

# Gas phase hydrogenation of maleic anhydride to tetrahydrofuran by Cu/ZnO/TiO<sub>2</sub> catalysts in the presence of *n*-butanol

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Received 21 September 2007; received in revised form 12 November 2007; accepted 26 November 2007

## Abstract

Cu/ZnO/TiO<sub>2</sub> catalysts were prepared via the coprecipitation method. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectrometry, temperature programmed reduction, and N<sub>2</sub> adsorption. The catalytic activity of Cu/ZnO/TiO<sub>2</sub> catalyst in gas phase hydrogenation of maleic anhydride in the presence of *n*-butanol was studied at 235–280 °C and 1 MPa. The conversion of maleic anhydride was more than 95.7% and the selectivity of tetrahydrofuran was up to 92.7%. At the same time, *n*-butanol was converted to butyraldehyde and butyl butyrate via reactions, namely, dehydrogenation, disproportionation, and esterification. There were two kinds of CuO species present in the calcined Cu/ZnO/TiO<sub>2</sub> catalysts. At a lower copper content, the CuO species strongly interacted with ZnO and TiO<sub>2</sub>; at a higher copper content, both the surface-anchored and bulk CuO species were present. The metallic copper (Cu<sup>0</sup>) produced by the reduction of the surface-anchored CuO species favored the deep hydrogenation of maleic anhydride to tetrahydrofuran. The deep hydrogenation activity of Cu/ZnO/TiO<sub>2</sub> catalyst increased with the decrease of crystallite sizes of CuO and the increase of microstrain values. Compensations of reaction heat and H<sub>2</sub> in the coupling reaction of maleic anhydride hydrogenation and *n*-butanol dehydrogenation were distinct.

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**Keywords:** Maleic anhydride; *n*-Butanol; Hydrogenation; Tetrahydrofuran; Cu/ZnO/TiO<sub>2</sub>

## 1. Introduction

Tetrahydrofuran (THF) is widely used both as a versatile solvent and as a raw material for the manufacture of poly-tetramethylene ether glycol (PTMEG), spandex fibers, and polyurethane elastomers [1–3]. The majority of tetrahydrofuran is produced by the following two processes: the furfural process and the Reppe process [1,3]. In the former, possibly carcinogenic furfural is used as the raw material; in the latter, explosive acetylene and possibly carcinogenic formaldehyde are used as the feed stocks. On the other hand, the severe reaction conditions and multi-step reaction pathways also make the above-mentioned production processes unfavorable. To overcome the disadvantages of the established processes, eco-friendly and economically alternative process is worthy of investigation. A very promising alternative to the established processes is the single stage hydrogenation of maleic anhydride

since maleic anhydride can be produced at a lower cost and on a large scale by partial oxidation of *n*-butane instead of benzene now [1,4–6].

Catalytic hydrogenation of maleic anhydride to succinic anhydride,  $\gamma$ -butyrolactone, 1,4-butanediol, and tetrahydrofuran has been an attractive research topic in the last decade since the hydrogenation products are important chemicals in the production of polymers, pharmaceuticals, and rubber additives, etc. [4,5,7,8]. Hydrogenation of maleic anhydride has been catalyzed by various kinds of catalysts, such as noble metals (Pd, Re, and Ru) in liquid phase at pressures between 1 and 5 MPa and temperatures between 190 and 240 °C [9–13], copper-based catalysts in liquid phase at pressures between 5 and 9 MPa and temperatures between 200 and 240 °C [7,9], and copper-based catalysts in gas phase at atmospheric pressure and temperatures between 210 and 280 °C [6,14,15]. The gas phase hydrogenation of maleic anhydride commonly used Cu/ZnO/M<sub>x</sub>O (Al, Cr, Ce, etc.) catalysts. During the above-mentioned researches, the high yield of  $\gamma$ -butyrolactone is generally achieved. However, tetrahydrofuran is usually produced with a lower yield and considered as a by-product.

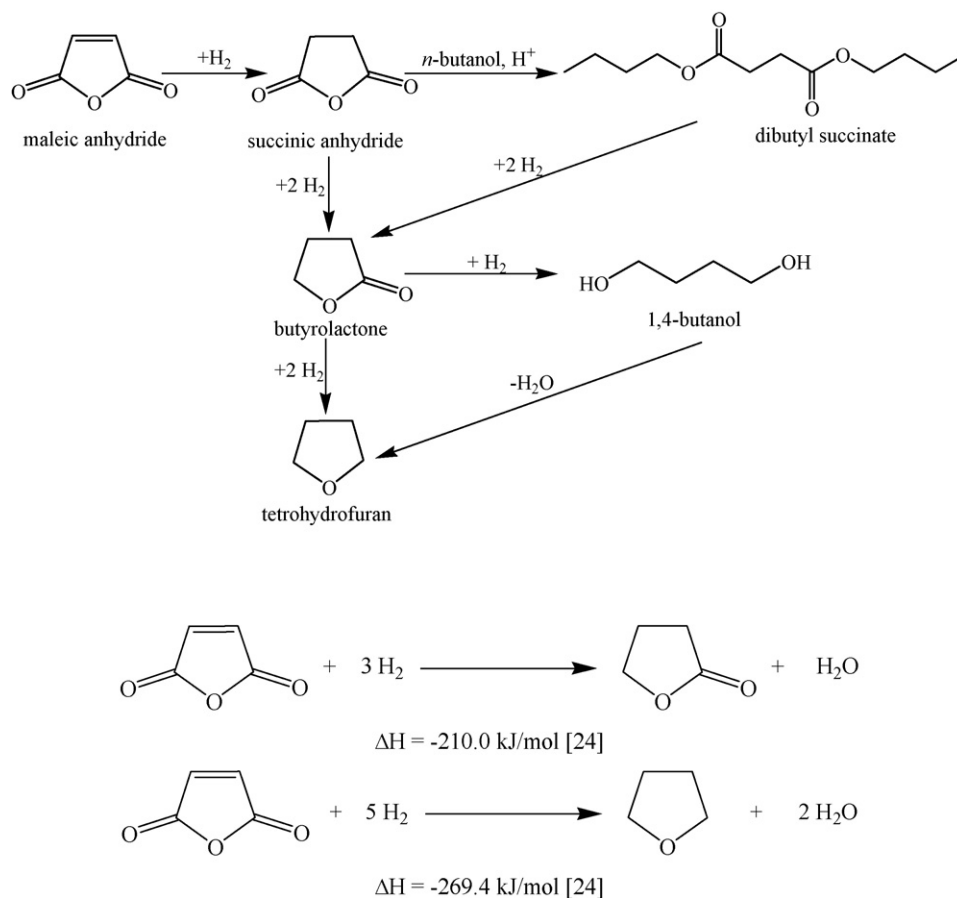
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To our best knowledge, there are no published papers dealing with the direct hydrogenation of maleic anhydride to tetrahydrofuran with a high yield except several patents [16,17]. Schlitter et al. [16] used Cu(Pd)/Al<sub>2</sub>O<sub>3</sub> catalysts for gas phase hydrogenation of maleic anhydride to tetrahydrofuran, the yield of tetrahydrofuran was up to 93% at a reaction temperature of 250 °C and the pressures ranging from 0.1 to 2 MPa. Budge and Pedersen [17] used Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub> as a catalyst for the hydrogenation of maleic anhydride to tetrahydrofuran in the presence of monohydric aliphatic alcohol such as ethanol and butanol at the reaction temperatures between 200 and 325 °C and the pressures between 1.5 and 5.0 MPa, the yield of tetrahydrofuran was up to 99.1%. Other relative method for the preparation of tetrahydrofuran is the hydrogenation of the derivatives of maleic anhydride, e.g. Müller et al. [3] reported that dimethyl maleate or dimethyl succinate was converted to tetrahydrofuran by Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst at a reaction pressure of 2.5 MPa and a reaction temperature of 220 °C. In the Müller's process, an extra esterification process of maleic anhydride is needed before the catalytic hydrogenation, giving a multi-stage process for tetrahydrofuran production. The patented literatures reveal that it is possible to directly hydrogenate maleic anhydride to tetrahydrofuran with a high yield. But the presence of noble metal palladium and polluting chromium in the catalysts is unfavorable in view of both the catalyst cost and the environmental protection.

According to the literatures for the preparation of tetrahydrofuran from maleic anhydride or its derivatives [3,16,17], a common feature exists, i.e. the investigated catalysts are composed of metallic copper (CuO), ZnO, and Al<sub>2</sub>O<sub>3</sub>. In the catalytic hydrogenation process, it is commonly believed that CuO supplies hydrogenation active sites and that ZnO and Al<sub>2</sub>O<sub>3</sub> play a role of support. For example, in the hydrogenation process of dimethyl maleic anhydride or dimethyl succinate to tetrahydrofuran, Müller et al. [3] suggested that Cu<sup>0</sup> catalyzes the hydrogenation and hydrogenolysis reactions yielding  $\gamma$ -butyrolactone and 1,4-butanediol and that Al<sub>2</sub>O<sub>3</sub> provides weakly acidic sites to promote the subsequent dehydration of 1,4-butanediol to tetrahydrofuran. But Lu et al. [18] have recently reported that TiO<sub>2</sub> with acidic sites-modified Cu/Al<sub>2</sub>O<sub>3</sub> catalyst was beneficial to the formation of  $\gamma$ -butyrolactone in the gas phase hydrogenation of maleic anhydride. The role of the supports is still at controversy.

It is well known that TiO<sub>2</sub> is a widely used material as a catalyst support or as a catalyst itself. It is reasonable to predict that TiO<sub>2</sub> as an alternative to Cr or Al present in copper-based catalyst should have a positive impact on the selective hydrogenation of maleic anhydride.

Recently, coupling of an exothermic hydrogenation reaction and an endothermic dehydrogenation reaction in one reaction system attracted researchers' interest in view of thermodynamics [19–21]. Copper-based catalysts can not only catalyze the



Scheme 1. Hydrogenation route of maleic anhydride [3,5,6,24].

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