Formic acid is one of the most desirable liquid hydrogen carriers. The selective production of formic acid from mono-saccharides in water under mild reaction conditions using solid catalysts was investigated. Calcium oxide, an abundant solid base catalyst available from seashell or limestone by thermal decomposition, was found to be the most active of the simple oxides tested, with formic acid yields of 50% and 66% from glucose and xylose, respectively, in 1.4% H$_2$O$_2$ aqueous solution at 343 K for 30 min. The main reaction pathway is a sequential forma- tion of formic acid from glucose by C–C bond cleavage involving aldehyde groups in the acrylic form. The reaction also involves base-catalyzed aldose-ketose isomerization and retro-aldol reaction, resulting in the formation of fructose and trioses including glyceraldehyde and dihydroxyacetone. These inter- mediates were further decomposed into formic acid or glycolic acid. The catalytic activity remained unchanged for further reuse by a simple post-calcination.

1. Introduction
The utilization of lignocellulosic biomass has been attracted much attention because environmental issues have become more serious.$^{[1,2]}$ So far, many efforts have been made to synthesize fuels from lignocellulose.$^{[1,4]}$ Gasification of lignocel- lulose biomass and subsequent Fischer-Tropsch reaction produce liquid biofuels, which are high-quality hydrocarbons.$^{[5,6]}$ Fast pyrolysis of biomass and successive catalytic upgrading such as hydrodeoxygenation afford bio-oils equivalent to light and heavy oil.$^{[7,8]}$ The former operates under high temperature and pressure, and the latter mostly needs an external supply of a large amount of hydrogen. In these regards, both conversion processes benefit only in mass production due to the advantage of scale; thus, a large amount of biomass needs to be treated at a chemical plant in industrial areas typically far from the forest, which causes additional energy consumption for transportation.$^{[9,10]}$ Although such liquid biofuels are applicable as fuels for aviation and ships, their use in automobiles would be declined in the future as the current demand for the energy transition in transport accelerates the use of renewable hydro- gen and electricity.$^{[11,12]}$

Formic acid is one of the most promising hydrogen carriers.$^{[13,14]}$ It can be produced from saccharides by selective oxidation$^{[15–18]}$ or carbon dioxide transformation, including catalytic hydrogenation,$^{[20–22]}$ electrochemical reduction,$^{[23,24]}$ and photocatalytic reduction.$^{[25–27]}$ In the former case, formic acid is obtained from monosaccharides regardless of the type, such as glucose, xylose, and mannose. Thus, both cellulose and hemicellulose, which are the main components of lignocellulose, can be utilized. Moreover, formic acid can depolymerize lignin,$^{[28]}$ which helps separate it from (hemi)cellulose and further utilize it. In the combination of lignocellulose depolymerization, the oxidative transformation of sugars to formic acid is expected to offer an opportunity for on-site conversion of biomass, which is much different from the conventional reductive process requir- ing the external supply of pressurized hydrogen. It is recently reported that mechanochemical depolymerization of lignocel- lose using citric acid as a homogeneous acid catalyst and successive hydrolysis-oxidation using hydrogen peroxide as an oxidizing agent in dimethyl sulfoxide at 453 K could afford a high yield of formic acid.$^{[29]}$

This study examined the selective production of formic acid from monosaccharides in water under mild reaction conditions at a temperature lower than 373 K by using heterogeneous catalysts. Although recent studies demonstrated a fairly good formic acid yield using homogeneous catalysts such as polyoxometalates under high pressure of oxygen$^{[20]}$ and LiOH in the presence of H$_2$O$_2$,$^{[31]}$ the use of heterogeneous catalysts is of importance because of suppressing the corrosion of the reactor and providing an opportunity to reduce not only the environ-
mental impact but also the economic cost. Here, we found that calcium oxide, an abundant solid material available from seashell or limestone by thermal decomposition, could efficiently catalyze the reaction and be reused after calcination.

2. Results and Discussion

2.1. Screening of Solid Catalysts for Formic Acid Production from D-Glucose

The oxidative production of formic acid from D-glucose using H₂O₂ as an oxidant was surveyed using various metal oxides, including alkaline earth metal oxides, rare-earth metal oxides, and transition metal oxides. The concentration of H₂O₂ was 0.9% which is very low and widely available. Although H₂O₂ is currently produced from hydrogen and oxygen via anthraquinone process, recent studies demonstrated that H₂O₂ could be obtained from H₂O and O₂ by photocatalytic system. Again, calcium oxide exhibited the highest activity among samples tested, and calcium hydroxide showed comparable activity, whereas calcium carbonate and calcium phosphate showed no activity. While Mg-Al hydrotalcite was also active for the reaction in water, the activity was much lower than that of calcium oxide in this study.

2.2. Effect of Reaction Conditions

The results showing the activity using alkaline earth metal oxides and Mg-Al hydrotalcite indicate that the catalytic activity is attributed to the solid basicity. The solid basicity of CaO was determined by a titration method. After immersion of CaO in toluene solution containing phenolphthalein overnight, an appropriate amount of benzoic acid was added until the color of the surface of CaO changed back. The amount of solid base sites was estimated to be 24 ± 3 μmol g⁻¹, indicating a significantly high turnover number of 1040.

Effect of reaction conditions including initial reactant concentration, reaction temperature, and amount of oxidant on the catalytic activity was investigated. Figure 2 shows the dependence of the catalytic activity of CaO on glucose concentration. The reaction was carried out at 343 K for 0.5 h. At a low glucose concentration of 2.8 mmol L⁻¹, a high yield of formic acid (61%) with the full conversion of glucose was achieved. With increasing glucose concentration, glucose conversion and formic acid yield were decreased, whereas fructose yield was increased. The rate of decrease in formic acid yield became gradual, and the yield has reached a plateau. At a high glucose concentration of 56 mmol L⁻¹, the formic acid yield was 36% with 84% glucose conversion.

Figure 3 shows the dependence of the activity on the reaction temperature. It was found that the reaction proceeded at 303 K, affording 21% yield of formic acid with 60% selectivity. No fructose formation was observed, indicating that

Table 1. Formic acid production from D-glucose using calcium compounds.³⁵

| Catalyst         | Glucose conversion/% | Formic acid yield/% | Glycolic acid yield/% | Glyceraldehyde yield/% | Fructose yield/% |
|------------------|----------------------|---------------------|-----------------------|------------------------|------------------|
| CaO              | 84                   | 36                  | 5                     | 5                      | 20               |
| CaO²⁻           | > 99                 | 45                  | 11                    | 12                     | 18               |
| Ca(OH)_2         | 83                   | 34                  | 8                     | 8                      | 24               |
| CaCO₃           | 0                    | 0                   | 0                     | 0                      | 0                |
| Ca₃(PO₄)₂       | 0                    | 0                   | 0                     | 0                      | 0                |
| Mg-Al hydrotalcite| 21                   | 2                   | 0                     | 1                      | 12               |

[a] Reaction conditions: D(+)-glucose (1.1 mmol, 0.20 g), metal oxide (0.20 g), H₂O₂ (5.5 mmol), water (20 mL), 343 K, 0.5 h. (b) 363 K, 2 h.
base-catalyzed glucose-fructose isomerization named Lobry de Bruyn-van Ekenstein transformation\[^{[36]}\] did not occur at near-room temperature. As the reaction temperature increased, glucose conversion and formic acid yield increased while the formic acid selectivity was decreased due to a simultaneous increase of fructose yield. Figure 4 shows the effect of the H\(_2\)O\(_2\) amount added on the reaction. With increasing H\(_2\)O\(_2\), the formic acid yield was increased, confirming that H\(_2\)O\(_2\) functioned as an oxidant agent. When 11.1 mmol of H\(_2\)O\(_2\) was used for the reaction, 56.4 % yield of formic acid was obtained. The amount of remained H\(_2\)O\(_2\) was analyzed by the UV absorption method.\[^{[37]}\] It was found that the amount of H\(_2\)O\(_2\) detected after the reaction was lower than 0.01 mmol for all cases, indicating that H\(_2\)O\(_2\) was consumed not only for the oxidative conversion of glucose into formic acid but also by self-decomposition.

**2.3. Reaction Pathway for Formic Acid Production**

Figure 5 shows the time course production of formic acid at different temperatures. At 363 K, the reaction was almost complete after 30 min, with a formic acid yield of 43% (Figure 5(a)). After 30 min, a slight increase of glucose conversion was observed, corresponding to fructose formation due to base-catalyzed glucose-fructose isomerization. It suggests that H\(_2\)O\(_2\) was rapidly consumed for 30 min, resulting in no further increase of formic acid production. As the reaction was fast at 363 K and in a low glucose/catalyst ratio of 1 (w/w), the reaction was then carried out at 343 K in a high glucose/catalyst ratio of 3 (w/w) to monitor product changes and consider the reaction pathway (Figure 5 (b)). At the initial stage of the reaction, formic acid was preferentially produced. For 5 min, the selectivity to formic acid was 53 % at half of the glucose conversion (51 %) with no fructose formation. For 30 min, the
formic acid yield was 39%, with the selectivity of 50%. Prolonged reaction time gradually increased formic acid yield to 45%, increasing glucose conversion to 90%. Simultaneously, glycolic acid was formed along with formic acid. The dependence of product selectivity is shown in Figure 5(c). It was found that the selectivity to formic acid was almost constant to ca. 50%, whereas the selectivity to glycolic acid was decreased with the increase of glucose conversion. While fructose was not formed at the initial stage of the reaction, the selectivity was increased until 30 min reaction and then gradually decreased for further reaction. Besides, it should be noted that the selectivity to others was high for 5 min and then decreased (not shown). These values were 27% for 5 min, 18% for 15 min, and 0% for 30 min. These could be attributed to intermediate species for direct formic acid production, which will be discussed later.

A possibility of further transformation of fructose, glyceraldehyde, and glycolic acid into formic acid was investigated. Table 2 lists the results of formic acid production from these substrates over CaO using H$_2$O$_2$ at 363 K for 2 h. The result of glucose conversion corresponds to that in Figure 5(a). Like glucose, a high yield of formic acid was obtained from glyceraldehyde. Thus, the reason that the yield of glyceraldehyde was low in Figure 5(b,c) is due to its rapid transformation. Formic acid was also formed from fructose. The yield was lower than that from glucose and glyceraldehyde, suggesting that fructose as a ketose was relatively a difficult substrate for further transformation into formic acid. This result is in good agreement with the results in Figure 5(b,c) because the fructose yield was moderate, and it was gradually decreased with the increase of reaction time. It was found that glycolic acid was hard to be converted, which is also in good agreement with the results in Figure 5 because the formed glycolic acid remained unchanged.

In the absence of H$_2$O$_2$, glucose is known to undergo base-catalyzed isomerization and retro-aldol reactions, resulting in the formation of fructose and trioses, including glyceraldehyde and dihydroxyacetone. Although formic acid could be obtained from fructose and glyceraldehyde as described above, the main pathway for formic acid production in the presence of H$_2$O$_2$ should be different because formic acid was mostly formed at the initial stage of the reaction with the increase of glucose conversion. A proposed reaction pathway is shown in Scheme 1. Isbell and Naves reported the formic acid formation from saccharides using alkaline hydrogen peroxide. Ebitani et al. suggested the same reaction mechanism for formic acid production using hydrotalcite catalyst. OOH$^-$ species formed by base attack the aldehydic carbon atom of the acyclic form of aldoses such as glucose and glyceraldehyde, resulting in the cleavage of carbon-carbon bond accompanied with the formation of formic acid. The remaining next lower aldose further undergoes decomposition by adding H$_2$O$_2$ with the formation of formic acid. This reaction pathway is considered the main route for formic acid production. During the sequential reaction, a variety of lower aldoses could be formed. In Figure 5(c), it was observed that the selectivity to others which are unidentified products, was high at the initial stage of the reaction, which could correspond to a variety of lower aldoses derived from glucose.

A similar reaction occurs for ketoses such as fructose and dihydroxyacetone with the formation of another carboxylic acid, glycolic acid, due to the bond cleavage between second and third carbon, which is in good agreement with the result that the relatively high yield of glycolic acid was obtained from fructose (Table 2). While glycolic acid formation was also observed from glucose and glyceraldehyde, it is likely due to isomerization to fructose or dihydroxyacetone.

2.4. Formic Acid Production from Other Saccharides and Reusability of the Catalyst

Mannose and xylose could be also efficiently converted into formic acid, as shown in Table 3. Yields of formic acid were 39%
from mannose and 66% from xylose. High selectivity to formic acid (84%) was obtained from xylose, probably due to the suppression of aldose-ketose isomerization.

The reusability of the catalyst was further investigated. Before reusing the catalyst, it was washed with water and ethanol, followed by drying at 353 K overnight in an oven. The results are shown in Figure 6. The activity was decreased after the first and second reuse. The analysis by XRD of the sample after the second reuse indicated a drastic change of the crystal structure, as shown in Figure 7. After reuse, the sample was transformed into CaCO$_3$ which is inactive for the reaction mentioned above (Table 1). Thus, after the second reuse, the sample was calcined at 1073 K before reuse. The XRD pattern of the re-calcined sample indicated a mixture of Ca(OH)$_2$ and CaO. As both exhibited comparable activity (Table 1), the sample gave the same activity as the fresh catalyst. It was demonstrated that the catalytic activity was fully recovered by a simple calcination.

### 3. Conclusion

Calcium oxide, a simple, widely available alkaline earth metal oxide, efficiently produced formic acid from glucose, fructose, mannose, and xylose in water using hydrogen peroxide as an oxidant under mild reaction conditions. The yield of formic acid was 52% from glucose and 66% from xylose, respectively. While the reaction includes aldose-ketose isomerization and retroaldol reaction, the main pathway is a sequential formation of formic acid from aldose by C–C bond cleavage involving aldehyde groups in the acyclic form. The catalyst could be reused without loss of activity by calcination before reuse.

### Experimental Section

#### Chemicals

$\alpha$-glucose (98%, Kishida), $\alpha$-fructose (99%, Wako), $\alpha$-mannose (99%, Wako), $\alpha$-xylose (99%, Wako), glyceraldehyde (>90%, Sigma-Aldrich), glycolic acid (97%, Wako), formic acid (98%, Wako), hydrogen peroxide (30%, Wako), and benzoic acid (99.5%, Wako) were used for the reactions and the analysis. Calcium oxide (CaO, 99.9%, Wako), hydroxide (Ca(OH)$_2$, 90%, Kishida), carbonate (CaCO$_3$, 99.95%, Wako), and phosphate (Ca$_3$(PO$_4$)$_2$, 98%, Wako) were used as catalysts. Other metal oxides, MgO (99.9%, Wako), SrO (95%, Wako), La$_2$O$_3$ (99.99%, Wako), CeO$_2$ (99.9%, Wako), TiO$_2$ (anatase, 98.5%, Wako), Nb$_2$O$_5$ (99.9%, Wako), SnO$_2$ (98%, Wako) and ZnO (99.9%, Wako) were also used as catalysts. Mg-Al hydrotalcite (Mg/Al = 3) was prepared by a conventional coprecipitation method using Mg(NO$_3$)$_2$·6H$_2$O (99%, Wako), Al(NO$_3$)$_3$·9H$_2$O (98%, Wako), Na$_2$CO$_3$ (99.5%, Kishida) and NaOH (98%, Kishida).

#### Catalytic Test

A quantity of 1.1 mmol of $\alpha$-glucose and 0.20 g of catalysts were put into 20 mL of water containing 5.5 mmol of H$_2$O$_2$ in a reactor.
vessel. The vessel was heated at 353–373 K for 0.5–2 h in an oil bath under stirring. After the reaction, the reaction mixture was analyzed by high-performance liquid chromatography (HPLC; LC-2000 plus, JASCO) equipped with a differential reactive index detector (RI-2031 plus, JASCO) with Aminex HPX-87H column (flow rate: 0.5 mL min⁻¹, eluent: 10 mmol L⁻¹ H₂SO₄).

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**Conflict of Interest**

The authors declare no conflict of interest.

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