1. Introduction

Biomass has attracted increasing interest as an alternative, renewable source of energy to counteract the depletion of fossil fuels. Biomass can be used as a chemical feedstock in various important commercial processes such as the production of biodiesel (fatty acid methyl esters), which typically involves transesterification of triglycerides from vegetable oils and animal fats with methanol, with glycerol as the major by-product. The by-product glycerol has low value due to the presence of impurities, so has prompted the development of technologies for effective use of biodiesel-derived glycerol waste.

Glycerol is a versatile platform chemical for the production of valuable C3 products via deoxygenation reactions. Generally, glycerol deoxygenation can proceed via two pathways, as shown in Fig. 1. Pathway I involves dehydroxylation reaction, also called deoxydehydration, which removes adjacent OH groups to give allyl alcohol and propylene. Pathway II involves dehydroxylation to produce acrolein, acetol (hydroxyacetone), carboxylic acids, aldehydes and ketones, and alcohols in the presence of hydrogen. Allyl alcohol is considered to be one of most valuable among these products for use as raw materials of resins, paints, coatings, polymers, and drugs.

The dehydration reaction of glycerol proceeds over various solid acid catalysts, such as Nb$_2$O$_5$, heteropolyacids, and zeolites, whereas the deoxygenation reaction to propanediols proceeds over transition metal catalysts including Pt, Ru, Ir-ReO$_x$, and Pt-WO$_x$. In contrast, few studies have investigated the selective production of allyl alcohol. Re-based catalysts, such as ReO$_x$-Au and organometalic rhenium complex, Nb-Si-V, V*/BEA, Ag/zeolite, and iron-based catalysts such as FeO$_x$-ZrO$_2$, Fe/$\gamma$-Al$_2$O$_3$, Fe/ZSM-5, and MoFe/KIT-6 exhibit high activity for allyl alcohol production. However, a hydrogen source is required to allow the dehydroxylation reaction to obtain allyl alcohol. Allyl alcohol production from glycerol over Re-based
catalysts was performed in a batch reactor under pressurized hydrogen atmosphere, and 91 C-mol% of allyl alcohol yield was achieved over ReO$_x$-Au/CeO$_2$ catalyst at 413 K and 8 MPa of H$_2$. However, the reaction system required dioxane solvent and long reaction time. In contrast, iron-based catalysts were commonly used for gas-phase glycerol conversion without addition of hydrogen donor. Presumably the hydrogen produced in-situ via catalytic reforming of glycerol is used for dehydroxylation, which limits the allyl alcohol yield. Addition of hydrogen source or sacrificial reductant, such as NH$_3$, formic acid, and oxalic acid, to the reaction system is effective to enhance the allyl alcohol yield. The allyl alcohol yield from glycerol over iron-loaded $\gamma$-Al$_2$O$_3$ was increased by around 10 % by co-feeding formic acid and oxalic acid. Formic acid may assist allyl alcohol production by stoichiometric addition to glycerol to form allyl formate as an intermediate for allyl alcohol.

Iron-based catalysts are considered to be promising due to the cost effectiveness and abundance of raw material. Our research group has reported glycerol conversion over iron oxide-based catalysts containing zirconium, aluminum, and potassium with simultaneous production of other valuable chemicals, such as carboxylic acids, aldehydes, and ketones. We found that glycerol conversion occurred on the iron oxide surface, and zirconia and alumina are responsible for the dispersion of the iron oxide particles. A 27 C-mol% yield of allyl alcohol from glycerol was achieved using 5 mol% potassium-loaded ZrO$_2$-FeO$_x$ catalyst at 623 K and $W_{cat}/F_{glycerol}$ (mass of the catalyst (g)/mass feed rate of glycerol (g/h)) ratio of 3 h. However, the optimal catalyst properties, such as crystal structure, type of acid sites, and potassium loading have not yet been investigated. Moreover, our previous study found the selectivity for polymerization products exceeded 30 C-mol%, limiting the efficient conversion of glycerol. Therefore, minimization of this side reaction would improve glycerol conversion and facilitate practical applications.

The present study investigated the chemical and physical properties of iron oxide during glycerol conversion over potassium-loaded iron oxide catalyst without the addition of zirconium or aluminum. Oxidation state, acid site type, and acid site content of the iron oxide and potassium-loaded iron oxide catalysts were studied to understand the reaction mechanism. In addition, the effects of potassium loading, $W_{cat}/F_{glycerol}$ value (i.e., contact time), and reaction temperature were studied on polymerization during glycerol conversion over iron oxide-based catalysts to minimize the side reaction and achieve maximum allyl alcohol yield.

2. Experimental

2.1. Catalyst Preparation and Characterization

All reagents were purchased from Wako Pure Chemical Industries, Ltd., Japan. Fe$_3$O$_4$ and FeO were used as purchased, whereas $\alpha$-Fe$_2$O$_3$ was prepared by a precipitation method using Fe(NO$_3$)$_3$·9H$_2$O and 10 wt% ammonia solution. Fe(NO$_3$)$_3$·9H$_2$O 44 g was dissolved in distilled water 600 mL and ammonia solution was added with a tube pump to the vigorously stirred Fe(NO$_3$)$_3$·9H$_2$O aqueous solution until pH 7 was reached. The mixture was further stirred for 1 h, and the precipitate was recovered by filtration, dried at 383 K overnight, and calcined at 773 K for 2 h in air. Potassium was loaded by an incipient wetness impregnation method. An aqueous solution of KNO$_3$ at the required concentration and $\alpha$-Fe$_2$O$_3$ was mixed, dried at 383 K overnight, and calcined at 773 K for 2 h. The prepared catalysts were denoted as K[y]/$\alpha$-Fe$_2$O$_3$, where y is the mol% of potassium on the catalyst.

The Brunauer-Emmett-Teller (BET) surface area of the catalyst was estimated from the N$_2$ adsorption isotherm at 77 K measured by a Belsorp-mini High Precision Volumetric Gas Adsorption Analyzer (MicrotracBEL J. Jpn. Petrol. Inst., Vol. 62, No. 6, 2019
The amount of potassium loading and crystal structure of the catalysts were analyzed by X-ray fluorescence (XRF Supermini; Rigaku Corp., Japan) and X-ray diffraction (XRD) (MiniFlex 600; Rigaku Corp., Japan), respectively. The concentration of solid acid sites on the catalyst was measured by ammonia temperature-programmed desorption (NH₃-TPD) using a quadrupole mass spectrometer (BELmass; MicrotracBEL Corp., Japan) directly connected to a catalyst analyzer (BELcat; MicrotracBEL Corp., Japan). The sample preheated at 823 K was exposed to an argon stream containing 1% NH₃ for 30 min at 373 K. The sample preheated at 823 K was exposed to an argon stream at a rate of 10 K/min. During heating, the effluent gas was monitored by the mass spectrometer to determine the amount of NH₃ released. The nature of the acid sites was identified by Fourier transform infrared (FT-IR) spectroscopy of pyridine-adsorbed catalysts (FT/IR-4100; JASCO Corp., Japan). The catalyst was placed on a heating cell and preheated to 723 K. Next, a sufficient amount of pyridine was injected into the cell at 298 K, followed by evacuation at the same temperature to remove weakly adsorbed pyridine. Diffuse reflectance spectra were obtained with a spectrometer equipped with a mercury cadmium telluride detector with an accumulation of 64 scans at 4 cm⁻¹ resolution. The obtained infrared spectra were converted to the Kubelka-Munk function.

2.2. Catalytic Conversion of Glycerol

Catalytic conversion of glycerol was carried out in a stainless-steel fixed-bed flow reactor for 2 h at 573-648 K under atmospheric pressure. The iron oxide-based catalyst (0.064-1.92 g) was pelletized, sieved to a size of 300-850 μm, diluted with glass beads with the same particle diameter to unify the catalyst bed volume, and placed in the reactor. Nitrogen was supplied as a carrier gas at 20 cm³ (standard temperature and pressure)/min, and 30 wt% glycerol aqueous solution was injected with a microsyringe at 2.0 mL/h, to give a specific Wcat/Wglycerol value (0.1-3 h). In most experiments, 30 wt% formic acid aqueous solution was also supplied to the reactor at 2.0 mL/h with a microsyringe. The typical molar composition of the feed stream was glycerol : formic acid : water : nitrogen = 3 : 6 : 70 : 21.

During the reaction, the liquid and gaseous effluents were collected in an ice-cooled condenser and in a gas pack, respectively. The liquid products were analyzed by a gas chromatograph (GC) (GC-2014; Shimadzu Corp., Japan) equipped with a flame ionization detector (FID) and a DB-WAX capillary column (Agilent Technologies, Japan). The gaseous products were quantified by a GC (GC-8A; Shimadzu Corp., Japan) equipped with a thermal conductivity detector and an active carbon column, and a GC-FID (GC-8A; Shimadzu Corp., Japan) equipped with a Porapak Q column. Because CO₂ could be produced from both glycerol and formic acid, the decomposition of formic acid over the iron oxide based catalyst under the same reaction conditions as the glycerol conversion was performed to check the amount of CO₂ produced from formic acid. The amount of CO₂ produced from glycerol was then estimated by subtracting the amount of CO₂ observed in the formic acid decomposition from that obtained in the glycerol conversion. The undetectable products, labelled as "undetectable" in the following figures, were the components collected as liquid product but not observed by GC. We considered that the "undetectable" product consisted of the polymerized products of glycerol and other products. The product yield was estimated from the number of carbon atoms in the glycerol fed to the reactor.

3. Results and Discussion

3.1. Changes in Chemical and Physical Properties of Iron Oxide Catalyst during Glycerol Conversion

3.1.1. Effect of Hydrogen-source Addition on Product Yields

Addition of hydrogen is reported to promote dehydroxylation of glycerol to form allyl alcohol⁴¹,⁴²,⁴⁹,⁵⁴, so we examined the conversion of glycerol in the presence and absence of a hydrogen source. Molecular hydrogen and formic acid, which is easily decomposed into hydrogen and carbon dioxide, were chosen as hydrogen sources⁵⁹. A preliminary experiment tested the decomposition of formic acid over the potassium-loaded iron oxide catalyst and observed formic acid conversion of 95.7%. Therefore, formic acid could act as the hydrogen source under the reaction conditions used. The reaction was performed over potassium-loaded iron oxide catalyst at 623 K and Wcat/Wglycerol of 3 h for 2 h using three different feed compositions: (a) feed containing 30 wt% formic acid aqueous solution at 2 mL-liq/h, (b) feed containing hydrogen gas at 10 cm³/min, and (c) feed without a hydrogen source. Figure 2 shows that, as expected, the allyl alcohol yield was increased by the addition of a hydrogen source, and the highest yield was obtained in the presence of formic acid. The yield of allyl alcohol was improved in the presence of excess amount of formic acid via formation of allyl formate with glycerol⁴¹,⁴²,⁵³,⁵⁵. In this reaction system, reaction temperature was as low as 508 K⁴², residence time was as short as 6 min⁵³, and formic acid and allyl formate were observed after the reaction. In contrast, almost all formic acid was decomposed in our reaction system, and the large amount of water in our reaction system could suppress allyl formate production. Therefore, we considered that allyl alcohol production proceeded not via the reaction pathway of formic acid addition to glycerol to form the allyl formate but the reaction pathway in which hydrogen...
from the decomposition of formic acid was directly involved in allyl alcohol production. Assuming that formic acid in the feed was completely decomposed to hydrogen and carbon dioxide, the hydrogen production rate was estimated to be 4.9 cm³/min, which was half the hydrogen feed flow rate used in conditions (b). Thus, the difference in product yield was not due to the different hydrogen concentration but rather to the different production rate of hydrogen atoms on the catalyst. Using formic acid, hydrogen atoms were formed on the catalyst by decomposition, whereas using hydrogen gas, chemisorption on the catalyst surface followed by dissociation is required to form hydrogen atoms. Thus, the higher effectiveness of formic acid in producing allyl alcohol from glycerol could be attributed to the facile decomposition of formic acid. Therefore, in subsequent experiments, glycerol conversion was performed with the addition of formic acid to the feed.

3.1.2. Effect of Oxidation State of Iron Oxide

To identify the optimal oxidation state of iron oxide for allyl alcohol production from glycerol, the reaction was carried out in the presence of formic acid at 623 K and W_{cat}/F_{glycerol} of 1 h for 2 h using FeO, Fe₃O₄, and α-Fe₂O₃ catalysts. Figure 3 shows that glycerol conversion was 96.7 C-mol% and 85.2 C-mol% over α-Fe₂O₃ and Fe₃O₄, respectively, whereas only a small amount of glycerol reacted over FeO. The yields of products from Pathway I (i.e., allyl alcohol and propylene; Fig. 1) were almost the same for α-Fe₂O₃ and Fe₃O₄, whereas higher allyl alcohol yield of 25.7 C-mol% was obtained in the reaction over Fe₃O₄. The yields of products from Pathway II (i.e., aldehydes, carboxylic acids, ketones, and acrolein) were 40.1 C-mol% for α-Fe₂O₃ and 27.9 C-mol% for Fe₃O₄. These results suggest that although the specific product yields depended on the catalysts, almost the same products from Pathways I and II were observed with α-Fe₂O₃ and Fe₃O₄ catalysts.

To further understand the effect of the oxidation state of iron oxide on the outcome of the reaction, the XRD patterns of α-Fe₂O₃ were recorded before and after glycerol conversion, as shown in Figure 4. Notably, the crystal structure of α-Fe₂O₃ changed from hematite to magnetite during glycerol conversion, indicating that the α-Fe₂O₃ phase transformed into Fe₃O₄. Reduction of α-Fe₂O₃ to Fe₃O₄ was reported to proceed during the glycerol conversion in addition to the formic acid co-feeding and the aqueous solution of the reactant, respectively, at 623 K. To check whether the change in crystal structure of iron oxide occurred and activity was reached at steady-state, long-term reaction at larger W_{cat}/F_{glycerol} value was tested. Figure 5 shows the product yield of glycerol conversion over α-Fe₂O₃ in the presence of formic acid at 623 K and W_{cat}/F_{glycerol} of 3 h for 6 h. The product was collected for every 2 h and the product yield shown in Figure 5 was the average of each 2 h period. The product yield was almost stable throughout the 6 h reaction, so the change in crystal structure of iron oxide.

Fig. 2 Effect of Hydrogen Source on Product Yields of Glycerol Conversion

Reaction temperature: 623 K, reaction time: 2 h, W_{cat}/F_{glycerol}: 3 h, catalyst: K[5]/α-Fe₂O₃, feed: 30 wt% glycerol aqueous solution (a) with 30 wt% formic acid aqueous solution (2 mL-liq/h), (b) with hydrogen gas (10 cm³/min), and (c) without a hydrogen source.

Reaction temperature: 623 K, reaction time: 2 h, W_{cat}/F_{glycerol}: 1 h, feed: 30 wt% glycerol aqueous solution (2 mL-liq/h) and 30 wt% formic acid aqueous solution (2 mL-liq/h).

Fig. 3 Product Yields of Glycerol Conversion over Various Iron Oxide-based Catalysts with and without Potassium Loading
proceeded quickly. Therefore, the magnetite structure of both \( \alpha\text{-Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) was considered to be responsible for their high catalytic activities as well as the similar types of compounds produced from glycerol. The BET surface area of \( \alpha\text{-Fe}_2\text{O}_3 \) after glycerol conversion was 13.9 m\(^2\)/g, which was larger than that of \( \text{Fe}_3\text{O}_4 \) after glycerol conversion (3.2 m\(^2\)/g). Thus, the larger surface area of \( \alpha\text{-Fe}_2\text{O}_3 \) might be responsible for the higher conversion of glycerol than over \( \text{Fe}_3\text{O}_4 \).

### 3.1.3. Effect of Potassium Loading on Acidic Properties of Catalysts

Dehydration of glycerol over \( \alpha\text{-Fe}_2\text{O}_3 \) proceeded at a higher rate than over \( \text{Fe}_3\text{O}_4 \), resulting in higher yield of propylene and products derived from Pathway II and lower yield of allyl alcohol. To suppress excess dehydration, the effect of potassium loading on \( \alpha\text{-Fe}_2\text{O}_3 \) on product yield was investigated, which is known to affect the reactions over \( \text{Fe}_3\text{O}_4\text{-ZrO}_2 \) catalysts\(^8\). Reaction over 1 mol% potassium-loaded \( \alpha\text{-Fe}_2\text{O}_3 \) (K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \)) was performed in the presence of formic acid at 623 K and \( \text{W}_{\text{cat}}/\text{F}_{\text{glycerol}} \) of 1 h for 2 h, giving a glycerol conversion similar to that over \( \alpha\text{-Fe}_2\text{O}_3 \), as shown in Fig. 3. However, the allyl alcohol yield over K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \) increased to 41.0 C-mol%, and product yields derived from Pathway II decreased to 27.5 C-mol%. These changes in products yield were consistent with the previous reports\(^8,30\). These results suggest that potassium was located on the acid sites of the catalyst, resulting in reduced number of acid sites where Pathway II and dehydration of allyl alcohol to propylene occur. In contrast, conversion of glycerol over 1 mol% potassium-loaded \( \text{Fe}_3\text{O}_4 \) (K[1]/\( \text{Fe}_3\text{O}_4 \)) was smaller than that over \( \text{Fe}_3\text{O}_4 \) and the allyl alcohol yield was not significantly changed, resulting in improvement of allyl alcohol selectivity by potassium loading. On the other hand, the ratio of product from Pathway I to that from Pathway II over K[1]/\( \text{Fe}_3\text{O}_4 \) was still smaller than that over K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \). Therefore, both the potassium loading and structure change during glycerol conversion were effective for the selective production of allyl alcohol.

To evaluate the effect of potassium loading on the catalyst properties, the crystal structure was investigated. The XRD spectra of the potassium-loaded iron oxide catalysts before and after glycerol conversion in Fig. 4, similar to the catalysts without potassium, showed that K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \) transformed into magnetite after glycerol conversion. Potassium loading does not generally affect the crystal structure of the catalyst, so the structure change occurred at a later stage. To elucidate the change in acid site concentration during the reaction over K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \) in the presence of formic acid, NH\(_3\)-TPD measurement of the iron oxide catalysts was performed. Figure 6(a) depicts the NH\(_3\)-TPD profiles of as-prepared \( \alpha\text{-Fe}_2\text{O}_3 \), K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \) before glycerol conversion, and K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \) after glycerol conversion. The acid site amount, represented by the area of the TPD curve, was smaller than 0.01 mmol/kg-cat for all catalysts, so that quantitative evaluation was impossible. Therefore we focused on the qualitative change of the acid site amount. Desorption of NH\(_3\) was observed from 375 to 450 K for \( \alpha\text{-Fe}_2\text{O}_3 \) whereas little NH\(_3\) desorbed from K[1]/\( \alpha\text{-Fe}_2\text{O}_3 \), suggesting that potassium loading reduced the number of original acid sites in \( \alpha\text{-Fe}_2\text{O}_3 \). In contrast, desorption of NH\(_3\) was...
observed from 430 to 475 K for K[1]/α-Fe$_2$O$_3$ after glycerol conversion with the magnetite structure, suggesting that acid sites were newly formed during glycerol conversion. The NH$_3$ desorption curve of K[1]/α-Fe$_2$O$_3$ after glycerol conversion was different from that of the original α-Fe$_2$O$_3$, so the properties of the acid sites newly formed during glycerol conversion could be different from those of the original sites. Compared with the NH$_3$-TPD profiles of iron-loaded zeolite and potassium-loaded ZrO$_2$-FeO$_{x}$, NH$_3$ desorption from K[1]/Fe$_2$O$_3$ was observed at lower temperature, suggesting that K[1]/Fe$_2$O$_3$ possessed relatively weaker Brønsted acid sites than the other iron-based catalysts reported.

To investigate the properties of the acid site, FT-IR measurement of the pyridine adsorbed on the iron oxide catalysts was conducted. Figure 6(b) shows that the FT-IR spectrum of pyridine-adsorbed α-Fe$_2$O$_3$ included a large peak around 1445 cm$^{-1}$ corresponding to Lewis acid sites and a small peak around 1542 cm$^{-1}$ corresponding to Brønsted acid sites. Notably, all peaks disappeared for K[1]/α-Fe$_2$O$_3$, indicating that almost all acid sites on α-Fe$_2$O$_3$ disappeared after potassium loading. After glycerol conversion in the presence of formic acid, the peak corresponding to Brønsted acid sites appeared again. These observations were consistent with the NH$_3$-TPD data. The mechanism of the formation of Brønsted acid sites is not fully understood, but we considered that the Brønsted acid sites could be formed by hydroxyl groups on the surface of iron oxide, which is likely to contain iron atoms with different valences, and adsorption of protons produced from formic acid and water on the surface defects. Based on these results, the changes in acid properties for α-Fe$_2$O$_3$ catalyst could be explained as follows: potassium loaded on the acid sites of α-Fe$_2$O$_3$ decreased the number of acid sites; then, the crystal structure changed from α-Fe$_2$O$_3$ to Fe$_3$O$_4$ with concomitant formation of new Brønsted acid sites during glycerol conversion. Therefore, potassium-loaded α-Fe$_2$O$_3$ was preferable for allyl alcohol production for two main reasons: (a) the potassium atoms occupied the original Lewis acid sites where dehydration Pathway II occurred; and (b) new Brønsted acid sites were formed with the structural change from α-Fe$_2$O$_3$ to Fe$_3$O$_4$ due to the hydrogen produced from formic acid during glycerol conversion. Consequently, the following experiments used potassium-loaded α-Fe$_2$O$_3$ catalyst.

3.2. Selective Allyl Alcohol Production from Glycerol with Suppression of Polymerization

Higher yield of allyl alcohol was obtained from glycerol using the potassium-loaded α-Fe$_2$O$_3$ catalyst, but various products undetectable by GC, mainly derived from polymerization of glycerol and deoxygenation products, were still formed (21.3 C-mol%) (Fig. 3). Thus, suppression of the polymerization reaction is important for further enhancing the allyl alcohol yield. Alkali catalysts are known to promote polymerization of glycerol, so excess potassium loading favors the polymerization of glycerol over allyl alcohol production. Moreover, polymerization of the products proceeds subsequent to glycerol conversion, so excess con-
tact time also promotes polymerization. Additionally, the reaction temperature is an important factor controlling the selectivity of the dehydroxylation, dehydration, and polymerization reactions. Thus, the effects of potassium loading, amount of catalyst, and reaction temperature on the allyl alcohol yield were investigated.

3.2.1. Effect of Amount of Potassium Loading

The product yield of glycerol conversion in the presence of formic acid over α-Fe₂O₃ with various potassium loadings at \( W_{\text{cat}}/F_{\text{glycerol}} = 1 \) h for 2 h at 623 K is shown in Fig. 7. Using α-Fe₂O₃ catalysts with potassium loading \( > 1 \) mol%, the yield of allyl alcohol remained unchanged with higher potassium loading, whereas the yield of products derived from Pathway II monotonically decreased. The small effect of higher potassium loadings on allyl alcohol yield may result from the saturation of the acid sites of α-Fe₂O₃ with 1 mol% potassium. The yield of undetectable polymerization products slightly increased with higher potassium loading, suggesting that the polymerization reaction proceeded on potassium. Therefore, the optimal potassium loading for allyl alcohol production was 1 mol%, which was adequate to remove the acid sites of α-Fe₂O₃ as displayed in Fig. 6(a), and 1 mol% potassium-loaded α-Fe₂O₃ catalyst was used in the following experiments.

3.2.2. Effect of Contact Time (\( W_{\text{cat}}/F_{\text{glycerol}} \)) and Reaction Temperature

The effect of the contact time (\( W_{\text{cat}}/F_{\text{glycerol}} \)) on the product yield and selectivity was examined by performing the reaction over K[1]/α-Fe₂O₃ in the presence of formic acid at 623 K for 2 h using different amounts of catalyst with the \( W_{\text{cat}}/F_{\text{glycerol}} \) value ranging from 0.1 to 3 h. Figures 8(a) and 8(b) illustrate the product yield and selectivity of glycerol conversion, respectively, at different \( W_{\text{cat}}/F_{\text{glycerol}} \). Conversion of glycerol increased with higher \( W_{\text{cat}}/F_{\text{glycerol}} \), reaching almost 100% at \( W_{\text{cat}}/F_{\text{glycerol}} = 1 \) h. At this value, the selectivities for the products obtained via Pathway I, Pathway II, and polymerization were 39.8, 26.9, and 21.3 C-mol%, respectively. Interestingly, these selectivities remained constant for lower \( W_{\text{cat}}/F_{\text{glycerol}} \) values. Generally, the selectivity of each product is independent of the conversion of the reactant in parallel reactions. Therefore, our observation that the selectivity remained unchanged at different \( W_{\text{cat}}/F_{\text{glycerol}} \) values up to 1 h suggests that polymerization of glycerol proceeded in parallel with Pathways I and II at low \( W_{\text{cat}}/F_{\text{glycerol}} \) values. On the other hand, with the increase in \( W_{\text{cat}}/F_{\text{glycerol}} \) value from 1 to 3 h, the selectivity of the polymerization products
increased remarkably whereas those of the products derived from Pathways I and II decreased, indicating that polymerization of the products, such as allyl alcohol, acetol, and acrolein, occurred at high $W_{\text{cat}}/F_{\text{glycerol}}$ values. The allyl alcohol yield increased with higher $W_{\text{cat}}/F_{\text{glycerol}}$ values from 0.1 to 1 h but decreased with higher $W_{\text{cat}}/F_{\text{glycerol}}$ values from 1 to 3 h. The polymerization reaction is generally accepted to occur simultaneously during glycerol conversion \(^8\),\(^{31}\) but which compounds were dominant to the polymerization reactants remained unclear. We found that most polymerized products were formed directly from glycerol and the polymerization reaction and other reactions occurred in parallel at low contact time, and polymerization of the products was also observed at higher contact time. The highest allyl alcohol yield of 39.8 C-mol% was obtained at $W_{\text{cat}}/F_{\text{glycerol}} = 1$ h, at which conversion of glycerol reached 100 % and no excess undesired reaction occurred.

Pathway I, Pathway II, and the polymerization reaction were found to occur as parallel reactions, so we thought that the reaction temperature would affect the product selectivity. To test this hypothesis, glycerol conversion was performed in the presence of formic acid over K[1]/α-Fe$_2$O$_3$ at $W_{\text{cat}}/F_{\text{glycerol}}$ of 1 h for 2 h at temperatures of 573, 598, 623, and 648 K, and the results are shown in Figs. 9(a) and 9(b). Both yield and selectivity of allyl alcohol increased at higher reaction temperatures from 573 to 623 K, suggesting that the activation energy of Pathway I was higher than that of other reactions. Therefore, high reaction temperature was favorable for increasing both yield and selectivity of allyl alcohol. On the other hand, the yield of allyl alcohol decreased and the yield of undetectable products increased at higher reaction temperatures from 623 to 648 K, suggesting that the polymerization reaction was dominant at temperatures above 623 K. The highest allyl alcohol yield was achieved at 623 K, at which the rate of Pathway I was higher than that of Pathway II, and the polymerization reaction was limited.

From these results, the optimal reaction conditions for allyl alcohol production from glycerol were determined to be: 1 mol% potassium-loaded α-Fe$_2$O$_3$ catalyst; $W_{\text{cat}}/F_{\text{glycerol}}$ value of 1 h; and reaction temperature of 623 K. Under these conditions, the allyl alcohol yield reached 39.8 C-mol%, the yield of Pathway II was 26.9 C-mol%, and the yield of polymerization products was 21.3 C-mol%. The allyl alcohol yield obtained in this study was greater than previously reported glycerol conversion over iron-based catalysts as follows: allyl alcohol yield was 11.6 C-mol% over Rb containing Fe loaded γ-alumina at $W_{\text{cat}}/F_{\text{glycerol}} = 0.3$ h and at 613 K\(^{30}\), 19.5 C-mol% over Fe/γ-Al$_2$O$_3$ at $W_{\text{cat}}/F_{\text{glycerol}} = 0.3$ h and at 613 K\(^{29}\), 26.8 C-mol% over Mo–Fe loaded zeolite at $W_{\text{cat}}/F_{\text{glycerol}} = 0.53$ h and at 613 K\(^{31}\), and 33.4 C-mol% over K/ZrO$_2$–Fe$_2$O$_3$ catalyst at $W_{\text{cat}}/F_{\text{glycerol}} = 3$ h and at 623 K in our previous study\(^8\). We considered that the higher yield of allyl alcohol was obtained due to optimization of the reaction conditions and using iron-oxide catalysts without metal oxide supports with stronger Brønsted acid sites than magnetite.

4. Conclusion

Selective production of allyl alcohol from glycerol over iron oxide-based catalyst was studied. The yield of allyl alcohol increased using potassium-loaded iron oxide with formic acid added to the glycerol feed. The potassium atoms occupied the Lewis acid sites of α-Fe$_2$O$_3$, and formic acid caused the reduction of iron oxide from hematite to magnetite during glycerol conversion with the formation of Brønsted acid sites, resulting in an increased yield of allyl alcohol.

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To further improve allyl alcohol production, the potassium loading on α-Fe₂O₃, contact time, and reaction temperature were optimized. Higher potassium loading from 0 to 1 mol% increased the allyl alcohol yield and decreased yield of dehydration products, suggesting that the number of Brønsted acid sites increased with fewer Lewis acid sites in the catalyst. On the other hand, potassium loadings higher than 1 mol% did not affect the allyl alcohol yield. Using contact time of <1 h, which gave incomplete glycerol conversion, allyl alcohol production, dehydration, and polymerization reactions were found to proceed simultaneously. In contrast, glycerol conversion at \( W_{\text{cat}}/F_{\text{glycerol}} \) values above 1 h resulted in increased polymerization. Moreover, the allyl alcohol yield increased with higher reaction temperature up to 623 K, whereas polymerization reaction was dominant above 623 K, resulting in lower yield of allyl alcohol and dehydration products.

The highest allyl alcohol yield of 39.8 C-mol% was achieved with glycerol conversion carried out in the presence of formic acid over 1 mol% potassium-loaded α-Fe₂O₃ catalyst at 623 K and \( W_{\text{cat}}/F_{\text{glycerol}} \) of 1 h.

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要 旨

酸化鉄触媒を用いたグリセリンからのアリアルアルコール選択合成反応系の最適化

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グリセリンはバイオディーゼル製造の主たる副生物であり、様々な有効化学原料の前駆体として注目を集めている。本研究では、固定床流速反応系においてα-Fe₃O₄触媒を用いたグリセリン転換を実施し、アリアルアルコール選択合成に対する酸化鉄系触媒の活性を評価した。グリセリンにジ酸を供給することで、グリセリン転換反応中にジ酸分解により生成した水素がα-Fe₃O₄をFe₃O₄に還元するとともにグリセリン脱ビドロキシル反応の水素源として利用され、高いアリアルアルコール収率を実現した。また、α-Fe₃O₄にカリウムを担持することで、アリアルアルコール収率が増加した。これは、α-Fe₃O₄の持つLewis酸点が担持したカリウムにより抑制され、反応中にFe₃O₄に還元されることでBronsted酸点が形成したためであることを示した。さらなるアリアルアルコール収率向上を目指し、カリウム担持量、接触時間（WHSV/Fe₃O₄）、反応温度による固定生成物の抑制を実施した。カリウム担持量1 mol%、接触時間1時間、反応温度623 Kにおいて、最大アリアルアルコール収率39.8 C-mol%を達成した。