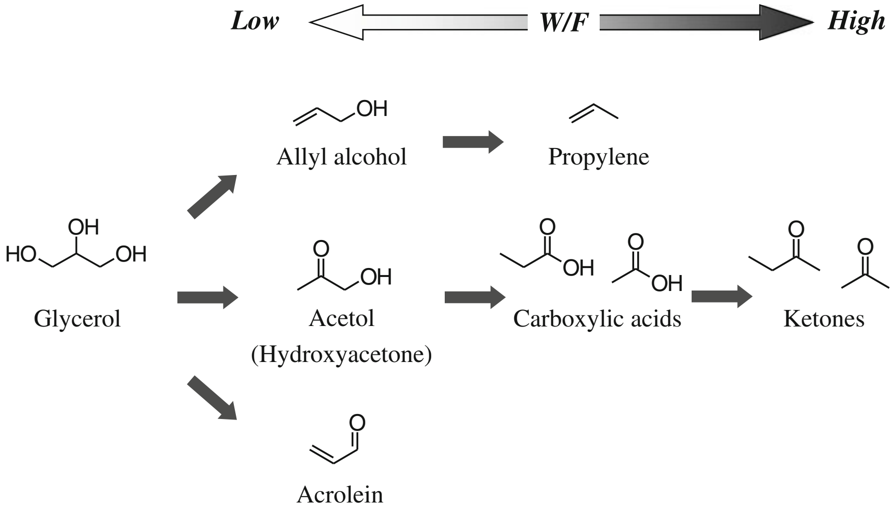

Fig. 5 Expected reaction paths of glycerol over ZrO_2–FeO_X

a similar reaction is possible over ZrO_2–FeO_X, and further study is required to clarify the reaction mechanism.

Application to the reaction of high concentrations of glycerol

From the viewpoint of reducing energy consumption, it is desirable to use a high-concentration glycerol solution as feedstock. However, using an excessive concentration of glycerol can lead to polymerization of glycerol during the reaction. To examine the application of ZrO_2(7)–FeO_X to the reaction of high concentrations of glycerol, the catalytic reaction was carried out for 6 h using a 50 wt% aqueous glycerol solution. Figures 6 and 7 show the product yields over time and the XRD patterns before and after the reactions over ZrO_2(7)–FeO_X, respectively. The conversion of glycerol and product yields were stable for 6 h and the catalyst retained its hematite structure after the reaction. Therefore, ZrO_2(7)–FeO_X can be used for the high concentration of 50 wt% glycerol.

Conclusions

Catalytic conversion of glycerol over ZrO_2–FeO_X was investigated. Useful chemicals, for example allyl alcohol, carboxylic acids, propylene, and ketones, were obtained from an aqueous glycerol solution as feedstock. Addition of ZrO_2 to FeO_X improved the catalytic activity and stability; the appropriate ZrO_2 content was 7–27 wt%. It was found that the reaction involved a series of consecutive reactions in which allyl alcohol and carboxylic acids were the intermediates. Moreover, the activity of ZrO_2(7)–FeO_X was stable over 6 h in the reaction of a high-concentration

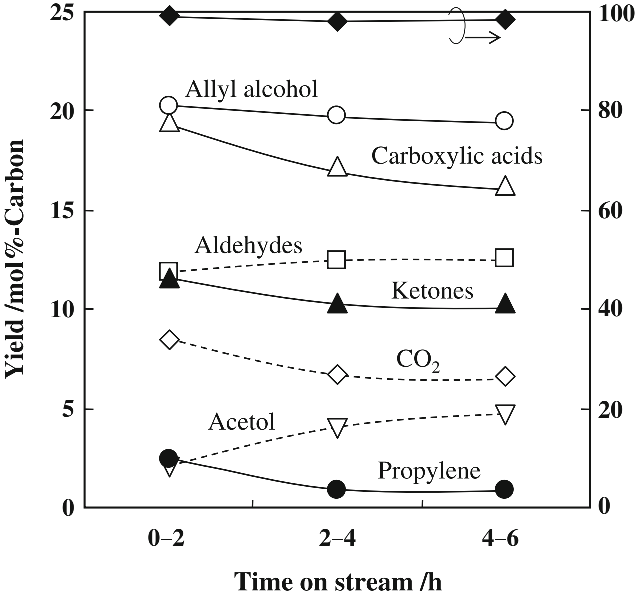

Fig. 6 Effect of time on stream on product yields during reaction of 50 wt% glycerol solution. Reaction conditions: $ZrO_2(7)–FeO_X$, $W/F = 1.0$ h

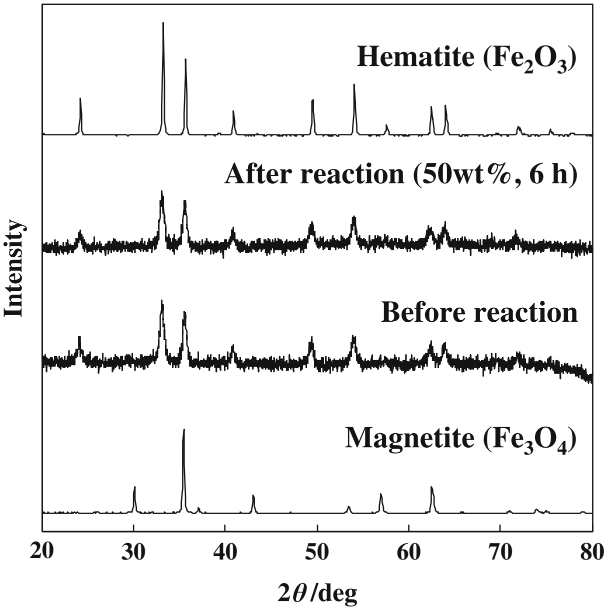

Fig. 7 XRD patterns of the catalysts before and after reaction of 50 wt% glycerol solution. Reaction conditions: $ZrO_2(7)–FeO_X$, $W/F = 1.0$ h, reaction time = 6 h

solution of 50 wt% glycerol. Therefore, ZrO_2–FeO_X is suitable for application to the conversion of a biodiesel-derived crude glycerol solution.

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