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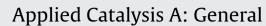
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# Vapor phase hydrogenation of 2-methylfuran over noble and base metal catalysts

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A B S T R A C T

Vapor phase hydrogenation of 2-methyl furan (2-MF) was carried out over barium-promoted copper chromite (Ba/Cu/Cr), Cu/Cr/Ni/Zn/Fe, Cu-Ru/C, 0.5 wt.% Pt/C (Pt/C), and 0.5 wt.% Pd/C (Pd/C) catalysts, respectively. The catalysts were characterized with respect to their specific surface areas by the $N_2$ BET method and solid-state structures by X-ray diffraction (XRD). The XRD data confirmed the formation of a mixed oxide in the copper-chromite catalyst and the presence of small Pt and Pd crystals (<5 nm by TEM) in the carbon-supported catalysts. The 2-MF hydrogenation was performed in vapor phase at atmospheric pressure in a continuous flow fixed bed tubular reactor at 140–350 °C employing the $H_2$/2-MF mole ratios in the 10–25 range. The results of 2-MF hydrogenation showed that the Ba/Cu/Cr, Cu/Cr/Ni/Zn/Fe, Cu-Ru/C and Pt/C catalysts were mainly active for furan ring opening leading mostly to 2-pentanone (2-PN) as well as small amounts of other products, such as 2-methyltetrahydrofuran (2-MTHF), 2-pentanol (2-PL), 1-pentanol (1-PL) and cracked hydrocarbons (butane and propane). On the other hand, the Pd/C catalyst was highly selective in 2-MF ring saturation leading to 2-MTHF as the main product below 220 °C, whereas it became increasingly selective to 2-PN, the ring opening product, at higher temperatures.

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## 1. Introduction

The catalytic transformation of biomass-derived oxygenated aromatics, such as substituted furans, to value-added chemicals and fuels is an important research area in green chemistry. It is highly desirable to develop novel catalysts and methods that enable control over the nature of functional groups in these biomass-derived molecules. Selective hydrogenation and hydrogenolysis of C—C and C—O bonds are important reactions for the conversion of substituted furans to useful chemicals. The objective of hydrogenolysis is to selectively break target C—C and/or C—O bonds, thereby producing more valuable, desired products.

Furan, furfural and their derivatives are very important biomass-derived aromatics that can be hydrogenated into a variety of specialty chemicals, solvents and alternative fuels. Selective hydrogenation of the C=C bond in the furan ring of furfural leads to the formation of tetrahydrofurfural, which can be converted into a diesel fuel component by self-aldol condensation [1]. Methyltetrahydrofuran can be also obtained by the selective hydrogenation of furfural ring which is a principal component of a P-series fuel [2]. 2-Methylfuran (2-MF) can be also produced by furfural hydrogenation at higher temperature than that employed to make furfuryl alcohol [3]. 2-MF appears as an unwanted by-product when furfuryl alcohol is made from furfural by the vapor phase hydrogenation over a copper-chromite catalyst at 135 °C and the yield of 2-MF increases when the reaction temperature is raised to compensate for the gradual reduction of catalytic activity [4]. The selectivity to the desired product in these hydrogenation reactions depends on the partial pressure of hydrogen and the nature of catalyst.

Hydrogenation of furan ring compounds over noble metals (Pt, Pd, Ir) is well known in the literature [5–12]. The first reported catalyst was platinum as a furfural hydrogenation catalyst in 1923 [13]. However, the fundamentals of surface reactions during hydrogenation of these heterocycles on noble and base metal catalysts are poorly understood as compared to elementary reaction steps on these surfaces involving benzene ring molecules. Tracy et al. [14] reported that furan, thiophene and pyrrole exhibit very different reaction pathways on Pd (1 1 1). Maris et al. [10,12] have shown that by using cinchonidine (CD)-modified Pd/Al$_2$O$_3$, a chirally modified metal catalyst, the enantioselective hydrogenation can be effectively achieved for furan and benzofurancarboxylic acid. Earlier studies in the literature [15–18] indicated that there was a problem of catalyst deactivation, as both palladium black and Pd/C deactivated rapidly due to carbon laydown.

Hydrogenation of olefinic and carbonyl groups of furan and its derivatives over copper-chromite catalysts has been reported

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[19–23]. Also, the cleavage of furan ring has been reported over copper-chromite and Pt oxide catalysts at low temperature and pressure [13,24]. Copper-chromite catalysts have been used extensively in various industrial processes, such as the partial hydrogenation of vegetable oils and fatty acids, as well as the decomposition or dehydration of alcohols [25]. The utilization of these catalysts in hydrogenation reactions stems from their ability to selectively hydrogenate carbonyl bonds while leaving unsaturated C=C bonds virtually untouched [19]. Ruthenium catalysts are frequently used for liquid phase hydrogenation of aromatic and carbonyl compounds [26–30]. Previously, it was reported that furan, methylfuran, α,α-dimethyl furan, ethylfuran and alkenefurans can be converted to saturated derivatives in good yields over Raney nickel catalysts under mild reaction conditions [31,32]. Papa et al. [33] in their study of hydrogenolysis of furan derivatives over Raney alloy and aqueous alkali found equal amounts of furan-ring hydrogenation and hydrogenolysis products. At atmospheric pressure, the hydrogenation of 2-alkylfurans over skeletal Cu-Al catalysts leads to the furan ring opening by breaking the C—O bond away from the alkyl group, whereas at high hydrogen pressure the cleavage of both C—C and C—O bond takes place leading to the formation of an aliphatic alcohol [34]. Paraffins were also observed over skeletal Cu-Al catalysts, probably due to dehydration of aliphatic alcohols followed by hydrogenation of olefin intermediates.

Therefore, these previous studies indicated that the nature of hydrogenation products of furan, 2-MF and their derivatives depends highly on the nature of catalysts and reaction conditions employed. However, very few reports have appeared to date on the topic of the vapor-phase hydrogenation of 2-MF [31,35,36] and the current fundamental understanding of the molecular relationships between the catalyst structure and the nature of alkylfuran hydrogenation pathways.

## 2. Experimental

### 2.1. Catalysts

The Cu/Cr/Ni/Zn/Fe = 43:45:8:3:1 (atomic ratio) catalyst was prepared by the co-precipitation method as reported by Zheng et al. [36] using Cu, Cr, Ni, Zn and Fe nitrates (Alfa Aesar, 99.9%, USA) as precursors. The Cu-Ru/C catalyst was prepared by incipient wetness impregnation method, where Ru and Cu were impregnated sequentially onto carbon black support (Vulcan-XC72 GP 3907, Cabot Corporation Ltd., USA) at the atomic Ru:Cu ratio = 3:2. RuCl$_3$·3H$_2$O (Alfa Aesar, 99.9%) and Cu(NO$_3$)$_3$·3H$_2$O (Alfa Aesar, 99.9%, USA) were used as the respective sources and the total metal content was 10 wt.%. The Ba/Cu/Cr, 0.5 wt.% Pt/C, and 0.5 wt.% Pd/C catalysts were obtained from BASF, USA.

### 2.2. Catalyst characterization

The BET surface areas of the catalysts were determined by the N$_2$ physisorption at liquid N$_2$ temperature employing a Micromeritics Tri-Star system. Prior to the measurements, the temperature was slowly ramped to 200 °C and the catalysts outgassed for 8 h. The phase composition of the catalysts was investigated by X-ray diffraction (XRD) (Siemens D500, CuKα). The TEM images were collected using Philips CM 20 electron microscope.

### 2.3. Catalytic tests

The hydrogenation of 2-MF was performed at atmospheric pressure in a continuous flow fixed bed tubular reactor employing quartz tubes, 250 mm in length and 7 mm i.d. Another quartz tube of 210 mm length and 3 mm i.d. attached to the first one served as outlet to facilitate faster removal of reactor effluent. The catalyst (0.2–2 g) was placed between quartz wool plugs inside the reactor. Prior to these tests, the catalysts were treated in situ at atmospheric pressure in the hydrogen flow of 20 cc/min, while the temperature was progressively increased from ambient to 340 °C, and then maintained for 2 h at 340 °C. A constant flow of 2-MF vapor (Sigma–Aldrich, 99%) was established by passing Ar through a bubbler (Kontes Kimble Chase LLC, Kontes Article No. 652230-0000) containing pure liquid 2-MF in a constant temperature bath (Fisher Scientific, Cat No. 14-462-10, Model 210, USA), and mixing the resulting 2-MF/Ar feed with hydrogen at the molar H$_2$/2-MF ratios in the 10–25 range. The 2-MF concentration in the feed was controlled by the bath temperature. The reactor was mounted inside a programmable electric furnace (Thermo Scientific, Lindberg/Blue M) and the axial temperature profile in the reactor was measured using a chromel–alumel thermocouple placed inside the catalyst bed. The reaction temperature was varied from 130 to 350 °C. The effluent was directly passed through the heated sampling valves to online GC–MS (Shimadzu, GCMS QP-5000) to determine the products stream composition. All stainless steel lines after the bath and the sampling valve of the GC-MS were heated to avoid condensation of the 2-MF reactant and products.

The reactor effluent was analyzed by GC–MS equipped with a capillary column (Supelco, 28473-U, SLB-5ms) of 30 m in length and 0.25 μ film thickness using ultrapure helium (Wright Brother Inc., Lot 9047-1) as the carrier gas. The injector and detector temperature was maintained at 230 °C. The products were identified using NIST Mass Spectrum Library 2008 (Shimadzu, Catalog No. 225-13290-91) and the total carbon balances agreed within ±5%.

The 2-MF conversion, selectivity and yield of the products were defined as:

Conversion (%) = [(Mole of 2-MF in the feed – Mole of 2-MF in the product)/Mole of 2-MF in the feed] × 100

Selectivity (%) = (Mole of the individual product/Total moles of the products) × 100

Yield (%) = (Selectivity × Conversion)/100

## 3. Results and discussion

### 3.1. Catalyst characterization

The BET surface areas of carbon-supported catalysts were higher than those of the other catalysts. The BET surface areas of Pt/C and Pd/C catalysts were 1182 m$^2$/g and 1188 m$^2$/g, respectively, whereas their total pore volume was 0.71 cm$^3$/g. The Ba/Cu/Cr, Cu/Cr/Fe/Ni/Zn and Cu-Ru/C catalysts were dense showing significantly lower BET surface areas of 47 m$^2$/g, 81 m$^2$/g and 64 m$^2$/g, respectively, and low pore volumes.

The XRD pattern of the copper-chromite catalyst shown in Fig. 1(A) agreed well with the pattern reported previously [19,37,38]. The peaks at 35.4° and 63° 2θ correspond to cupric chromite (CuCrO$_4$), whereas the peaks at 37.4° and 41.5° correspond to CuCrO$_2$ and CuO, respectively [19]. A weaker peak was detected at 22.3°, which corresponds to Cr$_2$O$_3$ [37]. The XRD pattern of the Cu/Cr/Fe/Ni/Zn catalyst, Fig. 1(B), corresponds to a disordered structure. The diffraction peaks corresponding to the binary Fe, Ni and Zn oxides were absent, suggesting that this catalyst probably contained an amorphous mixed metal oxide phase. The weak peaks observed at 35.4° and 63° 2θ suggested the presence of either CuCr$_2$O$_4$ (JCPDS #026-0509) or CuO (JCPDS #003-0898).

The diffraction peak observed at 25.3° 2θ for the Cu-Ru/C, Pt/C and Pd/C catalysts was assigned to that of the graphite phase (JCPDS #41–1487). Other peaks belonging to RuO$_2$, CuO, metallic Ru and metallic Cu were not detected for the Cu-Ru/C catalyst suggesting that the Ru- and Cu-containing phases were either disordered