Efficient Hydrogenation of Ethyl Lactate to 1,2-Propanediol over Ru–B/TiO_2 in Aqueous Solution

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Catalyst Ru–B/TiO_2 showed an excellently catalytic performance for the hydrogenation of ethyl lactate to 1,2-propanediol (1,2-PDO) under mild conditions (90 °C and 4.0 MPa H_2) without any additive. Especially, the activity of the catalyst was greatly improved in aqueous solution. The conversion of ethyl lactate was up to 98% and the selectivity to 1,2-propanediol was over 95%.

1,2-Propanediol (1,2-PDO) is an important industrial chemical, which is widely used as the raw materials to produce polymers, resins, and functional fluids (antifreeze, deicing). A commercial route to synthesize 1,2-PDO is the hydration of propylene oxide derived from propylene by either a chlorohydrin process or a hydroperoxide process.[1,2] Thus, to develop a cleanly and economically synthetic approach of 1,2-PDO is important. From renewable feedstocks, hydrogenolysis of glycerol is a useful route to prepare 1,2-PDO, but a challenging problem for this route is to look for an efficient catalyst as the reported catalysts generally show the low activity and selectivity.[3–6] Thus, the direct hydrogenation of lactic acid or lactates, which are easily obtained by fermentation of renewable sources such as agricultural crops and biomass streams, is a good green route to produce 1,2-PDO. In the hydrogenation of lactates, it is found that nickel and ruthenium catalysts are effective, but the reaction conditions are drastic. For example, the hydrogenation over Raney Ni must be performed in a high H_2 pressure of 25 MPa.[7–9] To use unsupported ruthenium black as catalyst, the hydrogenation could be achieved at 150 °C and 27 MPa and only gave a 1,2-propanediol yield of 84%.[10] Over Ru/C, 1,2-propanediol was obtained at the reaction temperature of 150 °C and hydrogen pressure of 14.5 MPa.[11] Recently, it was found that the introduction of tin was an effective method to improve the hydrogenation activity of ruthenium-based catalyst,[12–14] but the hydrogenation was still carried out under the conditions of 150 °C and 5.5 MPa. To our knowledge, an organic solvent is the best choice in order to obtain a good result for the hydrogenation of lactates to 1,2-PDO. In the present study, we first found that Ru–B/TiO_2 catalyst, prepared by the reduction impregnation method, was an excellent catalyst for the hydrogenation of ethyl lactates to 1,2-PDO. Especially, when the safe and environmentally friendly water was used as a solvent, the hydrogenation could quickly progress at the low temperature of 90 °C and hydrogen pressure of 4.0 MPa.

Catalyst Ru–B/TiO_2 was prepared by a reduction impregnation method. The alcohol solution of 10 mL containing $RuCl_3$ of 1.58 mmol was rapidly added to the flask containing TiO_2 (2.0 g), and then the mixture was reduced with an aqueous solution of $NaBH_4$ (a molar ratio of B to Ru was 10:1) at room temperature under the ultrasound agitation. At the end of reaction, the black precipitate was filtered, washed with distilled water, and dried under vacuum at 60 °C for 10 h. The filtrate was collected to determine the composition of the catalyst by ICP.

The hydrogenation of ethyl lactate was carried out in a 60-mL steel autoclave equipped with a glass liner and a magnetic stirrer. The desired amounts of catalyst, ethyl lactate, and solvent were charged to the reactor. The autoclave was flushed with pure hydrogen five times. When the designated reaction temperature was reached, hydrogen was fed to the desired pressure, the stirring rate was adjusted to 1500 rpm, and reaction timing began.

The contents of ruthenium and boron in catalyst were determined by ICP (IRIS Intrepid). Transmission electron microscopy (TEM) was carried out in a JEM-1200 apparatus at an accelerating voltage of 100 kV. X-ray diffraction spectra (XRD) were recorded with a PHILIPHS X'Pert MPD and Cu Kα was used as the radiation source at the voltage of 50 kV and the current of 30 mA. Samples were scanned in the range of $2\theta = 10$–$90°$ at a rate of 0.06°/s. All liquid samples were analyzed by gas chromatography (Agilent GC-6890) with a FID detector and a PEG-20M supelco column (30 m × 0.25 mm, 0.25-µm film). The conversion and selectivity are defined as following:

$$\mathrm{C}/\% = \frac{\text{ethyl lactate consumed}}{\text{ethyl lactate initially charged}} \times 100 \qquad (1)$$

$$\mathrm{S}/\% = \frac{\text{defined product}}{\text{ethyl lactate consumed}} \times 100 \qquad (2)$$

ICP analysis of the collected filtrate indicated that ruthenium and boron loading in this catalyst were 7.9 and 8.5 wt %, respectively. The transmission electron micrograph of Ru–B/TiO_2 exhibited that ruthenium particles were highly dispersed on TiO_2 in a size range of 5–10 nm and the electron diffraction of the selected metal particle did not show any diffraction spot.[17] The result indicated that the metal particles are amorphous alloy formed between Ru and B, which is consistent with the reported result.[12] The XRD pattern of Ru–B/TiO_2 exhibited no ruthenium particles were detected and this also indicated that ruthenium particles are amorphous and highly dispersed on TiO_2.

The effect of solvents on the hydrogenation of ethyl lactate is shown in Table 1. In all reaction solutions, the detectable byproducts were 1-propanol (*n*-PP), propionic acid (PA), and lactic acid (LA). According to the results in Table 1, the conversions in alcohol solvents are higher than that in *n*-hexane and dioxane. The catalytic activity of the catalyst in different solvents increases in the order of dioxane < *n*-hexane < ethanol < 2-propanol. Interestingly, an excellently catalytic performance of RuB/TiO_2 was exhibited with water as a solvent. The conver-

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Table 1. Effect of solvents on ethyl lactate hydrogenation

Solvent	Conversion /%	Selectivity/%				TOF /h
		1,2-PDO	*n*-PP	PA	LA	
EtOH[a]	28.7	73.8	4.2	7.1	14.7	4.6
i-PrOH[a]	56.7	90.0	2.7	1.4	5.8	10.9
n-Hexane[a]	23.1	83.4	3.7	2.8	10.2	4.2
Dioxane[a]	20.3	89.5	3.5	2.4	4.7	3.9
H_2O[a]	95.1	88.8	3.2	2.4	5.4	18.4
H_2O[b]	98.0	96.5	0.8	1.6	1.0	6.9

[a]Condition: T: 150 °C, P_{H2}: 4.0 MPa, time: 4 h, ethyl lactate: 0.5 mL, solvent: 1.5 mL, catalyst: 0.079 mmol, agitation rate: 1500 rpm. [b]T: 90 °C, P_{H2}: 4.0 MPa, time: 12 h.

sion of substrate was up to 95.1% and the selectivity of 88.8% to 1,2-PDO was satisfying. The amounts of by-product *n*-PP and PA in water were close to that in other solvents, but that of by-product LA was obviously lower than that in ethanol and hexane. The result indicated that the hydrogenation of ethyl lactate to 1,2-PDO was favorable in water and the presence of water did not promote the hydrolysis of substrate. Furthermore, the formation of LA in *n*-hexane and dioxane further proved that the production of LA was from the hydrogenolysis of C–O bond in ethyl lactate. The conclusion was also demonstrated by the existence of C_2H_6 in the gas chromatogram of vent gas. Fan et al.[12,13] found that monometallic catalyst Ru–B/γ-Al_2O_3 was not suitable for producing 1,2-PDO via the hydrogenation route of ethyl lactate as it only gave a selectivity of 50.7% to 1,2-PDO at a conversion of 78.7%. However, the activity of Ru–B/γ-Al_2O_3 and the selectivity to 1,2-PDO could be improved by introducing the second metal component tin into it. TOF increased from 2.9 h^{-1} over Ru–B/γ-Al_2O_3 to 5.4 h^{-1} over Ru–Sn–B/γ-Al_2O_3 catalyst.[12,13] In this case, the catalyst, in which the second metal composition was missing, still showed a high efficiency in water for the hydrogenation of ethyl lactate to 1,2-PDO and TOF was up to 18.4 h^{-1}. Even if the reaction temperature decreased to 90 °C and extended the time to 12 h, the conversion of 1,2-PDO reached 98.0% and the TOF (6.9 h^{-1}) was still higher than the reported value[12,13] (Table 2). To our knowledge, this is the best result for the hydrogenation of ethyl lactate to 1,2-PDO and this is the first discovery that water can play a great promotion role for the hydrogenation of ethyl lactate.

It is well known that water plays a key role in selective hydrogenation of benzene to cyclohexene and *p*-chloronitrobenzene (*p*-CNB) to *p*-chloroaniline (*p*-CAN).[15,16] In general, to obtain cyclohexene by the hydrogenation of benzene is difficult due to the thermodynamic reason. However, in aqueous solution, the hydrophilicity of the catalyst support leads to the existence of water films, in which the solubility of cyclohexene is lower than benzene, on the surface of the catalyst and re-adsorption or further hydrogenation of cyclohexene is depressed.[15] Similarly, in hydrogenation of *p*-CNB, water was proposed to perform the same function.[16] Therefore, in this study, we suggested that in aqueous solution the hydrophilicity of TiO_2 results in the formation of water film on the surface of the catalyst. Owing to the competitive adsorption of water on the surface of the catalyst and the probable hydrogen bond between 1,2-PDO and solvent water, it weakens the adsorption of 1,2-PDO or shortens the stay time of 1,2-PDO on the surface of the catalyst. As a result, the activity of the catalyst and the selectivity to 1,2-PDO is improved. In addition, the formation of hydrogen bond between water and ethyl lactate on the surface of the catalyst probably polarizes the C=O bond of carboxyl group, so that the attack of activated H_2 in the metal center to the carboxyl group of substrate is promoted.

Table 2. Effect of reaction time on lactate hydrogenation

Time /h	Conversion /%	Selectivity/%			
		1,2-PDO	*n*-PP	PA	LA
4[a]	20.3	89.5	3.5	2.4	4.7
8[a]	53.9	90.8	3.7	2.0	3.5
12[a]	69.9	91.3	3.9	1.7	3.0
4[b]	51.7	99.2	0	0.4	0.6
8[b]	72.6	97.2	0.3	1.2	1.3
12[b]	98.0	96.5	0.8	1.6	1.0

[a]Condition: T: 150 °C, P_{H2}: 4.0 MPa, time: 4 h, ethyl lactate: 0.5 mL, solvent: 1.5 mL, catalyst: 0.079 mmol, agitation rate: 1500 rpm. [b]T: 90 °C, P_{H2}: 4.0 MPa, time: 12 h.

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