Lactic Acid Production from Glucose over Y2O3-based Catalysts under Base-free Conditions

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1. Introduction

Environmental problems caused by the utilization of fossil resources have attracted much attention on the challenges posed by these limited resources and the development of ways to reduce CO₂ emissions. Alternative and renewable sources, based on carbon-containing chemical feedstocks, and new energy production methods are strongly desired. Recently, the production of fuels and chemicals from biomass resources, which are the most abundant, clean, and renewable sources, has garnered considerable interest because of their potential to reduce CO₂ emissions 1)–3).

Lactic acid (2-hydroxypropionic acid; LA) is a biomass-derived product receiving increasing interest. LA is a sugar-derived chemical that can be used as feedstock for the production of biodegradable polyester, poly(lactic acid), and several green solvents and commodity chemicals. Moreover, LA has value in the pharmaceutical, food, and detergent industries 4)–12).

For example, the dehydration of LA produces acrylic acid, which is widely known as a polymer raw material. Polycrlylates are used in various applications, including paints, adhesives, thickeners, detergent fibers, polyelectrolytes, absorbents, flocculants, and dispersants. Hydrogenation of LA yields 1,2-propanediol, which is used as a food additive, resin material, and in cosmetics. The oxidation of LA produces pyruvic acid, which is used in pharmaceuticals, agricultural chemicals, and food additives. The uses of lactides vary depending on the alcohol used to esterify LA. For example, methyl lactate is used as a solvent and detergent; ethyl lactate is used as a food additive and raw material for perfumes; butyl lactate is used as a food additive as well as a pharmaceutical and agricultural chemical.

The market growth of LA is expected in a sustainable society because the material has a low impact on the environment. The global production of LA in 2016 was approximately 1.22 million tons per year, and is expected to reach 1.96 million tons by 2025 12). Therefore, the increasing demand for LA has greatly stimulated its large-scale production, which poses a significant challenge for academic research and industry.

Methods to catalytic conversion of glucose into lactic acid (LA), which is a versatile platform chemical, have been widely investigated. Herein, various kinds of metal oxide catalysts were used for lactic acid (LA) production from glucose under strong homogeneous base-free conditions. Among the metal oxides tested, Y₂O₃ afforded LA in moderate yield (33 %) together with trioses (dihydroxyacetone and glyceraldehyde) and fructose. It was found that the Y₂O₃/SiO₂ catalyst can effectively catalyze the transformation of glucose into LA. Compared to Y₂O₃, the LA yield was remarkably improved (45 %). The characterization results showed that Y(OH)₃ was highly dispersed on the Y₂O₃/SiO₂ catalyst, acting as a Brønsted base and promoting LA formation from pyruvaldehyde (PA). Brønsted acid sites (hydroxyl groups) located at the interface between Y(OH)₃ and SiO₂ promoted the dehydration of trioses to form PA. The acid and base sites on the Y₂O₃/SiO₂ catalyst functioned in concert to ensure that the overall reaction proceeded efficiently.

Keywords
Yttrium oxide, Glucose, Lactic acid, Brønsted base, Brønsted acid

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Currently, LA is typically formed through two major production processes. The first is the bio-fermentation of glucose and sucrose using microorganisms. However, this process has several drawbacks: low production rate, the requirement of expensive enzyme catalysts, a large quantity of waste, costly separation, and the use of a stoichiometric amount of base for neutralization to maintain the preferable pH level for microorganisms. The second is the reaction of acetaldehyde with HCN or CO. However, this process has several drawbacks, such as high temperature, high pressure, and the use of toxic gases (HCN, CO). Owing to these drawbacks, significant efforts have been made to develop alternative chemical routes for LA production from renewable feedstocks such as glucose under mild reaction conditions.

Scheme 1 shows the reaction pathway to LA from glucose. Glucose is isomerized to highly reactive fructose and then converted to the triose sugars dihydroxyacetone (DHA) and glyceraldehyde (GLD). Both trioses can be obtained by the retro-aldol reaction of glucose, which is derived from cellulose, or by the oxidation of glycerol, which is the main by-product of biodiesel from triglycerides. Then, the trioses are dehydrated to form the intermediate pyruvaldehyde (PA). LA is thought to be formed via hydration and hydride shift. The retro-aldol reaction and its reverse reaction, the aldol reaction, are generally considered base-catalyzed reactions that can proceed quickly. In contrast, the dehydration of DHA or GLD followed by rearrangement is catalyzed by Brønsted and Lewis acids. Several groups have reported that PA is further transformed into LA, catalyzed by Lewis acids.

Recently, the catalytic production of LA and alkyl lactates from glucose by solid acid catalysts, strong homogeneous bases, and a combination of both have been investigated. However, a homogeneous base catalyst such as NaOH has several drawbacks, such as the requirement of high temperatures (573 K), excess strong base, and low recyclability. In contrast, in solid acid catalysts, it is necessary to improve both the reaction rate and the selectivity toward LA because of by-products such as carboxylic acids, C6 isomers, acidic aldol condensation products, dehydration products, and unidentified compounds. For example, the formation of 5-hydroxymethylfurfural (HMF) by dehydration of fructose, which proceeds on a strong Brønsted acid, and the formation of polymerization products such as humic substances proceed competitively with the formation of LA, resulting in reduced selectivity to LA. Therefore, understanding the relationship between the catalytic performance and acid-base properties is critical for designing an efficient catalyst for LA production from glucose, which is a multi-step reaction.

In this study, various metal oxide catalysts were prepared and used to transform D-glucose into LA under homogeneous base-free conditions. The correlation between the acid-base properties and the activity and selectivity of each reaction step, shown in Scheme 1, was investigated. Yttrium oxide was found to be active for the transformation of D-glucose into LA under base-free conditions.

2. Experimental

2.1. Materials

TiO\textsubscript{2} (JRC-TIO-15), Nb\textsubscript{2}O\textsubscript{5} (JRC-NBO-1), Al\textsubscript{2}O\textsubscript{3} (JRC-ALO-8), Zr\textsubscript{2}O\textsubscript{4} (JRC-ZRO-7), SiO\textsubscript{2} (JRC-SIO-13), and CeO\textsubscript{2} (JRC-CEO-2) were kindly supplied by the Catalysis Society of Japan. Mg-Al hydroxalcite (Mg/Al) was kindly provided by Kyowa Chemical Industry Co., Ltd. D-Glucose, DHA, and PA were respectively purchased from Tokyo Chemical Ind. Co., Ltd., EMD.
2. 2. Catalyst Preparation

Metal hydroxides (Mg(OH)$_2$, Zn(OH)$_2$, Y(OH)$_3$, Yb(OH)$_3$, Er(OH)$_3$, Gd(OH)$_3$, and La(OH)$_3$) were prepared from metal nitrates using 28% NH$_3$ (aq) as the precipitant. Metal oxides (MgO, ZnO, Y$_2$O$_3$, Yb$_2$O$_3$, Er$_2$O$_3$, Gd$_2$O$_3$, and La$_2$O$_3$) were prepared from hydroxides. The prepared hydroxides were calcined at 773 K for 3 h in air.

SiO$_2$-supported metal oxide catalysts (MgO/SiO$_2$, ZnO/SiO$_2$, and Y$_2$O$_3$/SiO$_2$) were prepared by the impregnation method. The metal nitrate was dissolved in 50 mL distilled water, and then 1.0 g SiO$_2$ was added. The resulting precipitate was vaporized and dried up at 353 K, and then calcined at 773 K for 3 h in air.

2. 3. Transformation of Sugars

The reaction was carried out in a glass vessel placed in a 50 mL stainless steel autoclave. The substrate (1.0 mmol) and the solid catalyst (200 mg) were stirred in 10 mL distilled water. After the reactors were sealed, air was purged with argon, and the reactors were pressurized to 1.0 MPa. D-Glucose, DHA, and PA were used as the substrates. The autoclave was placed in a heater at 343-473 K. The reactants and products were analyzed by high-performance liquid chromatography (HPLC; LC-2000, JASCO Corp.) using Aminex HPX-87H (Bio-Rad Laboratories, Inc.) (300 $\times$ 8.7 mm; flow rate: 0.6 mL min$^{-1}$; eluent: 10 mM H$_2$SO$_4$).

2. 4. Catalyst Characterization

X-ray diffraction (XRD) patterns of the catalysts were recorded using a Rigaku SmartLab diffractometer with Cu K$\alpha$ radiation. The samples were scanned in the range 2$\theta$ = 10-70$^\circ$ at 10$^\circ$ min$^{-1}$ and a resolution of 0.01$^\circ$. The Brunauer-Emmett-Teller (BET) specific surface area was estimated from N$_2$ adsorption isotherms obtained using a BELSORP-mini II (Microtac-BEL Corp.) at 77 K. The analyzed samples were evacuated at 573 K for 3 h prior to measurement. NH$_3$-temperature-programmed desorption (TPD) and CO$_2$-TPD were measured using a BELCAT II (Microtac-BEL Corp.). X-ray absorption spectroscopy (XAS) of the catalysts was performed at the BL01B1 beamline at SPring-8 (Hyogo, Japan). The ring energy was 8 GeV, and the stored current was 99.5 mA. Y K-edge (17.0 keV) XAS curves were recorded using Si(311) crystal monochromators. All spectra were obtained in transmission mode. Data reduction was performed using xTunes (Science & Technology Inst., Co.)$^{49}$.

Fourier transfer infrared (FT-IR) spectra were recorded using a FT/IR-4700 (JASCO Corp.) by a KBr pellet method. To prepare the hydrated sample, each sample was hydrated at 473 K for 0.5 h in 5 mL water under 1 MPa Ar, then dried at 353 K.

3. Results and Discussion

3. 1. Screening of Metal Oxides Catalysts

The catalytic activities of various metal oxides for the conversion of glucose into LA were surveyed. Figure 1 shows the XRD patterns of the metal-oxide catalysts. The physical properties (crystal structure and BET surface area) of the metal oxides, together with the acidity and basicity estimated from NH$_3$-TPD and CO$_2$-TPD, are shown in Table 1. A broad peak at approximately 20$^\circ$ was observed for SiO$_2$, which was attributed to amorphous silica. In addition to SiO$_2$, diffraction peaks due to each metal oxide appeared.

Table 1 BET Surface Area, Crystal Structure, Acidity, and Basicity of Metal Oxides

| Catalyst  | Surface area [m$^2$ g$^{-1}$] | Crystal system | Acidity [μmol g$^{-1}$] | Basicity [μmol g$^{-1}$] |
|-----------|-------------------------------|----------------|-------------------------|---------------------------|
| Y$_2$O$_3$ | 102 cubic                      |                | 37                      | 155                       |
| MgO       | 53 cubic                      |                | 26                      | 145                       |
| ZnO       | 93 monoclinic                 |                | 117                     | 112                       |
| Al$_2$O$_3$ | 168 cubic ($\gamma$-Al$_2$O$_3$) |                | 137                     | 24                        |
| TiO$_2$   | 58 tetragonal (anatase)       |                | 119                     | 3                         |
| Nb$_2$O$_5$ | 149 hexagonal (TT-Nb$_2$O$_5$) |                | 94                      | 0                         |
| ZnO       | 3 hexagonal                   |                | <1                      | <1                        |
| SiO$_2$   | 344 amorphous                 |                | 18                      | 0                         |

**Fig. 1 XRD Patterns of Metal Oxides**

(a) Y$_2$O$_3$, (b) MgO, (c) ZrO$_2$, (d) Al$_2$O$_3$, (e) TiO$_2$, (f) Nb$_2$O$_5$, (g) ZnO, (x 0.3), (h) SiO$_2$.

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Figure 2 shows the results of LA formation from glucose using a variety of metal oxides. The detected products were LA, DHA, GLD, fructose, and HMF. Among the metal oxides tested, Y$_2$O$_3$ gave the highest total yields of LA, DHA, GLD, and fructose, with a high conversion of glucose (ca. 100%). MgO, ZnO, CeO$_2$, and hydrotalcite gave a high LA yield with a high conversion of glucose (ca. 100%). In contrast,
TiO₂ and Nb₂O₅, which possess both Lewis and Brønsted acid sites⁴⁴),⁵⁰),⁵¹), produced a large amount of HMF with a small amount of LA and afforded intermediates, PA and GLD. ZrO₂ and Al₂O₃ mainly produced HMF, fructose, and LA, but the conversion of glucose was lower than that of other metal oxides. In the case of SiO₂, fructose was mainly detected with a low conversion of glucose (58%). This result suggests the presence of few acid sites with sufficient acid strength to dehydrate fructose to HMF. After the reaction, the solutions were colored dark yellow to brown, indicating extensive polymerization.

The effect of the reaction temperature on glucose conversion was investigated using a Y₂O₃ catalyst (Fig. 3). As the reaction temperature increased, the LA yield increased. However, the yields of DHA and fructose decreased with increasing temperature. DHA was observed at 473 K. Unidentified by-products were formed with yields higher than 50 %, regardless of the temperature. Many compounds have been reported as by-products, such as carboxylic acids, C₆ isomers, acidic aldol condensation products, dehydration products, and unidentified compounds presumed to be the polymerized product.

Figure 3 shows the time course of glucose conversion over the Y₂O₃ catalyst at 453 K. At the initial stage of the reaction (15 min), DHA was the main product. This suggests that DHA is more stable than GLD when fructose undergoes a retro-aldol reaction to triose. It has been considered that DHA is converted to the isomeric GLD via the enetriol intermediate¹⁷),¹⁸),²²),²₄). Onda et al. proposed a mechanism by which DHA and GLD are converted to PA by dehydration in the enetriol intermediate state when the reaction is catalyzed by hydrotalcite using glucose as a substrate at 323 K (Scheme 2)¹⁷),²₄). The yield of LA reached its highest value at 30 min and then decreased slightly.

3.2. PA and DHA Conversion

The catalytic activities of various metal oxides for the conversion of PA into LA were investigated. Figure 5 shows the results of LA formation from PA using various metal oxides at 363 K. The detected by-products were acetic acid and formic acid, formed through the retro-aldol reaction of PA. Basic metal oxide catalysts such as Y₂O₃ and MgO showed high LA yields even at temperatures as low as 363 K. In contrast, other metal oxide catalysts (ZrO₂, TiO₂, Nb₂O₅, and SiO₂) exhibited very low LA yields with low PA conversion. This suggests that PA can be smoothly converted to LA at base sites, even at 363 K.

The activities of rare-earth oxides and hydroxides were compared (Fig. 6). It is well known that rare earth oxides exhibit basic properties³⁰),⁵₂)~⁵₄). The rare
earth oxides and hydroxides were highly active in the PA conversion, even at 343 K. Among the rare-earth oxides and hydroxides tested, Y$_2$O$_3$ gave the highest LA yield.

The results of DHA conversion at 363 K and 423 K are shown in Fig. 7. LA and fructose were mainly formed by MgO and Y$_2$O$_3$ at 363 K, indicating that the aldol reaction proceeded preferentially from trioses (DHA) on the base sites. The conversion yield of DHA by MgO is much higher than by Y$_2$O$_3$. This implies that a large amount of unidentified by-products was formed by MgO. The oligomerization of fructose or trioses may proceed by strong base sites on MgO at 363 K. On the other hand, PA, together with a small amount of LA, was mainly formed on acidic Nb$_2$O$_5$ and TiO$_2$ catalysts.

At 423 K, the yields of LA and PA were significantly enhanced when Nb$_2$O$_5$ and TiO$_2$ catalysts were used. The TiO$_2$ catalyst exhibited a high LA yield of 53 % at a conversion of 98 %. The Nb$_2$O$_5$ catalyst afforded LA and PA yields of 35 % and 51 %, respectively, at 100 % conversion. These results indicate that the Nb$_2$O$_5$ catalyst can quickly convert DHA to PA, and the TiO$_2$ catalyst can smoothly transform PA to LA. Therefore, the nature of the active sites was deduced to be different for the TiO$_2$ and Nb$_2$O$_5$ catalysts.

On the other hand, the basic metal oxide catalysts increased the amounts of by-products other than LA, which could be considered as polymerization products. At 423 K, the polymerization of trioses competed with the conversion to PA, and the polymerization proceeded relatively more efficiently. In addition, the basic metal oxide catalysts barely produced PA, while a remarkable amount of PA was formed by the acidic catalysts (TiO$_2$ and Nb$_2$O$_5$). This result may be due to the lower activity of the acid sites than the base sites for PA conversion to LA, even at 423 K. In the case of ZrO$_2$, LA, PA, and fructose were observed because of the coexistence of acid and base sites on the surface of the ZrO$_2$ catalyst.

The effect of the reaction temperature on the DHA conversion reaction was investigated using a Y$_2$O$_3$ catalyst. Figure 8 shows the change in DHA conversion and yield of products at different temperatures between 343 K and 473 K. Fructose was mainly produced at temperatures below 400 K. Above 400 K, the yield of LA increased considerably, while that of fructose decreased rapidly. The yield of PA was low regardless of the temperature, suggesting that PA was immediately

GLD: glyceraldehyde, DHA: dihydroxyacetone, PA: pyruvaldehyde.

Scheme 2  Dehydration of Trioses to Pyruvaldehyde

![Scheme 2](image-url)
converted to LA on the Y₂O₃ catalyst. The selectivity for unidentified by-products increased above 423 K. This implies that the oligomerization and dehydration of triose to PA are in competition at high temperatures.

3.3. Possible Reaction Pathway

Based on the above considerations, a possible reaction pathway for the formation of LA from glucose over metal oxide catalysts is illustrated in Scheme 3. Both acid and base sites promote the isomerization of glucose to fructose (Step 1). Next, fructose is converted via two processes: one is the conversion to trioses by retro-aldol reaction (Step 2) and the other is the formation of HMF by the dehydration reaction (Step 3). Dehydration is catalyzed by strong Bronsted acid sites, as reported previously. In contrast, the retro-aldol reaction is more likely to proceed via base sites than acid sites. Then, the trioses are converted into three different products (Steps 5, 4, and 8) depending on the acid-base nature of the catalyst and the reaction temperature. The dehydration of trioses (Step 5) to form PA competes with the aldol reaction (Steps 4 and 8) to give fructose and oligomers; the aldol reaction may proceed relatively quickly when the concentration of trioses is high. The aldol reaction proceeds more easily at low temperatures for the basic metal oxide catalysts. Therefore, fructose is mainly formed from triose on the basic metal oxide Y₂O₃ (Step 4). At high temperatures, oligomerization proceeds competitively with dehydration catalyzed by acid sites. Finally, PA is converted to LA at both the acid and base sites (Step 6). This reaction mechanism strongly suggests that both acid and base sites are essential for the sequential reactions of LA formation from glucose.

3.4. Activity of Physical Mixture

The glucose conversion reaction was performed using a 1 : 1 (w/w) physical mixture of acid and base catalysts. Y₂O₃ was used as the basic catalyst, whereas Nb₂O₅ and TiO₂ were used as the acidic catalysts. Figure 9 shows the glucose conversion and product yield. For the physical mixture catalysts, the LA yield decreased compared to that of Y₂O₃ alone, and no HMF was formed. It is likely that fructose was immediately converted to trioses by Y₂O₃. In contrast, DHA and GLD were obtained without subsequent conversion to LA, indicating that the essential reaction step for LA production from glucose is the conversion of triose sugars. This reaction proceeds through the dehydration of DHA or GLD to PA. This result suggests that the physical mixture of catalysts did not demonstrate the synergetic function of the surface acid and base sites.

3.5. Activity of SiO₂-supported Catalysts

To demonstrate the synergetic function of the surface acid and base sites, silica-supported metal oxide catalysts (Y₂O₃/SiO₂, MgO/SiO₂, and ZnO/SiO₂) were prepared and used for the conversion of glucose to LA. For example, the generation of acid sites on MgO sup-
ported on SiO₂ has been reported. The loading amount of the metal oxides was fixed at 10 wt%.

**Figure 10** shows the results of LA formation from glucose using silica-supported metal oxide catalysts. Among the SiO₂-supported metal oxides tested, Y₂O₃/SiO₂ gave the highest LA yield (45 %) with a high glucose conversion (ca. 96 %). The LA yield increased by 1.5 times compared to Y₂O₃. In MgO/SiO₂, the LA yield was much lower, while the yields of trioses and fructose were much higher than with MgO. Small amounts of HMF and PA were also observed. The LA yield over ZnO/SiO₂ was slightly higher than that with ZnO. Trioses, fructose, PA, and HMF were also formed.

The effect of Y₂O₃ loading on LA formation from glucose was investigated (**Fig. 11**). The LA yield increased with Y₂O₃ loading up to 10 wt% and was main-

**3.6. Structure of SiO₂-supported Catalysts**

**Figure 12** shows the XRD patterns of the prepared Y₂O₃/SiO₂ catalysts with various Y₂O₃ loadings. No diffraction line attributable to Y₂O₃ was observed until the Y₂O₃ loading reached 10 wt%, indicating that the yttrium compounds were highly dispersed on SiO₂. However, above 10 wt%, broad diffraction lines due to the (222) plane of Y₂O₃ with a cubic crystal structure (PDF No. 00-005-0574) or the (101) plane of Y(OH)₃ with a hexagonal crystal structure (PDF No. 00-004-0213) were observed. This suggests that the yttrium compound (oxide or hydroxide) particles aggregated on the SiO₂ surface as the Y₂O₃ loading amount increased.

**Figure 13** shows the Y K-edge X-ray absorption

GLD: glyceraldehyde, DHA: dihydroxyacetone, PA: pyruvaldehyde, HMF: 5-hydroxymethylfurfural, AA: acetic acid, FA: formic acid.

Scheme 3 Possible Reaction Pathway
near edge structure (XANES) spectra of the Y$_2$O$_3$, Y(OH)$_3$, and Y$_2$O$_3$/SiO$_2$ catalysts. The Y K-edge XANES spectra of Y$_2$O$_3$ (cubic, YO$_6$ unit) and Y(OH)$_3$ (hexagonal, YO$_8$ unit) are different from each other owing to their different symmetries. The Y K-edge XANES spectra of Y$_2$O$_3$/SiO$_2$ are almost similar regardless of Y$_2$O$_3$ loading, indicating that the local structure of Y in Y$_2$O$_3$/SiO$_2$ is nearly identical to that of Y(OH)$_3$.

**Figure 14** shows $k^3$-weighted Y K-edge extended X-ray absorption fine structure (EXAFS) spectra and their Fourier transforms of Y$_2$O$_3$, Y(OH)$_3$, and Y$_2$O$_3$/SiO$_2$ catalysts. No significant changes in the EXAFS spectra of each Y$_2$O$_3$/SiO$_2$ catalyst appeared regardless of the Y$_2$O$_3$ loading. Moreover, the oscillation period was similar to that of Y(OH)$_3$, whereas it was quite different and much weaker than Y$_2$O$_3$. This indicates that the local structure of Y in Y$_2$O$_3$/SiO$_2$ is similar to that in Y(OH)$_3$. The oscillation amplitude decreased monotonically with $k$, and a weaker oscillation than that of Y(OH)$_3$ was observed in the region above 8 Å$^{-1}$. These results indicate that a smaller Y−(O)−Y contribution in Y(OH)$_3$ exists in the Y$_2$O$_3$/SiO$_2$ catalyst. This could be seen more clearly in the radial structure function (RSF; **Fig. 14**). The RSFs of the Y$_2$O$_3$/SiO$_2$ catalysts produced a peak at 1.8 Å corresponding to a Y−O linkage. For Y$_2$O$_3$ and Y(OH)$_3$, a peak appeared at 3.2 Å, corresponding to a Y−(O)−Y linkage. In the case of Y$_2$O$_3$/SiO$_2$ catalysts, no peak was observed in this region, suggesting that the supported Y(OH)$_3$ was in the form of fine particles.

### 3.7 Effect of Hydration on the Structure of Y$_2$O$_3$

The Y K-edge XAFS results indicated that Y(OH)$_3$ was highly dispersed on the Y$_2$O$_3$/SiO$_2$ catalysts. Hydration by water in air may take place easily to form the hydroxide. Since the conversion of glucose to LA is carried out in water as the solvent at high temperatures, the loaded Y$_2$O$_3$ on Y$_2$O$_3$/SiO$_2$ may change structurally to hydroxide during the reaction. **Figures 15 and 16** show the FT-IR spectra of dried and hydrated Y$_2$O$_3$/SiO$_2$ and Y$_2$O$_3$, respectively, compared with Y(OH)$_3$. The bands at approximately 3460 cm$^{-1}$ and 1640 cm$^{-1}$, originating from the O−H stretching vibration of the adsorbed water and O−H deformation vibration$^{62,63}$, respectively, appeared for hydrated Y$_2$O$_3$/SiO$_2$ (**Fig. 15(a)**) and hydrated Y$_2$O$_3$ (**Fig. 16(a)**). The bands at
570 cm$^{-1}$ and 480 cm$^{-1}$ are characteristic of the Y–O metal-oxygen stretching frequency of cubic Y$_2$O$_3$. For the hydrated Y$_2$O$_3$, the peak at 630 cm$^{-1}$ assignable to the Y–O–H stretching mode was clearly observed. This band is relatively weak for Y$_2$O$_3$/SiO$_2$ because of the low Y$_2$O$_3$ loading. These results indicate that some of the Y$_2$O$_3$ was converted to Y(OH)$_3$ under the reaction conditions. Therefore, yttrium in the Y$_2$O$_3$ and Y$_2$O$_3$/SiO$_2$ catalysts was considered to exist in the hydroxide state during the reaction.

### 3.8. Proposed Reaction Mechanism of LA Production over Y$_2$O$_3$/SiO$_2$ Catalyst

Based on the above discussion, we propose the following reaction mechanism for the one-step synthesis of LA from glucose using the Y$_2$O$_3$/SiO$_2$ catalyst.

As shown in Scheme 4(a), there are two possible mechanisms for the isomerization of glucose to fructose. It can be assumed that the isomerization proceeds efficiently, regardless of the acid-base properties of the catalyst. In the acid-catalyzed reaction, isomerization is thought to proceed by an ene-diol-type hydride shift after the adsorption of glucose on the acid sites. In contrast, in the base-catalyzed reaction, after glucose is adsorbed on the base site, the proton is abstracted, and the Lobry de Bruyn-van Ekenstein rearrangement occurs. Since the Y$_2$O$_3$/SiO$_2$ catalyst has both acid and base sites, it is possible that the reaction proceeds by either mechanism.

Then, the retro-aldol reaction in the formation of trioses from fructose is considered to proceed via the reaction mechanism proposed in Scheme 4(b). Fructose is converted to GLD and an enetriol intermediate through a retro-aldol reaction by the Bronsted base sites of Y(OH)$_3$, where the proton of the hydroxyl at β-carbon is abstracted to dissociate the C–C bond between the α- and β-carbons. The enetriol intermediate is
(a) Isomerization of glucose to fructose, (b) Fructose to trioses (DHA and GLD) and isomerization of DHA, GLD and enetriol, (c) Trioses to PA, (d) PA to LA.

GLD: glyceraldehyde, DHA: dihydroxyacetone, PA: pyruvaldehyde, HMF: 5-hydroxymethylfurfural, AA: acetic acid, FA: formic acid.

Scheme 4  Proposed Reaction Mechanism of LA Formation from Glucose over Y$_2$O$_3$-based Catalyst  (continued on next page)
transferred to DHA via keto-enol tautomerism (isomerization). GLD is also thought to be converted to the enetriol intermediate by keto-enol tautomerism (isomerization)\(^\text{17),22),24)}\). The enetriol intermediate is then dehydrated by the Brønsted acid sites at the interface between Y(OH)\(_3\) and SiO\(_2\) and converted to 2-hydroxypropenal, which is then converted to the keto isomer PA (Scheme 4(c))\(^\text{34),35),38}\). However, fructose and oligomers are competitively generated by the base site when the concentrations of trioses are high. Therefore, it is necessary to accelerate the dehydration process from trioses to PA to improve the LA yield.

Three different mechanisms have been proposed for the transformation of PA into LA. Hara and Nakajima proposed the ene-diol-type hydride shift mechanism and MPV (Meerwein-Ponndorf-Verley) reduction mechanism\(^\text{68)}\). Lewis acid sites play an essential role in these mechanisms. On the other hand, Xinhua et al. proposed a hydration and benzylic acid rearrangement mechanism that proceeds on the Brønsted base site (Scheme 4(d))\(^\text{15)}\). The activities of Y\(_2\)O\(_3\) and Y\(_2\)O\(_3\)/SiO\(_2\) for PA conversion to LA at 363 K were much higher than those of Nb\(_2\)O\(_5\) and TiO\(_2\), which are known to be water-tolerant Lewis acid catalysts. These results strongly suggest that Brønsted base sites on Y\(_2\)O\(_3\) and Y\(_2\)O\(_3\)/SiO\(_2\) can promote PA conversion to LA by the hydration and benzylic acid rearrangement mechanism.

Therefore, both acid and base sites are essential for the sequential reactions to obtain LA from glucose. The acid and base sites on the Y\(_2\)O\(_3\)/SiO\(_2\) catalyst function in concert to ensure that the overall reaction proceeds efficiently. In this sequential reaction, the essential reaction step for LA production from glucose is the conversion of the triose sugars DHA and GLD to PA.

4. Conclusion

In this study, various metal oxide catalysts were used to convert glucose to LA under strong homogeneous base-free conditions. Y\(_2\)O\(_3\) afforded the desired product, LA, in a moderate yield (33 %). The Y\(_2\)O\(_3\)/SiO\(_2\) catalyst, in which the acid and base sites on the catalyst act in concert, succeeded in producing LA in high yield (45 %) without the addition of a strong base such as NaOH. The characterization results showed that Y(OH)\(_3\) was highly dispersed on the Y\(_2\)O\(_3\)/SiO\(_2\) catalyst, acting as a Brønsted base and promoting LA formation from PA.

On the other hand, the Brønsted acid sites (hydroxyl groups) located at the interface between Y(OH)\(_3\) and SiO\(_2\) promoted dehydration of the enetriol intermediate derived from triose sugars (DHA and GLD) to form PA. The essential reaction step for LA production from glucose was the conversion of triose sugars to PA catalyzed by the acid sites. The acid and base sites on the Y\(_2\)O\(_3\)/SiO\(_2\) catalyst functioned in concert to ensure that the overall reaction proceeded efficiently. We found the Brønsted base sites of on Y\(_2\)O\(_3\)/SiO\(_2\) catalyst allows the
conversion of PA to LA to proceed rapidly even at 90 °C. Therefore, it was clearly shown that the formation of acid sites that can efficiently proceed the formation of PA by dehydration of trioses is an important issue to improve the yield of LA from glucose.

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要 旨

Y2O3系触媒を用いた均一系塩基フリー条件下でのグルコースからの乳酸合成

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グルコースを触媒法により乳酸（LA: Lactic acid）に変換する方法が広く研究されている。ここでは、さまざまな金属酸化物を触媒として水酸化ナトリウムなどの均一系の塩基を添加しない条件でその触媒作用を検討した。検討した金属酸化物のうち、Y2O3は収率33%で乳酸を与えた。このとき、トリオース（ジヒドロキシアセトンとグリセリアルデヒド）とフルクトオースが副生成物として得られた。Y2O3/SiO2触媒は、グルコースからLAへの変換を効率的に進行させ、LA収率45%を達成した。すなわち、Y2O3を比較してLA収率は顕著に向上した。構造解析の結果、触媒上には、Y(OH)3が高分子担持されており、担持されたY(OH)3は、プレステッド塩基として作用し、ピルプアルデヒド（PA）からのLAへの転換を効率的に促進することが分かった。また、Y(OH)3とSiO2の界面に存在するプレステッド酸部位（水酸基）は、トリオースからの脱水反応によるPAの生成に関与していると考えられる。Y2O3/SiO2触媒では、酸点と塩基点が協調的に機能することで、グルコースからLAへの多段階の反応を効率的に進行させたと考えられる。

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