A Comparative Study of the Divalent Transition Metal Oxide Supported on Magnesium Oxide Catalyst for Lactic Acid Production from Glucose

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Abstract. In order to achieve the lactic acid production of lower energy consumption, reactor corrosion rate, while being environmentally friendly and sustaining high catalytic activity of various divalent transition metal oxide (Cu, Co, Ni and Zn) supported on magnesium oxide having the hexadecyltrimethylammonium bromide (CTAB) as a capping agent was investigated, where the reaction was performed under mild conditions in an alkali additive-free environment. Among all of the divalent candidates, the ZnCTAB/MgO exhibits the highest activity with a glucose conversion of 64% at a 100°C and a lactic acid yield of 12% at 140°C, a pressure of 0.4 MPa, over 1 h of reaction time. This is due to the high basicity produced via the water chemisorption on such catalyst’s surface.

1. Introduction
Over the last decade, global warming and energy crisis are major concerns caused by the increase in atmospheric carbon dioxide content and the depletion of fossil fuels. These issues force the chemical industry to focus more on the necessity to change from the feedstock of fossil fuels based to renewable resources.

Biomass is one of the suitable renewable carbon resources because it contains adequate carbon-carbon bonds to produce useful chemicals. Moreover, it does not increase the carbon dioxide in the atmosphere, making it a cleaner choice than the energy produced from fossil-based [1]. The major component of lignocellulosic biomass (wood, straw, and grasses) is the C6-sugars (glucose, fructose, and mannose), which are interesting precursors for the use in a wide range of high-value chemicals production.

The lactic acid (2-hydroxypropionic acid, C₃H₆O₃) is an important natural organic acid, which has broad applications in food, pharmaceutical, and cosmetic industries and it is also a building block for the synthesis of many useful chemicals, e.g., pyruvic acid, acetaldehyde, acrylic acid, and propanoic acid [2]. In recent years, lactic acid has gained more attention as a major feedstock for the manufacture of biodegradable plastics [poly(lactic acid), PLA], which can be decomposed by bacteria, while exhibiting a good mechanical strength. Thus, it is a suitable choice for the replacement of petroleum-based polymers reducing the environmental impacts [3].
The lactic acid can be synthesized by two routes of either the fermentation of carbohydrates with microorganisms or the chemical synthesis. At present, over 90% of the industrial lactic acid production is by the fermentation of glucose from starch with enzyme or microbes. However, the biological process has some disadvantages, e.g., strict controls of reaction conditions, a long fermentation time, and difficult scale-up of the process. Hence, the chemical synthesis route is a more interesting choice [4].

Generally, in the chemical route, the lactic acid was synthesized via the hydrolysis of lactonitrile, formed by the reaction between acetaldehyde and hydrogen cyanide. This process generates a highly toxic cyanide compound that causes an environmental issue [5]. As a result, producing the lactic acid from biomass via the chemocatalytic systems has been proposed as a promising route.

It is well-known in a lactic acid production from sugar that the alkali is typically used as a catalyst. Various authors focused on the hydrothermal process with or without alkali solution and/or heterogeneous catalyst. They reported that the water in the subcritical and supercritical regions acts as an alkaline catalyst. Some researchers also studied the conversion of glucose into lactic acid at high temperature (above 250°C) for short time (60-90 s). In 2007, Yan et al. compared two alkaline catalysts including sodium hydroxide (NaOH) and calcium hydroxide [Ca(OH)2] at 300°C for 60 s. The highest lactic acid yield of 27% was obtained for 2.5 M NaOH [6]. To enhance the production of carboxylic acids from carbohydrates, Wang et al. (2013) used a metal oxide as an oxidant catalyst. They compared the oxidative potential of different metal oxides (CuO, Fe2O3, Al2O3, ZnO and TiO2) and found that CuO gave the best activity with yields of lactic acid, acetic acid, and formic acid of 37.1%, 9.4%, and 4.9% respectively at 300°C for 60 s with CuO of 1.5 mmol and NaOH of 2.5 M [1, 7]. The previous study performed the reaction under a high concentration of alkali causing the corrosion to the reactor and pollute to the environment. To solve this problem, Huo et al. (2014) suggested that transition metal ions could improve lactic acid production from glucose and decrease the NaOH concentration at the same time. They compared various transition metal ions of Ni2+, Zn2+, Co2+, Fe3+, Fe2+, Mg2+, Cd2+, Sn2+, and Cu2+ obtained from metal chloride compounds. The highest yield of 25% for lactic acid was obtained with 0.01 M Ni2+ and 0.01 M NaOH at 300°C for 1 min [8].

In addition, there are several researches that used solid catalyst without the addition of an alkali agent for such catalyst. They investigated the effect of calcination temperature on lactic acid yield (30%) was obtained with 0.6 mol/L Na2SiO3 at 300°C for 60 s [11]. Obviously, all previous studies were performed under extreme conditions, which has some disadvantage including high energy consumption, increase equipment investment and limitation for the scale-up. So, many studies at mild condition were carried out, i.e., lower temperature and longer time. In 2008, Onda et al. studied the effect of various metals (Ru, Cu, Ag, Pd, and Pt) supported on the activated carbon catalyst on the selectivity of lactic acid and gluconic acid from glucose. The Pt/C showed the highest activity with the lactic acid and gluconic yield of 47% and 46%, respectively at 80°C for 2 h under air bubbling [3]. They focused on another solid basic catalyst, the hydrotalcite. They investigated the effect of the calcination temperature of the catalyst. The result showed that the calcined hydrotalcite under air at 450°C gave the highest lactic acid yield (20%) at 50°C for 8 h with NaOH 50 mmol/L [12]. In 2015, Choudhary et al. used the magnesia supported-Cu oxide catalyst synthesized via a hydrothermal method, which makes the copper oxide species interacts strongly with the support. In addition, CTAB (hexadecyltrimethylammonium bromide) was used as the capping agent for such catalyst. They investigated the effect of calcination temperature on lactic acid production. From their result, CuCTAB/MgO calcined under air at 500°C gave the highest yield for lactic acid and exhibited the maximum number of Brønsted basic sites. The optimum condition for the reaction was 120°C for 1 h with 2.5 M of NaOH resulting in 70% of lactic acid yield. They reported
that CTAB favored the dispersion of metals on metal oxides and influenced the generation/regeneration of the active Cu species during calcination [13]. Li et al. (2017) studied the effect of common alkaline metal hydroxides (NaOH and KOH) and alkaline-earth metal hydroxides (Mg(OH)$_2$ and Ba(OH)$_2$) on lactic acid yield. They found that Ba(OH)$_2$ exhibited higher catalytic activity than NaOH and KOH in the same OH$^-$ concentration. They reported that the divalent Ba$^{2+}$ ion played an important role in the conversion of glucose to lactic acid. The highest lactic acid yield of 78.3% was obtained at 25°C for 48 h under a nitrogen atmosphere.

From the previous research, most of all introduced reaction with the addition of alkali solution and many types of research showed the important role of the divalent ion of the catalyst in glucose conversion to the lactic acid. These inspired us to improve heterogeneous catalyst for glucose conversion to lactic acid without the addition of the alkaline solution, which reduces the reactor corrosion problem while being less toxic to the environment and the catalyst can be reused. So, this research focuses on the investigation of the effect of various divalent transition metal oxides supported on magnesium oxide catalyst using CTAB as the capping agent on lactic acid production from glucose performed under mild temperature and pressure in an alkali-free environment.

2. Experimental

2.1. Chemicals

The D-(+)-glucose, D-(−)-fructose, hexadecyltrimethy-ammonium bromide (CTAB), magnesium oxide (MgO), copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$•3H$_2$O), cobalt(II) nitrate hexahydrate (Co(NO$_3$)$_2$•6H$_2$O), nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$•6H$_2$O), zinc acetate dihydrate (Zn(CH$_3$COO)$_2$•2H$_2$O), lactic acid, formic acid and acetic acid used as reactants and/or as standard agents for the analysis were purchased from S.M. Chemical Supplies Co., Ltd.

2.2. Catalyst preparation

All catalysts were synthesized by the hydrothermal method described by Choudhary et al. with some modification [13]. First, the MgO was dispersed in deionized water by sonication. Then, an aqueous solution of 1 mmol/g-catalyst of various metals [Cu(NO$_3$)$_2$•3H$_2$O, Co(NO$_3$)$_2$•6H$_2$O, Ni(NO$_3$)$_2$•6H$_2$O or Zn(CH$_3$COO)$_2$•2H$_2$O] was added dropwise into the dispersed MgO solution under vigorous stirring. Thereafter, an aqueous CTAB solution of 1 mmol/g-catalyst was added into the mixture and vigorous stirring was continued for 3 h. The mixture was added in a 3-L autoclave prior to the heating to 180°C, where it was maintained at such temperature for 24 h. Afterward, it was slowly cooled down to room temperature. The obtained solid was washed with deionized water until the pH of the filtrate solution reaches 7.0 prior to another washing with ethanol. The solid was dried overnight at room temperature before being calcined in air at 500°C for 6 h with a ramp rate of 10°C/min. The prepared catalyst is characterized as a metal (Cu, Co, Ni, and Zn) catalyst supported on the MgO having CTAB as the capping agent.

2.3. Catalytic reaction procedure

The reaction testing was conducted in a Teflon-liner-fitted 50-mL-stainless-steel autoclave. First, 0.36 g of catalyst was load into the autoclave before the 0.54 g dissolved glucose dissolved in 30 mL of deionized (DI) water was added. Afterward, the autoclave was sealed, followed by the purging with nitrogen (N$_2$) three times at 0.4 MPa. After the purging, the autoclave was placed in a preheated oil bath at 140°C and stirred with a magnetic stirrer at 400 rpm and reacted at 140°C for 1 h. After the reaction, the autoclave was cooled down to room temperature in an ice-water bath immediately. The resulting solution was filtrated with a 0.2 µm syringe filter and analyzed by the high-performance liquid chromatography (HPLC).
2.4. Product analysis
The resulting solution was analyzed by HPLC, Agilent LC 1100 using an Agilent Hiplex-H column equipped with a UV-detector with a wavelength of 195 nm used in the detection of glucose and fructose [14]. In addition, the wavelength of 210 nm was used to detect organic acids, i.e., lactic acid, formic acid, and acetic acid. A dilute sulfuric acid aqueous solution of 5 mM in deionized water was used as the mobile phase at a flow rate of 0.6 mL/min. The conversion and yield were determined from the calibration curve.

The glucose conversion and yield of organic acid were calculated from the following equation:

\[
\text{Conversion} (\%) = \frac{\text{Moles of introduced substrate} - \text{Moles of remained substrate}}{\text{Moles of introduced substrate}} \times 100
\]

\[
\text{Product yield} (\%) = \frac{\text{Moles of product} \times \text{Number of carbon in product}}{\text{Moles of introduced substrate} \times \text{Number of carbon in substrate}} \times 100
\]

2.5. Catalyst characterization
The crystal structure and X-ray diffraction (XRD) patterns were analyzed by an X-ray diffractometer (Bruker D8 Advance) using Cu Kα irradiation at a 20 angle between 10° and 80° with a step of 0.05°/s. The lattice parameter and d-spacing were calculated via the Bragg’s law.

Temperature programmed reduction (TPR) was used to determine the reducibility of the catalyst. In H₂-TPR experiments, 0.08 g of catalyst was placed into the U-tube quartz reactor and pretreated under nitrogen (flow 25 ml/min) at 250°C for 1 h to remove water and impurities in the catalyst. After cooling down to 30°C, the catalyst was heated from room temperature to 650°C at a rate of 10°C/min under a flow of 10%H₂/Ar mixture (25 ml/min), in which the consumption of H₂ was recorded by the TCD.

The basicity of the catalyst was measured by carbon dioxide temperature programmed desorption (CO₂-TPD) and the titration with benzoic acid. For CO₂-TPD, each catalyst (0.1g) was charged into the U-tube quartz reactor. It was pretreated at 450°C with a temperature ramp of 10°C/min for 1 h under flow of Helium at 25 ml/min to remove any physisorbed organic molecules. Then, it was cooled down to 60°C followed by the saturation with CO₂ (flow at 25 ml/min) for 30 min. After which, the gas was switched to helium (25 mL/min) to remove the physisorbed CO₂. When the baseline is constant, the temperature of the furnace was increased to 750°C with a temperature ramp of 10°C/min under a flow of helium at 25 ml/min. The obtained TPD profile was recorded with a thermal conductivity detector (TCD) (Micromeritics 2750). For the titration with benzoic acid, 0.025 g of catalyst was dispersed in the mixed solution of DI water and ethanol (4:1 v/v) in the Erlenmeyer flask. The phenolphthalein was added 1-2 drops to the solution as an indicator. Then, 0.5 M of benzoic acid was added dropwise until the pink colour of the solution disappeared. The volume of benzoic acid used was measured to calculate the amount of basic site (mmol/g-catalyst).

3. Results and discussion

3.1. Effect of type of transition metal oxide supported on magnesium oxide catalyst and the reaction temperature

3.1.1. Glucose conversion. The catalytic activity of various transition metal oxides supported on magnesium oxide under mild conditions is shown in figure 1. The reaction was performed at 100°C, 120°C, and 140°C for 1 h under N₂ at 0.4 MPa. It was found that the conversion of all catalysts was above 50% and increased to 100% with an increase in the reaction temperature. This suggested that the increase in reaction temperature enhanced the reaction of glucose conversion [15]. The ZnCTAB/MgO exhibited the highest activity for glucose conversion (64%), while the others follow the trend as NiCTAB/MgO > CoCTAB/MgO > CuCTAB/MgO.
3.1.2. Lactic acid yield. Figure 2 describes lactic acid yield from various transition metal oxides supported on magnesium oxide at 100°C, 120°C, and 140°C. An increase in reaction temperature increases the lactic acid yield for all catalysts as has been previously reported [13, 16, 17]. When the reaction was performed at a lower temperature (100°C and 120°C), the NiCTAB/MgO exhibited the highest selectivity in lactic acid production compared with other catalysts to an obtained lactic acid yield of 2.6% and 5%, respectively. In addition, ZnCTAB/MgO gave the highest lactic acid yield (12%) at a high reaction temperature of 140°C.
3.2. Catalyst characterization
Catalysts were characterized by XRD to determine the phase of the catalyst. The XRD patterns of various metal oxides supported on the magnesium oxide catalyst are reported in figure 3.

![XRD patterns of various divalent metal oxides supported on magnesium oxide catalyst.](image)

The different species are shown as MgO (●), CuO (●), Cu₂O (○), CoO (●), Co₃O₄ (◆), NiO (■) and ZnO (◆).

All catalysts displayed the characteristic peaks of MgO at 36.9°, 42.9°, 62.3°, 74.7°, and 78.6°. For CuCTAB/MgO catalyst (figure 3b), the oxide species of copper formed showed both the Cu₂O and CuO characteristics. The peaks for CuO were observed at 36.4° and 39.5°. For the CoO peak, (figure 3c) they are 36.8°, 42.8° and 62.2° with minor peaks at 31.3° and 65.2° suggested to be the Co₃O₄, while NiCTAB/MgO (figure 3d) showed all characteristics peaks of NiO which were aligned with the peak of the magnesium oxide at 36.8°, 42.8° and 62.2°. And the characteristic peaks of ZnCTAB/MgO (figure 3e) showed the ZnO characteristics at 31.7°, 34.4°, 36.2°, 36.7°, 42.8°, 47.4°, 56.5°, and 62.0°. From XRD patterns, it is noticeable that the peak of all metal oxide species was a coincidence with the peak of magnesium oxide indicating that the CuO, NiO, and ZnO were supported successfully on the MgO. The catalyst has a mixed oxide phase with no impurity presented [18].

The basicity of the catalyst was investigated from the temperature programmed desorption of carbon dioxide (CO₂-TPD) and the titration with benzoic acid. The CO₂-TPD profile and the amounts of basicity calculated from CO₂-TPD and benzoic acid titration are shown in figure 4 and table 1, respectively.
Figure 4. CO$_2$-TPD profile of various divalent metal oxides supported on magnesium oxide catalyst.

Table 1. Amounts of basicity which was calculated from CO$_2$-TPD and benzoic acid titration.

| Catalyst   | CO$_2$-TPD (µ mol CO$_2$/g cat) | Benzoic acid titration (mmol/g cat) |
|------------|---------------------------------|-------------------------------------|
| CuCTAB/MgO | 462.61                          | 3.8                                 |
| CoCTAB/MgO | 259.67                          | 1.9                                 |
| NiCTAB/MgO | 343.34                          | 2.6                                 |
| ZnCTAB/MgO | 403.17                          | 4.8                                 |

From CO$_2$-TPD profile, the basic strength of all catalysts was similar showing the CO$_2$ desorption peaks at the temperature lower than 300°C, indicating that metal oxide supported on magnesium oxide catalysts has weak basic strength. The trend in the amounts of basicity calculated from the CO$_2$-TPD were in the order of CuCTAB/MgO > ZnCTAB/MgO > NiCTAB/MgO > CoCTAB/MgO, while the trend obtained from the benzoic acid titration method is ZnCTAB/MgO > CuCTAB/MgO > NiCTAB/MgO > CoCTAB/MgO. This indicated that the basicity of ZnCTAB/MgO increased when the catalyst was added into the water as confirmed by Sengupta G. (1978) which reported the chemisorption of water on the surface of ZnO at 150°C. They found that at the surface of the catalyst, both Zn$^+$ and O$^-$ ions act as water adsorption sites. The dissociation of a water molecule into the •H and •OH radicals chemisorbed to ions on the ZnO surface generates the Zn(OH) species on the surface shown below[19].
The OH group generated at the surface may increase the amount of basicity, resulting in the highest activity found in the case of ZnCTAB/MgO. Choudhary et al. (2015) reported the mechanism of glucose conversion into lactic acid that the basicity of catalyst played a crucial role in the reaction pathway including the hydrolysis, isomerization, retro-aldol reaction, and the transformation into lactic acid. The reducibility of the catalyst has a role in the formation of pyruvaldehyde-complex form which is the intermediate prior to the formation of the lactic acid [13]. To understand the reducibility of the catalyst, the H$_2$-TPR was employed. The analyzed profiles of various transition metal oxides supported on magnesium oxide are shown in figure 5.

\[
\text{OH} \quad \text{H} \\
\begin{align*}
\text{ZnO} &+ \text{H}_2\text{O} \rightarrow \text{Zn} \quad \text{O} \\
\end{align*}
\] (3)

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**Figure 5.** H$_2$-TPR profiles of various transition metal oxides supported on magnesium oxide catalyst.

The CuCTAB/MgO exhibited a peak at a lower temperature than the other catalysts. The peak at the temperature of 220°C attributes to a well-dispersed CuO phase which can be easily reduced and at the peak of 270°C is reflected the reduction of larger CuO particles. Another small peak at 320°C is due to a low metal dispersion [20]. There is a reduction peak at 360-400°C for CoCTAB/MgO, which is ascribed to the reduction of Co$_3$O$_4$ [21]. For NiCTAB/MgO, the small reduction peak occurred at a temperature below 400°C, illustrating the bulk nickel oxide with low interaction with the support. The peak at temperatures higher than 700°C describes the incorporation of NiO with MgO support and the formation of NiO–MgO solid solution [22]. In addition, the ZnCTAB/MgO has a reduction peak at 330°C, 380°C, 560°C, and 680°C, which means that it is hardly reduced compared to the CuCTAB/MgO. However, the glucose conversion and lactic acid yield from ZnCTAB/MgO was higher than the CuCTAB/MgO catalyst. This observation suggests that the basicity of catalyst affects the lactic acid production from glucose more than the reducibility of the catalyst.
4. Conclusions
The investigation on the effect of different divalent transition metal oxide supported on magnesium oxide using CTAB as a capping agent on the glucose conversion to lactic acid found that the ZnCTAB/MgO exhibited the highest activity with a glucose conversion of 64% at 100°C, 0.4 MPa, and 1 h reaction time, whereas the lactic acid yield at 1 h of 12% at 140°C and 0.4 MPa was achieved. This catalytic system consumes less energy, lowers reactor corrosion, and is considered environmentally friendly because of the absence of alkali catalyst typically used in such reaction. A high activity achieved by the ZnCTAB/MgO was suggested to be caused by high basicity produced via water chemisorption on the catalyst’s surface.

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