Applied Catalysis A: General 475 (2014) 379–385

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

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

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ARTICLE INFO

*Article history:*
Received 21 September 2013
Received in revised form 29 January 2014
Accepted 30 January 2014
Available online 6 February 2014

*Keywords:*
Hydrogenation
Hydrogenolysis
2-Methylfuran
2-Methyltetrahydrofuran
2-Pentanone
Copper-chromium catalyst
Pt
Pd catalyst

ABSTRACT

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.

## 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/$Al_2O_3$, 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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http://dx.doi.org/10.1016/j.apcata.2014.01.054

[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, $\alpha$,$\alpha$-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. $RuCl_3 \cdot 3H_2O$ (Alfa Aesar, 99.9%) and $Cu(NO_3)_3 \cdot 3H_2O$ (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, CuK$\alpha$). 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 $\mu$ 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° $2\theta$ 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 $Cr_2O_3$ [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° $2\theta$ suggested the presence of either $CuCr_2O_4$ (JCPDS #026-0509) or CuO (JCPDS #003-0898).

The diffraction peak observed at 25.3° $2\theta$ 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

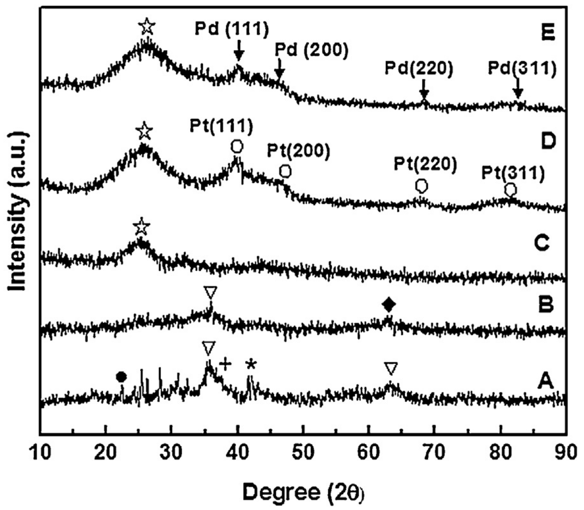

**Fig. 1.** XRD patterns of fresh catalysts: (A) barium-promoted copper chromite; (B) Cu/Cr/Fe/Ni/Zn; (C) Cu-Ru/C; (D) 0.5 wt.% Pt/C; (E) 0.5 wt.% Pd/C. The symbols are representing the difference phases as indicated: (▽) $CuCr_2O_4$, (+) $CuCrO_2$, (*) Cu°, (●) $Cr_2O_3$, (☆) Graphite, (♦) CuO, (O) Pt, (↓) Pd.

or present below the XRD detection limit. The XRD pattern of the Pt/C catalyst shown in Fig. 1(D) exhibited the characteristic diffraction peaks at 39°, 46°, 67° and 81° $2\theta$ which correspond to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the *fcc* Pt crystal structure, respectively [38–40]. The XRD pattern of the Pd/C catalyst shown in Fig. 1(E) similarly exhibited four weak peaks at 40°, 47°, 68° and 81° $2\theta$ corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections, respectively, of the *fcc* Pd structure [41–43]. The intensity of Pt and Pd peaks was low suggesting their small crystal size [41].

Fig. 2 shows the TEM images of the Pt/C and Pd/C catalysts. The low resolution TEM images showed the presence of roughly spherical metal nanoparticles of less than 5 nm in diameter uniformly distributed on carbon support. These TEM images confirmed the small Pt and Pd particle size suggested by the XRD patterns of Pt/C and Pd/C catalysts.

### 3.2. *Catalytic performance*

The catalytic data during 2-MF hydrogenation were collected by varying the reaction temperature, total feed flow rate, the $H_2$/2-MF mole ratio and the amount of catalyst, and shown in Figs. 3–7. The main products observed were 2-PN, 2-PL and 2-MTHF, which are products of both furan ring saturation as well as furan ring opening reactions. Minor amounts of other products, such as cracked hydrocarbons (butane and pentane), 1-PL and 1-butanone (1-BN) were also detected in some cases.

Fig. 3 shows the catalytic data for the hydrogenation of 2-MF over the Ba/Cu/Cr catalyst at two different $H_2$/2-MF mole ratios at 130–300 °C. These data indicated that 2-PN, 2-MTHF, 1-PL and 2-PL were major products below 220 °C, while above 220 °C the production of alcohols and 2-MTHF decreased with increasing reaction temperature and no alcohols were observed above 250 °C. Moreover, the yield of 2-PN decreased sharply from 66 to 20 mol.% above 250 °C and the pentane yield was enhanced dramatically to 80 mol.% as the reaction temperature was increased to 300 °C.

These results indicated that the product distribution was highly dependent on the reaction conditions used. Wilson [44] reported that 2-MTHF, 2-PN and 2-PL were major 2-MF hydrogenation products over Ni-based catalysts, whereas Wojcik [31] showed that 2-MTHF, 1-PL and 2-PL were major products at 200 °C over a Cu-Cr catalyst. Zheng et al. [36] have reported that 2-PN and 2-PL were the major products, while 2-MTHF and 1-PL were the minor products of 2-MF hydrogenation over the Cu-based catalyst.

In this study, the conversion of 2-MF over the Ba/Cu/Cr catalyst increased with reaction temperature and reached 100% at 300 °C and the $H_2$/2-MF mole ratio of 10, while the yield of 2-PN reach maximum of ca. 60 mol.% at 225 °C. A previous study of 2-MF hydrogenation [44] also showed that the main hydrogenation product over Ni-based catalysts at 100 °C was 2-MTHF with 86 mol.% yield, but as the temperature was further increased the 2-MTHF yield declined with a simultaneous increase in the yield of 2-PN. While pure copper catalyst was found to be inactive in the 2MF hydrogenation reaction, the copper-chromite catalyst showed 52% yield of 2-PN at 340 °C. However, the Ba/Cu/Cr catalyst employed in the present study showed a maximal 55 mol.% selectivity to 2-PN at 250 °C, whereas pentane was the main product at higher temperatures.

The yield of 2-PN dramatically decreased above 225 °C, while the pentane yield increased reaching >80 mol.% at 300 °C. The complete conversion of 2-MF was observed above 280 °C at the $H_2$/2-MF mole ratio of 20 with the maximum yield of 2-PN of ca. 70 mol.% at 250 °C. However, its yield declined sharply above 250 °C, which was accompanied by a significant increase in the yield of pentane. The maximum yield of 2-PN at both $H_2$/2-MF mole ratios was observed at 225–250 °C, while pentane production was favored at higher temperatures and higher $H_2$/2-MF mole ratios. Therefore, the product selectivity was highly dependent on the nature of catalysts as well as the reaction conditions. It should be noted that the yield of 1-PL and $C_3$-$C_4$ hydrocarbons was not significant over the Ba/Cu/Cr catalyst above 250 °C, whereas significant amounts of pentane were observed above 250 °C [45,46]. This result indicated that the Ba/Cu/Cr catalyst promoted furan ring opening by breaking the C—O bond at high temperatures. Liaw et al. [47] reported

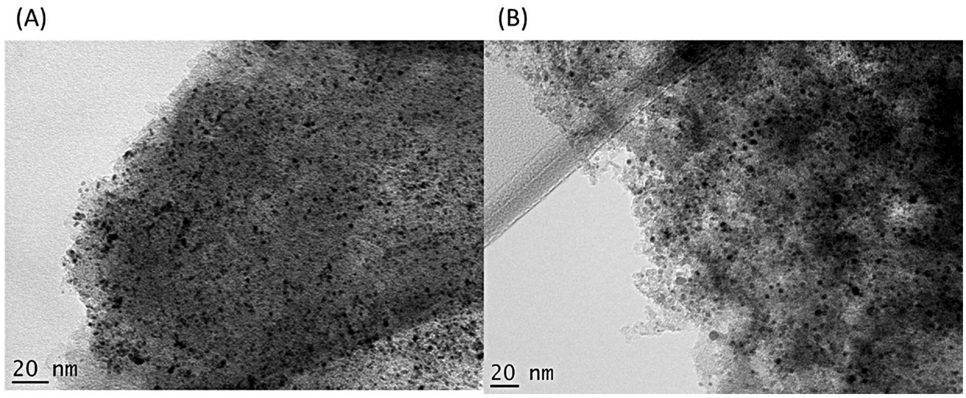

**Fig. 2.** TEM images of fresh catalysts: (A) 0.5 wt.% Pt/C; (B) 0.5 wt.% Pd/C.

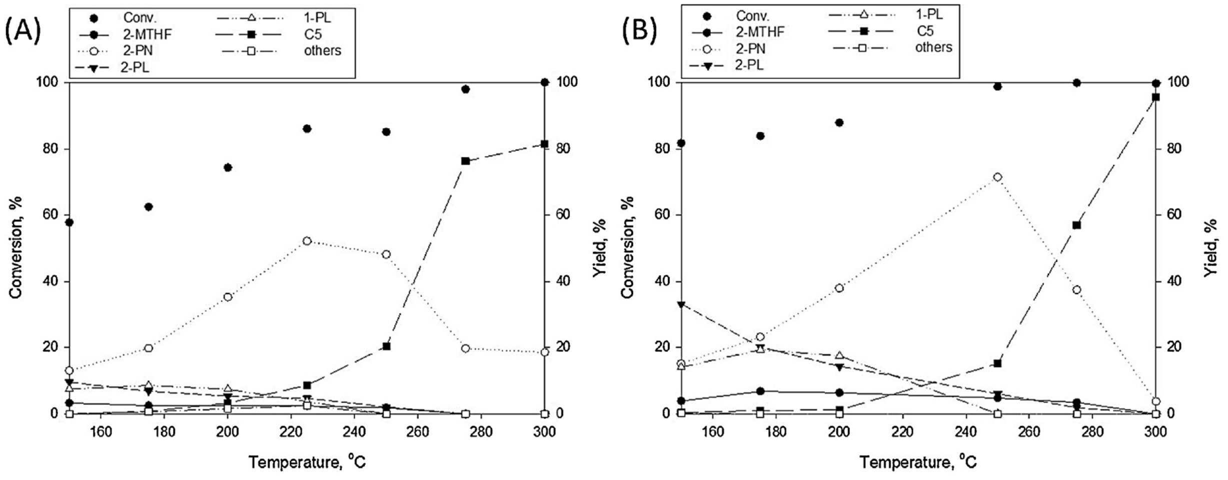

**Fig. 3.** Variation of 2-MF conversion and product yield over Ba/Cu/Cr catalyst at different temperature. (A) $H_2$: 2MF = 10; (B) $H_2$: 2MF = 15.

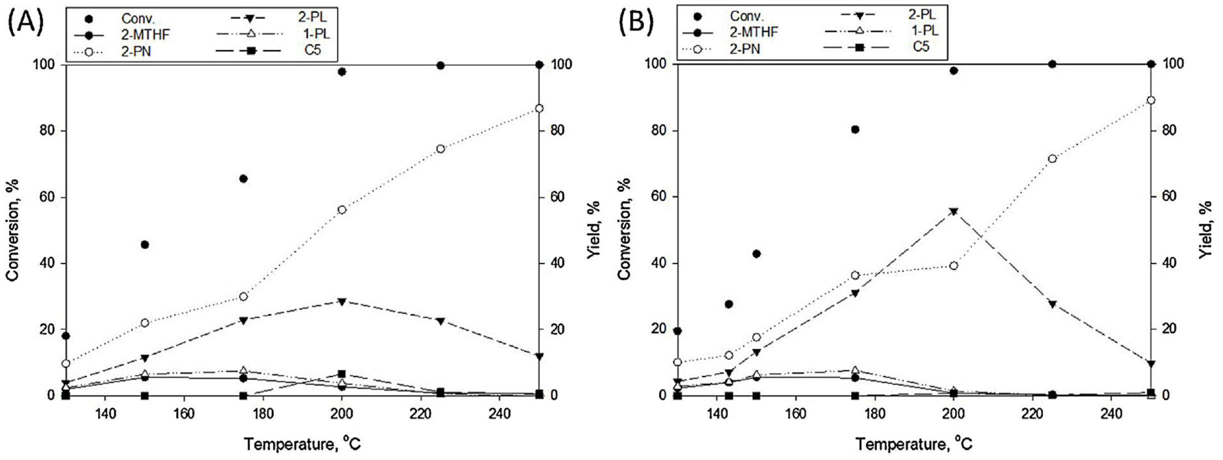

**Fig. 4.** Variation of 2-MF conversion and product yield over Cu/Cr/Ni/Zn/Fe catalyst at different temperature and $H_2$ to 2-MF mole ratio: (A) $H_2$: 2MF = 10; (B) $H_2$: 2MF = 15.

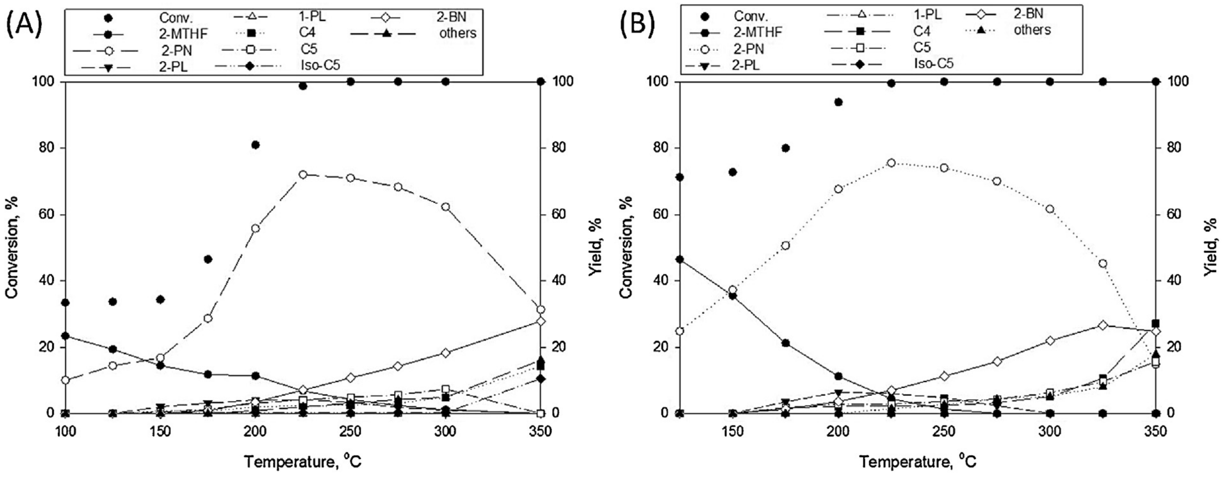

**Fig. 5.** Variation of 2-MF conversion and product yield over Cu-Ru/C catalyst at different temperature and $H_2$ to 2-MF mole ratio: (A) $H_2$: 2MF = 10; (B) $H_2$: 2MF = 20.

that Cr effectively promotes the hydrogenation of conjugated C=C bonds, while higher reactivity toward the C=O bond is the specific property of copper catalysts. Burnette [48] demonstrated that 2-MF can be converted to 2-MTHF, 2-PN and 2-PL over partially activated Raney nickel catalyst by hydrogenation at atmospheric pressure and 200 °C. Wojcik [31] reported that the copper-chromite catalyst had little or no effect on furan ring below 175 °C for furfural hydrogenation. However, the Ba/Cu/Cr catalyst employed in this study facilitated furan ring opening rather than the ring saturation reaction resulting in the high selectivity to 2-PN at atmospheric pressure. The maximum yield of 2-PN (70 mol.%) was observed at 250 °C at the $H_2$/2-MF mole ratio of 20 with 98% of 2-MF conversion.

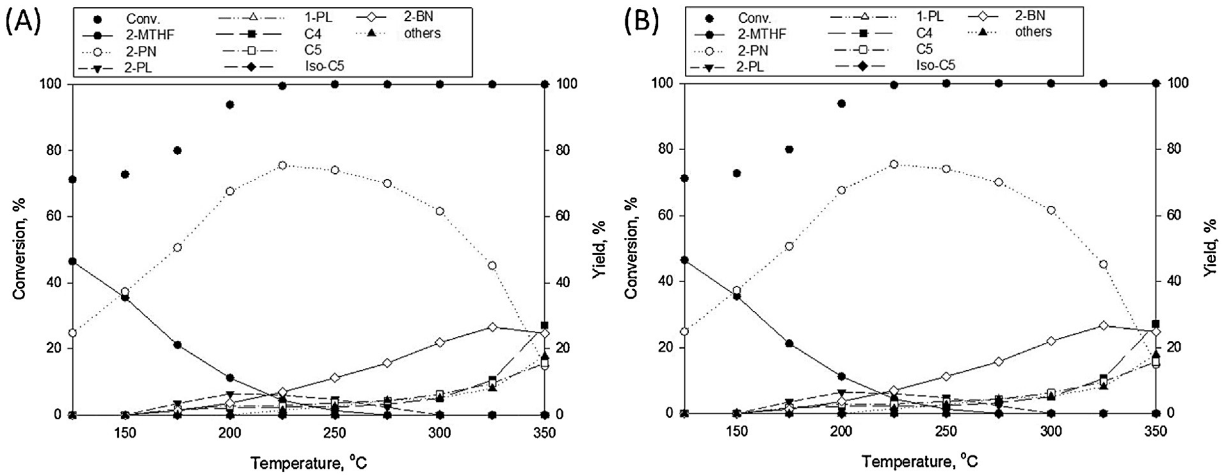

**Fig. 6.** Variation of 2-MF conversion and product yield over Pt/C catalyst at different temperature. (A) $H_2$ : 2MF = 10; (B) $H_2$ : 2MF = 25.

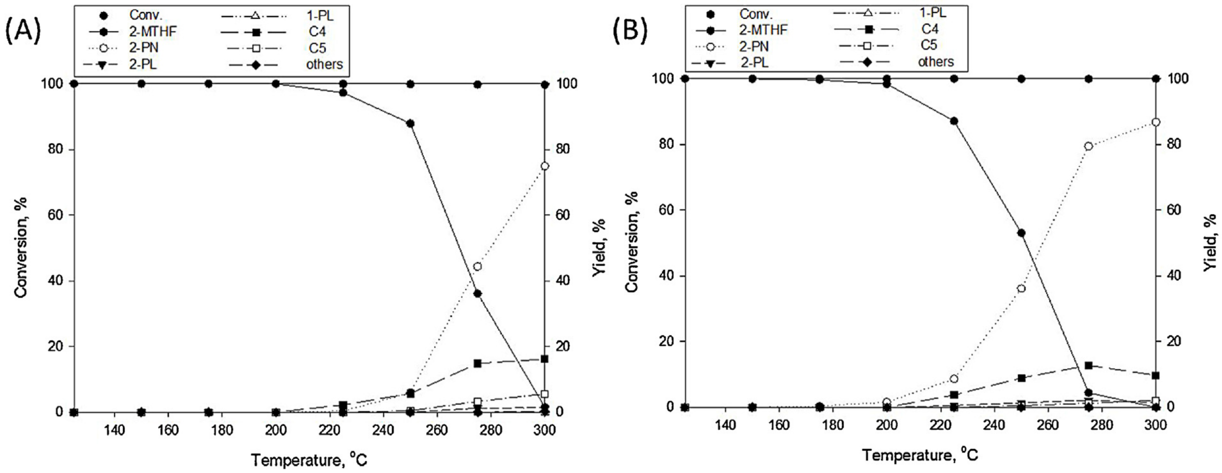

**Fig. 7.** Variation of 2-MF conversion and product yield over Pd/C catalyst at different temperature. (A) $H_2$ : 2MF = 10; (B) $H_2$ : 2MF = 25.

Therefore, excess hydrogen was beneficial for achieving a higher yield of 2-PN over the Ba/Cu/Cr catalyst.

The results of catalytic hydrogenation of 2-MF over the Cu/Cr/Ni/Zn/Fe catalyst at $H_2$/2-MF = 10 and 15 are shown in Fig. 4. At these $H_2$/2-MF mole ratios, the 2-MF conversion was almost 100% above 225 °C, and even 80–98% below 225 °C at a lower $H_2$/2-MF ratio of 10, which may be due to a higher contact time and the absence of inert support, such as carbon, in this catalyst. 2-PN and 2-PL were the primary products observed over the Cu/Cr/Ni/Zn/Fe catalyst, whereas trace amounts of 2-MTHF and 1-PL were also detected. The yield of 2-PN increased while the yield of 2-MTHF and 1-PL decreased with increasing temperature over the range of $H_2$/2-MF mole ratios investigated, whereas the yield of 2-PL passed through a maximum at ~200 °C. The yield of 2-PN varied in the range of 15–90 mol.% at 130–250 °C for both $H_2$/2-MF mole ratios. The maximum yield to 2-PL (56 mol.%) was observed at the $H_2$/2-MF mole ratio of 15 at 200 °C. The variation of the 2-PL yield with temperature indicated that the formation of 2-PL was temperature-dependent. It was previously reported that 2-PL is the product of 2-PN hydrogenation and the conversion of 2-PN to 2-PL is an equilibrium reaction that strongly favors 2-PN at atmospheric pressure over the entire temperature range investigated [36]. According to Zheng et al., 2-PN and 2-PL could be obtained with 57 and 25 mol.% yield at 250 °C. Our results indicated the same two major products; however, 2-PN can be obtained in a much higher yield (85 mol.%). The product distribution over the Cu/Cr/Ni/Zn/Fe catalyst demonstrated that significant quantities of both 2-PN and 2-PL formed simultaneously by furan ring opening below 200 °C. However, 2-PL formation decreased above 200 °C, while the 2-PN yield increased and reached ca. 90 mol.% at 250 °C. Moreover, this behavior did not depend significantly on the $H_2$/2-MF mole ratio. These observations may be due to the selective conversion of 2-MF to 2-PN as well as the conversion of 2-PL formed to 2-PN by the reverse reaction. However, at higher temperatures, the conversion of 2-MF to 2-PN was the dominant reaction and further hydrogenation of 2-PN to 2-PL was not significant. The large excess of hydrogen was not beneficial in terms of catalytic conversion of 2-MF and 2-PN yield over the Cu/Cr/Ni/Zn/Fe catalyst. Some 2-MTHF was also detected besides 2-PN and 2-PL at all $H_2$/2-MF mole ratios and low temperatures (<175 °C). The results obtained over the Cu/Cr/Ni/Zn/Fe catalyst indicated that both the ring saturation and ring opening were favorable at low temperatures (<175 °C), but ring opening became much more favorable at higher temperatures leading to highly selective formation of 2-PN.

In the case of the Cu-Ru/C catalyst, the main product was 2-PN and its yield reached a maximum at 225 °C at both high and low $H_2$/2-MF mole ratios (Fig. 5), while the yield of other products, such as 2-MTHF, 2-PL, 2-BN, and pentane, varied with reaction temperature. The 2-MF conversion was 100% at 250 °C for all $H_2$/2-MF mole ratios studied. The Cu-Ru/C catalyst exhibited similar catalytic performance to that reported by Wilson [44]. The main product over this catalyst was 2-PN and some isomerized hydrocarbons were observed at high temperatures (above 250 °C). For the $H_2$/2-MF mole ratio of 10, the conversion varied from 24 to 100% at 175–250 °C. At low reaction temperature (175 °C), the yield of 2-PN, 2-MTHF and 2-PL was 13, 4 and 3%, respectively. The formation of 1-PL was not observed over this catalyst, while significant amounts of 2-butanone (2-BN) were detected above 250 °C. As the reaction temperature increased, so did the yield of 2-PN, whereas the yields of other products, 2-MTHF and cracking products, i.e., butane, pentane and butanone, also showed temperature dependence. The 2-MTHF yield decreased with increasing reaction temperature, while the yield of the cracking products increased indicating that the hydrogenation of 2-MF over the Cu-Ru/C catalyst produces predominantly 2-MTHF at low temperature. At higher reaction temperatures, 2-MTHF is further cracked to produce shorter-chain hydrocarbons by C—C bond hydrogenolysis. Complete conversion of 2-MF was observed with a 70 mol.% yield of 2-PN at the $H_2$/2-MF mole ratio of 10 and above 250 °C, while other products were obtained in less than 5 mol.% yield, with the exception of 10 mol.% yield of 2-BN. Therefore, 2-MF is converted selectively to 2-PN over the Cu-Ru/C catalyst at ca. 225 °C. To investigate the effect of hydrogen concentration on the catalytic activity and product yield, 2-MF hydrogenation was carried out at a high $H_2$/2-MF mole ratio of 20. The results shown in Fig. 5(B) demonstrated that the catalytic activity was not significantly affected in the presence of a large excess of hydrogen, but the conversion of 2-MF and 2-PN yield were increased. Some cracking products, such as butane, pentane and butanone, were also detected, whereas 2-MTHF and 2-PL were not observed. The formation of the cracked hydrocarbons may occur due to the C—C bond hydrogenolysis of 2-MF in the presence of a large excess of hydrogen [45,46]. Therefore, in comparison to the Ba/Cu/Cr and Cu/Cr/Ni/Zn/Fe catalysts, the Cu-Ru/C catalyst was much more active and selective during 2-MF conversion to 2-PN at 225 °C and low $H_2$/2-MF ratios.

The results of 2-MF hydrogenation over the Pt/C catalyst at the $H_2$/2-MF mole ratios of 10 and 25 and 150–250 °C are shown in Fig. 6. The conversion of 2-MF ranged from 21 to 100% at the $H_2$/2-MF = 10 and the major products were 2-PN, 2-PL, 2-MTHF, and cracking products, such as butane and pentane, indicating that these transformations corresponded to both furan ring saturation as well as ring opening reactions. The selectivity to these hydrogenation products changed somewhat as the temperature increased in the 150–250 °C range. The product selectivity trends indicated that Pt metal is capable of promoting both furan ring saturation and ring opening reactions. 100% conversion of 2-MF was observed at 250 °C at the $H_2$/2-MF = 10, while the product yields were 69 mol.% (2-PN), 12 mol.% (butane and pentane), 10 mol.% (2-PL), 4 mol.% (2-MTHF), and 5 mol.% (1-PL). Our results for the 0.5 wt.% Pt/C catalyst are in excellent agreement with those of Shuikin et al. [49] which also reported 2-PN as the main product. The conversion of 2-MF increased somewhat up to 200 °C at the high $H_2$/2-MF mole ratio of 25 accompanied by a slight increase in the yield of cracked hydrocarbons. These results indicated that the over hydrogenation was enhanced over the Pt/C catalyst in the presence of a large excess of hydrogen, which contributed to the higher yield of cracked hydrocarbons. The hydrogenolysis of 2-MF was favored at high reaction temperatures, and significant quantities of cracked products (up to 20 mol.% yield) were produced at both low and high $H_2$/2-MF mole ratios.

The performance of the 0.5 wt.% Pd/C catalyst in 2-MF hydrogenation is shown in Fig. 7. The Pd/C catalyst was found to behave very differently as compared to other catalysts investigated. This catalyst was very active and selective in the furan ring hydrogenation that led to the complete conversion of 2-MF to 2-MTHF even at low reaction temperatures (<200 °C) and low $H_2$/2MF ratio. However, the yield of 2-MTHF dramatically decreased as the reaction temperature increased above 200 °C, while the formation of 2-PN and cracked hydrocarbons progressively increased at 100% 2-MF conversion. These results showed that the Pd/C catalyst is very active and selective for furan ring hydrogenation in 2-MF to 2-MTHF at low reaction temperatures. Excellent agreement was also observed with the results of a previous study that employed 0.5 wt.% Pd/C and demonstrated 84–97 mol.% yield of 2-MTHF up to 236 °C, whereas 2-PN formed increasingly above 273 °C [50]. Gaset et al. [15] reported that tetrahydrofuran (THF) can be obtained in high yield at low pressure over a charcoal-supported Pd catalyst. Starr and Hixon [16] also found that furan could be converted to THF quantitatively over palladous oxide-palladium black catalyst.

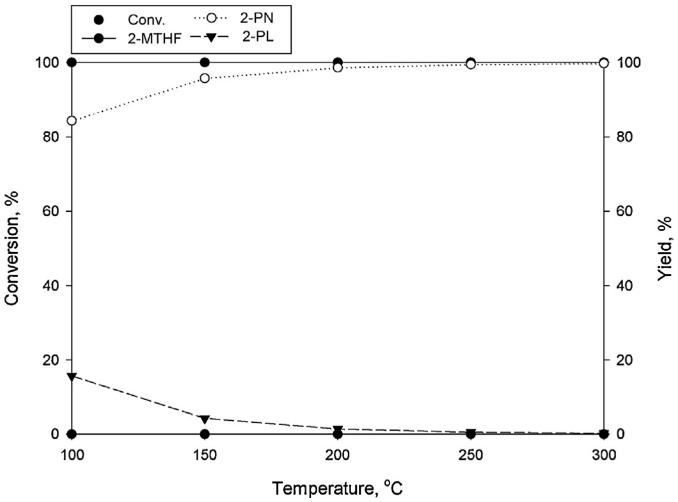

**Fig. 8.** Thermodynamic calculations of chemical equilibrium for 2-MF hydrogenation at $H_2$: 2MF = 10 and 100–350 °C.

It should be noted that the product distribution during 2-MF hydrogenation over the catalysts employed in this study significantly deviated from that expected for the chemical equilibrium. Fig. 8 shows the results of thermodynamic calculations for the chemical equilibrium between 2-MF, 2-MTHF, 2-PN, and 2-PL for the $H_2$/2-MF feed ratio of 10 and 100–350 °C. The pure component properties used in these calculations were taken from the Dortmund Data Bank [51]. The results of these calculations indicated that 2-MF would be completely converted to products at equilibrium under these reaction conditions. However, 2-PN is expected to be the most abundant product, whereas 2-MTHF and 2-PL would be present only in trace quantities. Therefore, high yields of several hydrogenation and hydrogenolysis products observed in this study suggest the promise of these catalysts for catalytic transformation of biomass-derived 2-methylfuran to value-added chemicals and fuels.

## 4. Conclusions

Vapor-phase hydrogenation of 2-MF was carried out over Ba/Cu/Cr, Cu/Cr/Ni/Zn/Fe, Cu-Ru/C, Pt/C and Pd/C catalysts as a function of temperature and $H_2$/2-MF mole ratios. This study showed that the Ba/Cu/Cr, Cu/Cr/Ni/Zn/Fe, Cu-Ru/C, and Pt/C catalysts were active for both furan ring opening and ring saturation reactions. However, 2-PN was the main hydrogenation product over these four catalysts. On the other hand, the Pd/C catalyst was highly active for the selective conversion of 2-MF to 2-MTHF at low temperatures and low $H_2$/2-MF ratio. A complete conversion of 2-MF was observed even at 125 °C with a 98 mol.% yield of 2-MTHF. The Ba/Cu/Cr catalyst was highly active and selective for the conversion of 2-MF into pentane at high reaction temperatures. The catalytic data confirmed that this catalyst facilitated the furan ring opening rather than the ring saturation reaction. A large excess of hydrogen was beneficial for obtaining a higher yield of 2-PN over the Ba/Cu/Cr catalyst. The results obtained over the Cu/Cr/Ni/Zn/Fe catalyst demonstrated that both ring saturation and ring opening took place at low temperatures (<200 °C), while ring opening became more favorable at higher temperatures resulting in a selective formation of 2-PN with a 90 mol.% yield at 250 °C, the yield of 2-PL over this catalyst showed a maximum of 60 mol.% at 200 °C and $H_2$/2-MF mole ratio of 15. The yield of the 2-PN was not significantly influenced by different $H_2$/2-MF ratios, while they affected the 2-PL formation. The use of excess hydrogen was not beneficial to produce 2-PN in the case of the Cu/Cr/Ni/Zn/Fe catalyst. The Cu-Ru/C catalyst showed high activity in both ring opening and ring saturation reactions at low temperature. At high reaction temperatures, C—C and C—O scission products formed increasingly over the Cu-Ru/C catalyst. The product selectivity trends over the Pt/C catalyst showed that the Pt catalyst has the tendency to promote both the furan ring opening and ring saturation reactions. Complete conversion of 2-MF was observed even at 220 °C resulting in a product mixture from both ring saturation and ring opening reactions. Furthermore, the Pt/C catalyst enhanced the over hydrogenation reaction in the presence of excess hydrogen, which contributed to the higher yield of hydrocarbon products.

Therefore, high yields of hydrogenation and hydrogenolysis products observed in this study indicated the promise of these noble and base metal catalysts for catalytic transformation of biomass-derived substituted furans to value-added chemicals and fuels.

## Acknowledgment

The financial support of this research was provided from the National Science Foundation under grant CBET-1236210.

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