A novel route for synthesis of γ-butyrolactone through the coupling of hydrogenation and dehydrogenation

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A coupling process of the hydrogenation of maleic anhydride and the dehydrogenation of 1,4-butanediol has been invented for the synthesis of γ-butyrolactone over a Cu–Zn catalyst, realizing optimal hydrogen utilization and better energy efficiency.

γ-Butyrolactone (GBL) is one of the important intermediates in fine chemical industrial practices, for example, for the synthesis of pyrrolidone, *N*-methylpyrrolidone, *N*-vinylpyrrolidone, herbicides, and rubber additives. There are two main routes for the production of GBL: the catalytic dehydrogenation of 1,4-butanediol (BDO) and the hydrogenation of maleic anhydride (MA). Both processes are mainly performed typically in multi-tubular fixed-bed reactors. In particular, the dehydrogenation of BDO is dominant in commercial applications.[1]

The catalytic hydrogenation of MA or its derivatives such as maleic acid, succinic anhydride or succinic maleate to GBL has frequently been reported in the literature.[2–10] The reaction equation of MA hydrogenation to GBL can be represented as follows:

$$\text{(structure)} + 3H_2 \longrightarrow \text{(structure)} + H_2O - 211 \text{ kJ mol}^{-1} \quad (1)$$
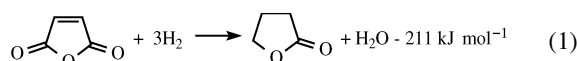
Reaction (1) shows that production of 1 mol GBL requires 1 mol MA and 3 mol H_2, releasing 211 kJ of heat. Owing to the strong exothermic nature of Reaction (1), it is difficult in the temperature control of the process, leading to apparent hotspots typically in a tubular fixed-bed reactor and lowering the selectivity to the desired product, GBL. In addition, a supply of hydrogen is needed.

The vapor phase catalytic dehydrogenation of BDO to GBL has also been described in the literature.[11–15] This reaction can be expressed as follows:

$$\text{(structure)} \longrightarrow \text{(structure)} + 2H_2 + 61.6 \text{ kJ mol}^{-1} \quad (2)$$
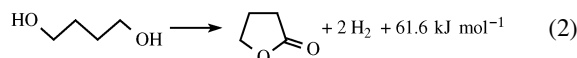
It is evident that production of 1 mol GBL requires 1 mol BDO, releasing 2 mol H_2 and requiring 61.6 kJ of heat. It should be noted that the reaction is practically irreversible under typical industrial operating conditions (H_2:BDO = 15, 1 atm, 200 °C, equilibrium constant K_p = 10^8). Owing to the endothermic properties of reaction (2), the increase of the LHSV (liquid hourly space velocity) of BDO is relatively limited by low external heat supply in a practical reactor. In addition, the hydrogen released from reaction (2) cannot be used properly in a single dehydrogenation process.

This work proposes an idea to combine reactions (1) and (2) in one catalytic process to achieve better thermal balances, the efficient use of hydrogen, and thus high overall efficiency. The combined reaction can be expressed as follows:

$$\text{(structure)} + 1.5 \text{(structure)} \longrightarrow 2.5 \text{(structure)} + H_2O - 119.6 \text{ kJ mol}^{-1} \quad (3)$$
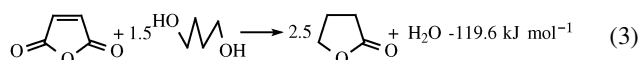
The above combined system can be practically realized on the basis of the fact that the hydrogenation of MA and the dehydrogenation of BDO could be carried out over the same Cu-based catalyst, and under similar reaction conditions.[6,7,13]

The hydrogenation of MA, the dehydrogenation of BDO and the coupling process were investigated in a fixed-bed reactor over a Cu–Zn catalyst, which was prepared by a co-precipitation method from copper nitrate and zinc nitrate. The reactor (600 mm long, 12 mm i.d.) was packed with 15 g catalyst (20–40 mesh). The reaction system had a buffer tank for collecting the tail gas and a pump for cycling hydrogen. In the beginning of all tests, N_2 was introduced to purge the reaction system, and was then replaced by 5%H_2/N_2(v/v) at 1 atm. The catalyst was pre-reduced by increasing the temperature from 25 to 270 °C at a rate of 20 °C h^{-1} and then keeping it at 270 °C for 2 h. After the reduction, the reactants were introduced into the reactor. Hydrogen in tail stream was recycled after the reaction products had been condensed. The products were collected at an ice trap and analyzed using a gas chromatograph GC-920 (Shanghai Analyzer Comp., China) fitted with a FID.

Table 1 Influence of temperature on MA hydrogenation to GBL

T/°C	265	270	290	300
MA conversion (%)	99.5	100	100	100
GBL selectivity (%)	87.4	93.2	90.6	85.2

Reaction conditions: 1 atm, LHSV = 0.1 h^{-1}, H_2:MA = 50:1 (mol/mol).

Table 1 shows that the conversion of MA is 100% and that the selectivity of GBL is > 90% at 270–290 °C.

The dehydrogenation of BDO at different temperatures is represented in Table 2. It indicates that the conversion of BDO is > 99.3% and the selectivity for GBL is > 97.6%. In order to check the thermal equilibrium status of the BDO dehydrogenation reaction [reaction (2)], the experiment under different hydrogen to BDO ratios was conducted, and the results are summarized in Table 3. It is clear that the conversion of BDO can reach 98.2% even under a large hydrogen mol ratio in the reacting mixture. For all conditions listed in Table 3, it is

Table 2 Influence of temperature on BDO dehydrogenation to GBL

T/°C	190	200	210	230	260
BDO conversion (%)	99.3	99.8	100	100	100
GBL selectivity (%)	98.8	99.6	98.3	98.1	97.6

Reaction conditions: 1 atm, LHSV = 0.5 h^{-1}, H_2:BDO = 15:1 (mol/mol).

Table 3 Influence of H_2:BDO ratio on the dehydrogenation of BDO to GBL

H_2:BDO (mol/mol)	10	15	25	45	85
BDO conversion (%)	100	100	99.6	99.1	98.2.
GBL selectivity (%)	97.2	97.8	98.0	98.2	98.8

Reaction conditions: 1 atm, LHSV = 0.5 h^{-1}, T = 240 °C. Equilibrium constant, K_p is > 10^8 under all conditions.

estimated that the thermal equilibrium constant, K_{p},† of BDO dehydrogenation is $> 10^{8}$, showing that this reaction is practically irreversible.

The coupling reaction results (Table 4) display that the total conversion of BDO and MA is 100%, and that the total selectivity to the desired product GBL is $> 98.1\%$. From Tables 1–3, it can be found that the selectivity to GBL from MA hydrogenation is increased by *ca.* 4%, and that the selectivity to GBL from BDO dehydrogenation is increased by *ca.* 1% due to the coupling effect. In the coupling process, hydrogen can be balanced within the system without substantially adding hydrogen (MA hydrogenation) and releasing hydrogen (BDO dehydrogenation).

Table 4 Influence of temperature on the coupling of BDO and MA to GBL

T/°C	220	230	240	255	275
Total conversion (%)	100	100	100	100	100
GBL selectivity (%)	98.5	98.6	98.4	98.3	98.1

Reaction conditions: 1 atm, LHSV = 0.25 h^{-1}, H$_2$:(BDO+MA) = 80:1 (mol/mol), BDO:MA = 1.5:1 (mol/mol).

In conclusion, the coupling process tested in this work has several advantages over the two conventional single processes, namely good energy efficiency and optimal hydrogen utilization. In addition, compared with the MA hydrogenation process, the coupling has a significantly lowered reaction temperature (normally 30–50 °C). This is because the rich active hydrogen species on the catalyst surface from BDO dehydrogenation promotes the MA hydrogenation reaction. The coupling may lead to other advantages, such as the increase of total selectivity to GBL and easy temperature control in a tubular fixed-bed due to its moderate heat release compared with the above single reaction processes. All of these results show good prospects for the commercial application of this innovation.

Notes and references

† Reminded by one of the referees, we have conducted an analysis of the theoretical equilibrium position of the dehydrogenation reaction of DBO at 200 °C and under other conditions as listed in Table 2. Owing to the lack of thermodynamic properties of BDO and GBL, we used a quantum chemistry approach (DFT/B3LYP/6-31*) to calculate the unavailable thermodynamic data. ΔG° (200 °C) for reaction (2) was then estimated as -23.50 kcal mol^{-1} for BDO, leading to a equilibrium BDO conversion of 99.9998%. This means that the dehydrogenation of BDO to GBL at atmospheric pressure is a practically irreversible reaction under our conditions.

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