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Catalytic Conversion of Biomass-derived Carbohydrates to Methyl Lactate by Acid-Base Bifunctional γ -Al₂O₃

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ABSTRACT. We report the catalytic conversion of biomass-derived carbohydrates to methyl lactate using metal oxides. The combination of Lewis acid-base sites on $\gamma\text{-Al}_2\text{O}_3$ is superior to several amphoteric oxides for the production of methyl lactate from both dihydroxyacetone and glucose in methanol. The successful production of methyl lactate from glucose by $\gamma\text{-Al}_2\text{O}_3$ is attributed to high densities of both acid and base functionalities that are essential for the promotion of the step-wise reaction, which consists of isomerization, retro-aldol, and dehydration reactions.

INTRODUCTION. Woody biomass is expected to be used as an alternative to fossil fuels due to its abundance and non-competitive nature against food supply. Given that wood-based biomass consists of mainly carbohydrates, efficient systems to produce commercially and industrially important chemicals from carbohydrates should be devised.¹⁻³

α -Hydroxy esters have significant appeal as renewable biomass-derived solvents and building blocks for polyesters;^{4,5} in particular, lactic acid (LA) has attracted much attention because its polymer (i.e., polylactic acid) exhibits renewable and biodegradable properties, and has thus emerged as an alternative to petroleum-derived plastics.⁶⁻⁸ Their increasing popularity is due in part to rising concern over the mass consumption of fossil feedstocks for the synthesis of conventional polymers. This situation has motivated many scientists to develop synthetic processes for LA derivatives from biomass-derived saccharides, including both LA itself and LA esters, the latter of which are also useful chemicals as green solvents and feedstock for polymers.⁹ Recently, many researchers have reported the one-pot synthesis of LA derivatives from mono- and disaccharides with Sn-containing beta type zeolites,¹⁰⁻¹² a Ga-doped Zn/H-nanozeolite Y,¹³ and Fe-doped SnO_2 ,¹⁴ where glucose, which can be obtained via depolymerization of polysaccharides,

is the most desirable reactant due to its low cost.⁷ This cascade transformation from glucose to LA derivatives involves multiple steps: i) isomerization of glucose to fructose, catalyzed by bases or Lewis acids,^{15,16} ii) base-catalyzed retro-aldol reaction of fructose to two C3 units, 1,3-dihydroxyacetone (DHA) and glyceraldehyde,^{17,18} and iii) the formation of LA derivatives via dehydration and subsequent 1,2-hydride shift, accelerated by Lewis acids¹⁹⁻²³ (Scheme 1). In our related work, we demonstrated that homogeneous Lewis acids catalyze intermolecular aldol condensation between DHA and aldehydes,^{24,25} which indicates that retro-aldol reactions could also be accelerated in the presence of Lewis acids because all aldol reactions are reversible. These mechanistic insights led us to infer that amphoteric oxides that possess both basicity and Lewis acidity would enable a one-pot conversion of glucose to desirable LA derivatives in water or alcohol. Here, we have examined methyl lactate (MLA) formation from DHA and glucose in methanol using some typical amphoteric oxides (Al_2O_3 , ZrO_2 , TiO_2 , SnO_2 , and CeO_2) reported to date as heterogeneous catalysts.

RESULTS AND DISCUSSION. These five metal oxides were initially tested for MLA formation from DHA in methanol (Table 1). The catalysts were prepared via a typical precipitation method using the corresponding metal nitrates, followed by calcination of the resultant precipitates at 773 K (see Experimental Section). Figure S1 shows powder X-ray diffraction (XRD) patterns of these catalysts. All samples have diffractions derived from the corresponding crystalline oxides, which indicates that stable oxide networks can be formed by a simple calcination treatment. Catalytic activities and surface areas of the resultant metal oxides are summarized in Table 1 and Table S1, respectively. Any catalytic reaction takes place only on the surface; therefore, the surface area of a heterogeneous catalyst is one dominant factor for its catalytic activity. After the catalysts were

calcined in air at 773 K, they could be categorized into three groups depending on the surface area: high surface area (γ -Al₂O₃ with 209 m² g⁻¹), medium surface area (monoclinic ZrO₂ with 74 m² g⁻¹, anatase TiO₂ with 85 m² g⁻¹, and SnO₂ with 58 m² g⁻¹), and low surface area (CeO₂ with 36 m² g⁻¹). A series of catalytic activities for DHA to MLA transformation can be roughly explained according to their surface areas, even if there are some differences in the density of Lewis acid sites. γ -Al₂O₃ exhibited the highest catalytic activity, due to its high surface area, and produced MLA in 62% yield (entry 2), which is comparable to the MLA yields obtained previously from investigation of a variety of heterogeneous catalysts.⁴ The catalyst was recovered for further reaction by centrifugation, washing with water, and drying at 373 K in an oven overnight. The Al₂O₃ was determined to be reusable and exhibited good methyl lactate selectivity even after the 3rd use (entries 4 and 5). Next, an aluminum precursor was simply calcined at different temperatures (573 K and 973 K) to control the crystallinity and surface area of the resultant Al₂O₃ catalyst. No significant differences were obtained in surface area and catalytic activity between the Al₂O₃ catalysts calcined at 773 K and 973 K. However, Al₂O₃ calcined at 573 K showed significantly lower activity than the other two oxides (entry 3 versus entries 1 and 2). This can be attributed to the acid-base properties of the resulting oxide. High-temperature calcination at higher than 773 K successfully formed the stable and amphoteric γ -Al₂O₃ phase, which has Lewis acid sites that are effective for MLA formation (Figures S1(b) and S1(c)). Two prominent diffraction peaks at $2\theta = 45.9^\circ$ and 66.6° correspond to the (400) and (440) planes of γ -Al₂O₃, respectively. In contrast, calcination of the aluminum precursor at 573 K gave low crystalline boehmite (AlOOH), one of aluminum hydroxide phases (Figure S1(a)). Several distinct peaks at $2\theta = 28.2^\circ$, 38.2° , and 49.0° could be assigned to the (120), (031), and (051) planes of boehmite, respectively. The crystallization phenomenon observed for Al₂O₃ is in good agreement with previous reports²⁶,

in which phase transition from boehmite to γ -Al₂O₃ occurs at temperatures higher than ca. 723 K. Boehmite is a basic oxide and the intrinsic Lewis acidity of boehmite is insufficient to catalyze MLA formation compared with γ -Al₂O₃. Therefore, γ -Al₂O₃ can be considered as the most effective catalyst for MLA formation from DHA.

Although all of the metal oxides used in this study are known to exhibit both Lewis acidity and basicity, the former is mainly required for the DHA-to-MLA transformation. Therefore, catalytic performance of these metal oxides calcined at 773 K for direct transformation from glucose to MLA in methanol, which requires both functionalities, was investigated. Al₂O₃ calcined at 773 K again afforded the highest MLA yield of 34% (entry 8) among the catalysts tested, which was as high as the yields in previous reports.^{7,9-14} In the case of glucose, the Al₂O₃ was also reusable and exhibited acceptable product yields (entries 11 and 12). This high MLA yield is characteristic of γ -Al₂O₃ because the activities of the other metal oxides are less than 15% (entries 13-16). The results summarized in Table 1 thus demonstrated that Al₂O₃ calcined at 773 K efficiently accelerates both DHA and glucose transformations to MLA.

To rationalize the high performance of the two γ -Al₂O₃ samples for the reactions, the acid-base properties of the Al₂O₃ samples calcined at 773 K and 973 K were investigated using Fourier transform infrared (FTIR) spectroscopy. Here, chloroform and pyridine were used as acidic and basic probe molecules, respectively. The samples were first dehydrated at 423 K for 1 h to remove physisorbed water, and then exposed to saturated CHCl₃ or pyridine vapour at room temperature until the intensities of the absorption bands for these molecules became constant. The pyridine or CHCl₃-saturated samples were then evacuated at room temperature for 1 h to eliminate physisorbed species on the surface. The original FTIR spectra of the dehydrated samples taken at

room temperature were used as background spectra to obtain the difference spectra shown in Figures 1 and 2.

Figure 1 shows difference FTIR spectra of CHCl_3 -adsorbed $\gamma\text{-Al}_2\text{O}_3$ catalysts at 773 K and 973 K.²⁷ The stretching mode of the CH bond, which generally appears at 3020 cm^{-1} , was shifted to 2980 cm^{-1} due to the interaction between the acidic proton of CHCl_3 and a basic site formed on $\gamma\text{-Al}_2\text{O}_3$. The pair of negative and positive bands at 3760 cm^{-1} and 3670 cm^{-1} is attributed to interaction of surface Al-OH groups with CHCl_3 through the formation of an acid-base adduct and/or a simple physisorbed species. Note that a new bending mode appeared at 1247 cm^{-1} , along with the original bending mode at 1220 cm^{-1} . Given that lattice oxygen has basicity available for the stabilization of CHCl_3 , two different species of adsorbed CHCl_3 can be proposed, as illustrated in the inset of Figure 2. The band at 1247 cm^{-1} has been assigned to CHCl_3 mutually coordinated with both the base and acid sites via the C-H and C-Cl groups, respectively.²⁸ Considering the size of the chloroform molecule, Lewis acid and base sites in this case are present in close proximity. On the other hand, the formation of a simple acid-base adduct between CHCl_3 and lattice oxygen gives a typical H-C-Cl bending mode at 1220 cm^{-1} , as also observed for gaseous CHCl_3 . Based on these observations, it can be concluded that the two $\gamma\text{-Al}_2\text{O}_3$ catalysts synthesized here have both Lewis acid and base sites. Lattice oxygen and/or Al-OH groups on the surfaces are regarded as base sites.

Pyridine adsorption experiments with FTIR measurements were also conducted for the dehydrated samples to characterize their Brønsted and Lewis acidities.^{29,30} Figure 2 shows difference FTIR spectra of the pyridine-adsorbed samples.³¹ A specific band at 1445 cm^{-1} , assignable to coordinated

pyridine with Lewis acid site, was clearly observed in both samples. However, no band at 1540 cm^{-1} was obtained, which suggests that these samples have no Brønsted acid sites.

FTIR characterization with probe molecules thus indicated that $\gamma\text{-Al}_2\text{O}_3$ samples have both Lewis acid and base sites and they are effective for MLA formation. Table 2 summarizes the surface areas, and the amounts of Lewis acid and base sites for two $\gamma\text{-Al}_2\text{O}_3$ samples. The amount of Lewis acid sites can be estimated based on sample weight, the area for coordinated pyridine species at 1445 cm^{-1} (Figure 2), and the molecular absorption coefficient ($1.71 \text{ cm } \mu\text{mol}^{-1}$)³² to be 0.16 mmol g^{-1} for both samples. The amounts of base sites were also estimated by acid-base titration using phenolphthalein as a color indicator to be 0.36 mmol g^{-1} (773 K) and 0.40 mmol g^{-1} (973 K). In addition, the results for TiO_2 and ZrO_2 catalysts reported in the previous paper were also included in Table 2 for comparison.³³ The amounts of Lewis acid sites on TiO_2 and ZrO_2 calcined at 673 K were 0.32 mmol g^{-1} and 0.04 mmol g^{-1} , respectively.

Among the catalysts tested, the use of $\gamma\text{-Al}_2\text{O}_3$ led to the generation of MLA from glucose in high yield. The roles of Lewis acid and base properties on $\gamma\text{-Al}_2\text{O}_3$ should be discussed with respect to the reaction mechanism, as shown in Scheme 1. Given that these catalysts exhibit similar Lewis acid and base properties to those used in this work, the catalytic activity for MLA formation from DHA cannot be simply explained by the amount of Lewis acid sites; Al_2O_3 (0.16 mmol g^{-1}) and ZrO_2 (0.04 mmol g^{-1}) gave higher MLA yields than TiO_2 (0.32 mmol g^{-1}), as shown in Table 1, entries 2, 4, and 5. This is probably due to the type of Lewis acid center,³⁴ the intrinsic Lewis acidities of unsaturated coordination aluminum and zirconium species on their respective oxides are more suitable for selective DHA conversion to MLA than those of titanium species on TiO_2 surface.

On the other hand, these three catalysts have similar Lewis basic sites, i.e., oxygen atoms in the lattice and/or hydroxyl groups. This suggests that there is no large difference in the base properties among these catalysts, and the activities are simply dependent on the density of base sites. A high density of base sites on γ -Al₂O₃ is potentially beneficial for glucose isomerization and the retro-aldol reaction of evolved fructose, as shown in Scheme 1. In addition, intrinsic Lewis acid catalysis and a high density of Lewis acid sites would also contribute to glucose isomerization and MLA formation from triose sugars (DHA and glyceraldehyde). The combination of such Lewis acid and base properties consequently makes γ -Al₂O₃ an active catalyst for the one-pot synthesis of MLA from glucose in methanol.

Finally, we investigated the influence of the Lewis acid sites of metal oxides on the reaction activity. Activation of a reactant by a Lewis acid is closely related to the energy level of the highest occupied molecular orbital (HOMO) of the reactant (nucleophile; DHA or glucose) and the lowest unoccupied molecular orbital (LUMO) of the Lewis acid (electrophile).³⁵ Thus, a small HOMO/LUMO energy gap means that the nucleophile reacts easily with the Lewis acid to form a stable Lewis acid–nucleophile complex. However, it is difficult to evaluate the LUMO of the Lewis acid formed on the surface of metal oxides; therefore, we examined the HOMO energy level of the water-soluble triflates, Al(OTf)₃, Zr(OTf)₄, and Ti(OTf)₄, based on density functional theory (DFT) calculations. These HOMO values are -3.21, -3.78, and -4.89 eV, respectively. Therefore, if the reaction systems are based on the simple Lewis acidic reaction, the reaction activity may be in the order Ti>Al>Zr. (Note that the amount of the Lewis acidity (Table 2) was also in the order of Ti>Al>Zr.) However, the results for the reaction activity as shown in Table 1 were Al>Zr>Ti. These results indicate that the transformation of DHA or glucose into methyl lactate is not based on the simple Lewis acidity but rather on acid-base cooperative catalysis.

CONCLUSION. We have successfully established a catalytic process for the efficient production of MLA from biomass-derived carbohydrates. When the conversion of DHA and glucose was demonstrated using several metal oxides, Al_2O_3 had the best performance, and the yields were 62 and 34%, respectively. The successful production of MLA from glucose over $\gamma\text{-Al}_2\text{O}_3$ is attributed to a high density of both functionalities that are essential for promotion of the step-wise reaction, which consists of isomerization, retro-aldol, and dehydration reactions. These results indicate that acid-base bifunctional catalysis on the $\gamma\text{-Al}_2\text{O}_3$ surface is effective for carbohydrate conversion.

Supporting Information

The supporting information is available free of charge on the ACS Publications website.

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The authors declare on competing financial interest.

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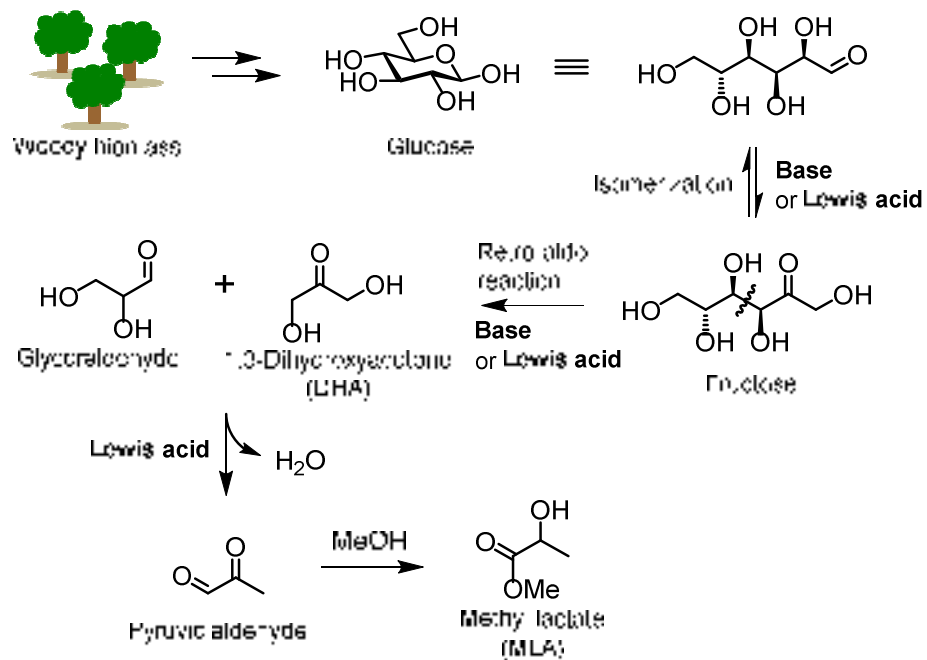
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Scheme 1. Reaction pathway for the conversion of glucose to methyl lactate.

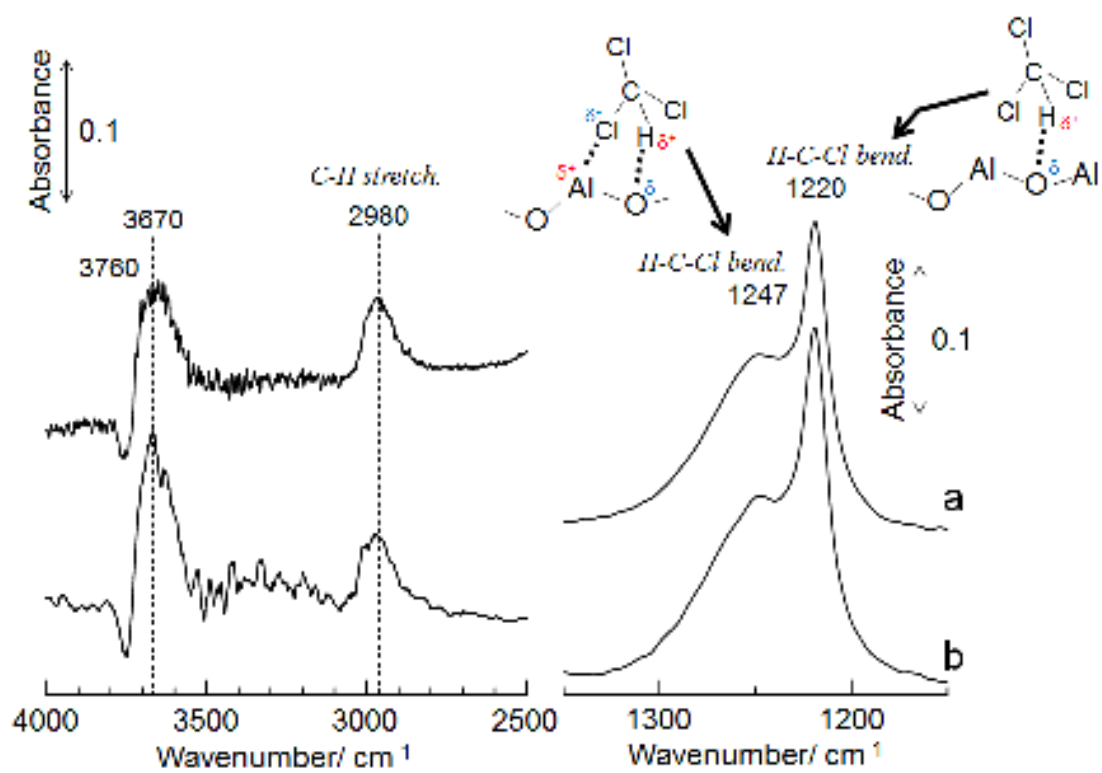


Figure 1. Difference FTIR spectra of CHCl_3 -adsorbed Al_2O_3 calcined at (a) 773 K and (b) 973

K.

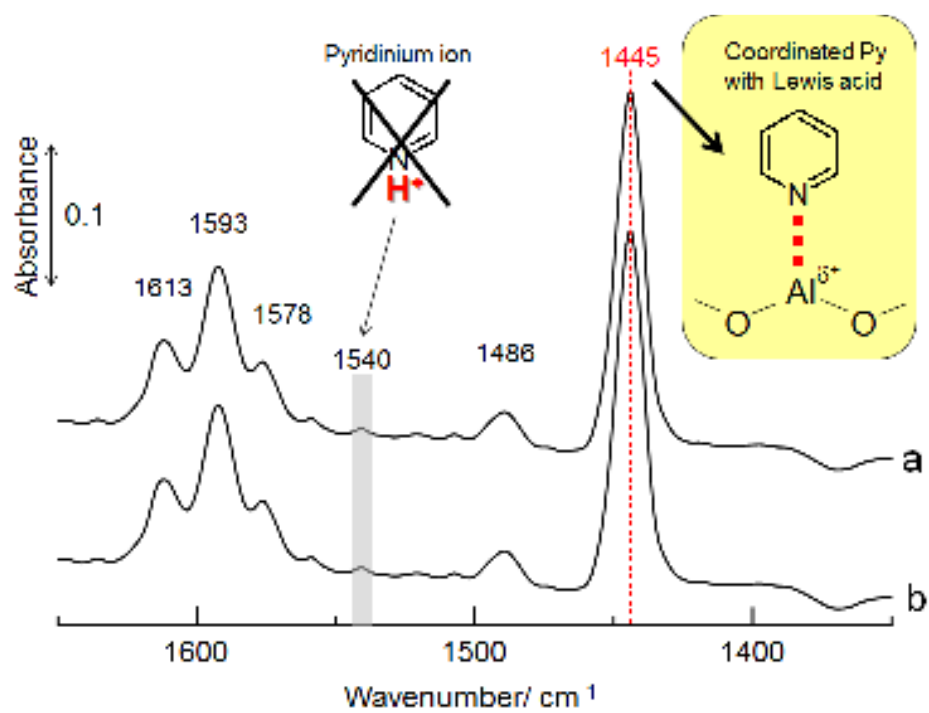


Figure 2. Difference FTIR spectra of pyridine-adsorbed Al₂O₃ calcined at (a) 773 K and (b) 973

K.

Table 1. Conversion of DHA or glucose into MLA with various metal oxides.^a

Entry	Calcination temp. [K]	Catalyst	Substrate	MLA yield [%] ^b
1	973	Al ₂ O ₃	DHA	54
2	773			62
3	573			25
4	773	Al ₂ O ₃ ^c		55
5		Al ₂ O ₃ ^d		42
6	773	ZrO ₂		41
7		TiO ₂		30
8		SnO ₂		32
9		CeO ₂		15
10	773	Al ₂ O ₃	Glucose	34
11		Al ₂ O ₃ ^c		25
12		Al ₂ O ₃ ^d		21
13		ZrO ₂		6
14		TiO ₂		10
15		SnO ₂		1
16		CeO ₂		14

^a Reaction conditions: DHA or glucose (55.6 mg), methanol (5.0 mL), catalyst (100 mg), naphthalene (0.156 mmol), Ar (5 atm), 6 h, 413 K for DHA, 433 K for glucose. All catalysts were calcined for 2 h, prior to use. Conversions of DHA and glucose were >99%, based on ¹H NMR analysis. ^b Carbon-based yield (%). The amount of MLA produced was determined by ¹H NMR analysis. ^c 2nd use. ^d 3rd use.

Table 2. Acid and base properties of metal oxides samples calcined at different temperatures.

Samples	Calcination temp. [K]	BET surface area [m ² g ⁻¹]	Acid amount ^a [mmol g ⁻¹]	Base amount ^b [mmol g ⁻¹]
Al ₂ O ₃	773	209	0.16	0.36
Al ₂ O ₃	973	151	0.16	0.40
TiO ₂ ^c	673	95	0.32	0.006
ZrO ₂ ^c	673	84	0.04	0.08

^a Pyridine-IR. ^b Acid-base titration. ^c See Ref. 33.