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Study on the reaction pathway in the vapor-phase hydrogenation of biomass-derived diethyl succinate over CuO/ZnO catalyst

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ABSTRACT

The reactivity of biomass-derived diethyl succinate and its main reaction intermediates was separately investigated in a fixed-bed reactor over CuO/ZnO catalyst, and some interesting results were obtained. Ethyl 4-hydroxybutyl succinate as an intermediate of diethyl succinate hydrogenation reaction was first detected, and it could be converted to 1,4-butanediol or polyesters. Additionally, propanol and butanol are mainly derived from 1,4-butanediol rather than gamma-butyrolactone. A comprehensive reaction pathway for the hydrogenation of diethyl succinate is proposed, which is significant for the design of new catalytic formulations. A CuO/ZnO + HY admixed catalyst exhibiting excellent performance was prepared according to the proposed reaction pathway.

1. Introduction

Gamma-butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF) are significant intermediate chemicals and solvents in food, pharmaceutical and textile industries [1]. These four-carbon chemicals are currently produced commercially through the Davy McKee process from maleic anhydride [2] or the traditional Reppe process [3]. Alternatively, these chemicals can be produced from the hydrogenation of biomass-derived succinic acid or its esters (dialkyl succinate), which is regarded as a promising and environmental-friendly route [4]. Succinic acid and its esters as important biomass-derived platform molecules can be produced through the fermentation of a number of renewable sources e.g. sugars and starches [4].

The vapor-phase hydrogenation of dialkyl succinate (DAS) has been subjected to numerous studies which mainly focus on screening and characterization of catalysts [5–12]. However, systematic studies addressing the reaction pathway of DAS hydrogenation reaction have not been published in the literature. There is still a lack of the full understanding and a consensus on the reaction pathway. Generally, it is thought that GBL, BDO and THF are consecutively formed with alkanol as co-product [5–12] in the hydrogenation reaction of DAS. There is equilibrium between GBL and BDO, and the ratio of BDO to GBL can be controlled by the choice of reaction conditions, with high pressures and low temperatures favoring BDO [5]. However, Turek et al. [12] suggested that THF could also be converted from GBL. Varadaraja [13] reported that THF was primarily formed via direct conversion of DAS over a silica surported copper-based catalyst. On the other hand, the origin of by-products such as propanol and butanol was still debated. Messori et al. [14] reported that these by-products were mainly derived from GBL. However, Deshpande et al. [15] suggested that propanol and butanol were converted from BDO. Additionally, it was suggested that DAS could react with BDO to form polymers which resulted in fouling and plugging of the unit [5,7], which indicated the complexity of reaction pathway. Scheme 1 illustrates the reaction pathway generally proposed for the hydrogenation of DAS, which is not comprehensive and contains some conflicting standpoints [5–15].

The aim of this work is to shed light on the reaction pathway of DAS hydrogenation. The reactivity of biomass-derived diethyl succinate (DES) and its main reaction intermediates was separately investigated in a fixed-bed reactor over CuO/ZnO catalyst to complement the reaction mechanism study.

2. Experimental

2.1. Catalyst preparation

The CuO/ZnO catalyst was prepared by the co-precipitation method. In a typical preparation procedure, a 1 M mixed solution of $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ was added into a 1 M Na_2CO_3 solution under stirring at 80 °C, until the pH reaching 7.5. After precipitation, the suspension was washed and filtered. The precipitate

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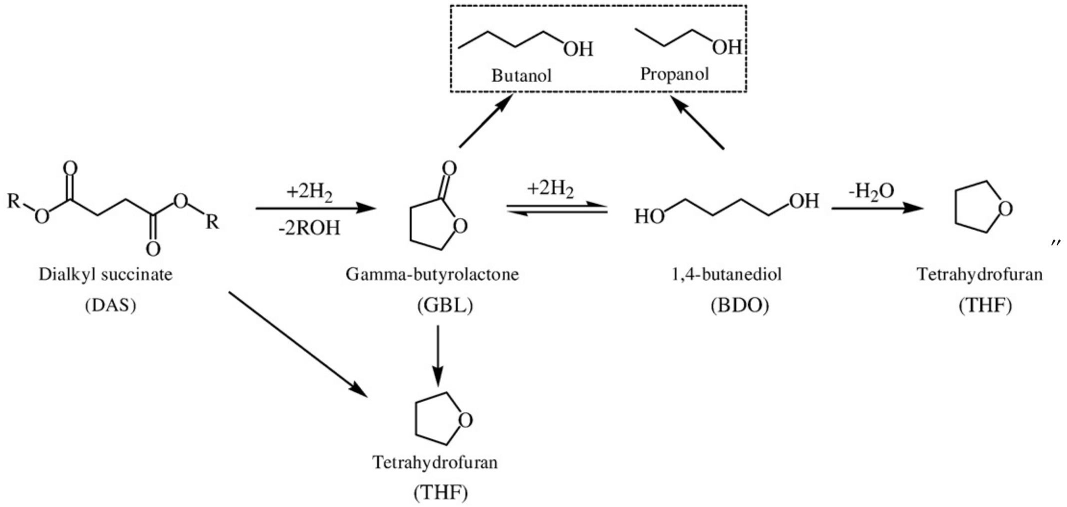


Scheme 1. Reaction pathway proposed in the literature for the hydrogenation of dialkyl succinate.

was dried at 110 °C for 12 h and then calcined at 450 °C for 5 h. The resulting catalyst was shaped by a tablet machine and then crushed to 20–40 mesh for catalytic test. The CuO/ZnO + HY catalyst was prepared by the physical-mixed method. The CuO/ZnO catalyst and HY zeolite were crashed to fine powders in agate mortar, respectively, and then the fine powders of both catalysts with appropriate mass ratio were further carefully kneaded for 30 min in agate mortar to form apparently homogeneous mixture of micro powders. The resulting mixture was pressed, crashed, and sieved to the particles (20–40 mesh).

2.2. Catalytic test

The catalytic tests were carried out in a fixed-bed reactor. Prior to reaction, all the catalysts were reduced in situ at atmospheric pressure with a 10% H_2/N_2 (v/v) gas mixture at 295 °C for 24 h. After reduction, the reactants were pumped to a vaporizer, mixed with pure hydrogen and then introduced into the reactor. The reaction products were analyzed using a SP-2000 gas-chromatograph and identified by a GC/MS (GC6890N/5973MSD, Agilent, USA).

3. Results and discussion

3.1. The effect of residence time on product distribution

Table 1 shows the DES conversion and product distribution at various residence times over CuO/ZnO catalyst. Variation of the residence time was achieved by changing the catalyst mass. As the conversion of DES increases with increasing residence time, the selectivity of GBL decreases, while the selectivity of BDO increases (Table 1). This indicates that GBL is firstly formed, and then converted to BDO, which is consistent with previous studies [6–9]. The effect of residence time on the selectivity of THF is inconspicuous due to the weak acidity of CuO/ZnO catalyst [6].

Table 1
Effect of the residence time on DES hydrogenation over CuO/ZnO catalyst[a].

Catalyst bed length (cm)	Residence time (s)	Conversion (%)	Selectivity[b] (%)				
			GBL	BDO	THF	EBS[c]	Others[d]
1.7	0.5	36.0	49.2	39.0	3.4	7.6	0.8
3.4	0.9	51.4	35.8	47.1	4.1	11.7	1.3
4.9	1.3	69.9	18.4	69.1	4.4	7.8	0.3
6.8	1.8	100	8.8	86.1	3.1	0	2.0

[a] Reaction conditions: 170 °C, 4.0 MPa, H_2/DES = 100 (molar ratio).

[b] Selectivity (%) = $C_i \cdot n_i / \sum(C_i \cdot n_i) \times 100$, C_i and n_i are the carbon atoms and molar quantity of liquid product i at the reactor outlet, respectively [12]. Ethanol and water are not taking into account.

[c] EBS = ethyl 4-hydroxybutyl succinate.

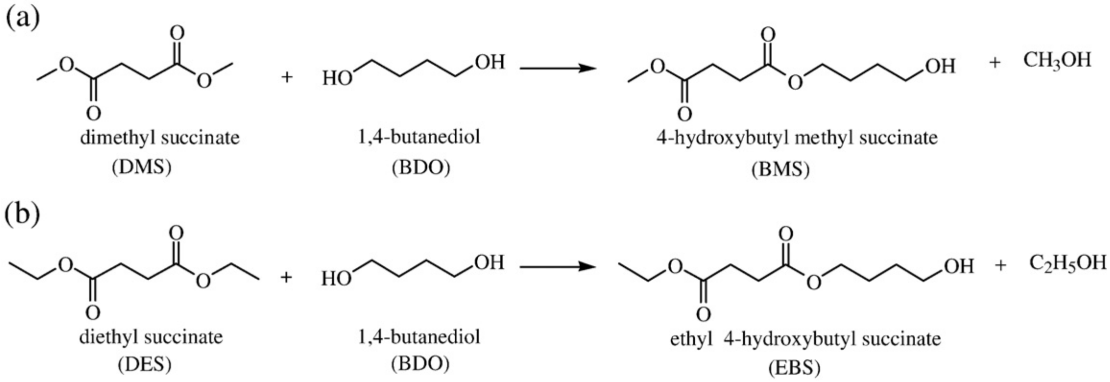
[d] Other products mainly propanol and butanol, etc.

Interestingly, in addition to GBL, BDO and THF, a product was first detected in the product mixture of DES hydrogenation, and it was identified to be ethyl 4-hydroxybutyl succinate (EBS) by GC/MS technique. EBS shows a relative low selectivity at short residence time, and the highest selectivity of EBS is obtained at a residence time of 0.9 s. However, the selectivity of EBS decreases to zero when residence time is improved to 1.8 s. These results suggest that EBS is an intermediate of the DES hydrogenation reaction because it can be further converted to BDO at long residence time.

Schlander et al. [5] attributed the dramatic carbon deficit to the formation of polyesters in the hydrogenation of dimethyl maleate, and proposed that 4-hydroxybutyl methyl succinate (BMS) could be formed via the transesterification of dimethyl succinate with BDO (Scheme 2(a)). However, BMS was not detected by the authors. Accordingly, EBS may be formed through the transesterification of DES with BDO (Scheme 2(b)). The transesterification of DES with BDO was investigated over CuO/ZnO catalyst under the reaction conditions applied for the hydrogenation of DES. However, the used temperature is low to avoid the occurrence of DES hydrogenation. It can be seen that DES shows a low conversion under the applied reaction conditions (Table 2). However, the conversion of DES is obviously improved when BDO is added to DES, and the main products are EBS and ethanol. These results prove that EBS is formed via transesterification of DES with BDO (Scheme 2(b)). In fact, EBS could further react with DES and BDO to polyesters [7], and some white polymeric materials were indeed found in the catalyst bed and colder parts of the unit.

3.2. Reactivity of GBL, BDO, THF and butanol

Usually, the by-products in the hydrogenation of the DES were reported to be butanol and propanol. However, a little of these by-products were detected over CuO/ZnO catalyst due to the low temperature applied. Additionally, it is difficult to determine the origin of by-products, because the mutual conversion between GBL and BDO takes place with a relatively high rate [5] in the process of DES hydrogenation, particularly at high pressure. Thus, the reactivity



Scheme 2. The formation pathway of 4-hydroxybutyl methyl succinate and ethyl 4-hydroxybutyl succinate.

of GBL and BDO was investigated separately at 260 °C, 0.1–2.0 MPa over CuO/ZnO catalyst to clarify the formation pathway of by-products. The reactivity of THF and butanol was investigated as well.

The hydrogenation GBL to BDO is thermodynamically limited at low pressure, and no BDO is detected at 0.1 MPa [5]. In addition, GBL shows low yields of propanol and butanol suggesting the high stability of GBL (Table 3). When pressure is improved to 2.0 MPa, the yield of BDO increases to 6.0% because the high pressure favors BDO formation [5]. At the same time, the yields of THF, propanol and butanol are obviously improved. These results suggest that THF and by-products are mainly derived from BDO rather than GBL [14]. When BDO is used as reactant, the yields of THF, propanol and butanol are higher than those of GBL under any reaction conditions. The equilibrium ratio of BDO to GBL is favored at high pressure, thus a lower conversion of BDO is observed at 2.0 MPa [5], and a lot of THF, propanol and butanol are obtained. It can be seen that the formations of THF, butanol and propanol are suppressed at 0.1 MPa, because most of BDO is converted to GBL [5,16,17]. This further confirms that BDO is the origin of THF and by-products. The hydrogenation of THF is characterized by low conversion value suggesting the high stability of THF [14,18]. Most of butanol is converted to propane and carbon monoxide over CuO/ZnO catalyst. Accordingly, BDO may be converted to propanol and carbon monoxide. In addition to THF, BDO can also be dehydrated to 3-buten-1-ol. Igarashi et al. [19,20] reported that 3-buten-1-ol could be produced from BDO over CeO_2 and ZrO_2 catalysts. It can be speculated that the 3-buten-1-ol formed from BDO is further hydrogenated to butanol over CuO/ZnO catalyst in the DES hydrogenation process.

Therefore, on the basis of the experimental results in this work and considering the existing literature, a proper reaction pathway for the hydrogenation of DES is proposed, which suggests that BDO plays a key role due to its high reactivity (Scheme 3). Besides cyclodehydration to THF, BDO can react with DES to EBS which can be further converted to polyesters or hydrogenated to BDO and GBL. Additionally, by-products such as propanol and butanol are also derived from BDO.

In industrial plant, the deposit of polyesters may result in fouling and plugging of catalyst bed and lines of unit [7], which may shorten the operation period and increase the production cost. However, how to avoid the formation of polyesters is still an open question in the hydrogenation of dialky succinate. In addition, the reduction of the yields of by-products is also significant to decrease the production cost. According to the proposed reaction pathway, the formation of polyesters and by-products can be suppressed if the formed BDO can be immediately converted to THF. However, CuO/ZnO catalyst exhibits a low reactivity for the cyclodehydration of BDO to THF due to its weak acidity [6]. It was reported that BDO could be selectively converted to THF by HY zeolite [21]. Thus, a CuO/ZnO + HY catalyst was prepared by the physical-mixed method for DES hydrogenation.

3.3. Catalytic performance of CuO/ZnO + HY admixed catalyst

Over CuO/ZnO + HY admixed catalyst, EBS is not detected, and no white polymeric materials are found in the catalyst bed or colder parts of the unit, which indicates the formation of polyesters may be avoided (Table 4). At 200 °C, a THF selectivity of 98.5% is obtained with complete conversion of DES, as the equilibrium between GBL and BDO is completely disturbed. In addition, the selectivities of by-products of CuO/ZnO + HY admixed catalyst are much lower than those of CuO/ZnO catalyst at high temperature because the formed BDO is immediately converted to THF.

Table 2
Product distribution of transesterification of DES with BDO[a].

Catalyst	DES conversion (%)	Yield (%)[b]					
		EtOH[c]	GBL	BDO	THF	EBS	Others
CuO/ZnO	5.8[d]	2.0	1.5	0.4	0.1	0	1.8
CuO/ZnO	31.6	13.9	1.8	–	2.1	12.2[e]	1.6

[a] Reaction conditions: 150 °C, 4.0 MPa, WHSV = 0.12 h^{-1}, H_2/DES = 200 (molar ratio), and DES/BDO = 1:0.7 (molar ratio).

[b] Yield (%) = $C_i \cdot n_i / C_{feed} \cdot n_{feed} \times 100$, C_{feed} and n_{feed} are the carbon atoms and molar quantity of feed, respectively [12].

[c] EtOH = ethanol.

[d] Reactant is only DES without BDO.

[e] The C_i of EBS is defined as 6 as only 6 carbon atoms are directly derived from DES.

Table 3
Reactivity of the main intermediates of DES hydrogenation[a].

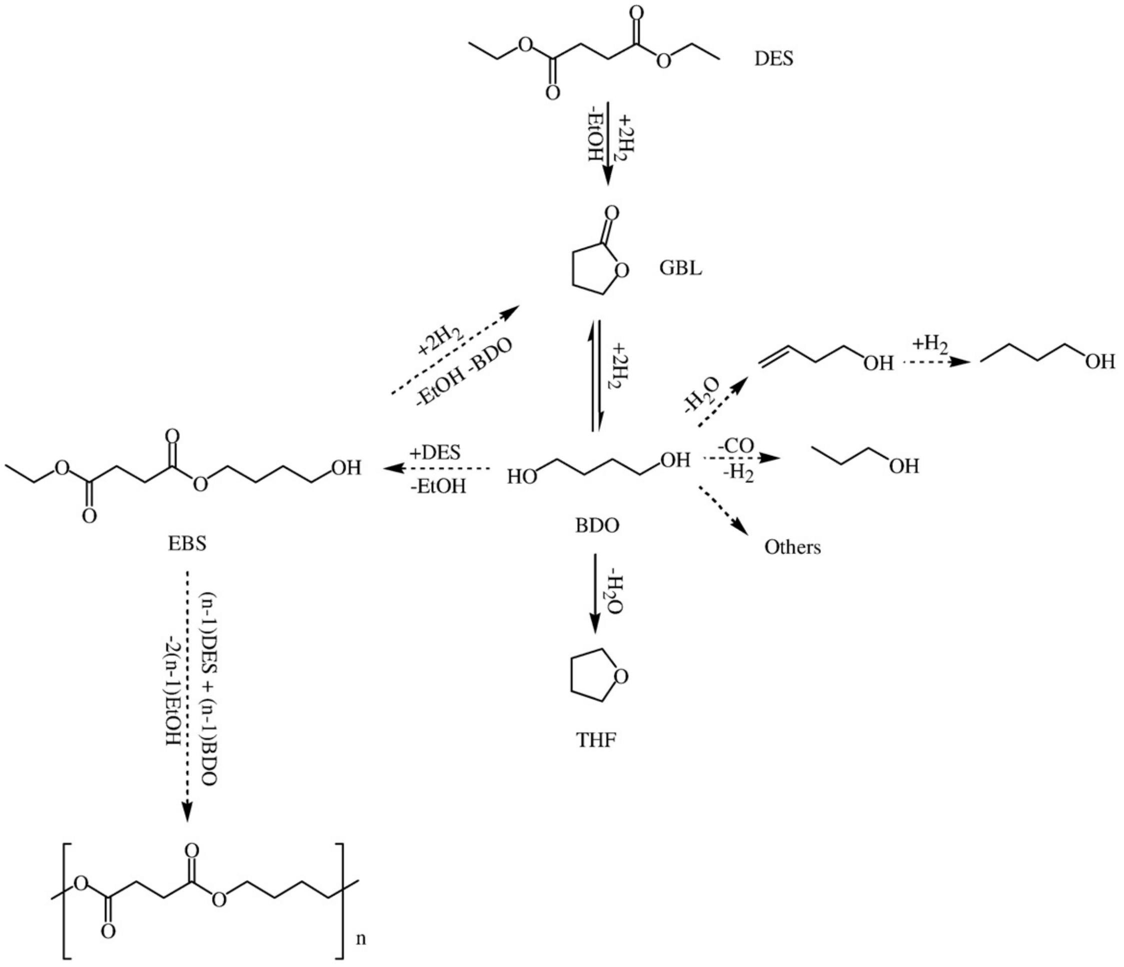
Feed stocks	Pressure (MPa)	Conversion (%)	Yield (%)[b]						
			GBL	BDO	THF	EtOH	PrOH[c]	BuOH[c]	Others
GBL	0.1	7.7	–	0	0	0	3.1	3.6	1.0
	2.0	47.0	–	6.0	9.6	0	10.8	17.8	2.8
BDO	0.1	96.5	77.2	–	2.1	0	6.7	5.3	5.2
	2.0	86.0	22.6	–	20.7	0	15.0	20.2	7.5
THF	2.0	5.0	–	–	–	1.4	0.4	3.1	0.1
BuOH	2.0	45.5	–	–	–	0	0	–	45.5 [d]

[a] Other reaction conditions: 260 °C, WHSV = 0.12 h^{-1}.

[b] The same as Table 2.

[c] PrOH = n-propanol, BuOH = n-butanol.

[d] Other products mainly propane and carbon monoxide, etc.



Scheme 3. Proper reaction pathway proposed for diethyl succinate hydrogenation. The broken lines represent the difference standpoints from Scheme 1.

4. Conclusions

The results of this work indicate that transesterification and hydrogenation reactions take place competitively in the process of DES hydrogenation. In addition to the consecutive formation of GBL, BDO and THF from DES hydrogenation, the formed BDO can react with the unconverted DES to EBS and polyesters. Interestingly, the EBS can be further converted to BDO and GBL, which indicates the hydrogenation of DES processes via a complicated netted reaction pathway. In addition, by-products such as propanol and butanol are mainly derived from BDO rather than GBL. These results are important to understand the mechanism and reaction pathway of DES hydrogenation, and provide an instruction for the design of new catalytic formulations. The formations of polyesters and by-products are significantly suppressed over CuO/ZnO + HY admixed catalyst, because the formed BDO is immediately converted to THF.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.catcom.2010.06.007.

Table 4
Catalytic performances of CuO/ZnO and CuO/ZnO + HY admixed catalysts[a].

Catalyst	Temperature (°C)	Conversion (%)	Selectivity[b] (%)						
			GBL	BDO	THF	EBS	PrOH	BuOH	Others
CuO/ZnO + HY[c]	170	44.9	38.3	0	59.7	0	0.6	1.3	0.1
	200	99.5	0.2	0	98.5	0	0.5	0.6	0.2
CuO/ZnO	260	100	31.6	2.8	22.7	0	7.8	16.3	18.8
CuO/ZnO + HY[d]	260	100	0	0	95.2	0	1.8	2.7	0.3

[a] Other reaction conditions: 4.0 MPa, WHSV = 0.12 h^{-1}, H_2/DES = 100 (molar ratio).
[b] The same as Table 1.
[c] HY zeolite content is 30 wt.%.
[d] HY zeolite content is 10 wt.%.

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