Letter

A new strategy for the efficient synthesis of 2-methylfuran and γ-butyrolactone

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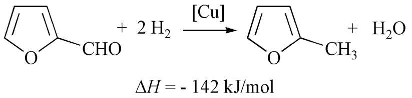
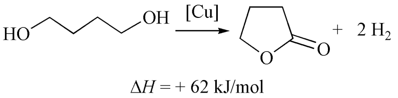
A novel process involving the coupling of the hydrogenation of furfural and the dehydrogenation of 1,4-butanediol has been studied in the vapor phase for the synthesis of 2-methylfuran (2-MF) and γ-butyrolactone (γ-BL) over the same Cu-based catalyst. It was found that hydrogen and heat energy are utilized with high efficiency in this process.

In this letter, we report a coupled catalytic process through hydrogen transfer between two reactants, 1,4-butanediol (BDO) and furfural, to produce two valuable products, 2-methylfuran (2-MF) and γ-butyrolactone (γ-BL), in an atom economic way from the viewpoints of both material and energy utilization. Catalytic hydrogenation transfer reactions have been widely investigated in the past, mostly for the reduction of organic compounds by using a hydrogen donor, which often leads to undesirable by-products.[1] In our coupled hydrogen transfer reaction, furfural (hydrogen acceptor) is reduced by the hydrogen from BDO (hydrogen donor) to form 2-MF, and at the same time, γ-BL is also the desired product from the BDO dehydrogenation. 2-MF is mainly used for the synthesis of crysanthemate pesticides, perfume intermediates and chloroquine lateral chains in medicinal intermediates, and the major production route is *via* the catalytic hydrogenation of furfural [eqn. (1)]. γ-BL is an important intermediate for the synthesis of pyrrolidone, *N*-methylpyrrolidone, *N*-vinylpyrrolidone, herbicides and rubber additives, and the catalytic dehydrogenation of 1,4-butanediol (BDO) to γ-BL is the dominant procedure in commercial applications [eqn. (2)].[2] Both processes are mainly performed in multi-tubular fixed-bed reactors.



(1)



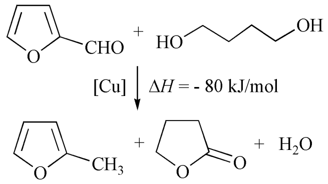
(2)

As shown in eqn. (1), the vapor-phase hydrogenation of furfural to 2-MF is exothermic by 142 kJ mol^{-1}. Due to the strongly exothermic nature of this reaction, temperature control over this process is very difficult and this leads to apparent hot spots, typically in an industrial tubular fixed-bed reactor, thus seriously lowering the yield to the desired product, 2-MF.[3–5] In addition, a supply of hydrogen to the system is needed.

The catalytic dehydrogenation of BDO to γ-BL shown in eqn. (2) is an endothermic process (61.6 kJ mol^{-1})[6–10] and the oxidative lactonization of diols to γ-BL like products has been reported.[11–13] In this reaction, the released hydrogen cannot be used effectively.

The new catalytic process combines reactions (1) and (2) into one catalytic system to significantly improve the yield of the catalytic hydrogenation of furfural, as well as leading to a better thermal balance and the effective usage of hydrogen through hydrogen transfer between the two reactants. In addition, this new catalytic process produces two desired products (2-MF and γ-BL) with a substantially increased hydrogenation yield, while the "no-hydrogen" (with hydrogen recycle but no hydrogen supply and release) operation also simplifies the technical procedure.

The combined reaction in eqn. (3) shows that producing 1 mol 2-MF and 1 mol γ-BL requires 1 mol furfural and 1 mol BDO, and is exothermic by 80.4 kJ mol^{-1}.



(3)

In addition to the perfect hydrogen mass balance, much easier temperature control in a practical reactor can also be expected than in the single furfural hydrogenation process, due to the lower heat release in the coupled system. In practice, this combined process can be carried out on the basis of the fact that the hydrogen transfer from BDO (hydrogen donor) to furfural (hydrogen acceptor) can be carried out over the same Cu–Zn catalyst and under similar reaction conditions.[14,15]

The separate furfural hydrogenation and BDO dehydrogenation reactions, as well as the coupled process, were carried out in a fixed-bed reactor over a Cu–Zn catalyst. Table 1 shows that almost complete conversion of furfural can be achieved over the present Cu-based catalyst. However, the yield of 2-MF varies substantially with operating temperature, with the best yield being 88.6% at 212 °C. Scheme 1 shows the complexity of the hydrogenation of furfural. It is clear that furfural hydrogenation can produce not only the desired product 2-MF but also other by-products, depending on the reaction

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Table 1 Influence of temperature on the hydrogenation of furfural to 2-MF.[a]

		% Yield					
T/°C	% Furfural conv.	2-MF	Pon[b]	Pol[c]	MTF[d]	FOL[e]	Other
190	99.8	75.2	0.9	1.5	8.5	13.6	0.3
200	100	81.5	4.5	4.6	6.7	2.2	0.5
212	100	88.6	2.7	4.8	3.3	–	0.6
225	100	85.2	2.5	8.7	3.1	–	0.5
235	100	82.7	2.1	11.8	2.7	–	0.7

[a] Reaction conditions: atmosphere, LHSV = 0.1 h^{-1}, H_2:furfural = 15:1 (molar ratio, recycling hydrogen), residence time = 9.6 s. [b] Pon = 2-pentanone. [c] Pol = 2-pentanol. [d] MTF = 2-methyl tetrahydrofuran. [e] FOL = furfuryl alcohol.

Table 2 Influence of temperature on the dehydrogenation of BDO to γ-BL.[a]

		% Yield		
T/°C	% BDO conv.	γ-BL	BuOH[b]	Other
190	99.7	98.8	0.8	0.4
200	99.9	98.7	0.9	0.4
210	100	98.6	0.9	0.5
230	100	98.3	1.2	0.5
240	100	98.1	1.3	0.6

[a] Reaction conditions: atmosphere, LHSV = 0.2 h^{-1}, H_2:BDO = 15:1 (molar ratio, recycling hydrogen), residence time = 4.5 s. [b] *n*-Butanol.

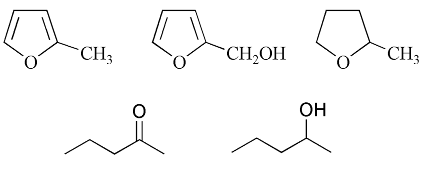
conditions[16–20] The non-uniform temperature profile in an industrial multi-tubular reactor generally lowers the yield of the desired product (2-MF)[16–20] to an extent that much lower yields are obtained than those in Table 1, for which the experiments were conducted in a laboratory micro-reactor.[16–20]

The dehydrogenation of BDO at different temperatures is shown in Table 2. The data indicates that the conversion of BDO is also nearly complete. Similar to the reported results,[21] the yield of the dehydrogenation reaction to γ-BL is very high (> 98%).

The coupled reaction was conducted using the same liquid hourly space velocity (LHSV), 0.1 h^{-1}, of furfural as that used in the single hydrogenation reaction test, and a BDO LHSV of 0.1 h^{-1} was also used to approach the stoichiometry of the coupled reaction [eqn. (3)]. It was observed that complete conversion of both furfural and BDO are reached (Table 3), indicating that the conversion efficiency for the hydrogenation of furfural has been maintained at the same level as in the single hydrogenation reaction (Table 1) with co-production of another important product, γ-BL through BDO dehydrogenation under the present operating conditions. Moreover, the coupled reaction has significantly improved the yield, especially from furfural to 2-MF, compared to those in the individual reactions (Table 1). At 210 °C, for example, the yield to 2-MF is raised by about 8%, and that to γ-BL is increased by about 1%. It is also seen that enhancement of the yield of 2-MF at 190 °C is more pronounced, by 15.6%.

Furthermore, the boiling point (at 101.3 kPa) of 2-MF is 63 °C and that of γ-BL is 204 °C, leading to easy separation of the product mixture from the coupled system, meaning less additional costs in the coupled process for industrial applications. These advantages may be of great interest for industrialization of the coupled synthesis of these two important products, 2-MF and γ-BL.

In order to explain the enhancement in the catalyst performance observed in the coupled reaction, we propose that the activated hydrogen species on the catalyst surface due to BDO dehydrogenation probably plays an important role in improving the yield of furfural hydrogenation. In an industrial process, other factors like an improved temperature profile along the reactor may further enhance the effect, suggesting the potential of coupled reactions in practical applications. Our further systematic investigations on the fundamentals of the coupling effect are expected to help explain this mechanism.



Scheme 1

In conclusion, we have demonstrated the feasibility of a coupled catalytic process, in which hydrogen transfer from BDO to furfural can be realized to produce 2-MF and γ-BL. Compared to conventional processes, the coupled process in this work has several advantages, such as improved yield, good energy efficiency and optimal hydrogen utilization. In addition, compared with the traditional furfural hydrogenation process, the coupled process can also be conducted at a lower reaction temperature (about 10–20 °C less) while leading to nearly the same efficiency. This shows that the rich activated hydrogen species on the catalyst surface from BDO dehydrogenation might promote the furfural hydrogenation reaction.[22] The coupled operation leads to other advantages, such as easy temperature control in a tubular fixed-bed reactor due to the moderate heat release compared to that of the single furfural hydrogenation reaction. In addition, the simplified technical procedure due to a "no-hydrogen-supply" operation shows improved technology. Further exploration is of both practical and theoretical importance.

Experimental

The catalyst mentioned in this study was prepared *via* the continuous precipitation method. In this preparation reaction, a solution of mixed $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ salts (1 M of total metal ions) was used as metal precursors with an atomic ratio of 1.3:1 (Cu:Zn), with a 1 M Na_2CO_3 solution added as the precipitating agent. Precipitation was performed at 65 °C, and the flow rates of the two solutions were adjusted to give a constant pH of about 7.5. The precipitate was aged for about 12 h at room temperature before filtering. The filtrated cake was washed with deionized water until no Na^+

Table 3 Influence of temperature on the coupling of the BDO and furfural reactions to give γ-BL and 2-MF.[a]

	% Conversion		% Yield	
T/°C	% Furfural	% BDO	2-MF[b]	γ-BL[c]
190	100	99.8	90.8	99.7
200	100	100	93.4	99.6
210	100	100	96.5	99.4
220	100	100	95.4	99.3
230	100	100	92.8	99.4
240	100	100	90.9	98.8

[a] Reaction conditions: atmosphere, LHSV (furfural + BDO) = 0.2 h^{-1}, H_2:(BDO + furfural) = 15:1 (molar ratio, recycling hydrogen), BDO:furfural = 1:1 (molar ratio), residence time = 4.7 s. [b] 2-MF yield = (moles of 2-MF produced) × 100/(moles of converted furfural). [c] γ-BL yield = (moles of γ-BL produced) × 100/(moles of converted BDO).

was detectable in the filtrate and subsequently dried at 110 °C for 24 h in air atmosphere. The dried catalyst was calcined at 400 °C for 5 h in a furnace. The fresh catalyst was shaped by a tablet machine and then crushed to 20–40 mesh for the reaction test.

The reaction was carried out in a fixed bed reactor (600 mm, i.d. 12 mm). The reaction system had a buffer tank for collecting the tail gas and a pump for cycling gas. Fifteen grams of catalyst was packed. At the beginning of all tests, N_2 was introduced to purge the reaction system and then replaced by a gas mixture containing 3%H_2 in N_2 at atmosphere pressure. The catalyst was pre-reduced by increasing the temperature from 25 to 250 °C at the rate of 10 °C h^{-1} and then staying at 250 °C for 5 h. After the reduction, the reactants were introduced into the reactor. The hydrogen in the tail stream was recycled after the reaction products had been condensed to keep the proper ratio of hydrogen to the main reactants [furfural, BDO, and (furfural + BDO), respectively]. The components in the products collected in the ice trap were identified with a VG Quattro CG/MS (Fisons VG Biotech, Manchester, England), and the contents (weight percentages) were determined by a GC-920 gas chromatograph (Shanghai Analyser Co., China) with a flame ionization detector (FID).

Acknowledgements

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22 An alternative explanation could arise from the "local" increment of the H_2 partial pressure (or the H_2:furfural molar ratio) on the catalyst surface, produced by the extra hydrogen evolving from BDO. We thank one referee for pointing out this possibility.