

Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran

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Abstract

The reactivity of furfural and its reaction intermediates is separately investigated in a fixed-bed reactor over a commercial catalyst (C₁: Cu/Zn/Al/Ca/Na = 59:33:6:1:1, atomic ratio) and a self-made multicomponent one (C₂: Cu/Cr/Ni/Zn/Fe = 43:45:8:3:1, atomic ratio). Some interesting results are obtained in this work. Firstly, both furfural and furfuryl alcohol can eliminate carbon monoxide to produce furan. Secondly, tetrahydrofuran and 2-methyltetrahydrofuran are all very stable, and *n*-butanol mainly derives from furan rather than tetrahydrofuran. Thirdly, 2-pentanone, 2-methyltetrahydrofuran, 1-pentanol and 2-pentanol are all the hydrogenation products of 2-methylfuran. Finally, with C₂ catalyst containing the Ni element, the main reaction product of tetrahydrofurfuryl alcohol is tetrahydrofuran, while δ -valerolactone is the main product with C₁ one. This work has unified some conflicting mechanisms and discussed the origin of some interesting products, which is important to understand the mechanism and reaction pathway of furfural hydrogenation, and to provide an instruction for the design of new catalytic formulations.

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1. Introduction

Furfural is a versatile compound in the fragrance industry, and the vapour phase hydrogenation of furfural is commonly used to produce 2-methylfuran, furfuryl alcohol and tetrahydrofuran [1,2]. 2-Methylfuran is an important intermediate in fine chemical industrial practices, which is mainly used for the synthesis of cysanthemate pesticides, perfume intermediates and chloroquine lateral chains in medical intermediates [3–5]. Furfuryl alcohol is mainly used for the production of dark thermostatic resins resistant to acids, bases and various solvents; liquid resins for galvanic bath-tube, and resins used for strengthening ceramics. It is also widely used as a solvent, e.g. phenolic resins or pigments of low solubility [2]. Tetrahydrofuran is mainly used as raw material for spandex fibers and polyurethane elastomers,

and as a solvent (it is a strong dissolving agent for both synthetic and natural resins) [6].

Many researchers [1,2,7–11] have reported some important results on the vapour phase hydrogenation of furfural, and recently we have developed a coupling process to synthesis 2-methylfuran and γ -butyrolactone simultaneously, in which the hydrogenation of furfural and the dehydrogenation of 1,4-butanadiol are combined at the same reactor [3–5]. However, furfural produces not only the desired products, but also many by-products of carbon monoxide, *n*-butanol, ethanol, pentanol, pentanone and so on both in the single process and the coupling one. Given the fact that the potential for enhancement of selectivity of the desired products by concentrating on the composition of catalysts as well as the operating conditions for the furfural hydrogenation [1–5,7–11] appears more or less limited, considerable effort should also be made into the reaction mechanism and the true origin of by-products. However, there are few experimental data reported in the open literature on the reaction pathway of vapour phase hydrogenation of furfural. In

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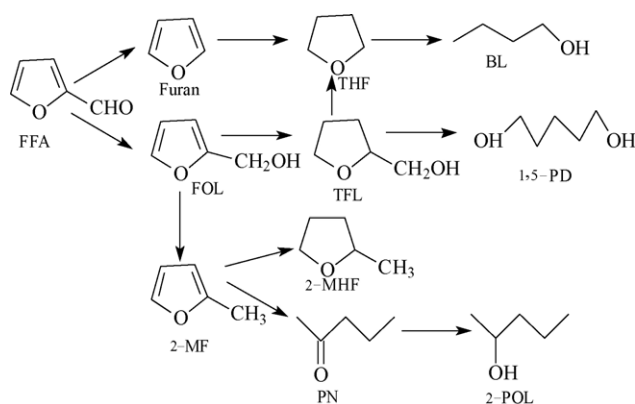


Fig. 1. Reaction pathway proposed in the literature for furfural hydrogenation. FFA, furfural; THF, tetrahydrofuran; BL, *n*-butanol; FOL, furfuryl alcohol; TFL, tetrahydrofurfuryl alcohol; 1,5-PD, 1,5-pentanediol; PN, 2-pentanone; 2-MHF, 2-methyltetrahydrofuran; 2-MF, 2-methylfuran; 2-PL, 2-pentanol.

addition, the debates about the origin of some by-products, such as *n*-butanol, carbon monoxide and ethanol, still exist. Fig. 1 illustrates the reaction pathway generally proposed for vapour phase hydrogenation of furfural [2,12–15], which is not comprehensive and contains some conflicting points.

In previous papers, some results on the behaviour of furfural and its reaction intermediates (such as, furfuryl alcohol, 2-methylfuran, tetrahydrofurfuryl alcohol) over Ni-Cu or Fe-Cu alloy catalysts are reported [12–15]. However, the alloy catalyst is unable to apply in industrial practices because of its serious deactivation phenomena. Cu-Cr catalyst has been successfully utilized for the hydrogenation reaction of furfural in practices [5,7], which exhibits excellent yield of 2-MF and long life. Cu-Zn catalyst is also an industrial catalyst for hydrogenation and has been traditionally used for methanol synthesis [16–21]. Recently, it has been used for the hydrogenation process other than methanol synthesis, and shows good performance [22,23]. During 2003–2004, we have successfully used the Cu-Zn catalyst for the hydrogenation of furfural [3,4].

The aim of this work is to unify some conflicting mechanisms, discuss the origin of some products, such as *n*-butanol, carbon monoxide and ethanol, and provide an instruction for the design of new catalytic formulations. In order to obtain general data, a commercial Cu-Zn catalyst (C_1) and a self-made multicomponent Cu-Cr one (C_2) are used. The two catalysts have been investigated in reaction conditions of industrial interest, which do not show any scale-up problems or deactivation phenomena with increasing time-on-stream. The reactivity of furfural and its main intermediates is separately investigated over the two catalysts to shed light on the reaction mechanism of furfural hydrogenation.

2. Experimental

2.1. Preparation of catalysts

The atomic compositions of the commercial catalyst (C_1) and of the self-made multicomponent one (C_2) were Cu/Zn/Al/Ca/Na = 59:33:6:1:1 and Cu/Cr/Ni/Zn/Fe = 43:45:8:3:1

(atomic ratio), respectively. C_2 was prepared via the coprecipitation method. In a typical preparation procedure, a solution of mixed $\text{Cu}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ (1 M of total metal ions) was used as metal precursors, with a 1 M $(\text{NH}_4)_2\text{CO}_3$ solution added as the precipitating agent. The flow rates of the two solutions were adjusted to give a constant pH of about 6.0. After precipitation, the suspension was maintained at 45 °C for 4 h to complete the aging step. The precipitate was washed, dried at 100–110 °C for 12 h and then calcined at 350 °C for 4 h in air atmosphere.

2.2. Catalytic test

The two fresh catalysts were shaped with a pressure of 40 MPa by a tablet machine and then crushed to 20–40 mesh. The catalytic tests were carried out in a tubular fixed-bed reactor (length of 500 mm and i.d. of 12 mm). Before the reaction, 5.0 g of catalyst packed in reactor was activated in situ at atmospheric pressure in a flow of H_2/N_2 (5:95, v/v) stream, and the temperature was progressively increased from ambient temperature to 270 °C. After reduction, the gas flow was switched to pure hydrogen. The reactants were pumped to a vapourizer, mixed with pure hydrogen and then introduced into the reactor. The liquid products in the ice trap were identified with a GC/MS (GC6890A/5973MSD, HP, USA), and the contents were determined by an Agilent 6890N (Agilent, HP) equipped with a flame ionization detector (FID) and a J&W DB-WAX 30 m × 0.32 mm capillary column. The gaseous products were determined by a SP-2000 gas chromatograph (Ruihong Analyser Co., Shandong, PR China) equipped with a flame ionization detector (FID) and a column (3.0 mm × 2.0 m) filled with Chromosorb 101, and a GC-920 gas chromatograph (Shanghai Analyser Co., PR China) equipped with a thermal conductivity detector (TCD) and a 13 × molecular sieve packed column (3.0 mm × 1.5 m).

3. Results and discussion

3.1. Reactivity of furfural and furfuryl alcohol

As shown in Table 1, the two catalysts are all active in the hydrogenation of furfural, exhibiting nearly complete conversion in the range of 200–300 °C. C_1 catalyst has better yield of 2-methylfuran than C_2 catalyst, with a maximum yield (87.0%) at 250 °C. There are some results [24–27] concerning the production of furan by decarbonylation of furfural over Pd or Pt-based catalysts. Literature [12] reported that Ni-Cu alloy catalyst exhibited high selectivity of furfural to furan when the temperature was over 200 °C. Furan is also produced over the Cu-based catalysts in this work, furthermore, C_2 catalyst produces more furan than C_1 one probably because of containing Ni element.

The conversion of furfuryl alcohol with the two catalysts is over 96% from 220 to 300 °C (Table 2). The yield of 2-methylfuran with C_1 catalyst is also higher than C_2 one, and C_2 catalyst also produces more furan than C_1 one. References [14,28] reported that tetrahydrofurfuryl alcohol could eliminate carbon monoxide and hydrogen to produce tetrahydrofuran

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