

Unique Approach for Transforming Glucose to C3 Platform Chemicals Using Metallic Iron and a Pd/C Catalyst in Water

Yoshiaki Hirano,* Yuka Kasai, Kunimasa Sagata, and Yuichi Kita

Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University,
1-1 Rokkodaicho, Nada-ku, Kobe, Hyogo 657-8501

E-mail: hirano@phoenix.kobe-u.ac.jp

Received: April 1, 2016; Accepted: June 1, 2016; Web Released: June 8, 2016



Yoshiaki Hirano

Yoshiaki Hirano received his M.E. degree from the Tokyo Institute of Technology in 1995. In 1995, he joined Nippon Shokubai Co., Ltd. He received his Master of Management of Technology degree (2010) from the Tokyo University of Science. In 2012, he moved to the endowed chair "Sustainable Chemistry" (Nippon Shokubai), established in the Department of Chemical Science & Engineering at Kobe University as an Assistant Professor. His research focuses on practical utilization technologies for renewable biomass resources to create new industrial fields by sustainable chemistry.

Abstract

In the utilization of biomass for fuels and chemicals, the key reactions involved are hydrogenolysis and deoxygenation using hydrogen. Unfortunately, the industrial use of molecular hydrogen is limited because of various drawbacks, such as high cost and considerable hazards associated with high-pressure operation. In this study, a unique chemical manufacturing process was proposed for inducing the hydrogenolysis and deoxygenation of biomass carbohydrates using hydrogen generated in situ from the reaction between metallic iron and water. From the results obtained, hydrogen generated in situ by metallic iron particles (hydrogen-generating agent) combined with a carbon-supported palladium catalyst (hydrogenation catalyst) transforms glucose to C3 platform chemicals, such as propylene glycol, hydroxyacetone, and lactic acid. Moreover, reaction conditions and mechanism were also evaluated. With the use of the proposed system, value-added chemicals were produced from biomass carbohydrates by using renewable sources of energy (such as hydrogen generated from the reaction between iron and water) without the complete dependence on fossil resources.

1. Introduction

For several industries, biomass carbohydrates are the most abundant sustainable resources of both energy and organic carbon. Since the last decade, because of the depletion of fossil resources as well as concerns surrounding greenhouse gas emissions, biomass has been rapidly utilized for the production of transportation fuels and value-added chemicals.^{1–4} In most cases, biomass has been utilized in three methods: power generation, thermochemical conversion (gasification or liquefaction), and biological conversion.

Carbohydrates, such as sugars, starch, cellulose, and hemicellulose, have an empirical formula of $C_m(H_2O)_n$ (where m can be different from n) and high oxygen content. For making them suitable for use as fuels and chemicals, it is necessary to decrease the oxidation state of biomass-derived materials via key reactions such as hydrogenolysis or deoxygenation,^{5,6} which result in the cleavage of C–C and C–O bonds by hydrogen or the removal of oxygen atoms from a molecule. For instance, the use of noble- or transition-metal catalysts has been reported for the conversion of carbohydrates, such as glycerol, glucose, sucrose, sorbitol, and cellulose, to various polyols.⁶

Nevertheless, these methods still exhibit various drawbacks, such as high cost, considerable hazards associated with high-pressure operation, low efficiency of hydrogen resulting from undesired side reactions, significant dependence on fossil resources, requirement for high-energy-intensive processes, and geographical constraints associated with hydrogen storage and transportation. In this regard, a number of methods have been proposed and intensively developed for the sustainable production of hydrogen: electrolysis of water using surplus power from natural resources (photovoltaics, hydraulic power, and wind power);^{7–9} thermolysis and photolysis of water by solar energy;^{7–9} thermochemical and biological conversion of biomass (gasification, pyrolysis, and fermentation);^{7–9} chemical looping of metals or using a metal oxide redox system, which is commonly referred to as the steam iron process.^{10,11} Zero-valent metals, such as Ge, Mo, W, Fe, Co, Ni, Cu, Zn, Al, Mn, as well as their oxides, have been previously investigated, and promising results have been demonstrated for the production of hydrogen by thermal water splitting.^{12–15}

A number of studies have been reported on reduction, hydrogenation, and hydrogenolysis using hydrogen generated in situ. For example, encouraging results have been observed in previously reported studies on the use of iron and zinc for the

reduction of organic and inorganic compounds such as nitroarenes,^{16,17} aryl chlorides,^{18,19} aldehydes,²⁰ and chlorinated hydrocarbons.²¹ Recently, Jin and co-workers have reported that CO₂ is reduced to formic acid or methanol by hydrogen generated in situ by the oxidation of metal powder (such as Fe, Zn, Al, and Mn) in water.^{22–27} In addition, they have reported a series of experiments on the conversion of biomass-derived materials to value-added chemicals under similar conditions.^{28–31} Feng and co-workers have reported the reduction of CO₂ to formic acid, acetic acid, and phenol with water in the presence of iron nanoparticles under mild hydrothermal conditions.^{32,33} Moreover, ever since Dumesic and co-workers demonstrated that hydrogen can be produced from sugars and alcohols using a platinum-based catalyst in water,³⁴ aqueous-phase reforming (APR)^{35–39} and catalytic-transfer hydrogenation (CTH)^{37,40–42} using hydrogen donor molecules have been investigated as efficient technologies for hydrogenation through the in situ generation of hydrogen for converting biomass-derived carbohydrates and bio-oil to fuels and chemicals. However, APR and CTH are hypothesized to exhibit disadvantages in terms of carbon efficiency, attributed to the consumption of a raw-material substrate or a hydrogen donor. More recently, some reduction and hydrogenation or hydrogenolysis reaction systems with CO and water have been employed as a source of hydrogen for the reduction of nitro compounds,⁴³ alkynes,⁴⁴ aldehydes,⁴⁵ and carboxylic acids,⁴⁶ and for the conversion of cellulose.⁴⁷

In this study, a unique chemical manufacturing process was proposed, which induces the hydrogenolysis and deoxygenation of biomass carbohydrates using hydrogen generated in situ via the chemical looping of a metal oxide redox. Typically, chemical looping occurs because of reduction and oxidation. As iron exhibits an advantage with respect to the thermodynamics of reactions conducted in water,¹⁴ as well as reduction starting from iron oxide,¹⁵ which is one of the most abundant metals on earth; it is the most promising material for producing hydrogen. A method well known for obtaining hydrogen from metallic iron and water, referred to the steam iron process ($3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$), has long been employed. Hence, we select iron metal and iron oxides as materials for chemical looping. As shown in Figure 1, the proposed process involves two steps. In the first step, biomass carbohydrates are

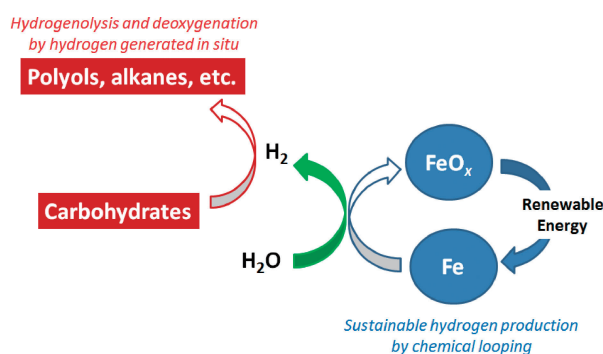


Figure 1. Hydrogenolysis by hydrogen generated in situ via the chemical looping of a metal oxide redox. FeO_x denotes iron oxide (divalent or trivalent), and Fe represents iron metal.

transformed to value-added chemicals (C2–C5 polyols and alkanes) via hydrogenolysis by hydrogen generated in situ from water, forming high-valence iron oxides (FeO_x). In the second step, the iron oxides can be reduced by a process powered by renewable sources of energy, such as solar thermal energy,^{48,49} solar hydrogen,^{12,13} reducing gas (CH₄, CO, H₂) from biomass gasification,^{50,51} and carbothermal reduction by biomass-derived tar or biomass itself.^{52–54}

In particular, it is possible to perpetuate the FeO_x redox cycle by using renewable energy. This new proposed process differs from conventional hydrogenation or reduction using pressurized hydrogen because it does not require an external hydrogen source. In addition, this method does not require high-purity and high-pressure hydrogen, and the supply of the hydrogen generated in situ prevents the consumption of energy for the production, storage, and transformation of hydrogen, as well as any hazardous risk involved with its handling. Thus, the hydrogen-free reaction system can be operated under mild pressure, resulting in improved, safer operation, as well as being cost-effective. Our proposed system could facilitate the sustainable production of industrial chemical products using renewable energy (in situ generation of hydrogen) from biomass carbohydrates as sustainable carbon resources without the dependence on fossil resources.

In this study, we demonstrated that the coexistence of metallic iron particles (hydrogen-generating agent) and a carbon-supported palladium catalyst (Pd/C, a hydrogenation catalyst) enables the transformation of glucose (a biomass-based carbohydrate) to C3 platform chemicals, such as propylene glycol (PG), hydroxyacetone (HA), and lactic acid (LA), using hydrogen generated in situ; PG,^{55–57} HA,^{58–60} and LA,^{61–63} examples of value-added products, are important chemicals for a wide range of applications in various industries, and recently, the development of novel chemical processes for their production from biomass has also attracted significant attention. Glucose (C₆H₁₂O₆) is the most abundant natural hexose, and it is of significance to directly synthesize C3 platform chemicals from glucose. We also demonstrated the reusability of our system via reuse experiments and evaluated reaction conditions and mechanism.

2. Experimental

2.1 Materials. All materials were purchased from commercial suppliers and used as received without any pretreatment or purification. Metallic iron particles with dimensions of 60–80 nm (NM-0019-UP, 99.9%); 5–9 μm (93-2601, 99.9%); and 75 μm (00737, 200 mesh, 99+%) were purchased from Ionic Liquids Technologies GmbH, Germany; Strem Chemicals, Inc., USA; and Alfa Aesar, UK; respectively. A carbon-supported 5 wt % palladium catalyst (Pd/C) was obtained from N. E. ChemCat Corporation, Japan. Glucose, fructose, HA, PG, glycerol, LA, 1,2-butanediol, 1,2-hexanediol, glycolic acid, and acetic acid of special grade were acquired from Wako Pure Chemical Industries, Ltd., Japan. Calibration standard gases were purchased from GL Sciences Inc., Japan.

2.2 Reaction Apparatus and Procedure. Experiments were conducted in a 64 mL stainless-steel autoclave (TSV-1, Taiatsu Techno Corporation, Japan) or a 100 mL Hastelloy autoclave (MMJ-100, OM Lab-Tech Co. Ltd., Japan). In a typical

run using the 64 mL autoclave, 180 mg of glucose (1 mmol), 335 mg of Fe metal particles (6 mmol), 30 mg of the 5 wt % Pd/C catalyst (Pd, 15 μ mol), and 36 mL of ultrapure water were loaded into the autoclave under anaerobic conditions. Second, the reactor was purged with nitrogen three times for expelling air, pressurized with 0.5 MPa of nitrogen, and heated to the designated temperature, which was maintained constant for the duration of the intended reaction, with stirring at 600–720 rpm. The temperature inside the reactor was monitored using a thermocouple. Approximately 30 min was required to reach the desired temperature, and approximately 1 h was required to cool the reaction vessel. “Reaction time” indicates the time between attaining the intended temperature and the beginning of cooling. For reuse experiments, the catalysts were collected by filtration and washed several times with water. Before the reuse experiments, the recovered catalysts were reduced in a flow apparatus with pure hydrogen (40 cm³ min^{−1}) at 723 K for 4 h, followed by drying under vacuum at 343 K.

2.3 Analytical Methods. After each reaction, the gaseous products were collected in a gas sampling bag and analyzed by gas chromatography (GC; GC-8A, Shimadzu Corporation, Japan) equipped with both silica gel and molecular sieve 5A columns, and a thermal conductivity detector. The liquid products were separated by centrifugation, decantation, and filtration using 0.45 μ m filters and then analyzed using two high-performance liquid chromatography systems (HPLC; 600 system, Waters Corporation, USA; Prominence system, Shimadzu Corporation, Japan) equipped with refractive index detectors. An Aminex HPX-87H column (ϕ 7.8 \times 300 mm; mobile phase: aqueous solution of 5 mmol L^{−1} formic acid; 0.7 mL min^{−1}; 313 K), and an Aminex HPX-87P column (ϕ 7.8 \times 300 mm; mobile phase: water; 1.0 mL min^{−1}; 358 K), both manufactured by Bio-Rad Laboratories Inc., USA, were used. The products were identified using standard substances and quantified by an external standard. The total amount of organic carbon dissolved in water (liquid products) was determined using a total organic carbon analyzer (TOC-L_{CSH/CSN}, Shimadzu Corporation, Japan). The yields of the products (mol %C) were calculated on the basis of carbon content:

$$\text{Yield [mol \%C]} = \frac{\text{number of C atoms in product}}{\text{number of C atoms in substrate}} \times \frac{\text{number of moles of product}}{\text{initial number of moles of substrate}} \times 100 \quad (1)$$

The catalysts were analyzed by X-ray powder diffraction (XRD) for determining the crystalline form using a diffractometer (SmartLab, Rigaku Corporation, Japan) with Cu K α radiation. Diffraction peaks were assigned in accordance with the Joint Committee of Powder Diffraction Standards (JCPDS) card file data. X-ray fluorescence (XRF) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were employed for determining the catalyst composition and amounts of dissolved metallic ions by using an X-ray fluorescence spectrometer (ZSX Primus II, Rigaku Corporation, Japan) with Rh K α radiation. Brunauer–Emmett–Teller (BET) analysis was conducted for determining the specific surface area of the catalysts by performing N₂ adsorption at 77 K using an adsorption analyzer (BELSORP-mini II, MicrotracBEL Corp., Japan). The

Fe and Ru metal particle sizes were obtained by scanning electron microscopy (SEM; S-4800, Hitachi High-Technologies Corporation, Japan) and field-emission electron microscopy (FE-TEM; JEM-2100F, JEOL Ltd., Japan), respectively. The used iron oxide (1 g) after two rounds of reuse experiments was heated with lignocellulosic biomass of empty fruit bunch (EFB) powder (0.5 g; elemental composition: C, 51.1 wt %; H, 6.1 wt %; O, 42.5 wt %; N, 0.3 wt %; dry ash free) in a flow apparatus with nitrogen (100 cm³ min^{−1}) at 1273 K for 2 h.

3. Results and Discussion

3.1 Generation of Hydrogen from Fe Metal Particles and Water. In a preliminary experiment, some iron metal particles with different particle sizes generated hydrogen under hydrothermal conditions, as shown in Figure 2. The amount of the generated hydrogen increased over time, and iron nanoparticles with dimensions of 60–80 nm were the most effective for hydrogen generation in terms of the formation rate and amount of generated hydrogen because their specific surface area was greater than those of larger iron particles. Hence, 60–80 nm iron nanoparticles are selected as the hydrogenation-generating agent in this study.

3.2 Transformation of Glucose Using Hydrogen Generated in situ. Figure 3 shows the transformation of glucose using Fe metal particles or a Pd/C catalyst or the combination of both Fe metal particles and a Pd/C catalyst (see Table S1 for details on the analysis). All of the glucose was converted to 100 mol %C.

The Fe metal particles resulted in a 19.3% yield of HA and a 16.4% yield of LA, while the use of only Pd/C resulted in a 20.2% yield of HA and a low yield (1.7%) of PG. Surprisingly, the combination of Fe metal particles and Pd/C catalyst resulted in the drastic increase in the PG yield (22.7%) along with a decrease in the formation of HA and LA. The total yield of C3 chemicals (PG, HA, and LA) was 34.6%. Notably, glucose was selectively transformed to PG even though the hydrogen generated in situ exhibited very low pressure (approximately 0.20–0.30 MPa). Thus, the Fe + Pd/C system enables

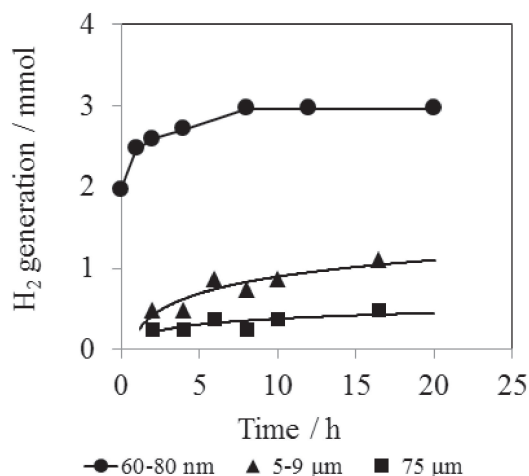


Figure 2. Generation of hydrogen using Fe metal particles of various sizes (60–80 nm, 5–9 μ m, and 75 μ m). Conditions: Fe, 335 mg (6 mmol); water, 36 mL; 453 K; 20 h; N₂, 0.5 MPa. Specific surface area: 60–80 nm, 8.7 m² g^{−1}; 5–9 μ m, 0.47 m² g^{−1}; 75 μ m, could not be measured.

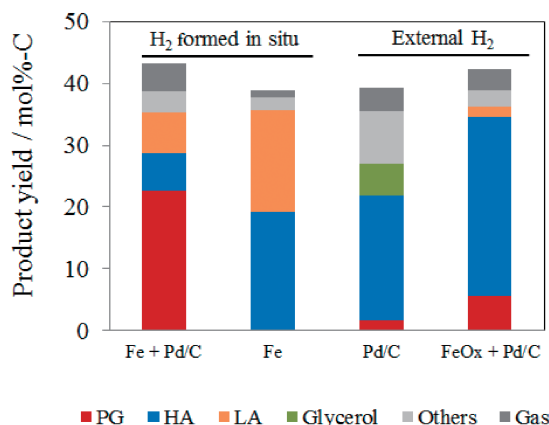
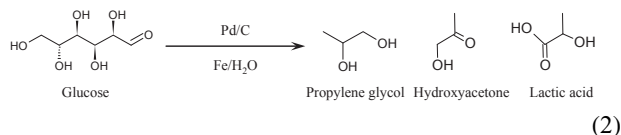


Figure 3. Transformation of glucose using Fe metal particles or a Pd/C catalyst or the combination of both Fe metal particles and Pd/C catalyst. Conditions: glucose, 180 mg; Fe, 335 mg; 5% Pd/C, 30 mg; water, 36 mL; 453 K; 20 h; N₂, 0.5 MPa. FeO_x + Pd/C: FeO_x from Fe after 20 h at 453 K; 5% Pd/C, 30 mg; N₂, 0.5 MPa; H₂, 0.2 MPa. Products: propylene glycol (PG); hydroxyacetone (HA); lactic acid (LA); other chemicals (1,2-butanediol, 1,2-hexanediol, glycolic acid, and acetic acid); gases (methane, ethane, propane, butane, carbon monoxide, and carbon dioxide). Maximum error: $\pm 2\%$. Liquid and gaseous product yields were determined by HPLC and GC analysis, respectively.

the transformation of glucose to PG, HA, and LA with the selective formation of PG, as shown in eq 2.



Interestingly, the activity of the in situ hydrogen system for PG formation was greater than that observed by the use of an external hydrogen source. A reaction was conducted using external hydrogen with iron oxide (FeO_x) generated from the metallic iron particles (Figure 4, the right-most column). The yield of PG from gaseous hydrogen was 5.6%, which is less than that (22.7%) observed with the use of in situ hydrogen. Recently, Jin and co-workers have reported a similar phenomenon for the Pd/C-catalyzed conversion of glucose to PG via water splitting with Zn.²⁹

3.3 Reusability of the Fe + Pd/C System. The reusability of the Fe + Pd/C system was examined by reuse experiments, and Figure 4 shows the results. Using a fresh catalytic system, the yield of PG increased from 17.3 to 23.9% in the first round of reuse (Reuse 1), and it remained constant at around 23% in the second and third rounds of reuse (Reuse 2 and 3). During the reaction, the oxidation state of metallic iron was changed, transforming to iron oxides. As shown in Figure 5, diffraction peaks assigned to magnetite, Fe₃O₄ (JCPDS card No. 01-085-1436), and metallic iron, Fe (JCPDS card No. 01-087-0721), were observed in the XRD patterns of the iron particles used in the reuse experiment (Figures 5b and 5d), while diffraction peaks corresponding to metallic iron were observed in the XRD patterns of fresh iron metal (Figure 5a) and the reduced system

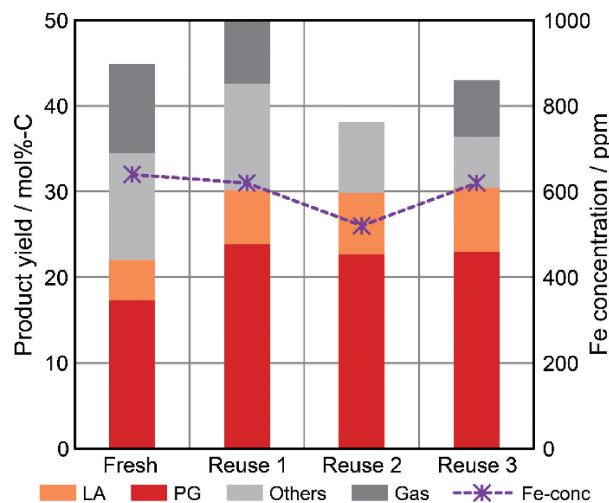


Figure 4. Reuse of the Fe + Pd/C catalyst system. Conditions: glucose, 360 mg; Fe, 670 mg; 5% Ru/C, 120 mg; water, 40 mL; 453 K; 20 h. The gas yield is not available for Reuse 2.

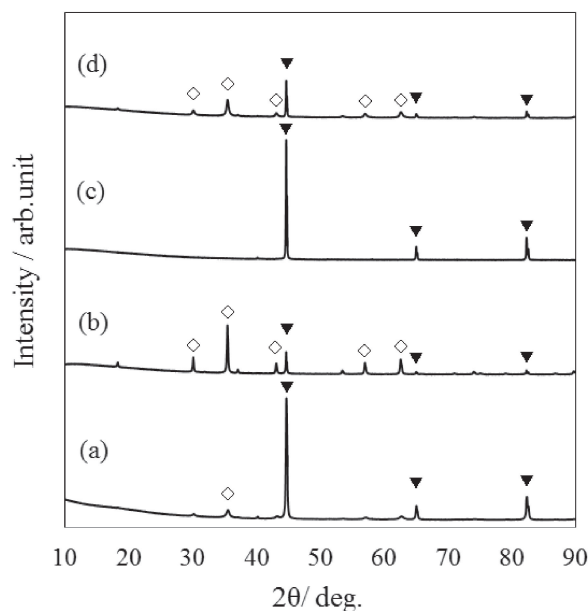
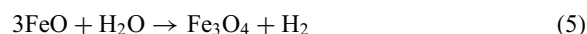
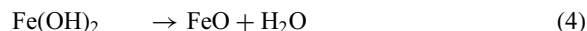
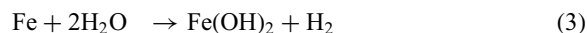


Figure 5. XRD patterns of iron materials: (a) fresh iron metal, (b) iron oxide after two rounds of reuse, (c) Fe + Pd/C reduced after three rounds of reuse; (d) Fe + Pd/C after four rounds of reuse. Peak assignment: ▼, Fe; ◇, Fe₃O₄.

(Figure 5c). These results imply that hydrogen is generated from the oxidation of metallic iron to magnetite by water.

In separate experiments, the regeneration of the used iron oxide to metallic iron was demonstrated by thermal treatment with lignocellulosic biomass as a practical method. As shown in Figure S1, from the XRD pattern of the treated sample, the used iron oxide was regenerated to metallic iron by thermal treatment with lignocellulosic biomass. Iron oxide is hypothesized to be directly reduced by syngas (H₂ and CO) or char formed during the thermal decomposition of biomass, although the method to regenerate the used iron oxide requires further investigation.

The mechanism of the iron–water reaction under hydrothermal conditions has been deduced from previous studies.^{64–66} Previously reported studies on zero-valent iron nanoparticles have demonstrated that during a liquid-phase reaction, Fe^{2+} is formed as iron hydroxide on a solid surface in water at ambient temperature.^{21,65} In addition, $\text{Fe}(\text{OH})_2$ is well known to be decomposed to FeO under nitrogen at approximately 473 K,⁶⁴ while $\text{Fe}(\text{OH})_2$ converts to magnetite (Fe_3O_4) in the absence of oxygen at temperatures of greater than 373 K (the sum of eqs 4 and 5: $3\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 2\text{H}_2\text{O}$); this transformation is known as the Schikorr reaction:^{65,66}



Total reaction:



The particle sizes of Fe and Pd from the reuse experiments appeared to be mostly unchanged (Table S3). Leaching of metals from the reuse experiments was also investigated from XRF and ICP-AES spectra. In all of the reuse experiments (see Figure 4, violet dotted line), the dissolved iron species was detected at a concentration of 520–640 ppm, indicating that the Fe species is possibly involved in the reaction. The roles of the Fe species are discussed in Section 3.5. On the other hand, the leaching of Pd metal species was not observed (not shown here). These results demonstrate that the Fe + Pd/C system is recyclable not only as a chemical-looping material (hydrogen-generating agent) but also as a hydrogenation catalyst.

3.4 Effects of Reaction Conditions. The effects of reaction conditions on the transformation of glucose using the Fe + Pd/C system were evaluated. Figure 6a shows the effects of temperature. The maximum yield of C3 chemicals was obtained at 433 K. HA was the major product obtained in 31.1% yield at 413 K. PG was the major product obtained in 22.7% yield at 453 K and in 23.9% yield at 473 K. At higher temperatures (473 and 493 K), the yields of gaseous products increased with the simultaneous decrease of the C3 chemical yield. At 493 K, the C3 chemicals further decreased with the increase of unknown products, assumed to be condensation products.⁶⁷ Thus, the optimal temperatures for the formation of HA and PG are 413 and 453 K, respectively. As needed, HA or PG can be synthesized by setting the temperature of the Fe + Pd/C system.

Figures 6b and 6c show the effects of the amounts of Fe metal particles and Pd/C for examining the selective formation of PG. When Pd/C was used without the addition of Fe metal particles, the yield of PG was 1.7%. The addition of Fe metal particles drastically promoted the formation of PG along with an increase in the amount of hydrogen generated, while the formation of HA decreased (Figure 6b); the effect attained saturation after the Fe amount reached 335 mg. The addition of Pd/C promoted the formation of PG along with a decrease in the formation of HA and LA (Figure 6c); the promotion effect attained saturation after the amount of Pd/C reached 30 mg. Thus, the optimal amounts of Fe metal particles and Pd/C for the formation of PG are 335 and 30 mg, respectively.

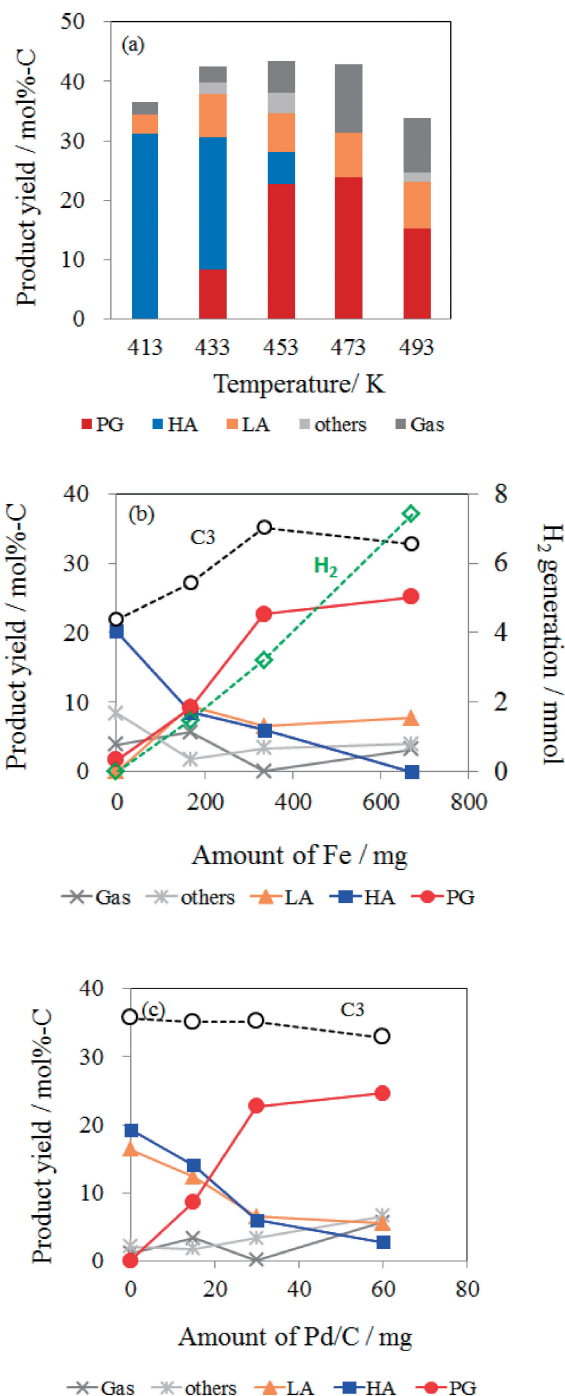
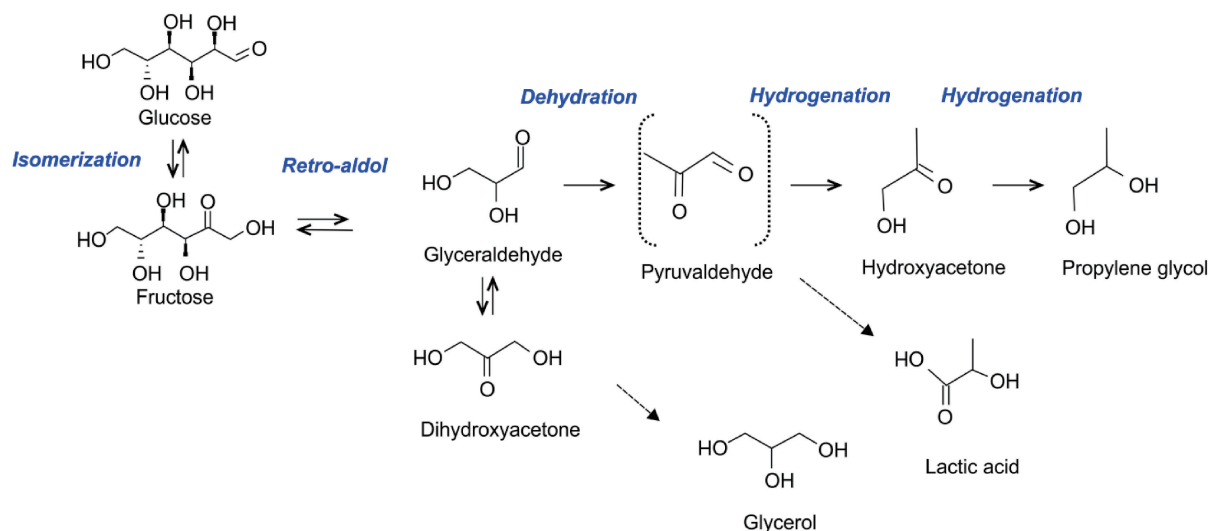


Figure 6. Effects of reaction conditions on the transformation of glucose in the Fe + Pd/C system. Conditions: glucose, 180 mg; water, 36 mL; (a) Fe, 335 mg; 5% Pd/C, 30 mg; 20 h, (b) 5% Pd/C, 30 mg; 453 K; 20 h, (c) Fe, 335 mg; 453 K; 20 h.

3.5 Reaction Mechanism—Roles of Metallic Iron Nanoparticles and Pd/C Catalyst. The roles of metallic iron and a Pd/C catalyst in the transformation of glucose were investigated. In addition, the changes in product yield with time were evaluated for the Fe + Pd/C system (see Figure S2). The results indicate that fructose and HA are the intermediate products in the formation of PG, and hydrogenation from HA



Scheme 1. Possible reaction pathway for the transformation of glucose using the Fe + Pd/C system.

Table 1. Transformation of various substrates using Fe or Pd/C, or both Fe and Pd/C^(a),b)

Entry	Substrate	Catalyst	Time /h	Conversion /mol %C	Product yield/mol %C				
					Fructose	HA	PG	Others	Gas
1	Glucose	Fe + Pd/C*	0	69.2	22.3	9.3	0.0	2.5	0.4
2	Glucose	Fe	0	59.0	23.7	7.7	0.0	0.0	0.1
3	Glucose	Pd/C*	0	15.1	0.0	0.0	0.0	0.0	0.5
4	HA	Fe + Pd/C	4	72.7	—	—	64.2	0.0	0.1
5	HA	Fe	4	12.6	—	—	4.9	0.0	0.0
6	HA	Pd/C + H ₂ 0.4 MPa	4	0.2	—	—	0.0	0.0	0.2

a) Reaction conditions: glucose, 180 mg; HA, 148 mg; Fe, 335 mg; 5% Pd/C, 30 mg or *60 mg; water, 36 mL; N₂, 0.5 MPa; 453 K. b) Abbreviations: HA, hydroxyacetone; PG, propylene glycol; Others, sum of 1,2-butanediol, 1,2-hexanediol, acetic acid, glycolic acid, and lactic acid; Gas, sum of C1–C4 alkanes, CO₂, and CO.

to PG is the rate-determining step, as demonstrated in our previous study using a ZnO + Ru/C system.⁶⁸ It is hypothesized that by using the Fe + Pd/C system, the transformation of glucose to PG also involved the isomerization of glucose to fructose, retro-aldol reaction of fructose to trioses (glyceraldehyde and HA can be formed from each other via consecutive keto–enol tautomerization⁶³), dehydration of glyceraldehyde to pyruvaldehyde, and hydrogenation of pyruvaldehyde to PG via HA (see Scheme 1).

The roles of both Fe and Pd/C during intermediate steps in the transformation from glucose to PG were also investigated. First, the isomerization of glucose to fructose was evaluated. As shown in Table 1, the use of Fe + Pd/C as well as only Fe afforded fructose in yields of 22.3 and 23.7%, respectively, at 453 K for 0 h (reaction time of 0 implies just after increasing the temperature), while no fructose was formed when only Pd/C was used. Thus, it is clear that Fe catalyzes the isomerization of glucose to fructose. As discussed in Section 3.3, the reaction mixture of glucose at 453 K for 20 h contained dissolved iron species at a concentration of around 600 ppm. The concentration of ferrous ions (Fe²⁺) in the reaction mixture was specifically determined to be approximately 600 ppm using a gas detector tube by the colorimetric method with 1,10-phenanthroline, indicating that a majority of the dissolved Fe species are estimated to be present as divalent cations. Wang

and co-workers have suggested that metal cations (including ferrous ions) catalyze a series of reaction steps, involving the isomerization of glucose to fructose, the retro-aldol reaction (the selective cleavage of the C3–C4 bond) of fructose to produce trioses, and the formation of lactic acid via pyruvaldehyde.⁶³ The role of homogeneous and heterogeneous Fe species was evaluated in separate experiments for the formation of HA and LA from glucose (see Table S2). Based on these results, homogeneous Fe species, such as ferrous ions, has been speculated to catalyze the transformation of glucose to LA via pyruvaldehyde, and pyruvaldehyde is immediately converted to HA in the presence of a hydrogenation catalyst and hydrogen.

Next, HA was used as a starting material. The yield of PG was 64.2% when the Fe + Pd/C system was used at 433 K for 4 h. No PG was formed using only Pd/C, and a yield of 4.9% for PG was obtained using only Fe. The Fe + Pd/C system clearly exhibited a synergistic effect for catalyzing the hydrogenation of HA to PG. Based on results reported in previous studies on the hydrogenation of carbonyl compounds over metal catalysts,^{69–71} the Fe species is speculated to activate the carbonyl group of HA molecules via the donation of electrons from unshared electron pairs of oxygen atoms to the electron-deficient Fe species, in agreement with the hydrogenation of the carbonyl group of HA molecules over the Pd metal catalyst. Richard and co-workers have reported that the activity and

selectivity of platinum for the liquid-phase hydrogenation of cinnamaldehyde to cinnamyl alcohol are improved by the addition of FeCl_2 .⁷⁰ They have also demonstrated that a part of iron atoms are deposited on Pt, as evidenced by the composition analysis of the metal particles determined by an energy-dispersive X-ray emission spectrometer attached to a scanning transmission electron microscope with a field-emission gun (FEG-STEM). For determining whether the Fe species was involved in the hydrogenation of HA to PG using the Pd/C catalyst, the distribution of iron and palladium atoms was measured by an energy-dispersive X-ray spectrometer (EDS) attached to a field-emission transmission electron microscope (FE-TEM) (see Figure S3). The results revealed that dissolved Fe species are deposited on the palladium catalyst, as has been reported previously.⁷⁰ Based on these results, metallic Fe and Fe species appear to play multiple roles in the transformation of glucose to PG, containing not only a hydrogen-generating agent, but also a degradation catalyst of glucose to trioses, and in the promotion of the hydrogenation of HA to PG with a Pd/C catalyst.

4. Conclusion

In this study, we developed a unique process for the hydrogenolysis or deoxygenation of biomass carbohydrates with hydrogen generated in situ using metallic iron and a palladium catalyst system. The Fe + Pd/C system led to the transformation of glucose to C3 platform chemicals (PG, HA, and LA) in 34.6% yield, with PG in 22.7% yield, at 453 K, as well as C3 platform chemicals in 34.4% yield, with HA in 31.1% yield at 413 K, without the addition of hydrogen from an external source. We hypothesized that iron played multiple roles—generating hydrogen, catalyzing the degradation of glucose to trioses, and assisting hydrogenation—while the palladium catalyst promoted the hydrogenation step, resulting in the formation of PG. We believe that this technique can be a complementary process and an alternative to most current applications of hydrogenation and reduction, which are limited by the hazards of high-pressure operation of hydrogen and the high cost of hydrogen storage and transformation. Currently, further studies on the enhancement of product yield and selectivity, improvement in the reusability of the Fe + Pd/C system, the reason for high activity of hydrogen generated in situ, the oxidation state of the active iron species, and the synergetic effect of Fe species with Pd/C are underway in our laboratory.

The authors gratefully acknowledge the financial support of JSPS KAKENHI (Grant-in-Aid for Exploratory Research) Grant No. 26620147 and an endowment fund by Nippon Shokubai Co., Ltd.

Supporting Information

Some figures and tables for the reaction results and the characterization of the Fe and Pd materials. This material is available on <http://dx.doi.org/10.1246/bcsj.20160114>.

References

- 1 J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 7164.
- 2 A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411.

- 3 G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044.
- 4 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484.
- 5 P. M. Mortensen, J.-D. Grunwaldt, P. A. Jensen, K. G. Knudsen, A. D. Jensen, *Appl. Catal., A* **2011**, *407*, 1.
- 6 A. M. Ruppert, K. Weinberg, R. Palkovits, *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 2564.
- 7 R. M. Navarro, M. C. Sánchez-Sánchez, M. C. Alvarez-Galvan, F. del Valle, J. L. G. Fierro, *Energy Environ. Sci.* **2009**, *2*, 35.
- 8 A. Thursfield, A. Murugan, R. Franca, I. S. Metcalfe, *Energy Environ. Sci.* **2012**, *5*, 7421.
- 9 J. Turner, G. Sverdrup, M. K. Mann, P.-C. Maness, B. Kroposki, M. Ghirardi, R. J. Evans, D. Blake, *Int. J. Energy Res.* **2008**, *32*, 379.
- 10 V. Hacker, R. Fankhauser, G. Faleschini, H. Fuchs, K. Friedrich, M. Muhr, K. Kordes, *J. Power Sources* **2000**, *86*, 531.
- 11 K. Otsuka, T. Kaburagi, C. Yamada, S. Takenaka, *J. Power Sources* **2003**, *122*, 111.
- 12 T. Kodama, N. Gokon, *Chem. Rev.* **2007**, *107*, 4048.
- 13 A. Steinfeld, *Sol. Energy* **2005**, *78*, 603.
- 14 M. Thaler, V. Hacker, *Int. J. Hydrogen Energy* **2012**, *37*, 2800.
- 15 K. Otsuka, S. Murakoshi, A. Morikawa, *Fuel Process. Technol.* **1983**, *7*, 203.
- 16 C. Boix, N. Poliakov, *J. Chem. Soc., Perkin Trans. 1* **1999**, *11*, 1487.
- 17 L. Wang, P. Li, Z. Wu, J. Yan, M. Wang, Y. Ding, *Synthesis* **2003**, *13*, 2001.
- 18 S. Mukhopadhyay, G. Rothenberg, D. Gitis, M. Baidossi, D. E. Ponde, Y. Sasson, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1809.
- 19 S. Mukhopadhyay, G. Rothenberg, D. Gitis, Y. Sasson, *Org. Lett.* **2000**, *2*, 211.
- 20 S. Mukhopadhyay, G. Rothenberg, H. Wiener, Y. Sasson, *New J. Chem.* **2000**, *24*, 305.
- 21 X. Li, D. W. Elliott, W. Zhang, *Crit. Rev. Solid State Mater. Sci.* **2006**, *31*, 111.
- 22 Z. Huo, M. Hu, X. Zeng, J. Yun, F. Jin, *Catal. Today* **2012**, *194*, 25.
- 23 F. Jin, Y. Gao, Y. Jin, Y. Zhang, J. Cao, Z. Wei, R. L. Smith, Jr., *Energy Environ. Sci.* **2011**, *4*, 881.
- 24 F. Jin, X. Zeng, J. Liu, Y. Jin, L. Wang, H. Zhong, G. Yao, Z. Huo, *Sci. Rep.* **2014**, *4*, 4503.
- 25 L. Lyu, F. Jin, H. Zhong, H. Chen, G. Yao, *RSC Adv.* **2015**, *5*, 31450.
- 26 L. Lyu, X. Zeng, J. Yun, F. Wei, F. Jin, *Environ. Sci. Technol.* **2014**, *48*, 6003.
- 27 X. Zeng, M. Hatakeyama, K. Ogata, J. Liu, Y. Wang, Q. Gao, K. Fujii, M. Fujihira, F. Jin, S. Nakamura, *Phys. Chem. Chem. Phys.* **2014**, *16*, 19836.
- 28 Z.-B. Huo, J.-K. Liu, G.-D. Yao, X. Zeng, J. Luo, F.-M. Jin, *Appl. Catal., A* **2015**, *490*, 36.
- 29 J. Wang, G. Yao, Y. Wang, H. Zhang, Z. Huo, F. Jin, *RSC Adv.* **2015**, *5*, 51435.
- 30 J. Xiao, Z. Huo, D. Ren, S. Zhang, J. Luo, G. Yao, F. Jin, *Process Biochem.* **2015**, *50*, 793.
- 31 L. Xu, Z. Huo, J. Fu, F. Jin, *Chem. Commun.* **2014**, *50*, 6009.
- 32 C. He, G. Tian, Z. Liu, S. Feng, *Org. Lett.* **2010**, *12*, 649.

- 33 G. Tian, H. Yuan, Y. Mu, C. He, S. Feng, *Org. Lett.* **2007**, *9*, 2019.
- 34 R. D. Cortright, R. R. Davda, J. A. Dumesic, *Nature* **2002**, *418*, 964.
- 35 R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, *Appl. Catal., B* **2005**, *56*, 171.
- 36 C. A. Fisk, T. Morgan, Y. Ji, M. Crocker, C. Crofcheck, S. A. Lewis, *Appl. Catal., A* **2009**, *358*, 150.
- 37 A. Martin, U. Armbruster, I. Gandarias, P. L. Arias, *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 9.
- 38 D. Roy, B. Subramaniam, R. V. Chaudhari, *Catal. Today* **2010**, *156*, 31.
- 39 S. Yin, A. K. Mehrotra, Z. Tan, *Biomass Bioenergy* **2012**, *47*, 228.
- 40 D. Scholz, C. Aellig, I. Hermans, *ChemSusChem* **2014**, *7*, 268.
- 41 Y. Wu, F. Gu, G. Xu, Z. Zhong, F. Su, *Bioresour. Technol.* **2013**, *137*, 311.
- 42 Y. Xu, J. Long, Q. Liu, Y. Li, C. Wang, Q. Zhang, W. Lv, X. Zhang, S. Qiu, T. Wang, L. Ma, *Energy Convers. Manage.* **2015**, *89*, 188.
- 43 L. He, L.-C. Wang, H. Sun, J. Ni, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem., Int. Ed. Engl.* **2009**, *48*, 9538.
- 44 S.-S. Li, X. Liu, Y.-M. Liu, H.-Y. He, K.-N. Fan, Y. Cao, *Chem. Commun.* **2014**, *50*, 5626.
- 45 A. Tlili, J. Schranck, H. Neumann, M. Beller, *Chem.—Eur. J.* **2012**, *18*, 15935.
- 46 L. Yu, X.-L. Du, J. Yuan, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *ChemSusChem* **2013**, *6*, 42.
- 47 J. Li, L. Liu, Y. Liu, M. Li, Y. Zhu, H. Liu, Y. Kou, J. Zhang, Y. Han, D. Ma, *Energy Environ. Sci.* **2014**, *7*, 393.
- 48 C. Hargus, R. Michalsky, A. A. Peterson, *Energy Environ. Sci.* **2014**, *7*, 3122.
- 49 P. Krenzke, K. Krueger, N. Leonard, S. Duncan, R. D. Palumbo, S. Möller, *J. Sol. Energy Eng.* **2010**, *132*, 034501.
- 50 R. W. Breault, E. R. Monazam, *J. Ind. Eng. Chem.* **2015**, *29*, 87.
- 51 S. Luo, C. Yi, Y. Zhou, *Renewable Energy* **2011**, *36*, 3332.
- 52 N. Kobayashi, L.-S. Fan, *Biomass Bioenergy* **2011**, *35*, 1252.
- 53 F. Li, L. Zeng, L.-S. Fan, *Fuel* **2010**, *89*, 3773.
- 54 S. Y. Luo, J. Fu, *J. Renewable Sustainable Energy* **2015**, *7*, 10.
- 55 M. A. Dasari, P.-P. Kiatsimkul, W. R. Sutterlin, G. J. Suppes, *Appl. Catal., A* **2005**, *281*, 225.
- 56 X. Wang, L. Meng, F. Wu, Y. Jiang, L. Wang, X. Mu, *Green Chem.* **2012**, *14*, 758.
- 57 Z. Zhang, J. E. Jackson, D. J. Miller, *Appl. Catal., A* **2001**, *219*, 89.
- 58 T. Deng, H. Liu, *J. Mol. Catal. A: Chem.* **2014**, *388–389*, 66.
- 59 A. K. Kinage, P. P. Upare, P. Kasinathan, Y. K. Hwang, J.-S. Chang, *Catal. Commun.* **2010**, *11*, 620.
- 60 C. R. Vitasari, G. W. Meindersma, A. B. de Haan, *Chem. Eng. Res. Des.* **2015**, *95*, 133.
- 61 M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B. F. Sels, *Energy Environ. Sci.* **2013**, *6*, 1415.
- 62 P. Mäki-Arvela, I. L. Simakova, T. Salmi, D. Yu. Murzin, *Chem. Rev.* **2014**, *114*, 1909.
- 63 Y. Wang, W. Deng, B. Wang, Q. Zhang, X. Wan, Z. Tang, Y. Wang, C. Zhu, Z. Cao, G. Wang, H. Wan, *Nat. Commun.* **2013**, *4*, 2141.
- 64 J. D. Bernal, D. R. Dasgupta, A. L. Mackay, *Clay Miner. Bull.* **1959**, *4*, 15.
- 65 U. R. Evans, J. N. Wanklyn, *Nature* **1948**, *162*, 27.
- 66 M. Ma, Y. Zhang, Z. R. Guo, N. Gu, *Nanoscale Res. Lett.* **2013**, *8*, 16.
- 67 M. Möller, P. Nilges, F. Harnisch, U. Schröder, *ChemSusChem* **2011**, *4*, 566.
- 68 Y. Hirano, K. Sagata, Y. Kita, *Appl. Catal., A* **2015**, *502*, 1.
- 69 V. Poncet, *Appl. Catal., A* **1997**, *149*, 27.
- 70 D. Richard, J. Ockelford, A. Giroir-Fendler, P. Gallezot, *Catal. Lett.* **1989**, *3*, 53.
- 71 W. Yu, H. Liu, M. Liu, Q. Tao, *J. Mol. Catal. A: Chem.* **1999**, *138*, 273.