New insight for reaction route of hydrogenation of maleic anhydride to γ-butyrolactone

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Received 1 April 2004; accepted 27 April 2004

A plausible reaction pathway for maleic anhydride (MA) hydrogenation is firstly proposed, which suggests that the CH_4 is produced by the methanation of CO formed during the reaction rather than direct de-carbonization of tetrahydrofuran, and MA cannot be directly decyclized, subsequently de-carbonized to C_3 compounds and CO. This work sheds light on the superficial phenomenon for MA liquid hydrogenation reported by other researchers, and may better explain the reaction process both in liquid and vapor phase MA hydrogenation. These results are important to understand the mechanism and reaction pathway of MA hydrogenation, and to facilitate the decrease of production cost in industrial plant.

KEY WORDS: maleic anhydride; selective hydrogenation; γ-butyrolactone; methanation.

1. Introduction

Hydrogenation of maleic anhydride (MA) is a significant industrial reaction as all its intermediate i.e., succinic anhydride (SA), and products *viz*., γ-butyrolactone (GBL), 1,4-butandiol (BDO) and tetrahydrofuran (THF), are chemicals of considerable industrial importance [1]. GBL is currently one of the most valuable alternatives to the environmentally harmful chlorinated solvents, and one of the most important intermediates in fine chemical industrial practices, for example, the synthesis of pyrrolidone, *N*-methylpyrrolidone, *N*-vinylpyrrolidone, herbicides and rubber additives. In addition, the butyrolactone ring is an integral building block of many natural products [2–4].

MA Hydrogenation is the most direct way to produce GBL without the use of hazardous materials. With the increasing demand of GBL, recently many researchers [5–10] have reported some important results on the MA hydrogenation, and during 2002–2003, we proposed a coupled works [11,12] of MA hydrogenation and/or BDO dehydrogenation for simultaneous synthesis of GBL. In addition, the patent references [13–16] show great interest in the nature and the compositions of catalysts as well as the operating conditions for the MA hydrogenation.

MA hydrogenation produces not only the intermediate of SA and the desired product of GBL, but also some by-products of *n*-butanol, butanoic acid and so on. These compounds mainly including SA and GBL can be further hydrogenated and de-carbonized to form C_3 compounds, i.e., *n*-propanol and/or propionic acid, meanwhile, an almost equivalent amount of C_1 compounds are always produced. Although the C_1 compounds mainly containing CO and /or CH_4 are the one of the many by-products during MA hydrogenation process, however, it can be gradually accumulated in the recycling tail gas system. When its content reaches a certain value (e.g. more than 10%) in recycled tail gas system of an industrial plant, the activity of catalyst will significantly decreases, which lead to low yield of the desired product of GBL. In order to keep these reaction systems maintaining sufficient effective H_2 content, the C_1 compounds formed during the reaction must be eliminated from this recycled tail system. This can be done by means of: (i) selective adsorption of tail gas; (ii) direct release of the tail gas. For the former method, it is critical important to identify the C_1 compounds and understand the mechanism of MA hydrogenation. The latter is an easy way, however, the H_2 consumption will dramatically increase, which results in considerable rise of production cost of GBL.

Though many attempts have been done on the mechanism of MA hydrogenation [17–19], however, a full understanding of the process is lacking, and the debate about the C_1 compound is still remains. Some authors [17,18] studied the reaction routes for liquid hydrogenation of MA to GBL and submitted that C_1 compound only was CH_4. A reaction pathway proposed in some literature [17–22] for MA liquid hydrogenation is shown in figure 1.

Messori *et al*. [19] studied the vapor hydrogenation of MA over Cu based catalyst, and hypothesized that the C_1 compounds are CO and/or CO_2. However, with this

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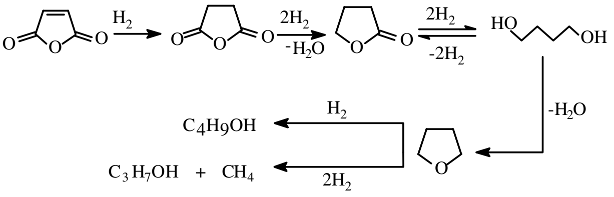

Figure 1. Reaction schemes of the liquid hydrogenation of MA.

assumption, it is difficult to explain fundamental reaction steps involved in the process, in which the C_1 compounds in gaseous by-products have several possible species. Now the references that possibly demonstrate what C_1 is, however, the influence of C_1 compounds on GBL yield, are still lacking.

Therefore, this work takes the form of an attempt to unify some conflicting mechanisms and other observations on the MA and its intermediates hydrogenation reaction pathway. MA vapor hydrogenation was generally carried out at higher H_2/MA molar ratio [19,23] in order to vaporize MA and to prevent the catalyst from coking. Without the recycle of reaction tail gas, the C_1 content is too low to be analyzed, and this is possible result that other researchers cannot efficiently detect C_1 compounds. Accordingly, in our work the tests utilizing either recycled tail gas or even lower H_2/MA molar ratio are adopted.

2. Experimental

2.1. Preparation catalysts

The Cu–Zn–Al catalyst of MA hydrogenation was prepared via continuous precipitated method. A mixed solution of $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ salts (1 M of total metal ions) were used as metal precursors with atomic ratio of 4.5 : 3.2 : 1, and 1 M Na_2CO_3 solution was added as the precipitating agent. Precipitation was performed at 75 °C, and the flow rates of the two solutions were adjusted to give a constant pH of ca. 7.5. The precipitate was aged for about 12 h at room temperature before filtering. The filtrated cake was washed with de-ion water until no Na^+ detected in the filtrate and subsequently dried at 110 °C for 24 h in air atmosphere. The dried catalyst was calcined at 450 °C for 5 h at a heating rate of 10 °C/h, and then shaped into Φ5×5 mm particle and 20–40 mesh by a tablet machine.

This Ni/γ-Al_2O_3 supported catalyst of methanation was prepared by simple pore volume impregnation. The commercial γ-Al_2O_3 support (BET surface area: 200 m^2/g, total pore volume: 0.76 cm^3/g; Nanjing Catalyst Co., P.R. China) was contacted with the solution of $Ni(NO_3)_2$ in deionized water, followed by drying at 110 °C for 11 h in air oven. The dried samples were calcined in air at 500 °C for 4 h at a heating rate of 2 °C/h. Finally, this Ni/ γ-Al_2O_3 (NiO 20%, wt.) catalyst was reduced at 400 °C for 5 h under 0.03 MPa in flowing H_2 (99.9%) at a heating rate of 10 °C/h.

2.2. Apparatus and procedures

The experiments of MA hydrogenation were carried out in a pilot-plant-scale reactor, which consisted of a single tube reactor (i.d. 40 mm, length 5 m), in which 5.5 kg Cu–Zn–Al catalyst was packed. The reactor was maintained at a desired temperature by circulating hot oil through the jacket of the reactor, and there was a buffer tank for collecting the tail gas and a pump for recycling gas. At the beginning of all tests, N_2 was introduced to purge the reaction system, and to replace the air in the reactor, and then replaced by mixed gas with 3% H_2 in the mixture of H_2 and N_2 at 0.03 MPa. The catalyst was pre-reduced *in situ* by increasing temperature from 25 to 130 °C at the rate of 15 °C/h and 130–280 °C at the rate of 5 °C/h, then keeping at 280 °C for 5 h. After the reduction, the mixed gas was replaced by pure H_2, and the vaporized MA and H_2 feeds were introduced into the reactor from the reactor top. The products coming out of the reactor were cooled and liquid products were collected in the knockout pot. The gases containing H_2 and CO from the reactor exit were further cooled with cooling brine and recycled back to the reactor through the recycling compressor. The components in the ice trap were identified with a VG Quattro CG/MS (Fisons VG Biotech. Manchester, England), and the contents were determined by a GC-920 gas chromatograph (Shanghai Analyser Co., China) equipped with a flame ionic detector (FID) and a column (3.2 mm × 2.0 m) filled with OV-101. The gaseous components (H_2, O_2, N_2, CH_4, and CO) were analyzed using an on-line GC equipped with a thermal conductivity detector (TCD) and a column filled with 13× molecular sieve.

Other control experiments, which showed that CH_4 was formed through methanation of between H_2 and CO produced during MA hydrogenation reaction, were devised in micro-reactors (i.d. 12 mm, length 600 mm) without tail gas recycle. Generally, 5.0 g catalyst (20–40 mesh) was packed in this micro-reactor.

3. Results and discussion

The experiments of MA vapor hydrogenation were carried out in a pilot-plant-scale reactor with recycled tail gas, and the pure H_2 was continuously conducted to this system to keep the reaction pressure equilibrium, in which 5.5 kg Cu–Zn–Al catalyst was packed. In one case, the tail gas of the MA hydrogenation was completely recycled into the reactor for 2.5 h instead of partly released to the atmosphere, and the experimental results were exhibited in table 1. Otherwise, the influences of CO content on MA hydrogenation to GBL with completely recycled tail gas were shown in figure 2.

Table 1
Effect of duration time on GBL yield and the accumulated CO content[a]

Duration (h)	Conversion (%)	Yield (%)			CO (%)
		GBL	C_3H_7OH	Others[b]	
0.5	100	93.2	2.2	4.6	1.2
1.0	100	92.9	2.2	4.6	2.4
1.5	100	92.8	2.2	4.6	3.6
2.0	100	92.5	2.1	5.3	4.8
2.5	100	91.2	2.1	6.6	5.9

[a] The MA vapor hydrogenation conditions: 275 °C, 0.03 MPa, liquid hourly space velocity (LHSV) = 0.04 h^{-1}, H_2/MA = 50/1 (molar ratio, recycling hydrogen).

[b] Other products: mainly *n*-butanol, SA, THF and butanoic acid etc.

In table 1, a 100% MA conversion with approximately 92% yield to GBL was obtained. The CO content became more and more in the recycled tail gas, after the feed stocks of pure H_2 and MA were conducted to this system with a completely recycled tail gas. The recycling H_2 tail gas was analyzed by GC, and the C_1 compound was identified to be only CO, which excluded the possibility of CO_2 and CH_4. Since the CO is produced by de-carbonization, it can gradually accumulate in the recycling tail system. If its C_1 content reaches a certain value in an industrial plant with recycled tail gas, the catalytic activity of MA hydrogenation will significantly decreases, which lead to low yield of the desired product of GBL.

From figure 2, while the CO contents increase from 2% to 35% in the mixed gases of H_2 and CO, MA hydrogenation activity significantly decreases from 100% to 88%, and this desired product yield of GBL greatly drops from 93% to 67% with the increase of SA intermediate from 0.2 to ca. 9%. In a word, the increase of CO content suppresses the activity of Cu–Zn–Al catalyst, which is a great disadvantage for the formation of desired GBL.

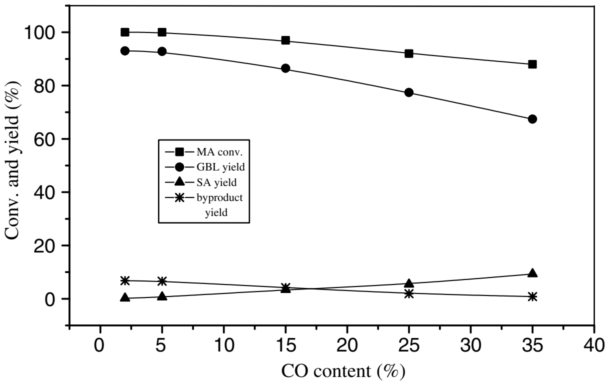

Figure 2. Influence of CO content on MA hydrogenation to GBL. [The MA vapor hydrogenation conditions: 275 °C, 0.03 MPa, LHSV 0.04 h^{-1}, H_2/MA molar ratio ca. 50/1 (recycling hydrogen); byproducts: *n*-propanol, *n*-butanol, propionic acid and butanoic acid etc.].

In addition, Messori *et al.* [19] report that the vapour hydrogenation of THF is characterized by low conversion values over Cu based catalyst (0.1 MPa, 245–275 °C) with the formation of ethanol together with ethane, while *n*-butanol is never detected. This literature result strongly indicates that THF is stable and CH_4 can not be formed under the usual reaction conditions for MA vapor hydrogenation. In this paper, they suggested that these compounds including MA, SA and GBL can be directly decyclized, subsequently de-carbonized to C_3 and C_1 compounds. However, in our tests (in table 1, and figure 2), there is no C_3 compounds with C=C bond in the products, and addition to this, the results of computational chemistry [24] also shows that hydrogenation of the C=C bond of MA to SA is much easier than the direct ring open of MA to C_3 and C_1 compounds. Thus, we hypothesize that probably both SA and GBL can be directly converted into C_3 compounds and CO through hydrogenation and the route of direct open of MA ring can be excluded. Finally, on the basis of the data reported in this work and also taking into account the existing literature [19,24] a proper pathway may be proposed for selective hydrogenation of MA to GBL and/or THF (figure 3), which may generally illustrate the reaction mechanisms for vapor phase of MA hydrogenation.

On the contrary, some literature [19] of MA liquid hydrogenation presented C_1 compound as CH_4. For example, Kanetaka *et al.* [17] studied MA hydrogenation at 240–280 °C over Ni catalyst, and proposed that THF was de-carbonized by over-hydrogenation and hydrogenolysis to both propanol and CH_4; Deshpande *et al.* [18] suggested that THF was over-hydrogenated and decyclizated to *n*-butanol, then de-carbonized to *n*-propanol and CH_4 at 250 °C over Ru and Co based catalyst. Some papers indicate that Ni, Ru and Co based catalysts are excellent activities of methanation [25–28] ($CO + 3H_2 \rightarrow CH_4 + H_2O$), therefore, we hypothesize that the CH_4 is not the primary product formed by THF over-hydrogenation. Instead, it is a secondary product and probably produced by methanation of CO formed during the reaction, since the conditions for MA hydrogenation mentioned above are in favor of methanation reaction.

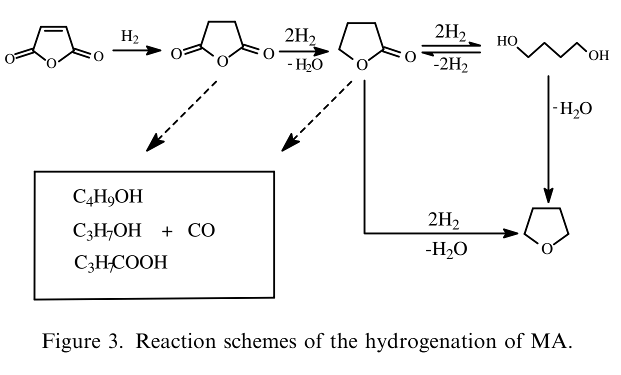

Figure 3. Reaction schemes of the hydrogenation of MA.

Table 2
Influence of temperature on the CO formation[a] and methanation[b]

T (°C)	Conversion (%)	Yield (%)			CO[c](%)	CH_4[d] (%)
		GBL	C_3H_7OH	Others		
275	100	96.2	1.1	2.7	0.4	0.4
285	100	94.9	1.5	3.6	0.5	0.5
295	100	93.5	1.8	4.7	0.6	0.6

[a] In the first reactor MA hydrogenation conditions: 0.03 MPa, LHSV = 0.16 h^{-1}, H_2/MA = 7/1 (molar ratio).
[b] In the second reactor CO methanation condition: 0.03 MPa, H_2/CO ratio ca. 200, GHSV 240 h^{-1}.
[c] The CO content of MA hydrogenation tail in the first reactor.
[d] The CH_4 content of Ni/Al_2O_3 reaction tail in the second reactor.

In order to verify the possible methanation reaction between H_2 and CO under MA hydrogenation conditions, two micro-reactors are devised in series without recycled tail gas. In the first micro-reactor, 5.0 g Cu–Zn–Al catalyst (20–40 mesh) was packed and reduced at the same conditions as above pilot-plant-scale test, and in the second reactor 5.0 g Ni/γ-Al_2O_3 (20–40 mesh) methanation catalyst was packed. After the two catalysts were reduced *in situ*, respectively, the reactants of MA and pure H_2 were introduced into the first micro-bed reactor with lower H_2/MA molar ratio. After the products was cooled and collected in the ice trap, the tail gases from the first reactor were adsorbed by commercial blue silica gel particles (diameter 2–3 mm, Qingdao Chemical Co. P.R. China) to eliminate the infection of trace organic compounds, and subsequently conducted to the second reactor packed with Ni/γ-Al_2O_3 methanation catalyst (reaction conditions: 275–295 °C, 0.03 MPa, H2/CO ratio ca. 200, GHSV 240 h^{-1}). These liquid and gaseous components were analyzed in agreement with pilot-plant-scale experiment. The experimental results are summarized in table 2.

As shown in table 2, the conversion of MA is nearly complete. The H_2 tail gas exited from the first micro-reactor is detected to contain CO rather than CH_4, in agreement with above pilot-plant-scale experiment. Nevertheless, only CH_4 can be detected from the H_2 tail gas exited from the second micro-reactor. These verified experiments show that the CO can be converted into CH_4 using methanation Ni/γ-Al_2O_3 catalyst, and probably demonstrate that CH_4 is a superficial by-product in MA liquid hydrogenation. This test results may be described by CO reaction pathway in figure 4.

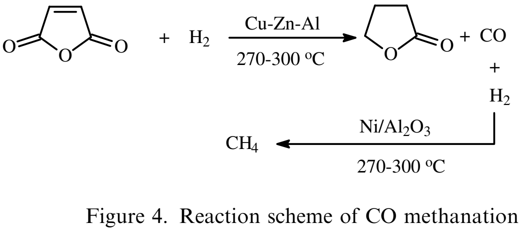

Figure 4. Reaction scheme of CO methanation.

4. Conclusions

The experimental results of pilot-plant-scale reactor and combined micro-reactor strongly indicate that CH_4 is not a primary product produced by over-hydrogenation, hydrogenolysis and de-carbonation of THF, instead, it is a secondary product and produced by methanation of CO formed during the MA hydrogenation reaction. Based on the results of this work and other literature, a plausible reaction pathway for MA hydrogenation is firstly proposed, which suggests that the CH_4 is formed by the methanation of CO formed during the reaction rather than direct de-carbonization of tetrahydrofuran, and only SA and GBL can be directly decyclized, subsequently de-carbonized to C_3 compounds and CO. We hypothesize that the CH_4 formation during MA liquid hydrogenation reported by other researchers is probably a superficial phenomenon, otherwise, it is the secondary product of CO methanation. This work probably can better explain the reaction process both in liquid and gaseous phase. These results are important to understand the mechanism and reaction pathway of MA hydrogenation, and to facilitate the decrease of productive costs in industrial plant with recycled tail gas. Our further systematic investigations will be expected to help explain this reaction mechanism.

Acknowledgments

We are indebted to the Natural Science Foundation of China (No. 20276077) and Shanxi Natural Science Foundation (No. 20021023) for financial support. The authors would like to thank Prof. M.X. Du for useful discussions, and providing both this Ni/Al_2O_3 catalyst of methanation and impregnation procedures.

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