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Hydrogenation of lactic acid to propylene glycol over a carbon-supported ruthenium catalyst

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ABSTRACT

Catalytic hydrogenation of lactic acid to propylene glycol is performed in a high-pressure batch reactor over ruthenium on various carbon supports (i.e., VulcanXC-72, ketjen black, CNTs, CNFs, and graphite) prepared using the incipient wetness impregnation method. The crystallinity of the synthesized catalyst is investigated via X-ray diffraction, and the particle sizes are determined using transmission electron microscopy. The surface areas of the synthesized catalysts are analyzed using the BET method; the catalytic activity correlates remarkably with the BET surface area. The yield of propylene glycol increases with pressure, and the highest yield is achieved at 130 °C. The catalytic activity is strongly dependent on the type of support. Among the catalysts tested, Ru on ketjen black shows the highest yield of propylene glycol.

1. Introduction

Lactic acid is a very useful raw material for the food and medical industries, and its consumption has increased steadily. The production of lactic acid by fermentation of biomass is important to meet the increasing demand. Via fermentation, lactic acid can be generated from renewable sources such as refined carbohydrates derived from agricultural crops [1,2] and waste biomass [3]. Lactic acid is known to be very reactive because it contains both hydroxyl and carboxy functional groups. Accordingly, it can be converted into a variety of chemicals through polymerization [3], condensation [4–6], dehydration [7], esterification [8,9], and oxidation [10].

Propylene glycol is widely used in foods, consumer products, and chemical applications and is produced industrially via the hydration of propylene oxide [11]. Propylene glycol production from lactic acid via a very good method was reported in the 1930s (Fig. 1). However, in general the catalytic conversion of lactic acid to propylene glycol requires high temperature and pressure. Dumesic et al. reported the conversion of lactic acid to propylene glycol over a silica-supported copper catalyst [12]. They proposed that hydroxyl acryl species were formed by dissociative adsorption of lactic acid; successive hydrogenation of the adsorbed species was thought to comprise the main mechanism for the production of propylene glycol.

Miller et al. [13] investigated the production of propylene glycol from lactic acid over various catalysts and reported a high yield of propylene glycol using ruthenium supported on activated carbon prepared via impregnation. According to their results, carbon is a promising support because of its inertness and stability in aqueous solution.

In the present work, ruthenium was supported on five different types of carbon (i.e., VulcanXC-72, ketjen black (KNB), carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphite) via the incipient wetness impregnation method. The resultant supported ruthenium catalysts were characterized by X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET) method, and high-resolution transmission electron microscopy (HR-TEM).

The catalytic activities of the catalyst towards the conversion of lactic acid into propylene glycol were investigated in a liquid-phase batch reactor, and the influence of the reaction temperature and pressure on lactic acid conversion was also studied. The main goal of this study is to investigate the effect of the support on the catalytic activity of ruthenium.

2. Experimental

2.1. Preparation and characterization of supported ruthenium catalyst

All carbon supports used in this study were obtained from commercial sources: VulcanXC-72 from Carbot International, ketjen black from Mitsubishi Chemical, CNTs from Iljin Nanotech,

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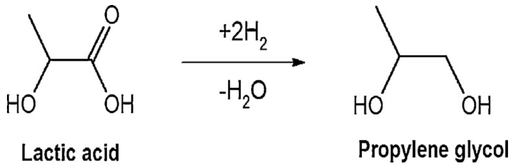

Fig. 1. Conversion of lactic acid to propylene glycol.

CM-95 and CNFs from Carbon Nano-material Technology, and graphite from Aldrich.

Prior to the impregnation of ruthenium, all carbon supports were immersed overnight in a stirred mixture of nitric acid and sulfuric acid (volume ratio of 3:1). After washing the resultant carbon in warm distilled water several times, the supports were placed in an oven at 100 °C and left overnight.

The ruthenium catalysts supported on various carbons were prepared using the incipient wetness impregnation method followed by drying at 100 °C. The ruthenium loading was 5 wt% for all the catalysts, and the dried powder was calcined at 500 °C for 4 h under flowing air. Prior to the reaction, all synthesized catalysts were reduced under flowing hydrogen at 400 °C for 4 h. After cooling, the catalysts were passivated in nitrogen for 30 min before being exposed to air [14].

All the synthesized catalysts underwent detailed analyses. The crystallinity of the synthesized samples was investigated using X-ray diffraction analysis (Rigaku, D/max-2200). A transmission electron microscope (JEOL/JEM2100F) was used to examine the surface morphologies and ruthenium particle sizes. The surface areas of the synthesized catalysts were determined using the BET method (ASAP 2020), and both the pore volumes and average pore sizes were calculated using the BJH model.

2.2. Hydrogenation of lactic acid

Liquid-phase catalytic hydrogenation of lactic acid to propylene glycol was performed in a 150 mL batch reactor at various reaction pressures (40–80 bar) and temperatures (110–170 °C).

A mixture of 1 M lactic acid solution (50 mL) and prepared catalyst (0.5 g) was placed into the reactor and agitated at 700 rpm. After purging the reactor with nitrogen for 5 min, the reactor was heated under flowing hydrogen. When the temperature reached the desired value, the hydrogen pressure was set to the specified pressure (40–80 bar) and the reaction was left for 6 h. The products were analyzed using a gas chromatograph (HP 6890) equipped with a flame-ionization detector. A free fatty-acid phase capillary column was used for the separation of the reactants and products.

3. Results and discussion

3.1. Characterization of supports and supported catalysts

X-ray diffraction analyses were performed on all samples; the XRD pattern of the CNT-supported ruthenium catalyst after reduction under hydrogen flow is shown in Fig. 2(a). For all the catalysts, two broad and strong peaks are evident at $2\theta = {\sim}25^\circ$ and 44°, which are assigned to the (0 0 2) diffraction of graphite carbon and the diffraction of the (1 0 1) planes of metallic ruthenium, respectively [15]. This indicates that the ruthenium in each catalyst was reduced to metallic ruthenium during thermal treatment under hydrogen flow.

Fig. 2(b) shows a TEM image of Ru/ketjen black after reduction under hydrogen flow. The Ru/ketjen black catalyst exhibited fairly uniform dispersion of small ruthenium species (less than 3 nm). Fine dispersion was also observed for the other carbon supports, and the average particle sizes of each catalyst, as measured from the TEM images, are summarized in Table 1. Before impregnation of ruthenium, all carbon supports were pretreated in a mixture of nitric acid and sulfuric acid. Many types of functional groups, such as hydroxyl groups, can form on the surface of carbon supports; these functional groups play an important role in the fine dispersion of ruthenium particles.

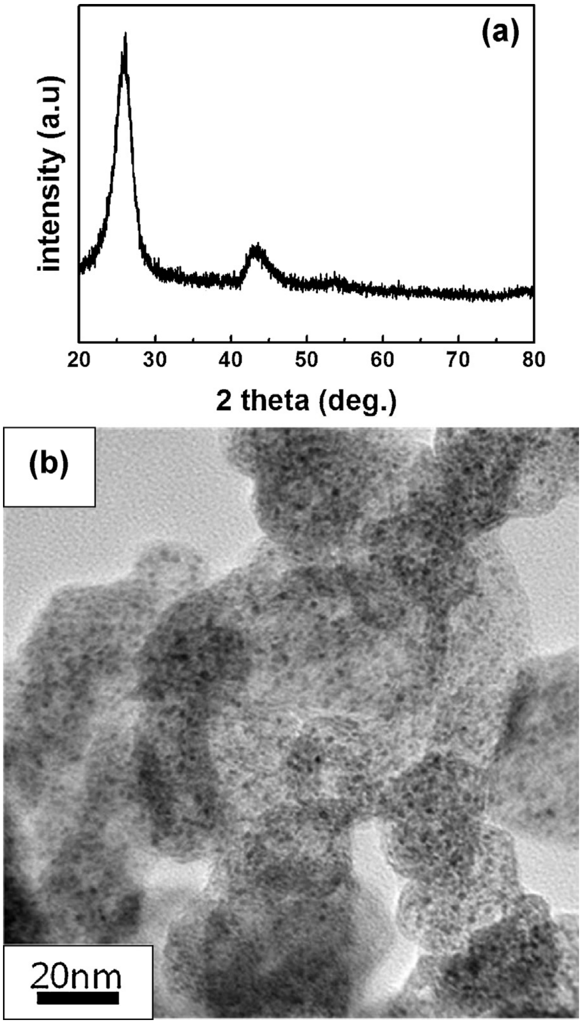

Fig. 2. (a) X-ray diffraction pattern of 5 wt% Ru/CNTs, and (b) a TEM image of 5 wt% Ru/ketjen black.

The BET surface areas, pore volumes, average pore sizes, and average particle sizes of the various carbon-supported ruthenium catalysts are listed in Table 1. Although the ruthenium particles were observed to be finely dispersed on all the carbon supports, the average particle size correlated remarkably with the surface area of the carbon support. Ketjen-black – supported ruthenium exhibited the highest surface area (1242.4 m^2/g), highest pore volume (5.54 cm^3/g), and smallest average ruthenium particle size (1.6 nm) of the investigated catalysts. The surface area of ketjen black is reported to be 1423 m^2/g, and this high surface area was maintained after the impregnation of ruthenium. In contrast, graphite-supported ruthenium showed the lowest surface area (17.2 m^2/g) and the largest average ruthenium particle size (10.4 nm), which is probably because of its high crystallinity and dense structure. Overall, the supports with larger surface areas exhibited smaller average ruthenium particle sizes. These results can be explained by the presence of functional groups that form on the surface of the carbon support during acid treatment. Larger carbon surface areas result in the formation of more functional

Table 1
BET surface areas, pore volumes, average pore sizes, and average Ru particle sizes of the synthesized catalysts.

	Ru/Vulcan	Ru/KNB	Ru/CNTs	Ru/CNFs	Ru/graphite
Average Ru particle size (nm)*	3.9	1.6	3.5	8.3	10.4
Surface area (m^2/g)	209.5	1242.4	225.5	118.0	17.2
Pore volume (cm^3/g)	0.49	5.54	1.26	0.18	0.05
Average pore size (nm)	9.4	17.9	22.5	5.9	11.6

* Average particle size was measured from TEM imasges.

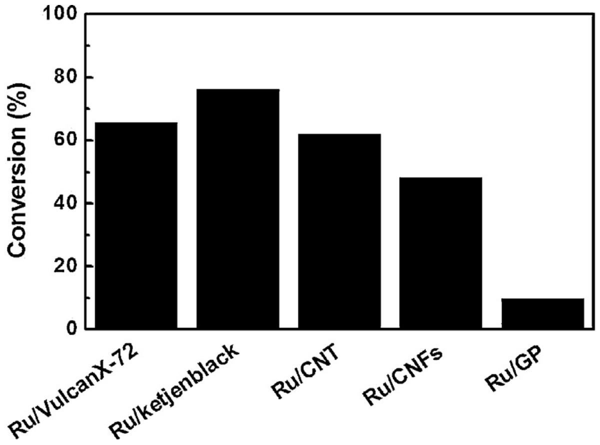

Fig. 3. Lactic acid conversion over various carbon-supported ruthenium catalysts. Reactant: 50 mL of 1 M lactic acid solution, reaction time = 2 h, temperature = 150 °C, and hydrogen pressure = 50 bar.

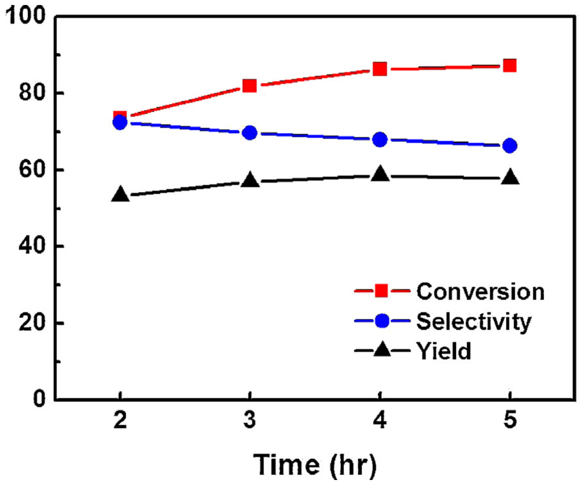

Fig. 4. Catalytic activity of 5 wt% Ru/ketjen black with respect to time on-stream. Reactant: 50 mL of 1 M lactic acid solution, temperature = 150 °C, and hydrogen pressure = 50 bar.

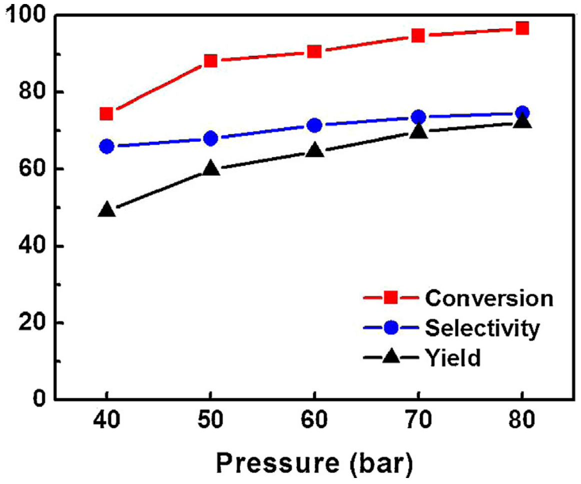

Fig. 5. Catalytic activity of 5 wt% Ru/ketjen black with hydrogen pressure. Reactant: 50 mL of 1 M lactic acid solution, reaction time = 4 h, and temperature = 130 °C.

groups causing the finer dispersion of ruthenium on the surface [16].

3.2. Hydrogenation of lactic acid to propylene glycol

Catalytic hydrogenation of lactic acid was performed in a high-pressure batch reactor. Fig. 3 shows a comparison of the lactic acid conversions over ruthenium supported on various carbons (i.e., VulcanXC-72, ketjen black, CNTs, CNFs, and graphite) after 2 h. The reaction temperature was 150 °C, and the hydrogen pressure was 50 bar for all catalysts except for graphite-supported ruthenium. Ruthenium supported on ketjen black showed the highest conversion (above 75%) of the catalysts tested. Interestingly, the catalytic activity correlated remarkably with the BET surface area: The higher the BET surface area, the higher the conversion of lactic acid. However, the correlation between the BET surface area and lactic acid conversion was not linear; for example, Ru/ketjen black showed a 10% increase in lactic acid conversion over that of Ru/Vulcan, but its BET surface is 6 times greater. These results can be explained by the amount of ruthenium loaded. For all catalysts, 5 wt% ruthenium was impregnated. If the loading amount is increased, the difference in the catalytic activities of the two catalysts would increase. The influence of the amount of ruthenium loaded on ketjen black on lactic acid conversion is currently under investigation.

The effect of the reaction time on catalytic activity (i.e., lactic acid conversion, propylene glycol selectivity, and propylene glycol yield) was investigated using the Ru/ketjen black catalyst (Fig. 4). The reaction temperature was 150 °C, and the hydrogen pressure was 50 bar. Lactic acid conversion increased with reaction time because the reaction was carried out in a batch reactor. The propylene glycol selectivity decreased slightly with time on-stream, implying that propylene glycol underwent further reactions with additional time. The other main products were propionic acid and 2-hydroxy propionaldehyde. Neither propanol nor C1 or C2 compounds were detected during the reaction. These results differ somewhat from those previously reported by Miller et al. [13]: they investigated lactic acid conversion over various catalysts and reported that, at temperatures below 170 °C, the only liquid product was propylene glycol and the major byproducts were light hydrocarbons (i.e., methane, ethane, and propane) [13]. Dumesic et al. [12] reported the hydrogenation of lactic acid at 100 °C over a silica-supported copper catalyst; the main byproducts of this reaction were propionic acid and 2-hydroxy propionaldehyde and no light C1 or C2 compounds were detected. The difference in product distribution can be explained by the different catalysts and reaction conditions as lactic acid conversion is strongly dependent on the catalyst and reaction conditions.

Fig. 5 shows the catalytic activity of 5 wt% Ru/ketjen black with respect to reaction pressure after 4 h at 130 °C. Both the lactic acid conversion and propylene glycol selectivity increased with

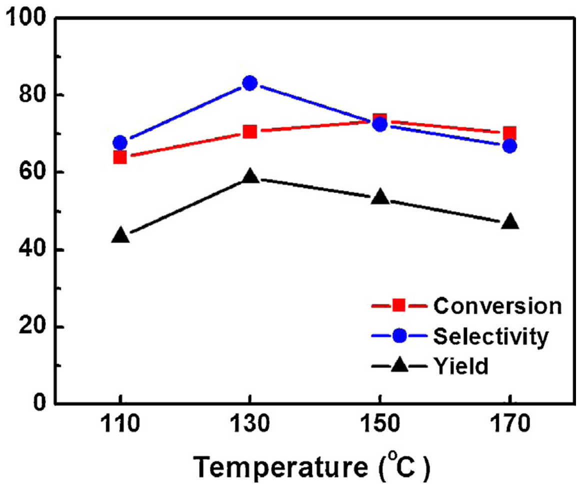

Fig. 6. Catalytic activity of 5 wt% Ru/ketjen black with reaction temperature. Reaction time = 2 h, Pressure = 50 bar.

reaction pressure. This is mainly because of the increased concentration of hydrogen in aqueous solution with increasing reaction pressure, which speeds up the reaction resulting in a higher propylene glycol yield. The optimal reaction pressure should primarily be determined by equipment cost.

The influence of the reaction temperature on the catalytic hydrogenation of lactic acid using 5 wt% Ru/ketjen black was investigated at 50 bar and is plotted in Fig. 6. In general, the conversion of lactic acid increased with reaction temperature in the range of 110–170 °C. However, the propylene glycol selectivity reached a maximum at 130 °C and then decreased with increasing temperature. The decreased selectivity at higher temperatures is attributed to secondary reactions involving propylene glycol. Because the hydrogenolysis of products competes with the hydrogenation of lactic acid over supported ruthenium catalysts, the selection of support and reaction conditions are very important.

4. Conclusions

Ruthenium catalysts supported on various carbons (i.e., VulcanXC-72, ketjen black, CNTs, CNFs, and graphite) were prepared using an incipient wetness impregnation method and employed for the hydrogenation of lactic acid to propylene glycol in a high-pressure batch reactor. The ruthenium particle size is strongly dependent on the BET surface area of the carbon support. Among the catalysts tested, ruthenium supported on ketjen black exhibited the highest catalytic activity because of its fine dispersion of ruthenium. The propylene glycol yield over ruthenium on ketjen black increased with increasing hydrogen pressure; the highest yield was achieved at 130 °C. It is concluded that propylene glycol can be efficiently produced from a bio-based chemical (i.e., lactic acid) using ruthenium supported on ketjen black.

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