

Hydrothermal Synthesis of 1-Butanol from Ethanol Catalyzed with Commercial Cobalt Powder

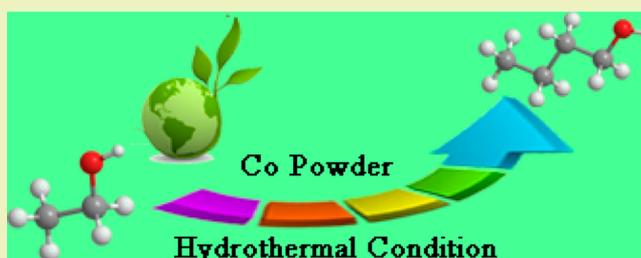
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Supporting Information

ABSTRACT: We reported a highly efficient conversion of ethanol to 1-butanol under hydrothermal conditions with commercial cobalt (Co) metal powder as a recyclable and inexpensive catalyst. The possible reaction pathways were explored. Moreover, it has been found that sodium bicarbonate is better than sodium hydroxide for the Guerbet reaction because the former led to less corrosion of reaction vessels and blocked the oxidation of the ethanol to acetic acid.

KEYWORDS: Ethanol, 1-Butanol, Cobalt powder, Green chemistry, Hydrothermal synthesis



INTRODUCTION

Because the coming energy shortage is the most serious crisis the world has ever faced,¹ the urgent need to explore alternative fuel sources has provoked interest in renewable biomass, to which substantial research efforts are being applied. Of particular appeal is the utilization of bioethanol because of the enormous amount produced from fermentation of different biomass materials and wastes.² Being viewed as the next oxygenate to replace ethanol in fuel applications,³ 1-butanol has superior fuel properties compared to ethanol, such as a higher heating value, lower volatility, and improved safety.⁴ Moreover, 1-butanol has been used in the production of paint, solvents, and plasticizers and also as the raw material for acrylic acid and acrylic esters.^{5,6}

Chemical synthesis of 1-butanol from ethanol is generally performed via a Guerbet reaction, in which higher alcohol is produced by the reaction of lower alcohol with itself or another alcohol.^{7–9} Because this reaction requires a catalyst, the recent research has focused on the exploration of a variety of catalysts, including Mg–Al mixed oxides,^{10,11} metal-modified Mg–Al mixed oxide,¹² alkali earth metal oxides, modified MgO,^{13,14} hydroxyapatites with different Ca/P molar ratios,^{15,16} etc. Herein, based on well-established hydrothermal methods,^{17–19} we utilized commercial Co metal powder as a cheap and recoverable catalyst together with NaHCO₃ to synthesize 1-butanol from ethanol with a good yield and high selectivity.

EXPERIMENTAL SECTION

All syntheses were conducted without stirring in a steel alloy autoclave (Fe–Cr–Ni alloy, GB1220-92) with an internal volume of 30 mL. Ethanol (99.7%, AR grade, Beijing Chemical Works), NaHCO₃ (99.5%, AR grade, Sinopharm Chemical Reagent Co., Ltd.), Co metal powder (99%, Sinopharm Chemical Reagent Co., Ltd., particle size = 1 μm), and ultrapure water were put into an autoclave. The filling volume remained 20 mL by adding ultrapure water. The

autoclave was sealed and placed in a furnace preheated to temperatures ranging from 140 to 240 °C, which led to an autogenous pressure of about 2 MPa. For changing the source of energy, the autoclave was powered with an in-house built solar unit. After heating for 1–30 days, the autoclave was removed and cooled to room temperature naturally. The pH value of the final solution was about 10. The components of the products in both the gas and liquid phases were identified using gas chromatography–mass spectrometry with electron ionization (GC-MS, Trace DSQ, Thermo Scientific Co.). The yield of products was calculated based on the number of carbon atoms in the product as follows

$$Y_i(\%) = \frac{n_i C_i}{2C_{\text{EtOH}}} \times 100$$

It should be pointed out that we identified most of the products, as substantiated by the carbon balance average (ca. 90%). The carbon balance was calculated as follows

$$C(\%) = \frac{2C'_{\text{EtOH}} + \sum_i n_i C_i}{2C_{\text{EtOH}}} \times 100$$

where n_i is the number of carbon atoms in the product, C_i is the concentration of product i in the final solution, C_{EtOH} is the initial concentration of ethanol, and C'_{EtOH} is the concentration of unreacted ethanol in the final solution. Because the amount of other products was less or below the experimental limit, we ignored their presence when calculating the selectivity to 1-butanol. The selectivity to 1-butanol was defined as²⁰

$$S_i(\%) = \frac{n_i C_i}{\sum_i n_i C_i} \times 100$$

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Table 1. Condensation of Ethanol to 1-Butanol over Different Catalysts^a

entry	catalyst	yield (mol %)					1-butanol selectivity %
		1-butanol	2-ethyl butanol	1-hexanol	2-ethyl hexanol	<i>n</i> -octyl alcohol	
1	Co	2.89	0.52	0.53	0.10	0.14	69
2	Ni	2.55	1.16	0.70	0.36	0.28	50
3	Raney Cu	0.93	0.25	0.15	0.05	0.04	65
4	Fe	0.75	0.10	0.14	0.01	0.04	–
5	copper chromite	0.33	0.09	0.05	0.04	0.03	–
6	CoCO ₃	0.82	0.13	0.16	0.02	0.05	–
7	Co ₂ O ₃	0.22	0.09	0.04	0	0	–
8	none	0.2	0.003	0.04	0	0	–
9	Co ^b	0	0	0	0	0	0
10	Co ^c	0	0	0	0	0	0

^aReaction conditions: 0.01 mol of NaHCO₃, 0.15 mol of ethanol, 11.24 mL of ultrapure water, 0.295 g of catalyst, and at 200 °C for 3 days. ^bThe reaction was carried out with ethanol, Co powder, and ultrapure water, but no NaHCO₃. ^cThe reaction was performed in pure ethanol without any water.

RESULTS AND DISCUSSION

Compositions of the products in both liquid and gaseous phases were identified with GC-MS. The GC-MS spectra showed that in the liquid phase 1-butanol was the main product, and 2-ethyl butanol, 1-hexanol, 2-ethyl hexanol, and *n*-octyl alcohol were the byproducts. However, no organic products were detected in the gaseous phase. A series of comparative experiments were conducted with different catalysts (Fe, Co, Ni, Raney Cu, copper chromite, CoCO₃, and Co₂O₃) (Table 1), among which Co powder showed the highest yield (2.89 mol %) and the best selectivity to 1-butanol (69%) (entry 1). The reaction could occur in the presence of a homogeneous catalyst (NaHCO₃) without a heterogeneous catalyst (e.g., no Co powder), but the obtained yield of 1-butanol was very low (only 0.2 mol %), which indicated that the steel alloy of autoclave was inert under the reaction conditions (entry 8). As for the other two reactions (i.e., entry 9, Co powder without NaHCO₃; and entry 10, using pure ethanol without water), no reaction happened due to the absence of an alkaline condition for the Guerbet reaction. We also carried out a comparative experiment with Co powder under mechanical stirring (rpm = 500) (see SI for details), only to obtain a lower yield of 1-butanol (0.1 mol %). We are aware of possible mass transfer limitations in the absence of stirring during catalytic runs, but the aim of our work is to demonstrate the feasibility of producing 1-butanol in a simple manner. More future work is needed to understand the stirring effect on the reaction rates.

The reaction conditions were optimized by varying the amounts of the ethanol (0.10–0.25 mol), NaHCO₃ (0.005–0.025 mol), and Co powder (0.005–0.015 mol). Figure 1 shows the influence of the added amount of ethanol. With the increased amount of ethanol, the concentration of the produced 1-butanol increased, reached the maximum (120 mmol/L), and remained constant even when 0.15 mol or more of ethanol was added. The effect of the added amount of NaHCO₃ is shown in Figure 2. The concentration of the produced 1-butanol increased dramatically when the added NaHCO₃ increased from 0.005 to 0.01 mol and slowly from 0.01 to 0.015 mol but decreased with the addition of more NaHCO₃ (>0.015 mol).

We studied the reaction rate of Co powder with various catalyst loadings. As shown in Figure 3, the reaction rate of Co powder decreased with increasing amounts of Co powder. This could possibly be because of mass transfer limitations due to the absence of stirring, which may limit catalyst surface

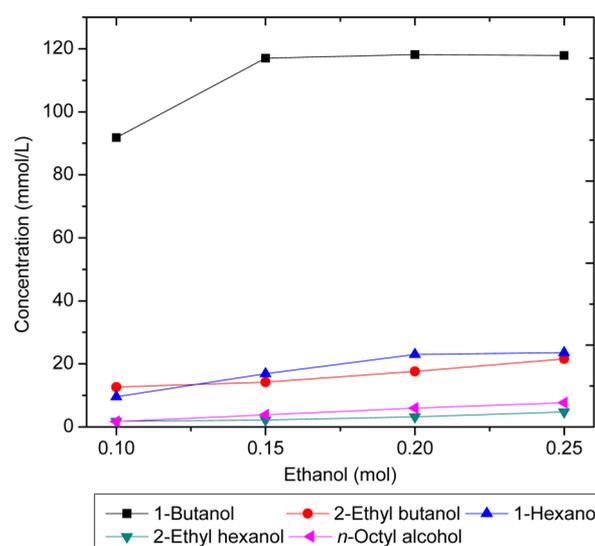


Figure 1. Effect of the added amount of ethanol on the concentration of products. (Reaction conditions: 0.01 mol of NaHCO₃ and 0.005 mol of Co powder at 200 °C for 3 days).

availability during reaction. In the optimized experiments above, the optimized hydrothermal reaction conditions were 0.15 mol of ethanol, 0.01 mol of NaHCO₃, and 0.005 mol of Co powder.

The effects of the reaction temperature (140–240 °C) and reaction time (1–30 days) were also investigated in Figures 4 and 5, respectively. In Figure 4, it was found that the yield of 1-butanol increased with longer reaction time, reached the maximum (9.8 mol %) after 20 days, and then remained constant, while the yield of the other products always kept rising, though slowly. However, the selectivity to 1-butanol decreased from 74% to 62% when the reaction time changed from 1 to 30 days. Figure 5 shows the variations of the yield of the products and selectivity to 1-butanol with a change in reaction temperature. As expected, the yield of 1-butanol increased from 1.2 to 5.5 mol % with the temperature changing from 140 to 240 °C. At the same time, the yield of 2-ethyl butanol, 1-hexanol, 2-ethyl hexanol, and *n*-octyl alcohol was also raised. The selectivity to 1-butanol increased from 50% to 74% when the reaction temperature increased from 140 to 180 °C and then remained constant (around 70%), even at a higher reaction temperature up to 240 °C.

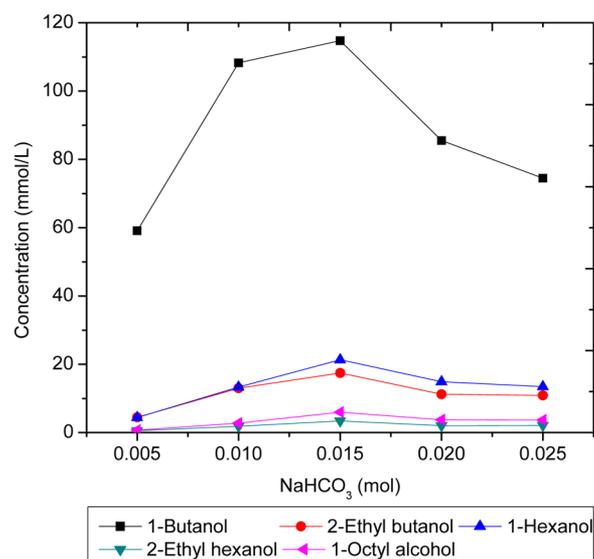


Figure 2. Effect of the added amount of NaHCO₃ on the concentration of products. (Reaction conditions: 0.15 mol of ethanol, 0.005 mol of Co powder, and 11.24 mL of ultrapure water at 200 °C for 3 days).

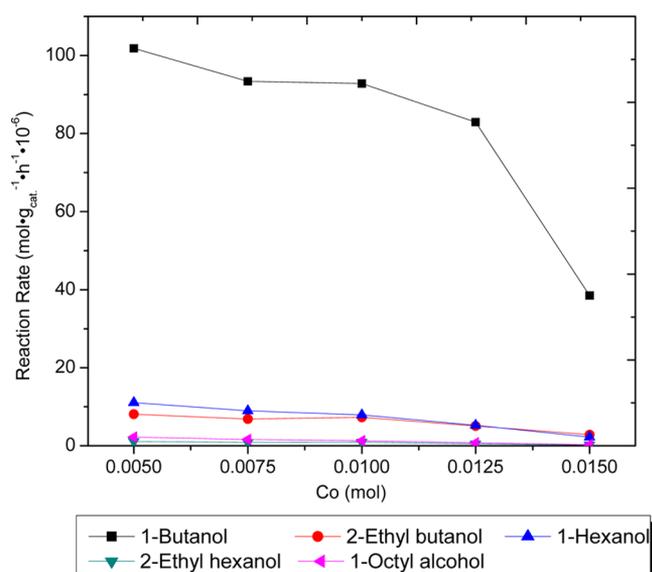


Figure 3. Reaction rate of Co powder with various catalyst loadings. (Reaction conditions: 0.15 mol of ethanol, 0.01 mol of NaHCO₃, and 11.24 mL of ultrapure water at 200 °C for 3 days).

Traditional Guerbet alcohols are produced by the dimerization of alcohols over alkali hydroxides or alkoxides,^{21,22} and when the starting alcohol converted into higher alcohol, a portion of the corresponding carboxylic acid was produced as byproduct. We found that when NaOH was used as a basic catalyst and the pH value was below 13, the Guerbet reaction did not occur, and the products were acetic acid and ethyl acetate. With the addition of more NaOH (i.e., pH > 13), the Guerbet reaction occurred, but the main product was acetic acid. Thus, we took NaHCO₃ as the catalyst in place of the traditional catalyst (i.e., NaOH, KOH). The advantage of using NaHCO₃ was less corrosion of reaction vessels as well as its blocking the oxidation of the ethanol to acetic acid. The powder X-ray diffraction (XRD) plots and Fourier transform infrared spectra (FTIR) showed that no change was found on

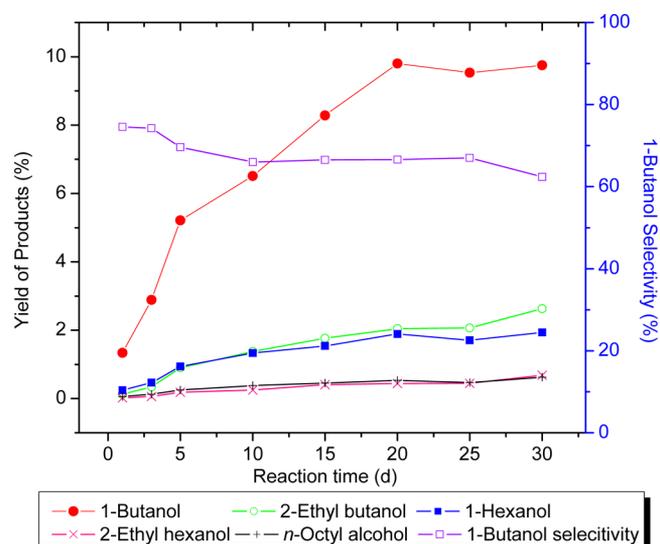


Figure 4. Variation of the yield of products and selectivity to 1-butanol as a function of reaction time. (Reaction conditions: 0.15 mol of ethanol, 0.01 mol of NaHCO₃, 0.005 mol of Co powder, and 11.24 mL of ultrapure water at 200 °C).

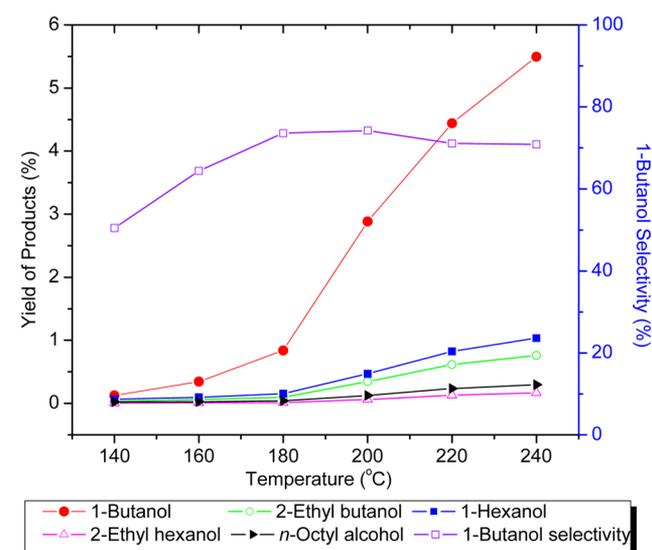


Figure 5. Influence of temperature on the yield of products and selectivity to 1-butanol. (Reaction conditions: 0.15 mol of ethanol, 0.01 mol of NaHCO₃, 0.005 mol of Co powder, and 11.24 mL of ultrapure water for 3 days).

the Co powder after the reaction. The Co powder after the reaction was collected and weighed. There was no loss of Co powder after the reaction. We used the collected Co powder for another two continuous runs, in which the yield of the products was similar to those at the first run (Figure 6). Thus, it can be considered that the catalytic power of the commercial Co metal powder remained practically constant even after three continuous runs.

It was found that there were tiny amounts of intermediates (i.e., acetaldehyde and crotonyl alcohol) in the products. To explore the mechanism of the conversion catalyzed by Co and NaHCO₃, we carried out a similar experiment except that 1-butanol was used instead of ethanol, in which the main products were 2-ethyl-2-hexenal, 2-ethyl-hexanal, 2-ethyl-hexanol, and 2-ethyl-2-hexen-1-ol (see Supporting Information

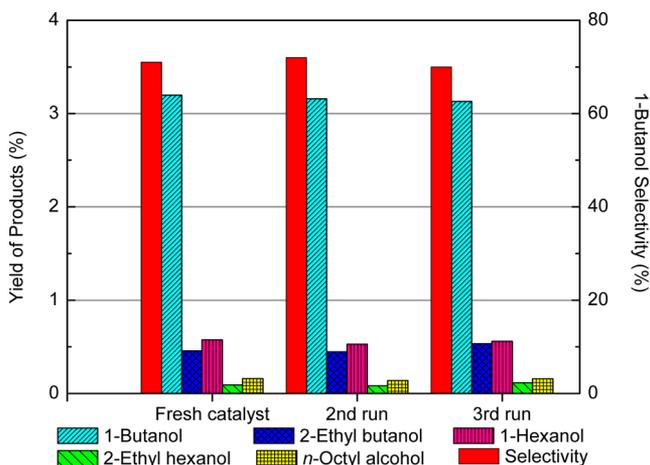
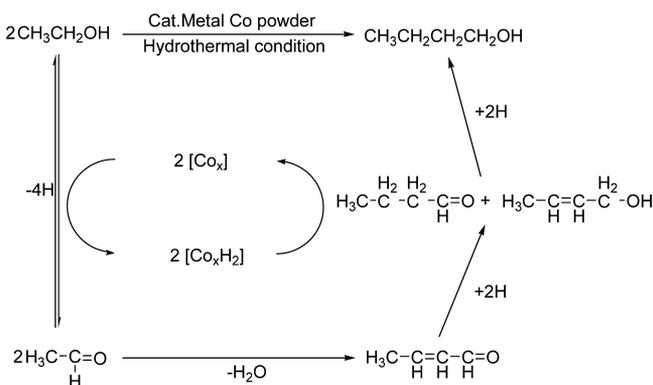


Figure 6. Reusability of Co powder catalyst. (Reaction conditions: 0.15 mol of ethanol, 0.01 mol of NaHCO_3 , 0.005 mol of Co powder, and 11.24 mL of ultrapure water 200 °C for 3 days).

for details). Therefore, the conversion catalyzed by Co and NaHCO_3 proceeded probably via three pathways including dehydrogenation, aldol condensation, and hydrogenation, which are illustrated in Scheme 1, in accordance with the

Scheme 1. Reaction Pathways for Co-Catalyzed Ethanol Conversion



“borrowing hydrogen” mechanism proposed by Williams.^{23,24} That is, the reaction started with “borrowing hydrogen” from alcohols to generate aldehyde together with a metal hydride (dihydride) intermediate, followed by aldol condensation of aldehyde to form α , β -unsaturated carbonyl compounds under alkaline conditions, and completed with the reduction of $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds by the previously formed metal hydride intermediate. Briefly, this process involved homogeneous base-catalyzed aldol condensation and (de)hydrogenation with Co powder. With respect to the fact that no net hydrogen was lost or gained during the reaction, the overall conversion was considered highly atom-efficient, and from the theoretical point of view, water was the only side product.

CONCLUSION

In conclusion, 1-butanol could be converted from ethanol with good yield and high selectivity using inexpensive commercial metal powder under hydrothermal conditions. Our reaction satisfied the green chemistry principles, including the one-step process, high atom economy, reduction of derivatives, use of renewable feedstock, reusable heterogeneous catalysts, and no

toxicity to human health and the environment. This work initiates the simple, cheap, and environmentally friendly production of 1-butanol from ethanol.

ASSOCIATED CONTENT

Supporting Information

Experimental procedure, GC-MS characterization for products, calibration curves of products for GC-MS, and method of calculation for the yield. Comparative experiment to entry 1 in Table 1: reaction with Co powder under stirring and the result of using 1-butanol as reactant. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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