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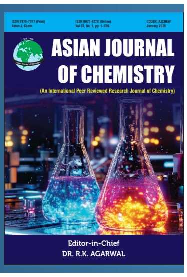

Furfural to 2-Methylfuran *via* Transfer Hydrodeoxygenation using 2-Pentanol over Cu-ZnO Nanowires: Extraction of Furfural and its Conversion to 2-Methylfuran

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The extraction of furfural from an aqueous solution and its conversion to 2-methylfuran through transfer hydrodeoxygenation (THDO) have been successfully carried out using a Cu-ZnO (30:70) catalyst in the vapour phase, utilizing 2-pentanol as extraction solvent and hydrogen. Due to the lower temperature of the reaction, the yield of 2-methylfuran and 2-pentanone was 83% and 90%, respectively. The carbon balance concerning furfural was >90%, which is higher than that of direct hydrodeoxygenation of furfural. The activity of catalyst and the yield of 2-methylfuran are associated with the number of surface active sites (Cu^0/Cu^+), as the high loading of catalyst produced a high yield of 2-methylfuran. The stability of the catalyst was studied for 23 h at 250 ºC and found to have stable activity. Moreover, the Lewis acidity of Zn^{2+} facilitates the process more easily and the final catalyst generated from aurichalcite is responsible for the increased number of copper sites on the catalyst's surface. Moreover, XPS analysis also proved the presence of more surface Cu^0 species and CHNS analysis confirmed the coke resistance of the Cu-ZnO catalyst.

Keywords: Aqueous furfural, 2-Pentanol, 2-Methylfuran, Hydrogen, Cu-ZnO, Biofuel.

INTRODUCTION

Diminishing conventional gasoline and jet fuel resources accompanied by increasing environmental concerns motivates the development of alternative ways to produce chemicals and fuels from abundantly available, renewable carbon-neutral resources. Production of high-value chemicals and biofuels from biomass is an alternative method to replace traditional petroleum-based fuels and chemicals [1]. Furan compounds such as furfural, furan and 5-hydroxymethylfurfural and alcohols are significant platform molecules involved in the process of biomass conversion [2]. Among them, furfural and 2-pentanol have the height research potential due to their high reactivity and versatility [3-5].

Furfural is naturally produced from xylose or xylan, which presents a large quantity of lignocellulose biomass. Typically, hydrolysis followed by dehydration of xylose over acid catalysts produces furfural [6]. In general, furfural extraction from the aqueous solution using alcohol is a promising process as reported [7] whereas furfural to 2-methylfuran (2-MF) reaction is mainly conducted under external hydrogen using supported metal catalysts [8-12]. It is confirmed that the reaction mixture can produce two important molecules such as 2-MF and 2-pentanone, the second one would produce only one product 2-MF, particularly under external hydrogen. Alcohols in the extraction mixture not only act as a solvent but also produce hydrogen. Hence, the extracted solution of furfural in alcohol can be further employed directly to transform furfural to 2-MF and alcohols to ketones *via* catalytic transfer hydrodeoxygenation (CTHDO) where no external hydrogen is required for furfural to 2-MF as alcohol dehydrogenation provide hydrogen and ketones. Subsequently, this reaction mixture can be further implemented in the cross-aldol condensation reaction. Hence, the usage of aliphatic alcohols in the furfural extraction followed by CTHDO should be an advanced method for the production of fuels from furfural and alcohols.

Further, the transformation of furfural to 2-MF using alcohols under nitrogen, as well as copper-based catalysts, has been employed to transform furfural to 2-MF. Due to a heavy carbon loss that can occur (*ca.* 30%) while using pure furfural under external hydrogen that leads to a low yield of desired products [9-12], recently, alternative research has been demonstrated using solvents mainly alcohols in the hydrogenation of furfural that enhanced the yield of 2-MF and maintained high carbon balance in vapour phase [13,14]. The increase in the yield of 2-MF is mostly attributed to the reduction of undesirable processes, including polymerization and decarboxylation. Moreover, the studies revealed that aliphatic alcohols such as isopropanol and 2-pentanol are highly desirable solvents for the hydrogenation of furfural under hydrogen. Interestingly, 2-pentanol is also an efficient solvent to extract furfural from an aqueous solution by directly obtaining furfural in 2-pentanol solution that can be applied as a feedstock for the transfer hydrodeoxygenation (THDO) reaction. Subsequently, a high yield of 2-MF can be achieved under a hydrogen-free environment. Catalytic production of 2-MF from furfural under nitrogen would be a challenging task.

According to the literature, the aurichalcite phase of Cu-ZnO catalysts showed excellent catalytic activity towards furfuryl alcohol in the presence of external hydrogen [15,16]. Chen *et al.* [17] reported a comprehensive review on the influence of catalysts and experimental conditions on the selective hydroconversion of furfural and 5-hydroxymethylfurfural into various chemicals. The study focused on both noble metal catalysts (Pt, Ru, Rh and Ir) and non-noble metal catalysts (Ni, Co, Cu, Mo and Fe), which were also utilized for the conversion of furfural to furfuryl alcohol. Recently, Yang *et al.* [18] primarily concentrated on the production of 2-MF from pure furfural through hydrodeoxygenation using a Cu-ZnO catalyst, yielding around 95% 2-MF at an LHSV of 1.5 h^{-1} under external hydrogen conditions. Most reports on the THDO of furfural predominantly resulted in a high output of furfuryl alcohol [19-22]. However, the present study aimed at THDO of furfural in the presence of 2-pentanol to produce two important products 2-MF and 2-pentanone simultaneously under an N_2 environment. The product mixture could be further processed into biofuels *via* hydroalkylation/alkylation followed by hydrodeoxygenation over a Ni-based catalyst.

The present work demonstrated a process for direct transformation of the extracted furfural from aqueous solution to 2-methylfuran (2-MF) without further purification process, which could be an economically and eco-friendly process. Furfural was extracted from a water solution using 2-pentanol and then conducted THDO using 30 wt.% Cu-ZnO catalyst under nitrogen in a vapour phase. The physico-chemical properties and stability of catalyst was analyzed by XRD, XPS and thermal programmed desorption (TPD) of NH_3.

EXPERIMENTAL

The chemicals, K_2CO_3 (Sigma-Aldrich, AR grade, 99%), $Cu(NO_3)_2{\cdot}3H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ (Loba Chemie, AR grade, 99%), was obtained from a commercial source.

Preparation of catalyst: The Cu-ZnO (30:70) catalyst was prepared by the precipitation-hydroxycarbonate gel method using K_2CO_3 as a precipitating agent. According to the reported procedure [2], for preparation of Cu-ZnO, the mixture of the required amount of metal nitrate solutions *i.e.*, $Cu(NO_3)_2{\cdot}3H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ was precipitated at pH 9 using 10 wt.% K_2CO_3. The hydroxycarbonate gels were thoroughly washed until no K^+ was detected in the filtrates. Subsequently, these gels were mixed in deionized water under constant stirring for 12 h. The resultant gel was filtered, dried in an oven at 393 K for overnight and then calcined in air at 773 K for 5 h.

Catalyst characterization: The XRD patterns of both the calcined and reduced catalysts were recorded on a Miniflex diffractometer (Rigaku Instruments, Japan) using Ni filtered $CuK\alpha$ radiation in the 2θ range of 10-80° at a scan rate of 2° min^{-1}. The average crystallite size of copper was calculated using the Debye-Scherrer's equation. The acidity of the catalysts was determined by thermal programmed desorption (TPD) studies on a home-made system. In a typical procedure, 100 mg of catalyst was subjected to 6% NH_3/He mixture gas at a flow rate of 30 mL min^{-1} with increasing of temperature up to 673 K at a linear ramp of 10 K min^{-1} and kept in isothermal condition for 0.5 h. The XPS was recorded for calcined and reduced catalysts (553 K for 3 h under hydrogen) using a Kratos-Axis 165 instrument with $MgK\alpha$ radiation ($h\nu = 1253.6$ eV) at 75 W. CHNS elemental analysis was carried out on Elementar, Model: VarioMicrocube to estimate the carbon content in the catalyst before and after the reaction.

Extraction of furfural from aqueous solution: The primary step for synthesizing 2-MF is the extraction of furfural from an aqueous solution using 2-pentanol as shown in Fig. 1. The dehydration of xylose in acidic conditions under aqueous medium produces furfural and it is expected to be around 15-20 vol.%, depending on the content of xylose [7]. For extraction of furfural, liquid-liquid extraction is a more desirable process than distillation due to the formation of azeotropes [23]. It is also important to observed that alcohols are highly suitable for extracting furfural from an aqueous solution than other solvents such as toluene, xylene, methylnaphthalene and benzaldehyde [24]. In this work, furfural extraction was carried out from a model solution of aqueous furfural by employing 2-pentanol as a solvent. To evaluate the efficiency of 2-pentanol and the yield of furfural, a model solution of aqueous furfural at 5 vol.% (5.7834 g) was initially generated, owing to its limited solubility in water (maximum 8 vol.%). Further, separately prepared a model solution that contains 10 vol.% of furfural. The extraction process was conducted using 2-pentanol in a stepwise process for the above two solutions. In each step, after the addition of 2-pentanol, the furfural-water-2-pentanol solution showed two layers as a result of aqueous and non-aqueous layers. The estimated yields of furfural in 2-pentanol from 5 and 10 vol.% samples are 84% and 90%, respectively. The required amount of 2-pentanol used for extraction is different for different furfural concentrations indicating that a higher concentration of furfural requires more 2-pentanol to extract furfural from an aqueous solution. In summary, the average yield of furfural in 2-pentanol is ~ 6 vol.%.

$$\text{Yield of FFA (\%)} = \frac{\text{Collected amount of FFA in 2-pentanol}}{\text{Total solution weight (2-petanol + FFA + water)}} \times 100$$

$$\text{Yield of 2-MF (\%)} = \frac{\text{Initial moles FFA} - \text{Final moles FFA}}{\text{Initial moles FFA}} \times 100$$

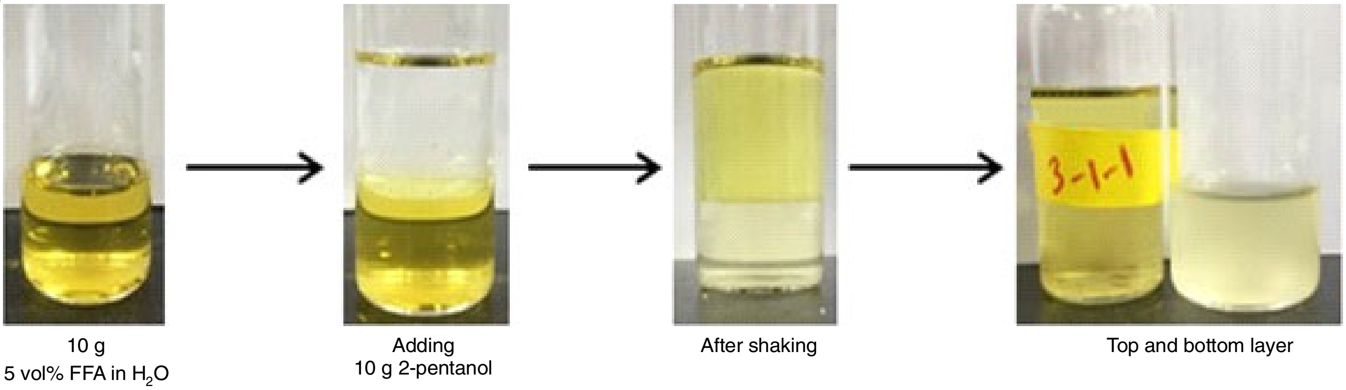


Fig. 1. Extraction of furfural from aqueous solution using 2-pentanol

Transfer hydrodeoxygenation of furfural solution to 2-methylfuran: Based on the extraction results, the amount of furfural in 2-pentanol is expected to be ~6 vol.%. Hence, the feed for tranfer hydrodeoxygenation (THDO) of furfural to 2-MF was fixed at 6 vol.% furfural in 2-propanol. The vapour phase THDO was conducted over Cu-ZnO (30:70) which is proved to be the best catalyst for hydrogenation of furfural to 2-MF under external hydrogen. However, no reports have been studied on the selective synthesis of mixture of 2-MF and 2-pentanone from furfural and and 2-pentanol under nitrogen in vapour phase. Typically, 1 g of catalyst was loaded between two quartz wool plugs in the middle of the reactor with glass beads. Then the reactor was put in a split furnace that controlled by J-type thermocouple. Next, the reactor was purged with N_2 gas for 15 min to get rid of air from the reactor. The catalyst was activated by *in situ* process at 270 ºC for 1 h, 5 ºC per min ramping rate, under pure H_2 gas with flow rate of 80 mL min^{-1}. When the activation process completed, the reactor was cooled down to reaction temperature. Then, the feed was fed in to the reactor using HPLC pump at a flow rate of 0.064 mL min^{-1}. The feed line from HPLC pump to reactor was covered with heating tape to ensure that the furfural solution would not be inside the line that leads to blocking the reactor. This mixture was analyzed using a GC-Shimadzu (gas chromatograph) equipped with an FID detector and an HP-INNOWAX column (50 m, 0.2 mm, 0.4 µm). The quantitative calculation for the acetone conversion and product selectivity was based on the method reported in our previous work. The product sample was collected every hour and quantified using a GC equipped with an FID detector. The products were identified by GC-MS.

RESULTS AND DISCUSSION

XRD studies: The XRD patterns of Cu-ZnO precursor, calcined and reduced form are shown in Fig. 2. As shown in the precursor phase the diffraction appears at 2θ of 13.08º (d = 4 0 0), 24.28º (d = 6 1 0), 27.48º (d = 5 11), 30.98º (d = 42 0) and 34.38º (d = 6 2 0) corresponds to the characteristic peaks of aurichalcite (AC) $(Cu,Zn)_5(CO_3)_2(OH)_6$ (JCPD card no. 17-0743).

This phase formation mostly appears in the ZnO-rich Cu-ZnO catalysts. Therefore, the present Cu-ZnO (30-70) catalyst is consistent with the previous reports [15-18]. In case of calcined and reduced catalysts, the predominate diffraction exhibited at 2θ = 31.88º (d = 1 0 0), 34.48º (d = 0 0 2), 36.38º (d = 1 0 1), 47.58º (d = 10 2), *etc.* could be attributed to ZnO (PDF# 36-1451). Whereas the peaks at 2θ = 35.68º (00 2), 38.78º (111) correspond to reflections of CuO (JCPD card no. 45-0937). The peaks located at 2θ = 43.38º and 50.48º could be ascribed to Cu (111) and Cu (2 0 0), respectively (JCPD card no. 04-0836).

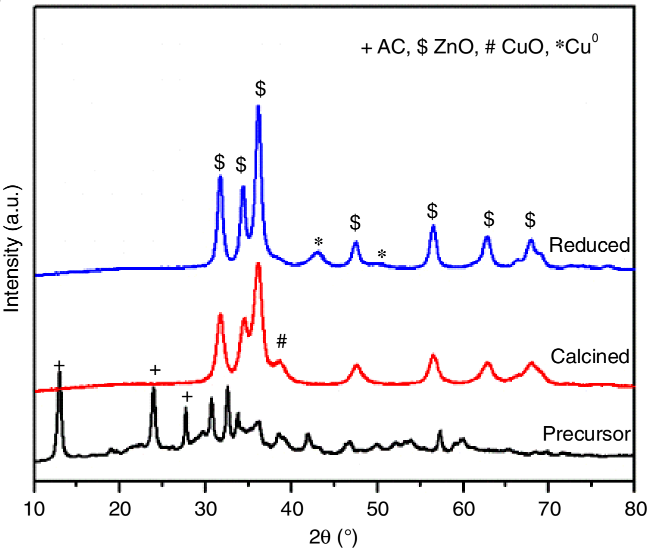


Fig. 2. XRD patterns of Cu:ZnO (30:70 mol.%) catalyst in various form

X-ray photoelectron spectroscopic (XPS) studies: The X-ray photoelectron spectroscopy (XPS) was studied to identify the oxidation states in the catalyst composition. The XPS analysis of the calcined and spent form of Cu-ZnO is shown in Fig. 3. It is well-known that a satellite peak at 940-945 eV in Cu 2p spectra corresponds to the presence of copper oxide, particularly Cu^{2+} ions. These species are more in calcined catalysts since it exhibited a very strong Cu^{2+}. However, the absence of satellite peaks in Cu 2p spectra of the spent catalyst indicates that Cu^{2+} was completely reduced to metallic copper (Cu^0) and/or Cu^{1+}. A weak satellite peak is noticed at 946.2 eV, which is ascribed to the presence of Cu(I) in the spent catalyst. The XPS of ZnO before and after the reaction would not change significantly as shown in Fig. 3b. However, a small quantity of ZnO is believed to exist in its reduced state, suggesting that

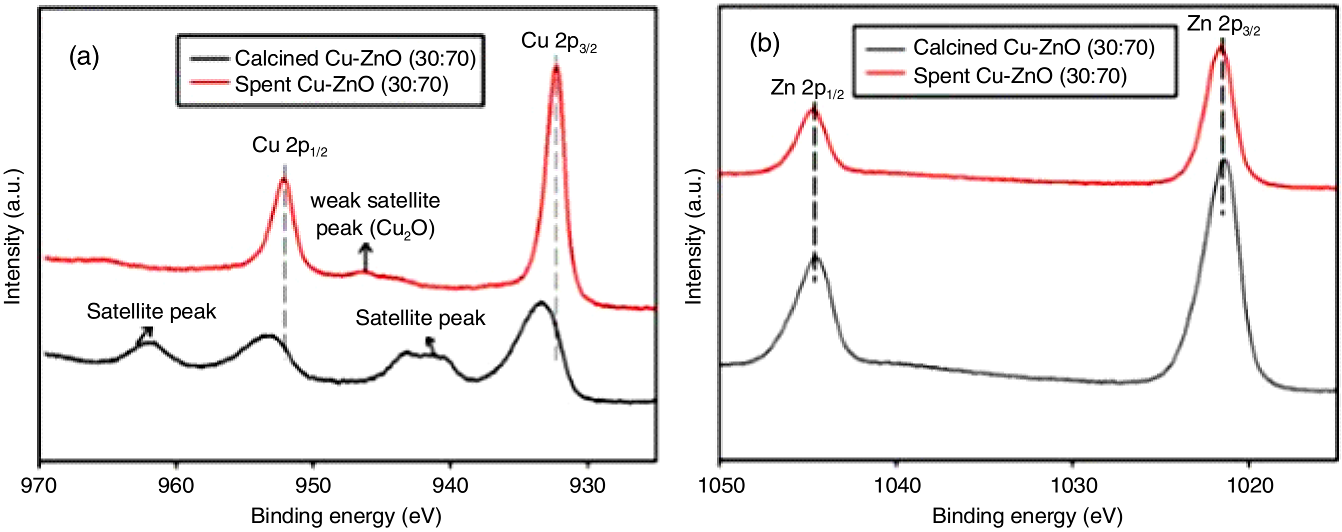


Fig. 3. XPS analysis of calcined and spent form of Cu:ZnO (30:70 mol.%): (a) Cu 2p and (b) Zn 2p

ZnO_x species are likely present on the surface of the used Cu-ZnO (30:70) catalyst [25].

Temperature programmed desorption (TPD) of NH_3: The surface acidity of catalysts plays a critical role in the product distribution in furfural hydrodeoxygenation [18]. Hence, the reduced Cu-ZnO (under pure H_2, 280 ºC for 3 h) catalyst acid sites were measured by TPD of NH_3 and mass signals corresponding to the NH_2^- and H_2O are shown in Fig. 4. The overlapping of the high-intensity peak at 410 ºC corresponds to either NH_4^+ or H_2O; the acidity of catalyst was measured by using only $m/z = 16$ peak and the calculated acidity is 24 µmol/g. It is well known that the xability of catalyst towards the hydrogenolysis for C-O bonds is related to the surface acidity of catalysts. The acidity in Cu-ZnO is associated with Brönsted acidity, since, in the reduced catalyst CuO is completely in metallic form or Cu^+ and has no vacant *d*-orbital ($3d^{10}$) whereas Zn^{2+} ion has ($3d^{10}$) a completely filled *d*-orbital, therefore, the Lewis acidity in the reduced catalyst is excluded. In general, oxide form of copper has shown Lewis acidity [18]. The acidity of spent catalyst was also examined and the results indicated a decreased acidity compared to the reduced catalyst, suggesting carbon deposition on the catalyst surface due to the breakdown of organic moieties during the reaction. This acid decrement might have effected to decrease the yield of 2-MF and increase furfuryl alcohol (FOL).

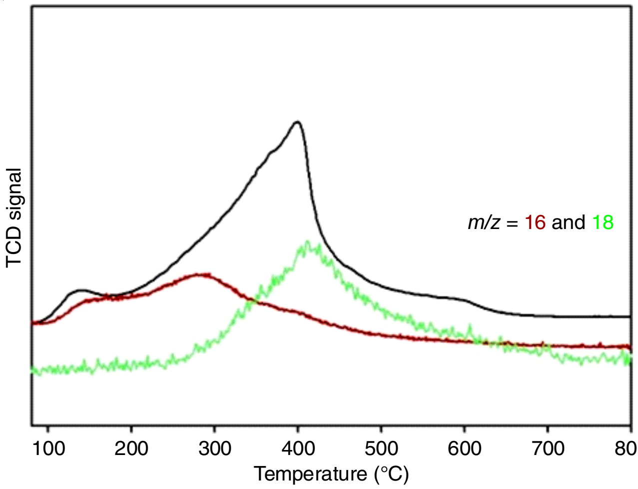


Fig. 4. TPD of NH_3 with m/z = 16 and 18 of Cu: ZnO (30:70 mol.%)

TEM studies: The Cu-ZnO (30:70) catalyst was analyzed by TEM analysis to insight into the morphology and copper distribution on ZnO. The TEM images (Fig. 5) clearly demonstrated that copper is distributed along ZnO look like needle like structure which indicates more separated ZnO whereas copper get more agglomeration in copper rich catalysts.

Optimized parameters

Effect of catalyst loading: Furfural (5 vol.%) in 2-pentanol feed was used as a feedstock to perform THDO over Cu-ZnO (30:70 mol.%) as shown in **Scheme-I**. The selective hydrogenation of furfural using 2-pentanol to 2-MF reveals the efficiency of the process. Initially, the effect of the catalyst amount was evaluated under nitrogen and the obtained results are shown in Fig. 6. Fig. 6a illustrates that with 0.5 g of catalyst, the furfural conversion is exceptionally high (98%) in the initial hours; however, the activity progressively diminished over time, ultimately reaching 84%. Similarly, 2-pentanol conversion is high at the beginning of the reaction, but then linearly decreases from 98% to 55% in the final hours of the reaction.

The yields of 2-MF and furfuryl alcohol follow an inverse trend over time, meaning that in the early hours, the yields of 2-MF and furfuryl alcohol are 79% and 5%, respectively, whereas, in the final hours, they reached 40% and 35%, respectively. In case of 1 g catalyst, the activity is highly stable for both furfural and 2-pentanol, with conversions of 94% and 80%, respectively, as shown in Fig. 6b. Remarkably, the maximum yields of 2-MF and furfuryl alcohol are 83% and 3%, respectively. The findings prompt an investigation into the impact of catalyst quantity on the reaction when it surpasses 1 g. Hence, the performance of 1.5 g of Cu-ZnO catalyst was evaluated and it was observed to achieve nearly 99% conversion of furfural and 2-pentanol, as shown in Fig. 6c. However, the 2-MF yield is not as high as with 1 g catalyst, probably due to the strong

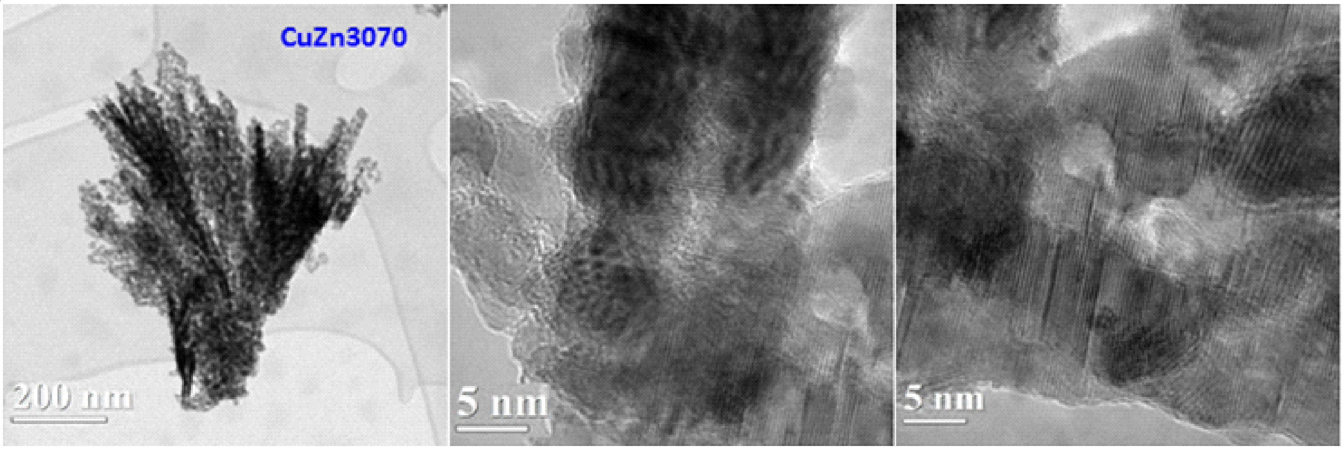


Fig. 5. TEM images of Cu-ZnO (30:70 mol.%) catalyst

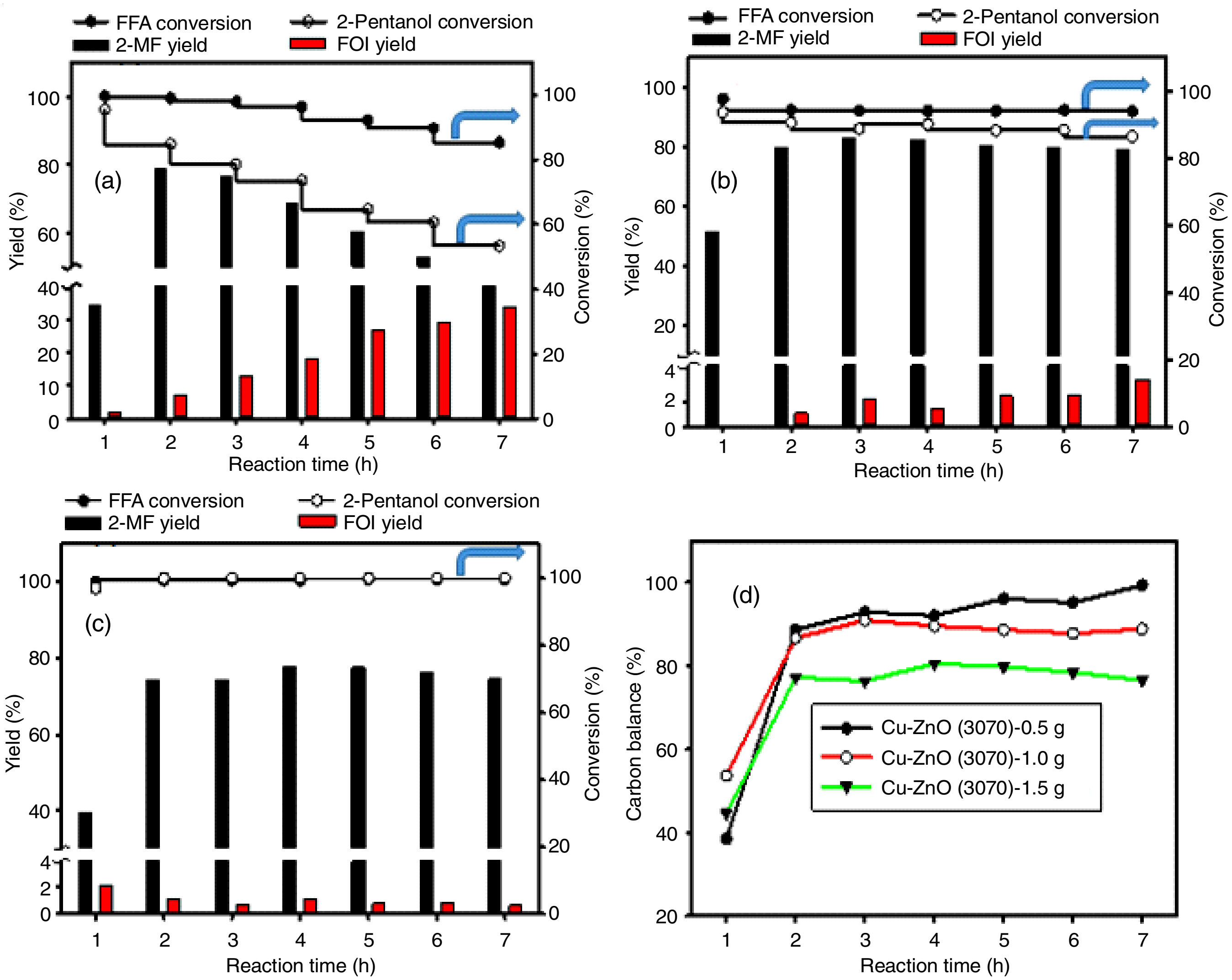
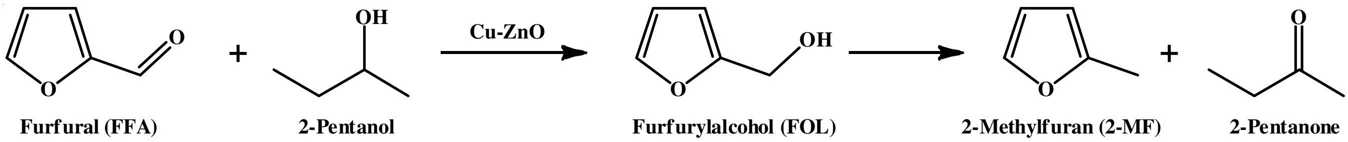
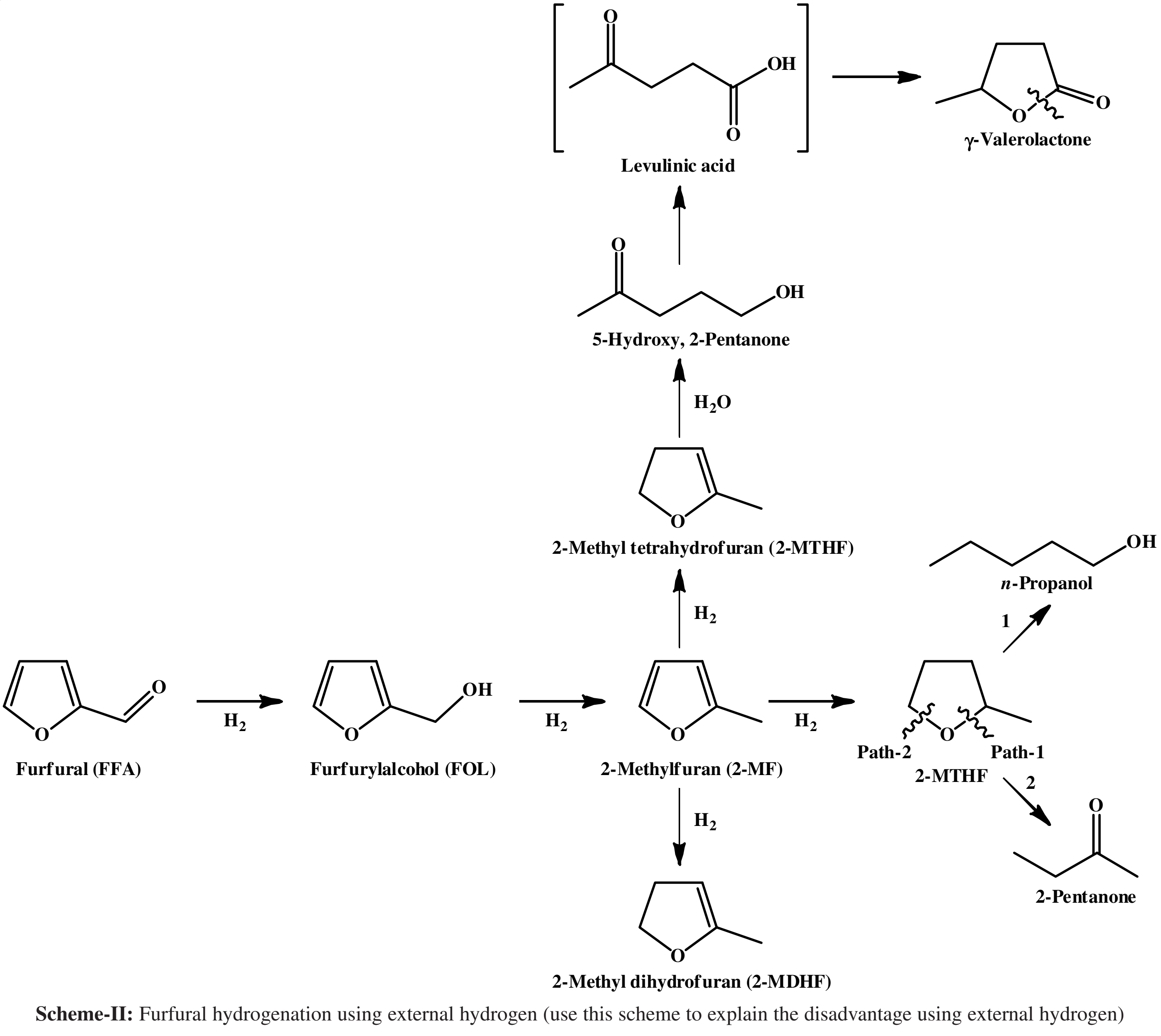


Fig. 6. Effect of catalyst loading in CTHDO of FFA to 2-MF using 2-pentanol over Cu-ZnO; (a) 0.5 g, (b) 1.0 g, (c) 1.5 g and (d) carbon balance



Scheme-I: Furfural hydrogenation using 2-pentanol (selective hydrogenation/hydrodeoxygenation) adsorption of reactant/product molecules on the surface of the catalyst. Moreover, the yield of furfuryl alcohol is the lowest under these catalytic conditions. Moreover, the carbon balance decreases linearly, as shown in Fig. 6d, from lower catalyst loading to higher catalyst loading, *i.e.* from 95% to 75%. This is consistent with the decrease in 2-MF yield despite the high conversion of furfural observed with the 1.5 g catalyst loading. Hence, THDO of furfural to 2-MF with the highest yield would be achieved with 1 g of catalyst. The hydrogenation of furfural in the presence of hydrogen exhibits a lack of selectivity, as illustrated in **Scheme-II**.

Effect of temperature: The role of temperature on THDO of furfural to 2-MF under 2-pentanol was studied in the temperature range of 200 to 250 ºC with 1 g Cu-ZnO as an optimum catalyst amount confirmed from the loading effect. Fig. 7 revealed a linear relationship between temperature and 2-MF yield. The conversion of both furfural and 2-pentanol were estimated as 97% and 58%, respectively, whereas, the yield of both 2-MF and furfuryl alcohol were 62 and 20%, respectively. When the reaction temperature increases from 200 to 225 ºC, no perceptible changes could be observed both in furfural conversion and 2-pentanol conversion but a significant change was observed in the yield of 2-MF that increased from 62% to 72% and furfuryl alcohol yield decreases from 20 to 10%. This result reflects the influence of temperature on hydrodeoxygenation of furfuryl alcohol to 2-MF particularly at higher temperatures. Moreover, dehydrogenation of 2-pentanol is an endothermic reaction hence during the reaction the actual catalyst bed temperature decreases to a lower temperature from the original reaction temperature mostly reaction at 200 ºC and 225 ºC. Therefore, the reaction at lower temperatures is favourable towards a higher yield of furfuryl alcohol. However, the reaction at 250 ºC maintained a stable temperature that tremendously enhanced both furfural and 2-pentanol conversions and led to the maximum 2-MF yield of 83%. These results demonstrated that high reaction temperature leads to cleavage of C-OH bond of furfuryl alcohol easily which is attributed to the high yield of 2-MF. Certainly, the maximum yield of 2-MF (~83%) is achie-



Scheme-II: Furfural hydrogenation using external hydrogen (use this scheme to explain the disadvantage using external hydrogen)

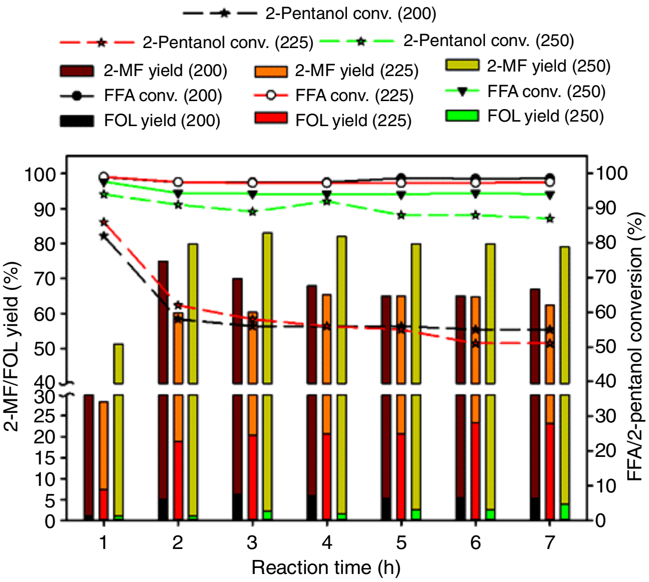


Fig. 7. Effect of temperature on THDO of FFA to 2-MF and carbon balance over 1 g Cu-ZnO; (a) 200 ºC (b) 225 ºC (c) 250 ºC and (d) carbon balance

ved at 250 ºC in the TOS study whereas simultaneously yielded 2-pentanone nearly 90%.

This product mixture is further evaluated for aldol condensation reaction as described as follows: The carbon balance follows an increasing order from 200 ºC to 250 ºC and the results are shown in Fig. 6d. In summary, CTHDO of furfural to 2-MF has a series of advantages relative to stand-alone hydrogenation and dehydrogenation reactions including: (i) one-pot simultaneous production of two valuable chemicals required for further aldol condensation, (ii) good thermal efficiency (*i.e.* heat transfer from exothermic hydrogenation to endothermic dehydrogenation), (iii) enhanced yields when compared pure hydrogenation of furfural and (iv) no consumption of external hydrogen.

Stability of Cu-ZnO catalyst: To study the stability of catalysts, the THDO reaction was carried out for 23 h over Cu-ZnO (30:70). A stable activity was observed for nearly 20 h with the maximum conversion of 99 and 80 % for furfural and 2-pentanol, respectively (Fig. 8). A maximum of 83% 2-MF yield with 90 % carbon balance is observed while >70% yield of 2-pentanone is achieved. However, a decrement in the activity after 20 h is attributed to the partial oxidation of Cu(0) or Cu(I) to Cu(II). In summary, the strong-metal support interactions and high surface copper active sites along with Cu(I) species are associated with the stability in hydrodeoxygenation and dehydrogenation of catalysts. Moreover, the acidity of the catalyst plays a vital role in the THDO.

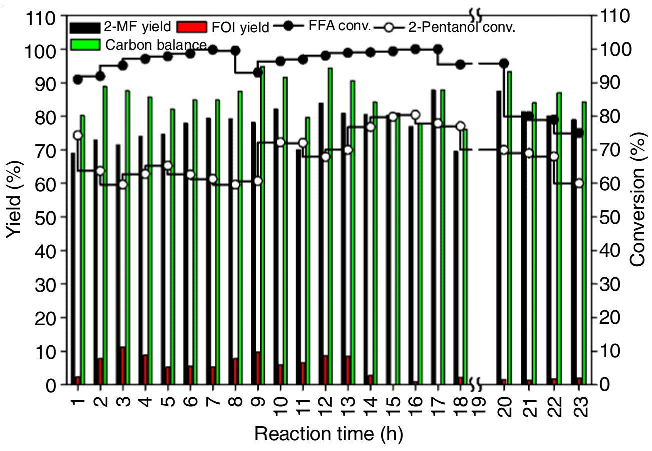


Fig. 8. TOS study of CTHDO of FFA to 2-MF and 2-pentanone to 2-pentanol over Cu:ZnO (30:70 mol.%) for 23 h

Conclusion

Furfural extraction using 2-pentanol from aqueous solution does not need to be purified to furfural to convert to 2-methylfuran (2-MF). The conversion of the solvent-involved process to 2-MF through transfer hydrodeoxygenation (THDO) has been effectively shown using a Cu-ZnO (30:70) catalyst. Both hydrodeoxygenation of furfural and dehydrogenation of 2-pentanol could be carried out simultaneously over Cu-ZnO without loss of activity for 20 h. The product mixture further can be used as a feed for a hydroxy-alkylation reaction where diesel-range chemicals (C_{10}-C_{16} hydrocarbons) can be synthesized, which is an alternative to the conventional petroleum-based fuels. The high stability of catalyst depends on the catalyst structure, aurichalcite phase, surface active species (Cu^0 or Cu^+) and the acid strength of the catalyst. In conclusion, furfural extraction using 2-pentanol followed by THDO without further purification has a great potential to produce two industrially important key chemicals in a single catalytic bed at atmospheric pressure.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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