

Article

Conversion of Cellulose to Lactic Acid by Using $\text{ZrO}_2\text{--Al}_2\text{O}_3$ Catalysts

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Abstract: Lactic acid has a wide range of applications in many industries, both as an ingredient and as an intermediate. Here, we investigated the catalytic conversion of cellulose to lactic acid by using heterogeneous mixed-oxide catalysts containing ZrO_2 . Although pure ZrO_2 has catalytic activity for the conversion of cellulose to lactic acid, the yield of lactic acid obtained is not satisfactory. In contrast, a series of $\text{ZrO}_2\text{--Al}_2\text{O}_3$ catalysts containing various percentages of ZrO_2 provided higher yields of lactic acid. The $\text{ZrO}_2\text{--Al}_2\text{O}_3$ catalysts had more Lewis acid sites and far fewer base sites than ZrO_2 . This suggests that the Lewis acid sites on $\text{ZrO}_2\text{--Al}_2\text{O}_3$ catalysts are more important than the base sites for the conversion of cellulose to lactic acid.

Keywords: cellulose; lactic acid; $\text{ZrO}_2\text{--Al}_2\text{O}_3$; zirconium oxide; aluminum oxide; biomass

1. Introduction

Biomass is a renewable organic resource that contains components that are essential for the production of many important chemicals and fuels [1–3]. Inedible lignocellulosic biomass is plant biomass that is mainly composed of cellulose, hemicellulose, and lignin. Currently, cellulose is the most promising component for biomass utilization because cellulose is the major component of lignocellulosic biomass [4–7].

Lactic acid is an organic compound that is used in large quantities as the food, cosmetic, pharmaceutical, and chemical productions [8,9]. Moreover, lactic acid is an important intermediate for conversion to other products such as propylene glycol, acrylic acid, and polylactic acid [8,10]. Conventionally, lactic acid is produced via the fermentation of sugars from starch [11]; however, the rate of production using this method is low, and the pH of the solution during fermentation must be kept in the range 5–7 to provide an environment suitable for lactic acid-fermenting bacteria. Thus, catalytic conversion of inedible cellulose is an attractive alternative to fermentation for the production of lactic acid.

Recently, several homogeneous catalysts (e.g., PbCl_2 and ErCl_3) have been investigated for their suitability for the conversion of cellulose to lactic acid [12,13]. These catalysts provide a high yield of lactic acid; however, their use in industries remains unrealized because of difficult separation of the products from the catalyst as well as the poor stability and recyclability of the catalysts. Therefore, heterogeneous catalysts for the conversion of cellulose to lactic acid are desired because products can be easily separated from this type of catalyst. Several heterogeneous catalysts have been reported to

have catalytic activity for the conversion of cellulose to lactic acid, such as LaCoO_3 , $\text{NbF}_5\text{--AlF}_3$, and AIW, which provided yields of lactic acid of 24%, 27%, and 28%, respectively [14–16]. However, these solid catalysts have a disadvantage that the metal species leach into solution during the reaction—2.4% of the Co and 1.5% of the La from LaCoO_3 [14] and 1.5% of the W from AIW [16] leached into solution. Additionally, these heterogeneous catalysts are relatively expensive, making their industrial use difficult. Previously, we reported a simple ZrO_2 catalyst for the conversion of cellulose to lactic acid (yield, 21.2%) that did not leach metal species into the reaction solution [17]. In addition, the ZrO_2 catalyst was stable in hot water. However, the yield of lactic acid obtained with this catalyst was less than those reported for the heterogeneous catalysts. Thus, the aim of the present study was to examine how to increase the yield of lactic acid obtainable with ZrO_2 -based catalysts. Dispersion of active species on supports such as metal oxides is a common means of increasing the catalytic activity of heterogeneous catalysts. Therefore, here we compared the catalytic activity of a series of mixed-oxide catalysts containing various amounts of ZrO_2 (5%, 10%, or 20%) on an Al_2O_3 support with that of pure ZrO_2 . We found that the 10% $\text{ZrO}_2\text{--Al}_2\text{O}_3$ catalyst showed activity for the production of lactic acid from cellulose with a product yield of 25.3%, which was cheaper than the reported heterogeneous catalysts.

2. Results and Discussion

2.1. Effect of Ball-Milling Treatment on Cellulose Conversion

In this paper, pulverization of cellulose by ball-milling has been applied for the increase of cellulose conversion [18–20]. The conversion of cellulose was only 25% in the case of un-milled cellulose (473 K, 6 h, without catalysts) and increased to 86% by the ball-milling treatment of cellulose. Figure 1 shows XRD patterns of un-milled and milled cellulose. The cellulose crystallinity was decreased by the ball-milling treatment as revealed by the peak broadening at $2\theta = 22.6$ degree (crystalline plane 002) in XRD patterns (Figure 1) [19,21], indicating that the cellulose conversion increased with decreasing cellulose crystallinity. In the reaction pathway, cellulose was firstly hydrolyzed to soluble glucose; thus, cellulose with high crystallinity was hydrolyzed very slowly at 473 K from the result of the low conversion of un-milled cellulose.

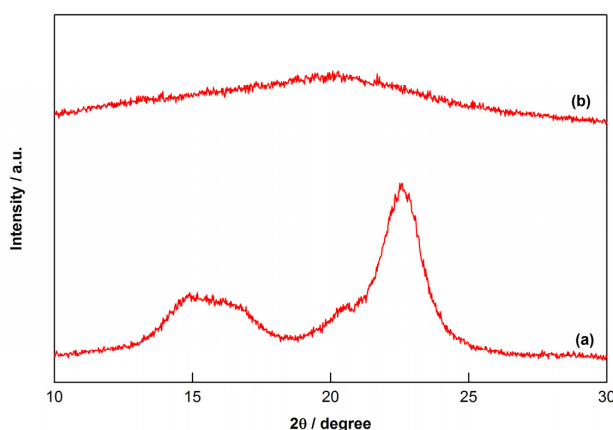


Figure 1. XRD patterns of (a) un-milled cellulose and (b) milled cellulose.

2.2. Catalytic Conversion of Cellulose to Lactic Acid by Using $\text{ZrO}_2\text{--Al}_2\text{O}_3$

Previously, we investigated the catalytic conversion of cellulose to lactic acid by using various transition metal oxides (i.e., ZrO_2 , Al_2O_3 , TiO_2 , Fe_3O_4 , V_2O_5 , CeO_2 , Y_2O_3 , Tm_2O_3 , HfO_2 , Ga_2O_3 , MgO , La_2O_3 , Nb_2O_5 , and Ta_2O_5) [17]. Of these catalysts, ZrO_2 had the highest catalytic activity (lactic acid yield, 21.2%; reaction temperature, 473 K). Therefore, in the present study, we examined the use of an Al_2O_3 support to increase the catalytic activity of ZrO_2 for the conversion of cellulose to lactic acid. The yields of lactic acid obtained with $\text{ZrO}_2\text{--Al}_2\text{O}_3$ mixed-oxide catalysts containing

different percentages of ZrO_2 at 473 K were higher than those obtained by using the individual metal oxides, indicating that the dispersion of active ZrO_2 species on the Al_2O_3 support increased the catalytic activity of ZrO_2 (Figure 2). The maximum yield of lactic acid (25.3%) was obtained when 10% ZrO_2 - Al_2O_3 was used as the catalyst. The yield of lactic acid increased slightly as the amount of ZrO_2 on the Al_2O_3 support was increased from 5% to 10%; however, the yield decreased as the amount of ZrO_2 was increased to 20%, indicating that the yield of lactic acid may decrease further as the percentage of ZrO_2 on the support increases.

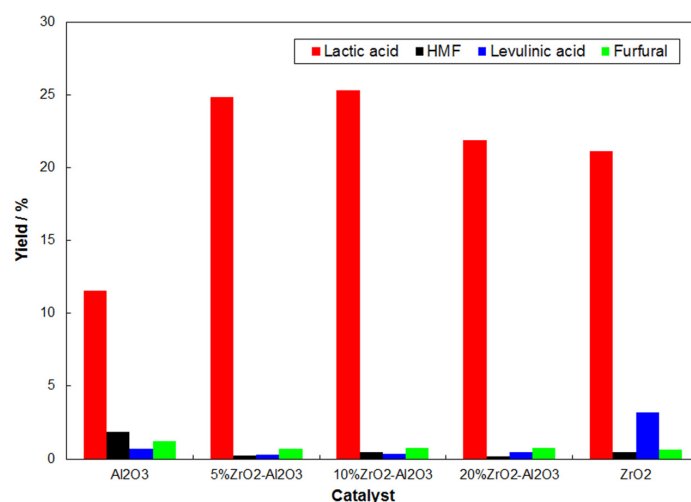


Figure 2. Product yields obtained by using Al_2O_3 , ZrO_2 , or ZrO_2 - Al_2O_3 mixed-oxide catalysts for the conversion of cellulose to lactic acid. Reaction conditions: ball-milled cellulose, 0.5 g; catalyst, 1.0 g; water, 50 g; reaction temperature, 473 K; reaction time, 6 h. HMF, 5-hydroxymethylfurfural.

2.3. Reaction Conditions

Next, we optimized the reaction conditions to obtain the highest possible yields of lactic acid with 10% ZrO_2 - Al_2O_3 used as the catalyst. Figure 3 shows the product yields obtained as a function of reaction time. The yield of lactic acid increased for up to 6 h, after which it decreased due to decomposition or polymerization of lactic acid.

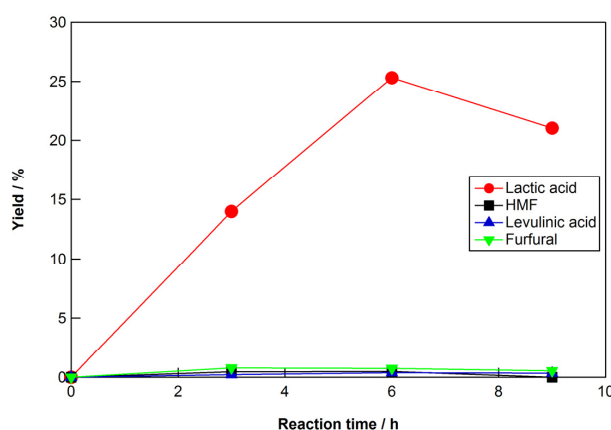


Figure 3. Product yields obtained when 10% ZrO_2 - Al_2O_3 was used as the catalyst as a function of reaction time. Reaction conditions: ball-milled cellulose, 0.5 g; catalyst, 1.0 g; water, 50 g; reaction temperature, 473 K. HMF, 5-hydroxymethylfurfural.

Figure 4 shows the product yields obtained as a function of reaction temperature. The maximum yield of lactic acid (25.3%) was obtained at 473 K. At the lowest temperature examined (i.e., 453 K), the cellulose conversion reaction proceeded very slowly. At the highest temperature examined (i.e., 493 K), the yield of lactic acid was less than that at the optimum temperature because the lactic acid was likely decomposed at this temperature.

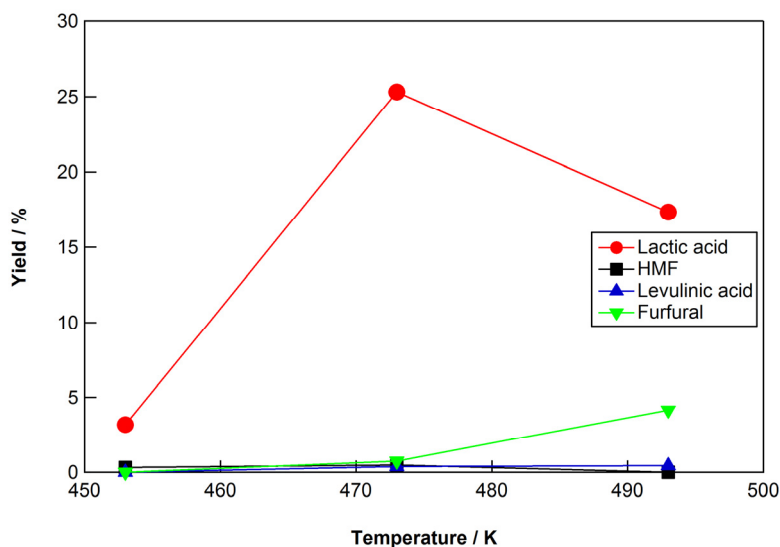


Figure 4. Product yields obtained when 10%ZrO₂–Al₂O₃ was used as the catalyst as a function of reaction temperature. Reaction conditions: ball-milled cellulose, 0.5 g; catalyst, 1.0 g; water, 50 g; reaction time, 6 h. HMF, 5-hydroxymethylfurfural.

Finally, we investigated the reusability of the 10%ZrO₂–Al₂O₃ catalyst for repeated conversion of cellulose to lactic acid. After the reaction with the optimized conditions (473 K, 6 h), the recovered solid, which contained the used 10%ZrO₂–Al₂O₃ catalyst and any unreacted cellulose, was heated at 673 K for 15 h under an air atmosphere to remove carbon-based material accumulated on the surface of the catalyst. The yield of lactic acid obtained by using the reused 10%ZrO₂–Al₂O₃ catalyst at 473 K for 6 h was 31.7%, which was higher than the yield obtained from the first reaction. One possible reason is that the calcination of the 10%ZrO₂–Al₂O₃ catalyst after the reaction would eliminate contamination on the surface, resulting in the higher lactic acid yield. This result suggests that the 10%ZrO₂–Al₂O₃ catalyst is recyclable.

2.4. Characterization

Next, we characterized the ZrO₂–Al₂O₃ catalysts to further understand their catalytic activity. The X-ray diffraction (XRD) patterns of the catalysts are shown in Figure 5. In the XRD patterns of the three ZrO₂–Al₂O₃ catalysts, peaks at 46.0° and 66.5° were attributed to γ -Al₂O₃ [22]. In the XRD patterns of 10%ZrO₂–Al₂O₃ and 20%ZrO₂–Al₂O₃, peaks at 30.3° and 50.7° were attributed to tetragonal ZrO₂ [23]; however, these peaks were not seen in the XRD pattern of 5%ZrO₂–Al₂O₃, indicating that ZrO₂ was either highly dispersed or in the amorphous phase in this catalyst. The XRD pattern for pure ZrO₂ revealed that it was in the monoclinic phase (Figure 5d).

In our previous paper, we hypothesized that the properties of the acid and base sites on ZrO₂ play an important role in the catalytic activity of this oxide for the conversion of cellulose to lactic acid [17]. Therefore, we examined the acid and base properties of the ZrO₂–Al₂O₃ catalysts by means of temperature-programmed desorption of ammonia (NH₃-TPD) and temperature-programmed desorption of carbon dioxide (CO₂-TPD), respectively. Figure 6 shows NH₃-TPD profiles of the ZrO₂–Al₂O₃ and ZrO₂ catalysts. The NH₃ desorption temperatures of the three ZrO₂–Al₂O₃ catalysts

were all 470 K, which was similar to that of ZrO_2 , indicating that the acid sites on the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and ZrO_2 catalysts were weakly acidic Lewis acid sites [24] (Figure 6). The shoulder peaks at 550 K were observed in the case of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ catalysts, which were ascribed to slightly stronger acid sites than weakly acid sites (peak at 470 K). The slightly stronger acid sites might be located on the boundary between ZrO_2 and Al_2O_3 . Although the XRD analysis revealed that the crystal phase of ZrO_2 differed depending on whether it was in pure or mixed-oxide form, the NH_3 desorption temperatures revealed that the acid strength was almost the same irrespective of form.

The desorption temperatures of CO_2 from the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and ZrO_2 catalysts were in the range 340–450 K (Figure 7), indicating that the base sites on the ZrO_2 catalysts were weakly basic [25]. The amount of CO_2 desorbed from the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ catalysts was smaller than that desorbed from the ZrO_2 catalyst.

Table 1 shows the amounts of acid and base sites on the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and ZrO_2 catalysts. The $\text{ZrO}_2\text{-Al}_2\text{O}_3$ catalysts had more acid sites but far fewer base sites than the ZrO_2 catalyst. In our previous paper, we suggested that the retro-aldol reaction (the conversion of fructose to glyceraldehyde and dihydroxyacetone)—the key step in the conversion of cellulose to lactic acid—involved both the acid and base sites on the ZrO_2 catalyst [17]. However, the $\text{ZrO}_2\text{-Al}_2\text{O}_3$ catalysts had more acid sites and far fewer base sites than did ZrO_2 . We discuss the reaction pathway in the next section.

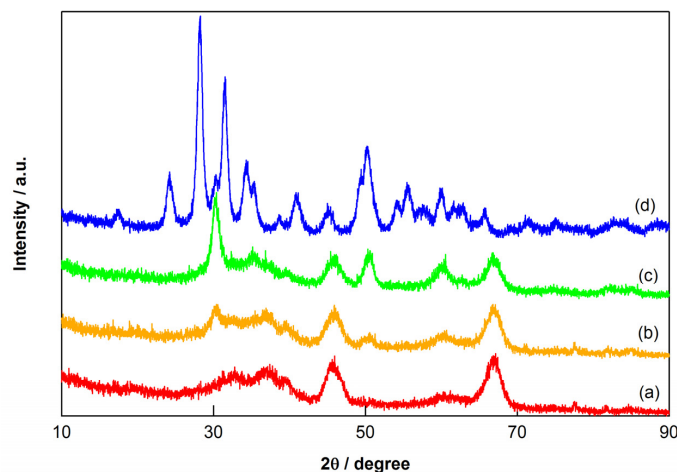


Figure 5. X-ray diffraction patterns of (a) 5% $\text{ZrO}_2\text{-Al}_2\text{O}_3$, (b) 10% $\text{ZrO}_2\text{-Al}_2\text{O}_3$, (c) 20% $\text{ZrO}_2\text{-Al}_2\text{O}_3$, and (d) ZrO_2 .

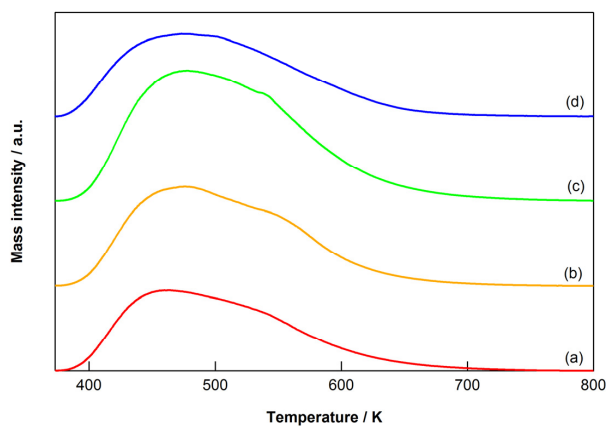


Figure 6. Temperature-programmed desorption of ammonia profiles of (a) 5% $\text{ZrO}_2\text{-Al}_2\text{O}_3$, (b) 10% $\text{ZrO}_2\text{-Al}_2\text{O}_3$, (c) 20% $\text{ZrO}_2\text{-Al}_2\text{O}_3$, and (d) ZrO_2 .

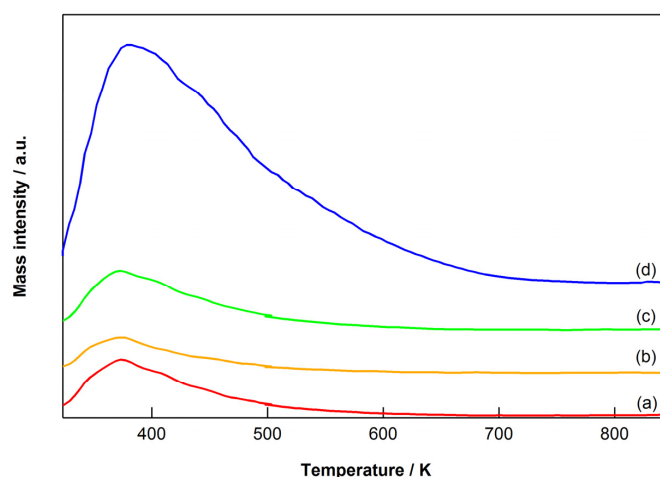


Figure 7. Temperature-programmed desorption of carbon dioxide profiles of (a) 5%ZrO₂-Al₂O₃, (b) 10%ZrO₂-Al₂O₃, (c) 20%ZrO₂-Al₂O₃, and (d) ZrO₂.

Table 1. Properties of the ZrO₂-Al₂O₃ and ZrO₂ catalysts.

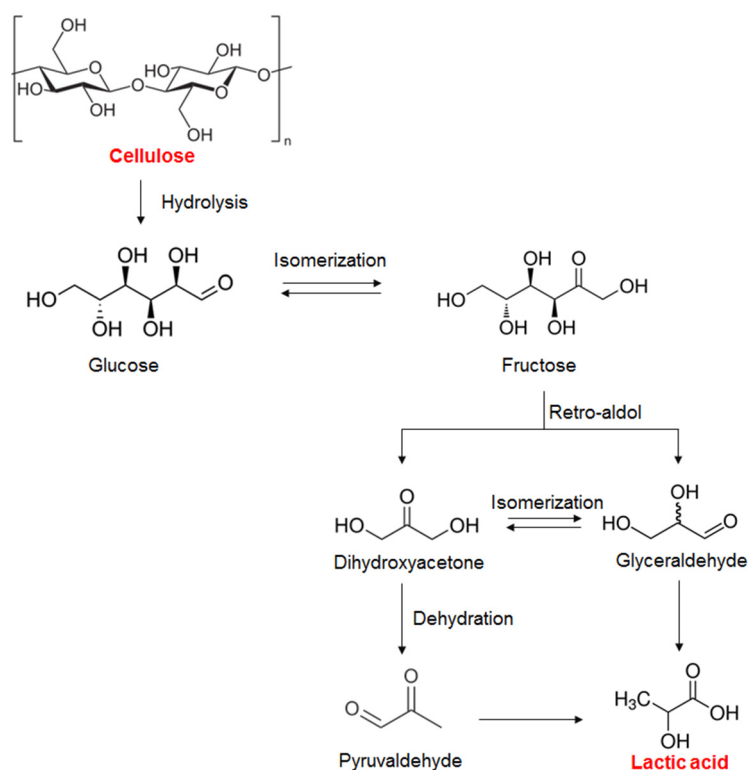
Catalyst	Surface Area ¹ /m ² g ⁻¹	Crystal Phase of ZrO ₂ ²	Amount of Acid Sites ³ /mmol g ⁻¹	Amount of Base Sites ⁴ /mmol g ⁻¹	Yield of Lactic Acid ⁵ /%
5%ZrO ₂ -Al ₂ O ₃	135	-	0.109	0.093	25.0
10%ZrO ₂ -Al ₂ O ₃	126	Tetragonal	0.131	0.057	25.3
20%ZrO ₂ -Al ₂ O ₃	130	Tetragonal	0.180	0.098	21.9
ZrO ₂ ⁶	101	Monoclinic	0.118	0.485	21.2

¹ Reported by manufacturer; ² Determined by XRD; ³ Determined by temperature-programmed desorption of ammonia (NH₃-TPD); ⁴ Determined by temperature-programmed desorption of carbon dioxide (CO₂-TPD);

⁵ Reaction conditions: ball-milled cellulose, 0.5 g; catalyst, 1.0 g; water, 50 g; reaction temperature, 473 K; reaction time, 6 h; ⁶ Presented in reference [17].

2.5. Reaction Pathway

The conversion of cellulose to lactic acid is a multi-step reaction (Scheme 1). First, cellulose is converted to glucose by hydrolysis, which can be catalyzed by acid catalysts [26,27]. Then, glucose is isomerized to fructose by a Lewis acid or basic catalysts [28]. The key step in the conversion pathway from cellulose to lactic acid is the conversion of fructose to glyceraldehyde and dihydroxyacetone via a retro-aldol reaction involving C-C bond cleavage, which can be enhanced by Lewis acids [29,30]. In a previous paper, we hypothesized that the combination of acid and base sites on ZrO₂ enhanced the conversion of fructose to glyceraldehyde and dihydroxyacetone [17]. However, in the present study, the yield of lactic acid obtained from cellulose by using the ZrO₂-Al₂O₃ catalysts did not appear to depend on the relative amount of acid and base sites. That is, the ZrO₂-Al₂O₃ catalysts provided a higher yield of lactic acid than did the ZrO₂ catalyst, even though they had more acid sites and far fewer base sites than did ZrO₂ (Table 1). This indicates that the number of base sites is not important for the catalytic conversion of cellulose to lactic acid with ZrO₂-Al₂O₃ catalysts. Furthermore, although the Lewis acid sites on the ZrO₂-Al₂O₃ catalysts played an important role in the conversion of cellulose to lactic acid, the yield of lactic acid obtained was not proportional to the number of acid sites. This suggests that dispersion of ZrO₂ on a Al₂O₃ support and accessibility to the acid sites on the catalyst are the most important factors for the conversion of cellulose to lactic acid when using ZrO₂-Al₂O₃ catalysts. Further studies are required to elucidate the details of the relationship between the active sites and the product yield and also the reaction mechanism.



Scheme 1. Reaction pathway for the conversion of cellulose to lactic acid.

In the final step of the reaction pathway, glyceraldehyde and dihydroxyacetone can be converted to lactic acid at 463 K without a catalyst [17]. However, the conversion of pyruvaldehyde to lactic acid is reported to require a catalyst with Lewis acid sites [31,32], which a ZrO_2 -based catalyst could provide.

Previously, we reported that we used a ZrO_2 catalyst to convert cellulose to lactic acid with a yield of 21.2% [17]. However, this yield of lactic acid was less than that obtained with other reported heterogeneous catalysts (24% yield of lactic acid using LaCoO_3 [14], 28% using AlW [16], and 27% using $\text{NbF}_5\text{--AlF}_3$ [15]). In the present study, we found that by using the 10% $\text{ZrO}_2\text{--Al}_2\text{O}_3$ catalyst we could obtain a yield of lactic acid of 25.3%, which was comparable with the yields using the reported catalysts. One advantage of the 10% $\text{ZrO}_2\text{--Al}_2\text{O}_3$ catalyst is that it can be obtained in lower cost than the reported heterogeneous catalysts. Additionally, a few percentages of the metal species in the reported catalysts leached into solution during the reaction. Conversely, the Zr species was not leached out from ZrO_2 into water during the reaction [17].

3. Materials and Methods

3.1. Materials

ZrO_2 (ZRO-7; reference catalyst from Catalysis Society of Japan) and mixed oxides containing ZrO_2 and Al_2O_3 (5% $\text{ZrO}_2\text{--Al}_2\text{O}_3$, 10% $\text{ZrO}_2\text{--Al}_2\text{O}_3$, and 20% $\text{ZrO}_2\text{--Al}_2\text{O}_3$) were obtained from Daiichi Kigenso Kagaku Kogyo Co., Ltd. (Osaka, Japan). Aluminum oxide (Al_2O_3) was obtained from Sigma-Aldrich Co., LLC (St. Louis, MO, USA). These materials were used without pretreatment.

3.2. Catalytic Reaction

Cellulose (microcrystalline cellulose; Merck KGaA, Darmstadt, Germany) was pulverized with a ball mill at 60 rpm. The conversion of cellulose to lactic acid was carried out in a stainless steel batch reactor with an inner volume of 100 cm³ (MMJ-100; OM Lab-Tech, Tochigi, Japan), as described in a previous paper [17]. Briefly, the reactor was loaded with ball-milled

cellulose (0.5 g), catalyst (1.0 g), and water (50 g); purged with nitrogen gas (0.1 MPa); and then heated to 453–493 K for 3–9 h with screw stirring. After the reaction was allowed to run, the resulting mixture was filtered to separate the liquid from the solid. The quantitative analyses of lactic acid, levulinic acid, 5-hydroxymethylfurfural, and furfural in the liquid fractions were carried out with a gas chromatograph (GC-2014; Shimadzu, Kyoto, Japan) equipped with a flame ionization detector and an InertCap capillary column (GL Sciences Inc., Tokyo, Japan). The chemicals in the liquid fraction (e.g., glucose) were analyzed by using a high-performance liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a refractive index detector (RID-10A; Shimadzu, Kyoto, Japan), an ultraviolet/visible detector (SPD-20AV; Shimadzu, Kyoto, Japan), and a Rezex RPM-Monosaccharide Pb+2 column (Phenomenex Inc., Torrance, CA, USA). The product yields were calculated based on moles of carbon as follows:

$$\text{Product yield (\%)} = \frac{(\text{Moles of carbon atoms in each product})}{(\text{Moles of carbon atoms in cellulose used})} \times 100 \quad (1)$$

$$\text{Conversion (\%)} = \left(1 - \frac{(\text{Weight of solid residue}) - (\text{Weight of solid catalyst})}{(\text{weight of cellulose used})} \right) \times 100 \quad (2)$$

3.3. Catalyst Characterization

XRD patterns of the catalysts were determined by using a Rigaku SmartLab XRD system (Rigaku, Tokyo, Japan) with Cu K α radiation in the 2 θ range of 5–90°.

NH₃-TPD profiles were determined with a TPD-1-AT instrument (Bel Japan, Inc., Osaka, Japan) with an online quadrupole mass spectrometer. Samples (ca. 0.05 g) were pretreated at 773 K in flowing helium for 1 h, saturated in flowing 5% ammonia diluted with helium (0.5 cm³ s^{−1}) at 373 K for 30 min, and then treated at 373 K in flowing helium (0.83 cm³ s^{−1}) for 1 h. The samples were then heated at a constant rate of 10 K min^{−1} from 373 to 953 K while the amount of NH₃ desorbed was detected.

CO₂-TPD profiles were determined with a Micromeritics 3FLEX 3500 chemisorption analyzer (Micromeritics, Norcross, GA, USA) with an online quadrupole mass spectrometer. Samples (ca. 0.2 g) were pretreated at 773 K in flowing helium for 1 h, saturated in flowing CO₂ (0.5 cm³ s^{−1}) at 323 K for 30 min, and then treated at 323 K in flowing helium (0.83 cm³ s^{−1}) for 1 h. The samples were then heated at a constant rate of 10 K min^{−1} from 323 to 953 K while the amount of CO₂ desorbed was detected.

4. Conclusions

Compared with using pure ZrO₂ as the catalyst (yield, 21.2%), a greater yield of lactic acid was obtained from cellulose by using a 10%ZrO₂–Al₂O₃ catalyst (yield, 25.3%) and optimized reaction conditions (reaction temperature, 473 K; reaction time, 6 h). XRD analysis revealed that the 10%ZrO₂–Al₂O₃ catalyst contained tetragonal ZrO₂ and γ -Al₂O₃. NH₃-TPD and CO₂-TPD analyses revealed that all three ZrO₂–Al₂O₃ catalysts had more Lewis acid sites and far fewer base sites than did ZrO₂. This suggests that the number of Lewis acid sites on the ZrO₂–Al₂O₃ catalysts was more important than the number of base sites for the conversion of cellulose to lactic acid.

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Author Contributions: P.W. and A.Y. conceived and designed the experiments; P.W. performed the catalytic reaction experiments; O.S. and N.M. analyzed the data; K.S. performed the NH₃-TPD study; P.W., P.R., and A.Y. wrote the paper; all the authors discussed the results and commented on the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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