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[Review Paper]

Conversion of Glycerol into Useful Chemicals over Iron Oxide-based Catalyst

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Catalytic conversion of glycerol with iron oxide-based catalysts was investigated for the production of useful chemicals. The catalytic reaction was carried out in a fixed-bed flow reactor at 623 K under atmospheric pressure. Useful chemicals such as allyl-alcohol, propylene and ketones were produced from glycerol through two main pathways: formation of allyl alcohol and propylene (Pathway I), and formation of hydroxyacetone and acrolein (Pathway II). Hydroxyacetone in Pathway II is easily converted into carboxylic acids followed by ketonization to form acetone, methyl ethyl ketone and pentanone. An increase in the *W/F* (weight ratio of catalyst to feedstock) value allowed the consecutive reactions to progress and the final products were 24 mol%-carbon of propylene and 25 mol%-carbon of ketones. Moreover, addition of alkaline metals to the catalyst increased the yield of allyl alcohol. This study demonstrates the production of useful chemicals from glycerol (crude glycerol and reagent glycerol). The effects of catalyst composition and experimental conditions on these yields are discussed, based on investigations of the reaction pathways and mechanisms.

Keywords

Biomass conversion, Glycerol, Allyl alcohol, Propylene, Iron oxide catalyst

1. Introduction

Biomass has emerged as a potential stable source of carbon in response to concerns about the depletion of fossil resources and global warming. Consequently, processes using biomass as a renewable energy feedstock^{1)~5)} are being developed to produce biodiesel fuel as a potential replacement for fossil fuels. Biodiesel is usually produced by trans-esterification of triglycerides, *e.g.*, vegetable oils and animal fats, with methanol, in which three moles of methanol per mole of triglyceride are stoichiometrically required to yield three moles of fatty acid alkyl ester, *i.e.*, biodiesel, and one mole of glycerol. Accordingly, development of an efficient utilization method for the glycerol byproduct is needed.

Glycerol is one of the major platform chemicals in a biorefinery and conversion of glycerol into useful chemicals has much investigation^{6)~16)}. Most studies have concentrated on converting glycerol into acrolein^{6)~8)}, hydroxyacetone (acetol)⁹⁾, or 1,2- and 1,3-propanediol^{10)~12)}. Acrolein and acetol are produced through gas-phase dehydration of glycerol over acidic catalysts including heteropolyacids and zeolites, and copper metal catalysts, respectively. 1,2- and 1,3-Propanediol are obtained through hydrogenolysis of glycerol over sup-

ported Ru, Rh, and Pt catalysts. Additionally, allyl alcohol has been synthesized from glycerol^{13)~16)} over an iron oxide (hematite, α -Fe₂O₃) catalyst.

We have developed a zirconia-iron oxide catalyst, ZrO₂-FeO_x, for the catalytic conversion of biomass resources, and succeeded in producing phenol and ketones from tar derived from plant biomass^{17)~21)}, sewage sludge²²⁾, and fermentation residue^{23),24)}, in which ZrO₂ loaded on FeO_x is important for the high catalytic performance and stability. Moreover, we have succeeded in producing useful chemicals, including propylene, allyl alcohol, carboxylic acids, and ketones, from glycerol using ZrO₂-FeO_x catalyst^{25)~27)}.

Allyl alcohol and propylene are useful and valuable chemicals obtained from glycerol through a characteristic reaction using iron oxide catalyst. The ZrO₂-FeO_x catalyst is very active for reactions involving organic compounds with hydroxyl and carboxyl groups, so this catalyst may also be applicable to the catalytic conversion of glycerol into useful chemicals through two main pathways, formation of allyl alcohol^{14),25)~27)} and propylene (Pathway I), and dehydration of glycerol to form hydroxyacetone and acrolein (Pathway II)^{28)~32)}. Hydroxyacetone (acetol) is easily converted into carboxylic acids (acetic and propionic acids), which are then further reacted to form ketones (acetone, methyl ethyl ketone and pentanone) *via* ketonization^{24),33)}.

The present study describes the production of useful chemicals from glycerol (crude glycerol and reagent

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glycerol) and determination of the catalytic reaction mechanism. First, $\text{ZrO}_2\text{-FeO}_x$ catalysts were employed to produce useful chemicals from crude glycerol and the effects of the ZrO_2 content in the catalyst and of W/F values (weight ratio of catalyst to feedstock) on the yields of useful chemicals were examined²⁶⁾. Catalytic conversion of model compounds of the intermediates in the glycerol conversion was also carried out to investigate the reaction pathways²⁵⁾. Useful chemicals such as allyl alcohol, carboxylic acids, propylene, and ketones were obtained from glycerol. The reaction involved a series of consecutive reactions, which involved allyl alcohol and carboxylic acids as the intermediates. Finally, different alkali metals, including Na, K, Rb, and Cs, were added to the $\text{ZrO}_2\text{-FeO}_x$ catalyst to increase the yield of allyl alcohol²⁷⁾. K-supported $\text{ZrO}_2\text{-FeO}_x$ and K-supported $\text{Al}_2\text{O}_3\text{-FeO}_x$ catalysts were used for further studies and the effects of K content on the product yield were explained, based on investigation of the reaction mechanism to produce allyl alcohol over the iron oxide catalyst.

2. Experimental

2.1. Catalyst Preparation and Characterization

Zirconia-iron oxide ($\text{ZrO}_2\text{-FeO}_x$) catalysts with different ZrO_2 contents were prepared by a coprecipitation method using appropriate nitric salt [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$] aqueous solutions and ammonia solution. All reagents were purchased from Wako Pure Chemical Industries, Ltd., Japan, and were used without further purification. To prepare $\text{ZrO}_2\text{-FeO}_x$ catalyst, 10 wt% ammonia solution was added using a micro-pump to the mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ aqueous solution with continuous stirring until the pH of the solution reached 7.0. The solution was stirred for an hour and then filtered. The obtained precipitates were dried at 383 K for 24 h and calcined at 773 K for 2 h in an air atmosphere. The ZrO_2 content in $\text{ZrO}_2\text{-FeO}_x$, which was varied in the range of 0-65 wt%, was analyzed by an X-ray fluorescence analyzer (XRF Supermini; Rigaku Corp.). The catalysts are here described as " $\text{ZrO}_2(Y)\text{-FeO}_x$," where Y is the weight percent of the supporting ZrO_2 . The FeO_x catalyst without ZrO_2 , ZrO_2 catalyst without FeO_x and alumina-iron oxide [$\text{Al}_2\text{O}_3(7.0)\text{-FeO}_x$] catalyst were also prepared by the same method for comparison.

The $\text{ZrO}_2\text{-FeO}_x$ precursor (before calcination) was used to prepare alkali metal-supported catalysts by an impregnation method with an alkali content of 1.0 mol% based on the total amount of Zr and Fe. The K content was varied in the range of 0-10 mol%, described here as " $\text{K}[Z]/\text{ZrO}_2\text{-FeO}_x$ " where Z was the K content (mol%). The aqueous solution of the appropriate alkali metal nitrate was added to the $\text{ZrO}_2\text{-FeO}_x$ precursor, and the mixture was 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 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 with an X-ray diffractometer (JDX-8020; JEOL Ltd.). The acidic property of the catalysts was evaluated by the temperature-programmed desorption profile of ammonia ($\text{NH}_3\text{-TPD}$) method using a quadrupole mass spectrometer (BEL-mass; Bel Japan, Inc.) combined with a catalyst analyzer (BEL-cat; Bel Japan, Inc.). The sample was pretreated in Ar flow at 823 K. After cooling to 373 K, NH_3 was introduced for 30 min and the sample was subsequently heated at 10 K min^{-1} up to 823 K under a flow of Ar.

2.2. Catalytic Conversion of Glycerol

Catalytic conversion of glycerol over different catalysts was carried out in a fixed-bed flow reactor for 2-6 h at a reaction temperature of 623 K under atmospheric pressure. Catalysts were pelletized and processed into particle sizes of 300-850 μm . N_2 gas was introduced as a carrier gas at the flow rate of 20 cm^3/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 0-10 h. Aqueous glycerol 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 liquid and gas products were collected with an ice trap and a gas bag, respectively, in each experimental run. The liquid products were analyzed with a gas chromatograph equipped with a flame ionization detector (GC-2014; Shimadzu Corp.) and a gas chromatograph mass (GC-17A GCMS-QP5050) equipped with a DB-Wax capillary column. The gas products were analyzed using gas chromatographs with thermal conductivity (TCD) and flame ionization detectors (FID) (GC-8A; Shimadzu Corp.) equipped with activated charcoal and Porapak Q columns, respectively. N_2 used as the carrier gas was collected in the gas bag, so nitrogen was used as an internal standard in GC analysis with the TCD detector, in which CO , CO_2 , CH_4 and H_2 produced during the glycerol conversion were quantified. CH_4 , propylene, and other hydrocarbon gases were also quantified by GC with the FID detector using standard curves. Liquid products were identified by GC with the FID detector, in which 2-propanol and 1,2-butanediol were used as internal standards. The product yields were calculated based on the amount of glycerol fed to the reactor.

2.3. Crude Glycerol

Figure 1 shows the components in the crude glycerol. The total amount of the carbon in crude glycerol was measured by a CHN elemental analyzer (Costech, ECS

4010). Concentrations of glycerol, methanol, and free fatty acids were measured by the same GC system as that used for analysis of liquid products, and the concentration of potassium was evaluated by XRF. The components in the crude glycerol were also measured by high performance liquid chromatography (HPLC LC-2000; JEOL Ltd.) with KC-811 and HG-5 columns.

The weight percent of carbon in the crude glycerol was 54 wt% as measured by the elemental analyzer. Low molecular weight components in the crude glycerol were methanol and glycerol identified by HPLC. Heavy molecular weight components consisted of palmitic acid, oleic acid, linoleic acid, stearic acid and their methyl esters. The weight percent of glycerol was 37 wt%, and the other major components were methanol (8 wt%), free fatty acids (25 wt%) and potassium (4 wt%), based on the GC and XRF analyses.

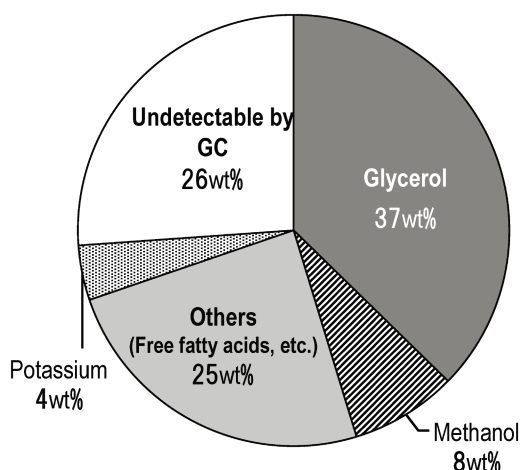


Fig. 1 Components of Crude Glycerol

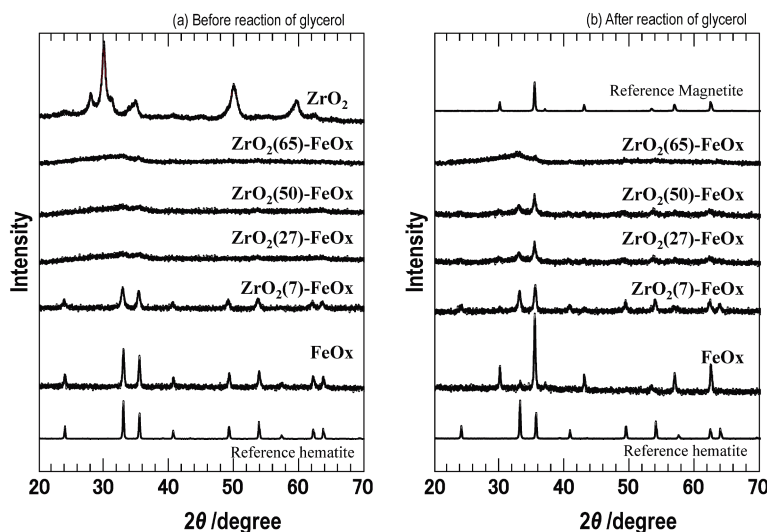
The concentration of free fatty acids was evaluated by assuming all contained free fatty acids were palmitic acid. The weight ratio of methanol to glycerol measured by HPLC was 4.7, which was almost the same value as the ratio measured by GC (4.6). Hydrocarbons (26 wt%) undetectable by GC analysis were considered to be polymeric glycerol, other free fatty acids and their methyl esters, and acyl-glycerol.

3. Conversion of Crude Glycerol into Useful Chemicals

3.1. Effect of Catalyst Composition on Catalyst Properties^{25),26)}

Figure 2(a) shows the X-ray diffraction patterns of $\text{ZrO}_2\text{-FeO}_x$ catalysts with different ZrO_2 concentrations, with ZrO_2 and FeO_x for comparison. The crystal sizes of the iron oxide (with hematite structure) and the BET surface areas of the catalysts are listed in Table 1.

ZrO_2 and FeO_x showed the peaks corresponding to tetragonal ZrO_2 and $\alpha\text{-Fe}_2\text{O}_3$ (hematite), respectively, whereas $\text{ZrO}_2\text{-FeO}_x$ catalysts showed only the peaks corresponding to hematite. The domain sizes of FeO_x ($\alpha\text{-Fe}_2\text{O}_3$) in the catalysts calculated by Scherrer's equation from the patterns were 32 nm and 16 nm at ZrO_2 concentrations of 0 wt% and 7 wt%, respectively. However, catalysts with concentrations of ZrO_2 above 27 wt% showed no peaks corresponding to ZrO_2 , and only slight peaks corresponding to hematite. These results indicated that the ZrO_2 particles were highly dispersed among the FeO_x particles, resulting in suppression of the sintering and crystal growth of iron oxide during calcination. Consequently, the surface area of

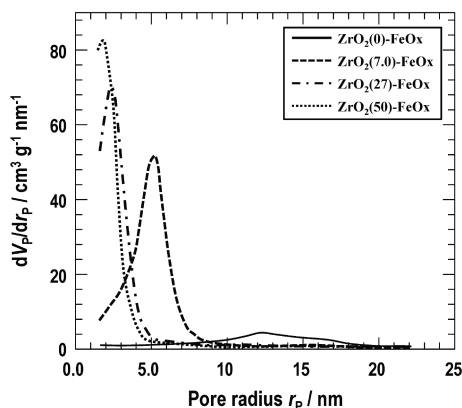


Reaction conditions: $\text{ZrO}_2(Y)\text{-FeO}_x$ (Y : 0-65 wt%), $W/F = 5$ h, reaction time = 2 h.

Fig. 2 X-ray Diffraction Patterns of the Catalysts before (a) and after (b) the Reaction of 10 wt% Crude Glycerol Solution

Table 1 Crystal Size and BET Surface Area of FeO_x of $\text{ZrO}_2\text{-FeO}_x$ Catalysts with Different ZrO_2 Concentrations

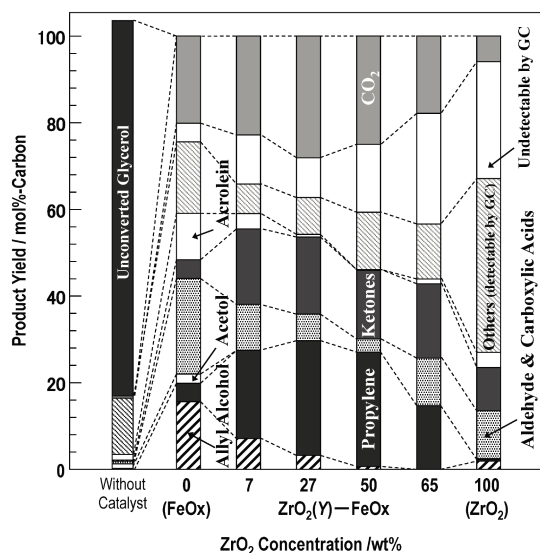
	ZrO_2 concentration in $\text{ZrO}_2\text{-FeO}_x$ catalyst [wt%]					
	0.0	7.0	27	50	65	100
Crystal size of FeO_x (Hematite) [nm]	32	16	-	-	-	-
BET surface area [$\text{m}^2 \text{g}^{-1}$]	14	56	124	143	149	88

Fig. 3 Pore Size Distribution of $\text{ZrO}_2\text{-FeO}_x$ Catalysts with Different ZrO_2 Content

the $\text{ZrO}_2\text{-FeO}_x$ catalyst was larger than those of ZrO_2 and FeO_x catalysts and increased with higher ZrO_2 concentration up to a maximum value of 140–150 m^2/g at the ZrO_2 concentration of 50–65 wt%.

Figure 3 shows the pore-size distributions of $\text{ZrO}_2\text{-FeO}_x$ catalysts calculated by the BJH method using the N_2 adsorption isotherm. FeO_x without ZrO_2 had a mean pore radius of 12 nm. With higher ZrO_2 content, the pore sizes drastically decreased to below approximately 5 nm and the pore volumes increased. These changes in pore size and volume resulted from the suppression of iron oxide sintering by ZrO_2 . As discussed above, the $\text{ZrO}_2\text{-FeO}_x$ catalyst consisted of small crystalline iron oxide particles on which ZrO_2 was highly dispersed. As the ZrO_2 content increased, the crystal size of the iron oxide decreased, leading to the formation of mesopores among the FeO_x particles. Since the size of the mesopores was large enough for the diffusion of glycerol molecules, the glycerol molecules could reach the active sites on the catalyst regardless of the presence of impurities contained in the crude glycerol (such as methanol and free fatty acids).

Figure 4 shows the effects of the catalyst composition of $\text{ZrO}_2\text{-FeO}_x$ on the product yield after reaction of 10 wt% crude glycerol solution at $W/F = 5.0$ h for 2 h. Reaction of crude glycerol solution without catalyst resulted in glycerol conversion of as low as 14 mol%-carbon and no formation of useful chemicals. In contrast, reaction using ZrO_2 , FeO_x , and $\text{ZrO}_2\text{-FeO}_x$ as catalysts resulted in complete glycerol conversion and formation of useful chemicals, including allyl alcohol,

Reaction conditions: 10 wt% crude glycerol solution, $\text{ZrO}_2(\text{Y})\text{-FeO}_x$ (Y: 0–65 wt%), $W/F = 5$ h, reaction time = 2 h.Fig. 4 Effect of ZrO_2 Content of $\text{ZrO}_2\text{-FeO}_x$ on the Product Yields

carboxylic acids, ketones, and acrolein as liquid products, and propylene as a gaseous product. ZrO_2 catalyst mainly produced carboxylic acids and ketones, whereas FeO_x and $\text{ZrO}_2\text{-FeO}_x$ produced allyl alcohol and propylene, in addition to the products above. Moreover, the yield of these chemicals using $\text{ZrO}_2\text{-FeO}_x$ was markedly improved compared to those obtained using only ZrO_2 or FeO_x .

Based on the above results, the expected catalytic functions for each component in the glycerol conversion over $\text{ZrO}_2\text{-FeO}_x$ are summarized in Fig. 5. Allyl alcohol and carboxylic acid were mainly produced over FeO_x catalyst. Moreover, adding a small amount of ZrO_2 to FeO_x enhanced the production of propylene and ketones. Addition of 7 wt% of ZrO_2 to FeO_x sharply increased the yields of propylene and ketones, and the total product yields of the useful chemicals reached the highest value of 60 mol%-carbon. However, adding 50 wt% of ZrO_2 resulted in lower product yields. Reaction using $\text{ZrO}_2(65)\text{-FeO}_x$, the catalyst with the largest surface area, decreased the total product yields of the useful chemicals to 45 mol%-carbon, presumably due to the lower proportion of FeO_x in $\text{ZrO}_2\text{-FeO}_x$, leading to decreases in allyl alcohol and propylene yields.

Figure 2(b) shows the X-ray diffraction patterns of

the catalysts after conversion of glycerol. The $\text{ZrO}_2\text{-FeO}_x$ catalysts showed diffraction peaks due to hematite ($\alpha\text{-Fe}_2\text{O}_3$) in addition to magnetite (Fe_3O_4). We previously reported that organics adsorbed on the $\text{ZrO}_2\text{-FeO}_x$ surface were oxidatively decomposed using the lattice oxygen in FeO_x , which was regenerated by active oxygen species produced from H_2O over ZrO_2 ^{34),35)}. The crude glycerol used as the present feedstock contained glycerol as well as impurity hydrocarbons such as methanol and free fatty acids, so that oxidation of these hydrocarbons simultaneously occurred over the catalyst during the conversion of glycerol. Moreover, as shown in Fig. 3, in contrast to $\text{ZrO}_2(27)\text{-FeO}_x$ and $\text{ZrO}_2(50)\text{-FeO}_x$, the pore size of the $\text{ZrO}_2(7)\text{-FeO}_x$ was large enough to allow diffusion of hydrocarbon molecules such as glycerol and free fatty acids.

The present study showed that crude glycerol solution could be successfully converted into useful chemicals using $\text{ZrO}_2\text{-FeO}_x$, and the optimum ZrO_2 content was 7 wt%.

3. 2. Effect of the W/F Value on Product Yields and Reaction Pathways²⁶⁾

Figure 6 shows the effect of the W/F value (weight of catalyst/feed rate) on the yield of major products from the reaction of 10 wt% of crude glycerol solution over $\text{ZrO}_2(7)\text{-FeO}_x$ for 2 h. The product yields from crude glycerol conversion in Fig. 6 are listed in Table 2

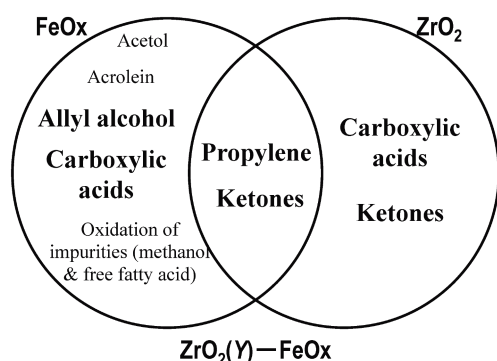
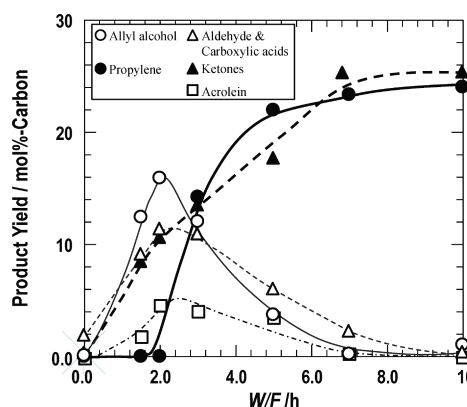


Fig. 5 Expected Catalytic Components for Each Product in Glycerol Conversion over $\text{ZrO}_2\text{-FeO}_x$

in more detail. The compositions of aldehydes, carboxylic acids, and ketones are listed in Table 3. The product yields of allyl alcohol, aldehydes and carboxylic acids increased with W/F value up to 2 h. These yields reached maximum values around W/F of 2 h and then decreased, indicating that these products were intermediates. Moreover, the yield of acrolein was less than 5 mol%-carbon and decreased with W/F values above 3 h. As listed in Table 3, the carboxylic acids consisted of acetic, propionic and butyric acids. The major ketones were acetone (C3 ketone) and methyl ethyl ketone (C4 ketone), and only a slight production of pentanone (C5 ketone) was observed. With W/F values above 7 h, the yield of the intermediates sharply decreased and the products were propylene and ketones, which were the final products in the series of reactions. With W/F of 10 h, 24 mol%-carbon of propylene and 25 mol%-carbon of ketones were obtained. Chemicals produced from biomass in biomass-refinery processes are sometimes obtained as water-organics mixtures, so separation and/or purification of the obtained chemicals from water is necessary. Purification of glycerol from crude glycerol is quite difficult due to the impurities contained in the solution and the arbitrary solubility of



Reaction conditions: 10 wt% crude glycerol solution, $\text{ZrO}_2(7)\text{-FeO}_x$, reaction time = 2 h.

Fig. 6 Effect of the W/F Value on the Yield of Major Products

Table 2 Effect of W/F Value on Product Yield of Glycerol Conversion over $\text{ZrO}_2\text{-FeO}_x$ Catalyst

W/F ^{a)} [h]	Product yields [mol%-carbon]						
	Allyl alcohol	Propylene	Hydroxyacetone (Acetol)	Aldehyde and carboxylic acids	Ketones	Acrolein	Others ^{b)}
0.0	0.09	0.00	1.03	1.87	0.30	0.00	13.0
1.5	12.5	0.00	1.46	9.11	8.46	1.88	27.1
2.0	15.9	0.00	0.30	11.4	10.6	4.61	19.4
3.0	12.0	14.2	0.27	10.9	13.5	4.08	10.8
5.0	7.12	20.3	0.00	10.6	17.4	3.54	6.83
7.0	0.23	23.4	0.00	2.22	25.3	0.38	10.4
10	1.03	24.1	0.00	0.37	25.4	0.08	15.5

a) Weight ratio of catalyst ($\text{ZrO}_2\text{-FeO}_x$) to feed rate of glycerol in crude glycerol solution.

b) Unidentified hydrocarbons detectable by GC.

Table 3 Compositions of Produced Aldehydes, Carboxylic Acids and Ketones

W/F [h]	Composition of aldehyde and carboxylic acids [mol%-carbon]				Composition of ketones [mol%-carbon]		
	Acetaldehyde	Acetic acid	Propionic acid	Isobutyric acid and butyric acid	Acetone	Methyl ethyl ketone	Pentanone
0.0	66.3	0	33.7	0	100	0	0
1.5	28.4	16.3	40.6	14.7	39.7	52.0	8.3
2.0	25.9	16.8	40.0	17.3	45.3	45.4	9.3
3.0	29.2	0	56.3	14.5	41.4	52.3	6.3
5.0	31.4	13.6	44.2	10.8	48.1	46.6	5.3
7.0	48.2	0	51.8	0	40.7	52.7	6.6
10	100	0	0	0	44.8	47.8	7.4

Table 4 Yields of Major Products and Conversion after the Reactions of Model Compounds

Model compound (reaction conditions)	Conversion [mol%-carbon]	Product yields [mol%-carbon]											
		Allyl alcohol	Propylene	Hydroxyacetone (Acetol)	Carboxylic acids			Ketones			Acrolein	Others	Undetectable by GC
					Acetic acid	Propionic acid	Other acids	Acetone	Methyl ethyl ketone	Pentanone			
Hydroxyacetone (Acetol) (10 wt%, W/F = 1.0 h)	79.5	0.00	0.03	20.5	4.15	16.8	1.06	10.0	1.25	1.68	0.00	10.1	30.4
Allyl alcohol (10 wt%, W/F = 10 h)	99.1	0.90	59.7	0.00	0.60	0.26	0.04	2.45	1.50	0.24	2.80	2.61	13.6
Acrolein (10 wt%, W/F = 1.7 h)	57.5	0.00	0.06	0.00	0.00	0.00	0.00	0.21	0.05	0.00	42.5	1.62	52.9

Reaction conditions: $\text{ZrO}_2(7)\text{-FeO}_x$, reaction time = 2 h.

glycerol in water. In catalytic conversion using the iron oxide catalysts, the major final products are propylene and ketones obtained by increasing the amount of the catalyst. Propylene is simply separated from the system as a gaseous product, and ketones are easily separated by distillation. Accordingly, the conversion of crude glycerol over iron oxide catalysts would be effective as part of the biomass-refinery process.

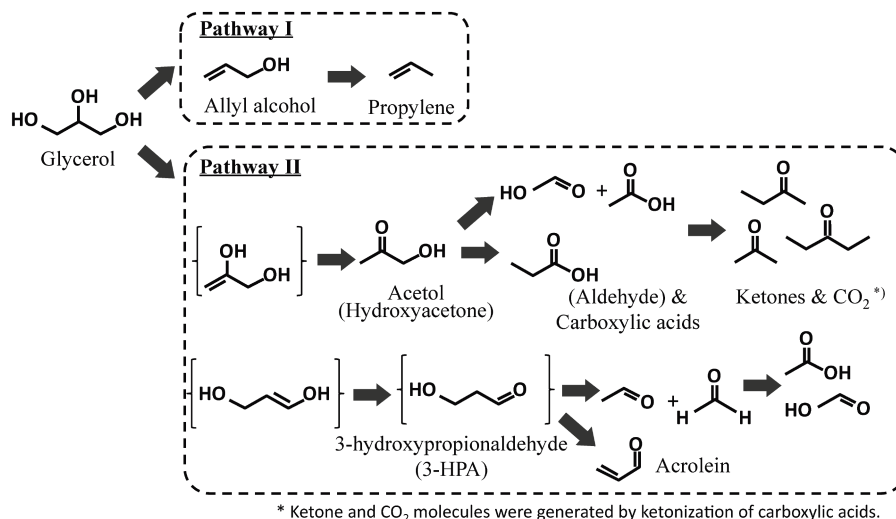
The reaction pathways were investigated by catalytic reactions using model compounds. Table 4 lists the model compounds and yields of the main products after reaction over $\text{ZrO}_2(7)\text{-FeO}_x$. Acetol (hydroxyacetone), formed by dehydration of glycerol, was mainly converted to carboxylic acids and ketones. Carboxylic acids are selectively converted into ketones over $\text{ZrO}_2\text{-FeO}_x$ ¹⁹, in which two molecules of carboxylic acids react to produce one molecule of ketone and CO_2 . Therefore, carboxylic acids and ketones were considered to be consecutively produced from acetol over the catalyst. Moreover, the products obtained from acetol conversion were almost the same as the products listed in Tables 2 and 3. Accordingly, acetic and propionic acids were produced directly from glycerol, whereas butyric acid was probably produced by the reaction of propionic acid and methylene radical, which was produced by ketonization. Acetone was produced from two molecules of acetic acid through ketonization, and methyl ethyl ketone and pentanone were produced by ketonization of “acetic acid and propionic acid” and “two molecules of propionic acid,” respectively^{19),24)}.

Allyl alcohol was selectively converted into propylene, whereas the conversion of acrolein was relatively low compared with that of acetol and allyl alcohol. These results are in good agreement with the results shown in Fig. 6. The hydroxyl group of allyl alcohol was presumably dehydrated to form propadiene on the acid sites of the catalyst, then immediately hydrogenated to produce propylene. Based on the results shown in Fig. 6 and Table 4, the expected reaction routes of glycerol over $\text{ZrO}_2\text{-FeO}_x$ are shown in Fig. 7. Two main reaction pathways are considered to occur: formation of carboxylic acids from acetol followed by ketonization, and formation of allyl alcohol and propylene. Moreover, possible reaction routes to produce formic acid are shown in Fig. 7, which will be discussed later.

4. Conversion of Glycerol into Allyl Alcohol and Reaction Mechanism

4.1. Alkaline Metal-loaded $\text{ZrO}_2\text{-FeO}_x$ Catalyst for Production of Allyl Alcohol²⁷⁾

In our previous study, catalytic reactions of organic-containing water solutions (pyroligneous acid) derived from the slow pyrolysis of cedar woodchips were carried out using $\text{ZrO}_2\text{-FeO}_x$ catalyst¹⁹⁾. $\text{ZrO}_2\text{-FeO}_x$ catalyst has high activity for the selective production of ketones (acetone and 2-butanone) from pyroligneous acid. However, the presence of metal impurities such as K and Mg in the pyroligneous acid inhibits the catalytic activity for oxidation of hydrocarbons with heavy

Fig. 7 Expected Reaction Pathways for Glycerol over $\text{ZrO}_2\text{-FeO}_x$ Table 5 Product Yields Obtained for Different Alkali Metal-supported $\text{ZrO}_2\text{-FeO}_x$

Alkaline metal on $\text{ZrO}_2\text{-FeO}_x$	Glycerol conversion [%]	Yield in Pathway I [mol%-carbon]		Yield in Pathway II [mol%-carbon]			
		Allyl alcohol	Propylene	Hydroxyacetone (Acetol)	Carboxylic acids and aldehyde	Ketones	Acrolein
-	100	13.7	5.9	1.2	24.8	9.2	6.3
Na	100	20.2	4.3	0.2	16.4	9.7	4.8
K	98.8	20.7	4.4	2.1	16.5	8.1	3.9
Rb	100	19.6	4.8	0.0	14.8	11.7	3.6
Cs	99.8	19.7	4.4	1.0	16.7	10.4	3.2

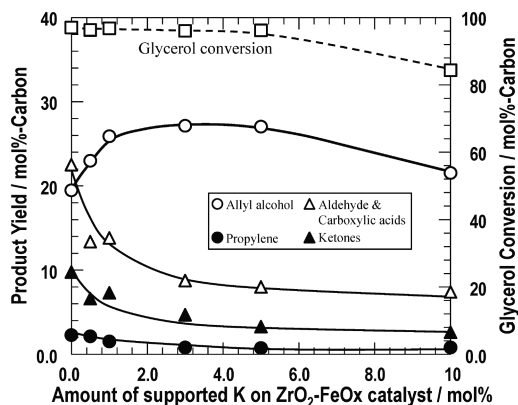
Reaction conditions: 30 wt% glycerol solution, alkali metal-supported $\text{ZrO}_2\text{-FeO}_x$, $W/F = 3$ h, reaction time = 6 h.

molecular weight as well as ketonization. In the bio-diesel fuel production process, alkali metals such as sodium (Na) or potassium (K) hydroxides are used as catalysts in the transesterification reaction. Therefore, crude glycerol derived from biodiesel fuel production process contains these alkali metal ions³⁶, as shown in **Fig. 1**. In the catalytic conversion of crude glycerol, these alkali metal ions deposit on the catalyst surface. Accordingly, the effect of loading of alkali metal on product yields was investigated.

$\text{ZrO}_2\text{-FeO}_x$ and Na-, K-, Rb-, and Cs-supported $\text{ZrO}_2\text{-FeO}_x$ were used to convert reagent glycerol solution (30 wt%) for 6 h at W/F of 3 h. **Table 5** shows the product yields of Pathway I (allyl alcohol and propylene) and Pathway II (acetol, carboxylic acids, ketones and acrolein) obtained using $\text{ZrO}_2\text{-FeO}_x$ and different alkali metal-supported $\text{ZrO}_2\text{-FeO}_x$ catalysts with alkaline metal content of 1.0 mol% based on the total amount of Zr and Fe. In our previous research concerning conversion of pyrolygneous acid solution using $\text{ZrO}_2\text{-FeO}_x$, the decrease in catalytic activity was observed due to the deposition of alkaline metals on the catalyst¹⁹. In contrast, almost complete glycerol conversions were obtained for $\text{ZrO}_2\text{-FeO}_x$ and all alkali metal-supported $\text{ZrO}_2\text{-FeO}_x$ catalysts. Moreover, ad-

dition of alkaline metals on the catalyst affected the product yields. $\text{ZrO}_2\text{-FeO}_x$ catalyst yielded approximately 20 mol%-carbon *via* Pathway I and 42 mol%-carbon *via* Pathway II. In comparison, all alkali metal-supported $\text{ZrO}_2\text{-FeO}_x$ catalyst showed higher product yields *via* Pathway I (25 mol%-carbon), and remarkably lower product yields *via* Pathway II (30 mol%-carbon). Interestingly, the allyl alcohol yield considerably increased from 13.7 mol%-carbon to approximately 20 mol%-carbon.

K was selected for further studies from all the alkali metals investigated, because KOH is commonly used as a catalyst for bio-diesel fuel production. The effect of K content on the dehydration of glycerol was studied. $\text{K}[Z]/\text{ZrO}_2\text{-FeO}_x$, where K content Z varied from 0 to 10 mol%, was used to convert 30 wt% glycerol solution for 2 h at W/F of 1 h. **Figure 8** shows the glycerol conversions and the yields of typical products obtained for $\text{K}[Z]/\text{ZrO}_2\text{-FeO}_x$ ($Z = 0\text{-}10$ mol%). The glycerol conversions were higher than 96 % with K content of 0-5 mol% and higher K content caused only a moderate drop in the conversion down to 84 %. Furthermore, addition of K caused drastic decreases in the acetol, carboxylic acid, ketone, and aldehydes yields, and this trend was greater at higher K content. On the other



Reaction conditions: 30 wt% glycerol solution, K[Z]/ZrO₂-FeO_x (Z = 0-10 mol%), W/F = 1 h, reaction time = 2 h.

Fig. 8 Effect of K Content on the Product Yields

hand, increasing the K content of ZrO₂-FeO_x to 3-5 mol% resulted in a remarkable increase in allyl alcohol yield up to 27 mol%-carbon. Alkaline metals contained in crude glycerol will be deposited on the surface of ZrO₂-FeO_x catalyst during the crude glycerol conversion. While the product composition depended on the amount of K on the catalyst, as shown in Fig. 8, useful chemicals involved in Pathways I and II could be produced. In addition, glycerol dehydration (Pathway II) and allyl alcohol dehydration were effectively suppressed by the addition of K.

Since glycerol dehydration is considered to proceed on the acid sites of catalysts, its suppression should result from decreased acidity of the catalyst, which could be confirmed by temperature-programmed desorption of ammonia (NH₃-TPD) profiles as shown in Fig. 9. Desorption of NH₃ from the catalyst was observed, indicating that acid sites for dehydration of glycerol were present. The amount of desorbed NH₃ decreased significantly with higher K content, which in turn resulted in further decreases in the acidity of the catalyst. Additionally, the peak position of the NH₃-TPD profile was shifted to a lower temperature at higher K content. These results indicated that the acidity of ZrO₂-FeO_x was reduced by the addition of K, leading to suppression of the glycerol dehydration.

4.2. Reaction Mechanism

Useful chemicals related to Pathways I and II were obtained in accordance with the dehydration of glycerol over the ZrO₂-FeO_x catalyst, as shown in Figs. 6 and 7. On the other hand, the hydroxyl groups exhibiting acidic properties were neutralized by K ions over the ZrO₂-FeO_x catalyst, as shown in Fig. 9. However, since significant amounts of the dehydration products (hydroxyacetone, carboxylic acid and acrolein) were still obtained, acidic sites must have persisted on the catalyst surface for the glycerol dehydration to proceed. Moreover, the yield of products in Pathway I increased

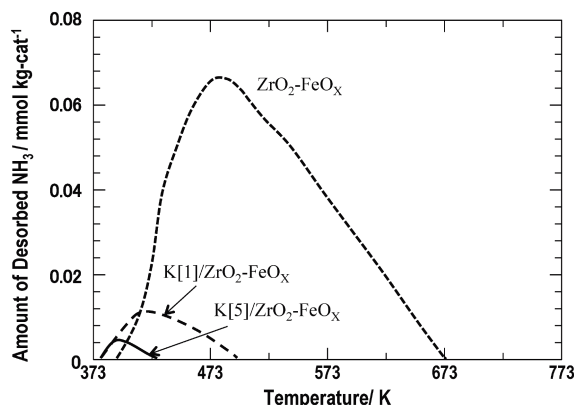


Fig. 9 NH₃-TPD Profiles for ZrO₂-FeO_x, K[1]/ZrO₂-FeO_x, and K[5]/ZrO₂-FeO_x

in the glycerol conversion over K/ZrO₂-FeO_x catalyst. Accordingly, glycerol dehydration over K/ZrO₂-FeO_x catalyst must take place on newly formed hydroxyl groups, possibly due to the partial reduction of Fe(III) to Fe(II), which are the catalytic sites to produce allyl alcohol (Pathway I). In fact, a change in the crystal phase from hematite to magnetite was observed after glycerol conversion as shown in Fig. 2(b).

Considering the fact that no external hydrogen is added to the system, the reduction of iron oxide must involve the reaction intermediates and the iron oxide surface. To confirm this, aqueous glycerol solution with acetol, acrolein, acetic acid, or formic acid aqueous solutions were pumped through the reactor at W/F of 3 h, where *F* and *W* are the feed rate of glycerol solution and the weight of K[5]/ZrO₂-FeO_x catalyst, respectively. The effects of addition of these intermediates on the propylene and allyl alcohol yields (Pathway I) are shown in Table 6. Addition of acrolein or acetic acid did not increase the allyl alcohol yield. In contrast, addition of acetol slightly increased the allyl alcohol yield, whereas addition of formic acid definitely increased the allyl alcohol yield to 33 mol%-carbon.

Since Pathway I was enhanced during glycerol conversion over the K/ZrO₂-FeO_x catalyst without addition of formic acid, formic acid must be formed during the glycerol conversion. There are two possible ways to produce formic acid in Pathway II. Firstly, glycerol can be dehydrated to form the unstable intermediate 3-hydroxypropionaldehyde (3-HPA). 3-HPA can further dehydrate to produce acrolein, but can also form acetaldehyde and formaldehyde through a reversed aldol condensation²⁸⁾, followed by oxidation of formaldehyde with the lattice oxygen of FeO_x to form formic acid. Secondly, acetol formed from glycerol dehydration can further react to give acetic acid and formic acid. Acetol can also isomerize to form propionic acid³⁷⁾. Formic acid can further decompose into CO₂

Table 6 Propylene and Allyl Alcohol Yields and Hydrogen Selectivity for the Reactions of Glycerol after Addition of Different Intermediates

Catalyst	K[5]/ZrO ₂ (7)–FeO _x						K[5]/Al ₂ O ₃ (7)–FeO _x	
	Feed	Glycerol	Glycerol and hydroxyacetone (30 wt%)	Glycerol and acrolein (20 wt%)	Glycerol and acetic acid (20 wt%)	Glycerol and formic acid (30 wt%)	Glycerol and formic acid (50 wt%)	Glycerol and formic acid (30 wt%)
Propylene yield [mol%-carbon]	0.6	1.3	1.1	1.0	1.1	1.1		12.9
Allyl alcohol yield [mol%-carbon]	25.4	28.4	23.6	26.7	33.4	35.9		30.2
Total yield in Pathway I [mol%-carbon]	26.0	29.7	24.7	28.8	34.5	37.0		43.1
Hydrogen yield ^{a)} [mol%]	4.1	2.1	3.4	2.1	18.5	25.0		15.5

a) Yield of generated hydrogen gas based on total hydrogen atoms contained in feedstock.

Reaction conditions: K[5]/ZrO₂-FeO_x and K[5]/Al₂O₃-FeO_x, W/F = 3 h, reaction time = 2 h.

and H₂ over a catalyst, and hydrogen atoms are formed during this process³⁸⁾. Gaseous hydrogen molecule yield based on the total hydrogen atoms contained in the feed stock (*e.g.* eight and two hydrogen atoms per glycerol and formic acid molecule, respectively) are listed in **Table 6**. Interestingly, hydrogen gas was generated during glycerol conversion without external addition of the intermediates and formic acids. Moreover, addition of formic acid enhanced the generation of hydrogen gas. Therefore, hydrogen atoms on the catalyst surface may participate in the reduction of iron oxide and production of allyl alcohol from glycerol, and others are generated as H₂ gas, as listed in **Table 6**.

Hydrogen atoms derived from formic acid are apparently important in our current reaction system and the reduction of iron oxide from Fe(III) to Fe(II) probably forms OH groups on the catalyst surface. A possible reaction mechanism on the iron oxide surface is illustrated in **Fig. 10**. In the K/ZrO₂-FeO_x catalyst, the hydroxyl groups exhibiting the acidic properties are neutralized by K ions before initiation of reaction as shown in **Fig. 9**. After glycerol conversion starts, the hydrogen atoms are produced mainly by formic acid, which was formed by decomposition of the intermediates in glycerol conversion. Then, iron oxide (Fe(III)) is reduced by hydrogen to form Fe(II) and a hydroxyl group on Fe(III) [(i) in **Fig. 10**], which adsorbs the glycerol molecule [(ii) in **Fig. 10**]. Dehydration and extraction of the hydroxyl groups of glycerol simultaneously occur to form allyl alcohol [(iii) in **Fig. 10**]. On the other hand, if only dehydration of glycerol occurs, acetol and acrolein are formed in accordance with Pathway II.

The effects of the amount of formic acid added to the reaction system on the product yield related to Pathway I (allyl alcohol and propylene) are summarized in **Table 6**. Larger amounts of formic acid increased the yield of products related to Pathway I. Moreover, using K/Al₂O₃-FeO_x catalyst, the yield reached approximately 43 mol%-carbon. These results indicate that the num-

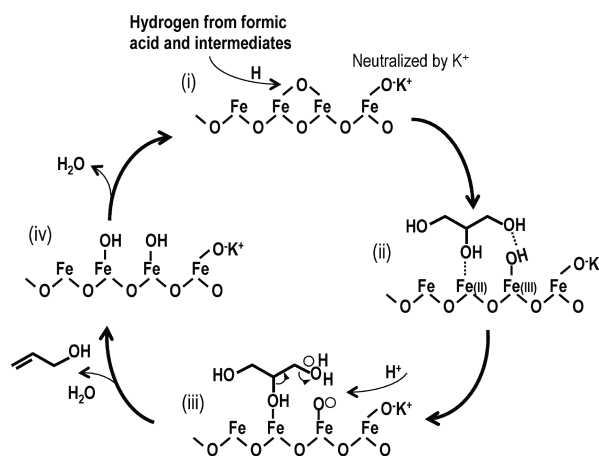


Fig. 10 Possible Reaction Mechanism for Allyl Alcohol Formation from Glycerol over Iron Oxide-based Catalyst

ber of dehydration/adsorption sites increased with higher concentration of hydrogen atoms on the catalyst. The active sites for allyl alcohol production from glycerol on the K/Al₂O₃-FeO_x catalyst were formed efficiently by addition of formic acid.

As discussed above, since the hydroxyl groups exhibiting acidic properties are neutralized by K ions in the iron oxide catalyst, addition of ZrO₂ and Al₂O₃ inhibits the sintering of iron oxide to preserve high surface area of the catalyst. During glycerol conversion, the hydrogen atoms are produced mainly by formic acid, so that iron oxide (Fe(III)) is reduced by hydrogen to form Fe(II) and a hydroxyl group on Fe(III). The dehydration of glycerol proceeds on these newly formed hydroxyl groups on the iron oxide surface, so that useful products are formed through Pathways I and II regardless of the deposition of alkaline metals during the reaction. Moreover, the newly formed active sites [Fe(III)-OH and Fe(II)] are active in the formation of allyl alcohol (Pathway I), leading to increased allyl alcohol yield. Further investigation of the activity of iron oxide including additives (ZrO₂ and Al₂O₃) and the

specific mechanism of allyl alcohol formation are still ongoing in our laboratory.

5. Conclusion

Catalytic conversion of glycerol was performed under nitrogen gas flow with different iron oxide-based catalysts. $\text{ZrO}_2\text{-FeO}_x$ successfully converted crude glycerol into useful chemicals such as propylene, allyl alcohol, carboxylic acids, and ketones. The catalytic activity and stability were improved by adding ZrO_2 to FeO_x and the optimum ZrO_2 content was found to be 7-27 wt%. Higher W/F value allowed the consecutive reactions to proceed and the final products were propylene and ketones.

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. All alkali metal-supported $\text{ZrO}_2\text{-FeO}_x$ catalyst gave considerably higher allyl alcohol yields and suppressed glycerol dehydration. K-supported $\text{ZrO}_2\text{-FeO}_x$ was selected for further studies regarding allyl alcohol yield. Higher K content increased the allyl alcohol yield up to 27 mol%-carbon and the yield of dehydration products drastically decreased. Glycerol dehydration proceeded on the acid sites of the catalysts, so allyl alcohol was presumably formed over the hydroxyl groups newly formed by reduction of iron oxide. Considering that no external hydrogen was added to the system, the hydrogen atoms were produced mainly by further reaction of formic acid, which was formed by decomposition of the intermediates in glycerol conversion. External addition of formic acid was effective in increasing allyl alcohol yield. The maximum yields of products related to Pathway I (allyl alcohol and propylene) reached 43 mol%-carbon using $\text{K/Al}_2\text{O}_3\text{-FeO}_x$ catalyst.

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要 旨

酸化鉄系触媒によるグリセロールからの有用化学物質合成

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酸化鉄系触媒によるグリセロールからの有用化学物質合成を実施した。反応実験は反応温度 623 K, 常圧下, 固定床流通式反応器にて実施した。グリセロールからの有用化学物質転換反応では, 主にアリルアルコール, プロピレン, ケトン類が得られた。これらの有用化学物質は反応経路 I (アリルアルコール, プロピレン) と反応経路 II (ヒドロキシアセトン, アクロレイン) に従って生成し, 経路 II に含まれるヒドロキシアセトンは容易にカルボン酸へと転化し, カルボン酸のケトン化反応によりケトンへと転化された。W/F 値 (触媒量/供給原料比) を

増加させると, アリルアルコールからのプロピレン生成, およびカルボン酸からのケトン生成の各逐次反応が進行し, 生成物はプロピレン (収率約 24 mol%-Carbon) とケトン類 (収率約 25 mol%-Carbon) に収束した。また, アルカリ金属を触媒に添加することにより, アリルアルコールの収率が効果的に向上することを見出した。本論文では, 試薬グリセリン, および粗製グリセリンからの有用化学物質合成を報告するとともに, 触媒組成と反応条件が生成物収率に及ぼす影響を反応機構の観点から議論する。

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