Single-step catalytic conversion of furfural to 2-pentanol over bimetallic Co-Cu catalysts

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Abstract

The conversion of biomass derived furfural to 2-pentanol, a useful organic solvent and precursor for various types of fuels, was demonstrated with ~71.1% yield in a single step over a Co-Cu/Al$_2$O$_3$ catalyst at 240 °C and 45 bar H$_2$ pressure. The catalyst demonstrated sustained activity and selectivity for four subsequent recycles without regeneration. Co was proposed as the primary active site that enabled hydrodeoxygenation of furfural to produce methyl furan followed by ring opening, while Cu mitigated product degradation that occurred on pure Cu catalysts.

Keywords: furfural, hydrodeoxygenation, fuel precursors, bimetallic catalysts, metal-metal interactions.

Introduction

The transformation of lignocellulosic biomass to renewable chemicals and fuels has potential to reduce reliance on fossil resources, and mitigate environmental concerns.[1-3] Extensive research has been reported on chemical approaches for converting biomass to C6 and C5 sugars and further to renewable platform chemicals, 5-hydroxymethylfurfural (HMF) and furfural (FF).[4-7] In particular, FF can only be commercially synthesized from biogenic sugars, thus its catalytic conversion to furanics and alcohols has gained significant interest.[8-10] Several reports have shown catalytic conversion of FF to furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFOL), methylfuran (MF), methyltetrahydrofuran (MTHF), and pentanediols over solid catalysts.[11-19] These renewable chemicals could potentially replace petroleum derived chemicals in various sectors such as polymers industries, drug synthesis, and transportation fuels.[1]

Long chain alcohols, particularly pentanol isomers, have gained interest for use as gasoline additives because of their high energy density and low hygroscopicity compared to ethanol. In particular, 2-pentanol (2-POL) has been highlighted as a useful organic solvent, a feedstock for P-series fuels, and diesel range alkanes.[20-22] There are reports of biomass-derived C4 and C5 alcohol production using aminoacids via biosynthetic pathways.[21, 23] However, we are not aware of previous reports for selective one-pot chemical catalytic conversions of FF to 2-POL, likely due to the difficulty of obtaining high selectivity in the required sequential bond activation steps. This process requires the selective hydrogenolysis of FF to MF, followed by ring opening rather than ring hydrogenation, as the formation of MTHF or THFOL via ring hydrogenation makes ring opening kinetically challenging, see Scheme 1. A primary difficulty in this conversion is that most catalysts that are effective for hydrogenolysis and ring opening will also drive subsequent ring hydrogenation.

Here we demonstrate that Cu-Co/Al$_2$O$_3$ bimetallic catalysts operating at 240 °C and 45 bar H$_2$ pressure can selectively convert FF to 2-POL with ~72% yield and show stable performance through multiple recycles. By comparison to monometallic Cu, Ni, and Co catalysts and to bimetallic Cu-Ni and Ni-Co catalysts, it is proposed that Co plays the primary role of controlling the selective pathway of HDO followed by ring opening to form 2-POL and that Cu primarily acts as to mitigate product degradation. These results, in combination with our previous analysis of Cu-Ni bimetallic catalysts for MF formation,[7, 11, 19] suggest that Cu based bimetallic catalysts are a useful platform for the development of tunable and stable catalysts for selective conversion of oxygenated multifunctional hydrocarbons.
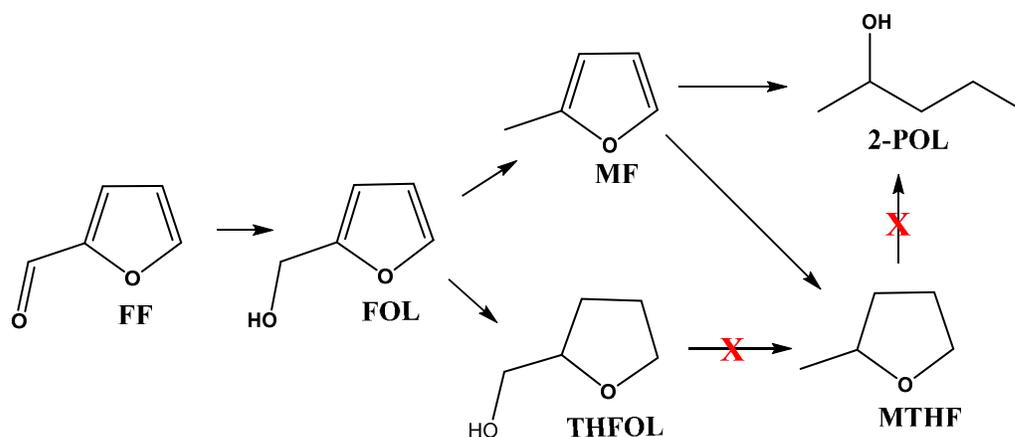
**Scheme 1**. Single-step catalytic conversion of FF to 2-POL.

Results and Discussion

Al$_2$O$_3$ supported monometallic (5 wt.%) Cu, Ni, and Co and bimetallic (5-5 wt.%) Cu-Ni, Co-Cu, and Co-Ni catalysts were synthesized by impregnation, as reported previously.[11] The resulting X-ray Diffraction (XRD) spectra of the monometallic catalysts shown in Figure 1(a) provide clear evidence of metallic Cu formation due to a peak associated with Cu(111) at 43.3° in the Cu/Al$_2$O$_3$ catalyst, but only weak diffraction peaks from the metals were seen for Ni/Al$_2$O$_3$

and Co/Al$_2$O$_3$ due to overlapping diffraction peaks with the support.[11, 24, 25] For the bimetallic Cu-Co and Cu-Ni catalysts, diffraction peaks were observed at 43.9° and 44°, respectively, which fall between the expected diffraction peaks of the pure metals, see Figure 1(b). Furthermore, the Cu(111) diffraction peak at 43.3° was weakened significantly for both bimetallic catalysts. This provided evidence that bimetallic domains were formed for the Cu-Co and Cu-Ni catalysts. However, it was more difficult to distinguish Co-Ni bimetallic diffraction peaks, which also fall in the region of 44.2 to 44.5 and overlapped with support Al$_2$O$_3$ diffraction peaks.[26]

To substantiate the formation of the bimetallic species and metal-metal interaction, H$_2$-TPR experiments were performed (Figure 1(c&d)). TPR spectra of the monometallic catalysts show peaks that are consistent with previous reports and have been assigned in literature.[11, 27-29] Compared to TPR spectra of the monometallic catalysts, the reduction peak temperatures were all shifted to lower temperature for the bimetallic catalysts. The peak shift was most prominent for Cu-Co/Al$_2$O$_3$, where a single broad H$_2$-consumption peak was observed at 188 °C. This is evidence that Cu promoted the reducibility of CoO$_x$ in both reduction steps (Co$_3$O$_4$ to CoO and then CoO to Co) by forming bimetallic or alloy particles.[25, 30] For Cu-Ni/Al$_2$O$_3$, three distinctive reduction peaks were observed. The low temperature peak is assigned to CuO reduction, similar to monometallic Cu, and the peak at 381 °C corresponds to a reduction of NiO$_x$, which was promoted by interaction with Cu. In addition, the intermediate temperature reduction peaks at ~250 °C were attributed to bimetallic Cu-Ni domains. In the case of Co-Ni/Al$_2$O$_3$, the low temperature reduction peak at 247 °C was assigned to reduction of Co-Ni bimetallic particles, while reduction peaks at 349 °C and 460 °C were attributed to weakly interacting phases of Ni and Co, respectively. The XRD and H$_2$ TPR spectra for the bimetallic catalysts show clear

evidence of bimetallic particle formation, rather than co-existence of monometallic particles on the support.
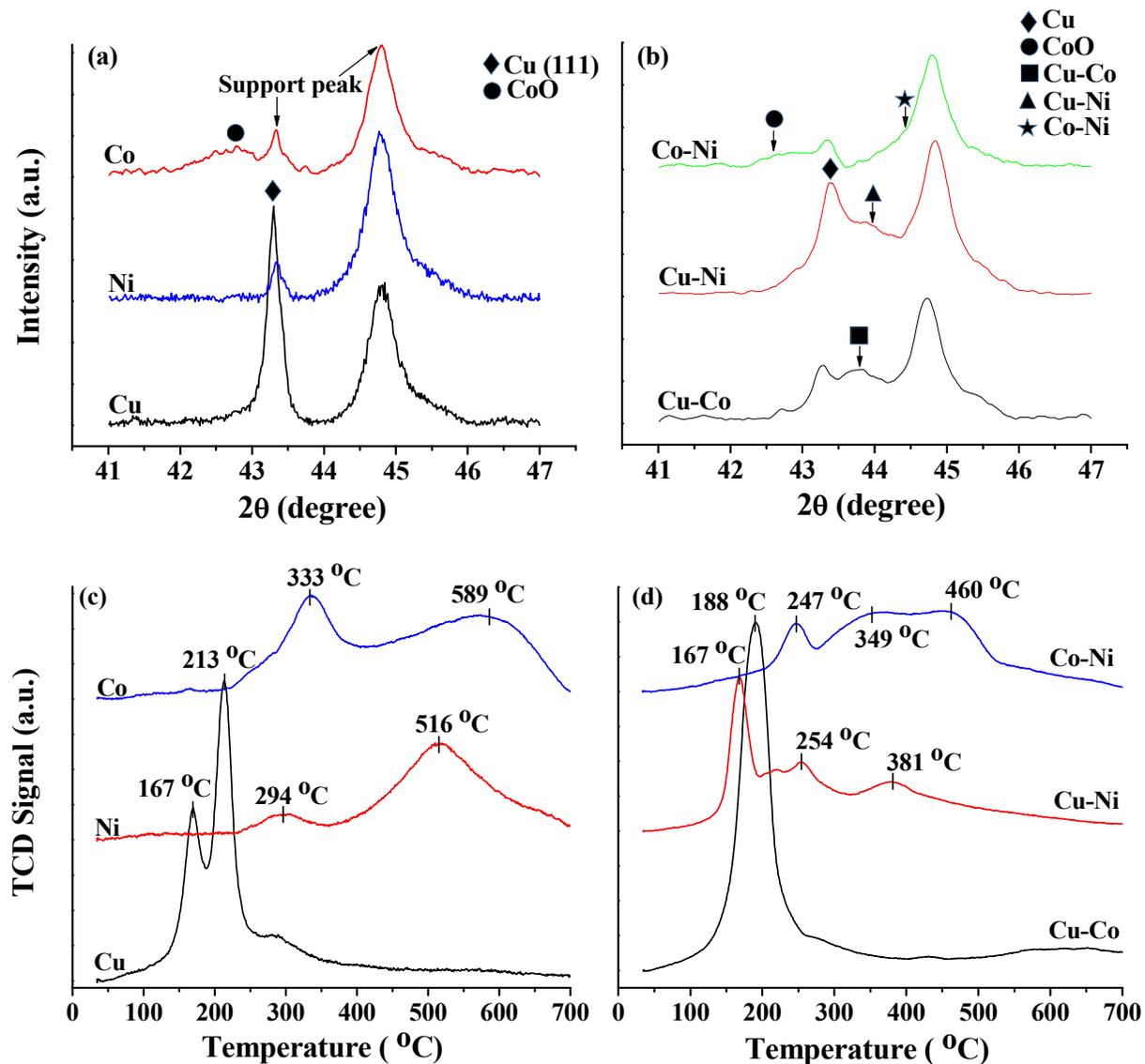
Figure 1. XRD spectra of reduced (a) monometallic Cu, Ni, and Co on Al_2O_3 catalysts and (b) bimetallic Cu-Ni, Co-Cu, and Co-Ni on Al_2O_3 catalysts. H_2-TPR spectra of (c) monometallic Cu, Ni, and Co on Al_2O_3 catalysts and (d) bimetallic Cu-Co, Cu-Ni, and Co-Ni on Al_2O_3 support catalysts. H_2 consumption values increased in the order of Cu/Al_2O_3, (0.674 mmol/g) < Ni/Al_2O_3, (0.809 mmol/g) < Co/Al_2O_3, (1.149 mmol/g) < $Cu-Ni/Al_2O_3$, (1.558 mmol/g) < Co-Cu/Al_2O_3, (1.857 mmol/g) < $Co-Ni/Al_2O_3$, (2.023 mmol/g), consistent with the weight loadings and oxide stoichiometry.

With the aim of driving 2-POL production from FF, which requires multiple bond activation steps, reactions were performed at 240 °C, which is higher than our previous studies and most in literature.[17] Figure 2 shows FF conversion and product yield as a function of time (0.5, 2, and 12 hours) over monometallic Cu, Ni, and Co/Al_2O_3 catalysts at 240 °C. 90% of FF was converted within 0.5 hours on Cu(5%)/Al_2O_3 with FF HDO to produce FOL and MF as the primary products, Figure 2(a). Increasing reaction time to 12 hours increased the MF yields to 92.5%. These results were consistent with our previous reports (Table S1) and the known repulsive interaction of Cu with the FF furan ring, which resulted in the carbonyl group HDO being the selective pathway. [11, 19] However, when the reaction was performed at 200 °C on Cu/Al_2O_3 with a reaction time of 8 hours, 18% yield of FOL and 75% yield of MF was observed demonstrating that increasing the reaction temperature to 240 °C simply acted to drive FOL conversion to MF with higher rates (Table S1).

Monometallic Ni and Co/Al_2O_3 exhibited higher FF conversions than Cu/Al_2O_3 (Figure 2(b and c)), with complete FF conversion within 0.5 hours. MTHF was the primary product on Ni/Al_2O_3 at 0.5 and 2 hours reaction times with a maximum 63% yield of MTHF observed at 2 hours and a small amount (~10% yield) of THFOL and 2-POL. Interestingly, we previously showed that THFOL was the major product on Ni/Al_2O_3 at 200 °C, suggesting that the reaction temperature modified the preferred reaction pathway (Table S1). It is proposed that the higher reaction temperature and H_2 pressure used here modified the primary adsorption geometry of FF to a more upright geometry which facilitated C-O hydrogenalysis followed by MF ring hydrogenation, rather than ring hydrogenation after FOL formation. It is worth noting that to the best our knowledge this is highest MTHF yield from FF reported for a non-noble metal catalyst, which is of interest due to the similar solvent properties of MTHF compared to THF and

toluene.[31-34, 35] However, prolonging the reaction time to 12 hours showed detrimental influence on yields of MTHF and total quantified products (68.9%). We expect that remaining unknown products were caused by decarbonylation followed by C-C bond cleavage.
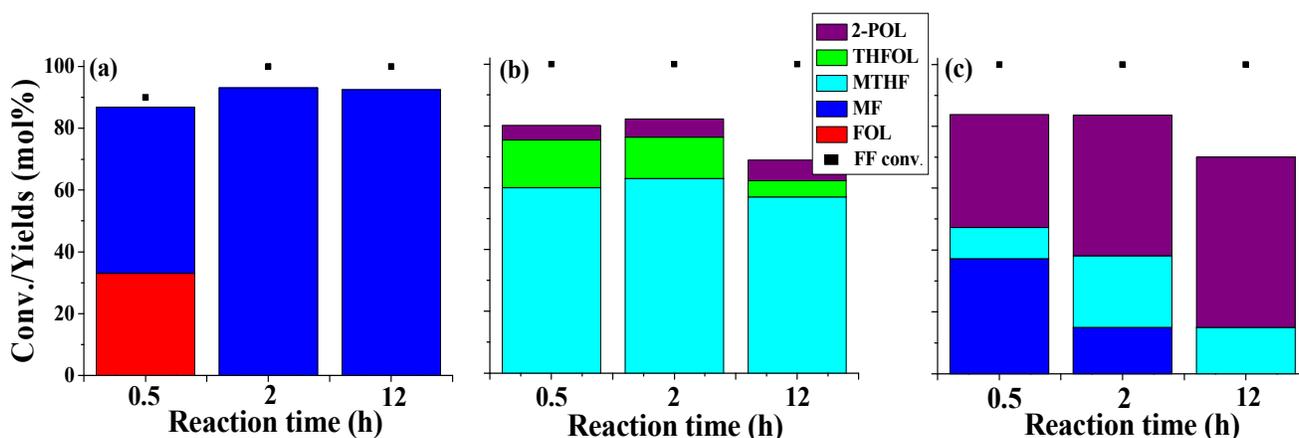
Figure 2. FF conversion and product yields on monometallic (a) Cu, (b) Ni, and (c) Co on Al_2O_3 catalysts. All reactions were run with a FF loading of 1 g and catalyst loading of 0.3 g in 25 mL of 1,4-dioxane as a solvent at temperature of 240 °C for 0.5-12 hours and an H_2 pressure of 35 bar.

Co/Al_2O_3 showed similar activity as Ni/Al_2O_3, but significantly different product distribution. An equal amount of MF (37.2%) and 2-POL (36.5%) was observed at 0.5 hours reaction time, in addition to 10.1% yields of MTHF. Increasing the reaction time promoted 2-POL formation at the expense of MF, with a maximum 55.3% yield of 2-POL observed at 12 hours. When Co/Al_2O_3 was used as a catalyst at 200 °C reaction temperature and 2 hours reaction time, 50% yield of MF, 5% yield of MTHF and 26% yield of 2-POL were observed, suggesting that increased reaction temperature influenced the sequential conversion of MF to 2-POL and promoted the production of MTHF. As compared to Ni/Al_2O_3, the enhancement in 2-POL yields from FF over Co/Al_2O_3 is hypothesized to be caused by preferential interaction of

the C_1-O bond instead of olefinic groups on Co surface sites, which facilitated MF ring-opening

reaction rather than MF ring hydrogenation as seen on Ni. This was in good agreement with the

theoretically calculated adsorption energies for atomic oxygen on transition metals where oxygen

adsorbs by ~0.5 eV stronger on Co than Ni, while C binds similarly on the two metals.[36, 37] Thus,

the more oxophilic nature of Co as compared to Ni enabled the MF ring opening pathway, rather

than ring hydrogenation pathway.

Further, we hypothesized that the reaction from MF to 2-POL occurred through the

unsaturated C5 alcohol followed by the formation of the saturated C5 alcohol, 2-POL, as a final

product, although it was difficult to detect the unsaturated C5 alcohols because the rate of

hydrogenation was much faster than the MF ring opening reaction over Co catalysts. Prolonging

the reaction to 12 hours for Co/Al$_2$O$_3$ further facilitated C-C and C-O cleavages, similar to Ni,

thereby reducing the quantifiable product yields to 65 %. Reactions at 200 °C and 220 °C for 2

hours on Co/Al$_2$O$_3$ catalysts resulted lower yields of 2-POL, and further diverted the reaction to

pentanediols as side products (Figure S2).

Figure 3 shows FF conversion as a function of time over bimetallic Cu(5%)-Ni(5%),

Co(5%)-Cu(5%), and Co(5%)-Ni(5%)/Al$_2$O$_3$ at 240 °C, 35 bar H$_2$ pressure. Figure 3(a)

demonstrates that Cu-Ni/Al$_2$O$_3$ showed enhanced activities compared to Cu/Al$_2$O$_3$, Figure S2, as

we showed previously.[11, 19] The product distribution at 0.5 hours resembled a mixture of the

monometallic Cu and Ni/Al$_2$O$_3$ catalysts, although the lack of FOL production likely suggested

that Ni promoted H$_2$ dissociation and spillover of atomic H onto Cu resulted in higher rates of

FOL conversion to MF. This suggested that the bimetallic particle surfaces consisted of a

mixture of both Cu and Ni domains. Continuing the reaction to longer times resulted in increased

MTHF yields, which in comparison to our previous reports, showed that higher reaction

temperatures facilitated FF HDO to MF instead of FF ring hydrogenation to THFOL (Figure 3), as was seen for Ni/Al$_2$O$_3$ (Figure 2(b)).
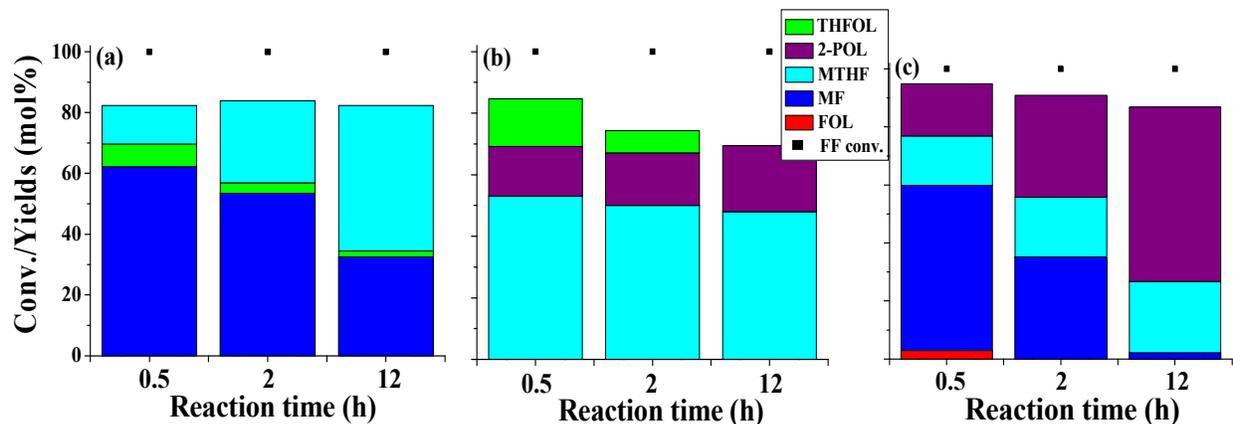
Figure 3. FF conversion and product yields on Al$_2$O$_3$ supported bimetallic (a) Cu-Ni, (b) Co-Ni , (c) and Cu-Co catalysts. All reactions were run with an FF loading of 1 g, a catalyst loading of 0.3 g, 25 mL of 1,4-dioxane as a solvent, a temperature of 240 °C, and an H$_2$ pressure of 35 bar.

The reactivity of Co-Ni/Al$_2$O$_3$ shown in Figure 3(b) resembled Ni/Al$_2$O$_3$ in Figure 2(b), where MTHF was produced at 53.1% yield at 0.5 hour reaction time and the remaining products were 15.5% THFOL and 16.1% 2-POL. In comparison to monometallic Ni/Al$_2$O$_3$, 2-POL formation was slightly enhanced for Co-Ni/Al$_2$O$_3$. However, the product distribution remained similar after 12 hours, with MTHF as the major product, although we also observed that THFOL had degraded into several unknown byproducts. The resulting conversion of FF on Co-Ni/Al$_2$O$_3$ at 12 hours resembled a mixture of products similarly from Ni/Al$_2$O$_3$ and Co/Al$_2$O$_3$, with no promotion of either MTHF or 2-POL yield.

Comparing the reactivity of Co-Cu/Al$_2$O$_3$ (Figure 3(c)) to Co/Al$_2$O$_3$ (Figure 2(c)), 2-POL formed at a slower rate over Co-Cu/Al$_2$O$_3$, but with increased yields at longer reaction times. Furthermore, at short reaction times, it was seen that the addition of Cu to Co/Al$_2$O$_3$ reduced the formation of side products (the non-quantified products). At 12 hours reaction time, 59.6% yield

of 2-POL was observed (compared to 55% for Co/Al$_2$O$_3$) with only a 14% yield of non-quantified products (compared to 35% for Co/Al$_2$O$_3$). Thus, it was concluded that the addition of Cu to Co/Al$_2$O$_3$ minimized product degradation to unwanted byproducts, which ultimately promoted the yield of 2-POL. It was also worth noting that the time dependent reactivity in Figure 3(c) demonstrated that MF was an intermediate for MTHF and 2-POL formation, and that ring opening was preferred on Co.

To improve 2-POL yields over Co-Cu/Al$_2$O$_3$, FF conversion was studied as function of H$_2$ pressure at 240 °C and 12 hours reaction time (Figure S3). 2-POL yields increased with increasing H$_2$ pressure to 45 bar, resulting in a maximum 71.1% yield of 2-POL. Direct production of 2-POL from FF has only been sparsely commented on in literature and we are not aware of previous reports with significant 2-POL yields quantified. Further increasing H$_2$ pressure to 55 bar showed a negative influence on 2-POL yields and promoted ring hydrogenation to increase THFOL and MTHF yields.

Recyclability studies were conducted at 2 and 12 hours reaction times (Figure 4) to explore Co-Cu/Al$_2$O$_3$ stability under the optimized reaction conditions (45 bar H$_2$ and 240 °C). Complete FF conversion was observed for both reaction times. Although FF is the starting material, 2-POL formation occurs through MF as an intermediate, regardless of the production of other FF-derived products. At 2 hours reaction time MF was not completely converted to 2-POL, thus these conditions are suitable to analyze catalyst stability in the context of *in-situ* produced MF conversion to 2-POL. There was no observed change in reactivity for 2 or 12 hours reaction time during 4 sequential catalyst recycles (Figure 4(a) and (b)). This demonstrated that the Cu-Co/Al$_2$O$_3$ catalysts were reasonably stable for the high yield production of 2-POL.
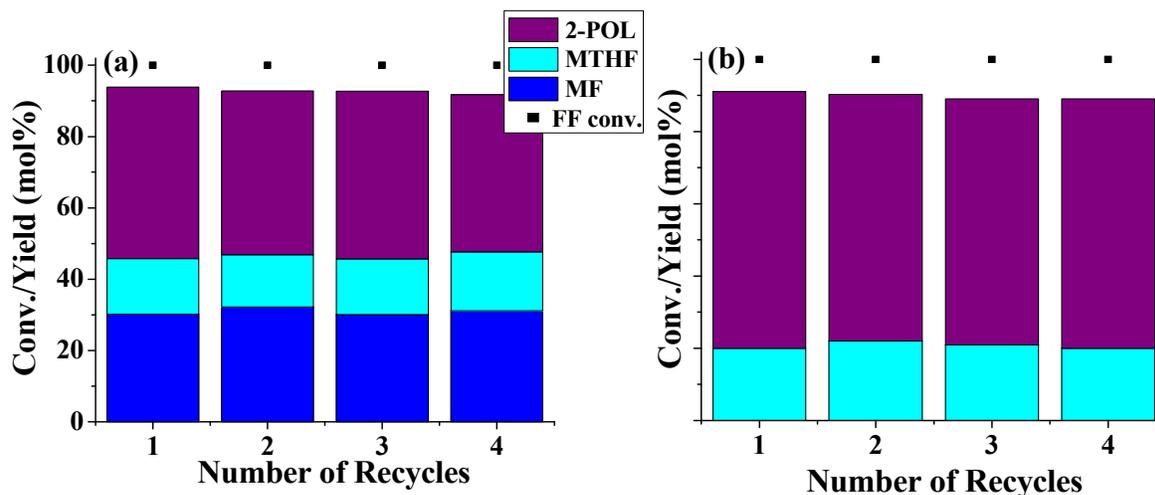
Figure 4. FF conversion and product yields as a function of number of catalyst recycles for Cu-Co/Al$_2$O$_3$ catalysts recycled after (a) 2 h and (b) 12 h reaction time. Reaction conditions were a FF loading of 1 g, catalyst loading of 0.3 g, 25 mL of 1,4-dioxane as a solvent, a temperature of 240 °C, H$_2$ pressure of 45 bar.

The high 2-POL yield observed on Co-Cu/Al$_2$O$_3$ is in contrast to recent reports on similar catalysts, suggesting that reaction conditions and catalyst pretreatment strongly influenced the resulting reactivity. For example, Cu-Co-Al mixed metal oxides that were reduced at 400 °C were examined for FOL (which is the initial and common intermediate in all pathways considered here, see Scheme 1) conversion at 140 °C, where it was seen that ~62% yields of pentanediols formation occured.[38] In that study, it was argued that CoO$_x$ was critical for this process. In another study, Co-Cu/Al$_2$O$_3$ catalysts were reduced at 280 °C prior to FF HDO and it was proposed that existing of Cu-CoOx species facilitated 78% selectivity to MF at 220 °C when using 2-propanol as a solvent.[39] 2-propoanol is more polar than 1,4-dioxane solvent, but unstable and can induce oxidation of the catalyst *in-situ*.[40] To identify the source of differences between our observations of high 2-POL yield and other reports, the reactivity of Co-Cu/Al$_2$O$_3$ was examined as a function of reaction temperature and reduction conditions.

At 180 °C, 45 bar H_2 pressure, and following 450 °C reduction temperature FF was converted over our Co-Cu/Al_2O_3 catalyst to 23.4% yield of pentanediols (combined yields of 1,2 pentanediol and 1,5 pentanediol), in addition to a mixture of THFOL(24.9%), MTHF(22.2%) and 2-POL (22.5%) (Figure S4). While increasing the reaction temperatures to 210 °C and to 240 °C, 2-POL yields were increased with expense of THFOL and pentanediols (Figure S4). This directly demonstrated that reaction temperature is important for controlling selectivity in FF conversion over Co-Cu/Al_2O_3 catalysts. The influence of reduction temperature was also examined by pretreating the Cu-Co/Al_2O_3 at 150 °C, 300 °C and 450 °C for 3 hours in H_2, and conducting FF conversion reactions at 240 °C (Figure S5). Catalysts pretreated at 150 °C and 300 °C resulted 57.5% and 55.3% of 2-POL yields, respectively, including MF (10.2% and 10.6%) and MTHF (22.7% and 25.2%), as other products. This is in contrast to the ~72% 2-POL yields observed over catalysts reduced at 450 °C. This suggested that metallic Co species facilitated complete MF conversions to 2-POL at longer hours (12 hours), while the retained existence of CoO_x species stabilized MF. Based on these results it is proposed that the high selectivity to 2-POL observed here for Cu-Co/Al_2O_3 resulted from a combination of complete Co reduction, increased reaction temperature compared to previous reports, and the use of a stable solvent that did not oxidize the catalyst.

Conclusions:

In this study, monometallic and bimetallic supported Cu, Ni, and Co catalysts were investigated for the single step conversion of FF to 2-POL. At 240 °C and 35 bar H_2 pressure, FF HDO to MF (92.5%) is the selective path over Cu/Al_2O_3 catalysts, whereas FF HDO followed by ring hydrogenation (MTHF, 63% yields) is favored on Ni/Al_2O_3 catalysts. Co/Al_2O_3 catalysts

facilitated FF HDO followed by furan ring opening and formed 2-POL as the major product due to the preferential adsorption of MF through oxygen (C_1-O bond) on Co active sites. 2-POL yields were maximized at ~72% by using Cu-Co/Al_2O_3 bimetallic catalysts and operating at 240 °C and 45 bar H_2. It is proposed that Co played the primary role of controlling the selective pathway of HDO followed by ring opening to form 2-POL and that Cu minimized product degradation.

Acknowledgements

Conflict of interest. There are no conflicts to declare.

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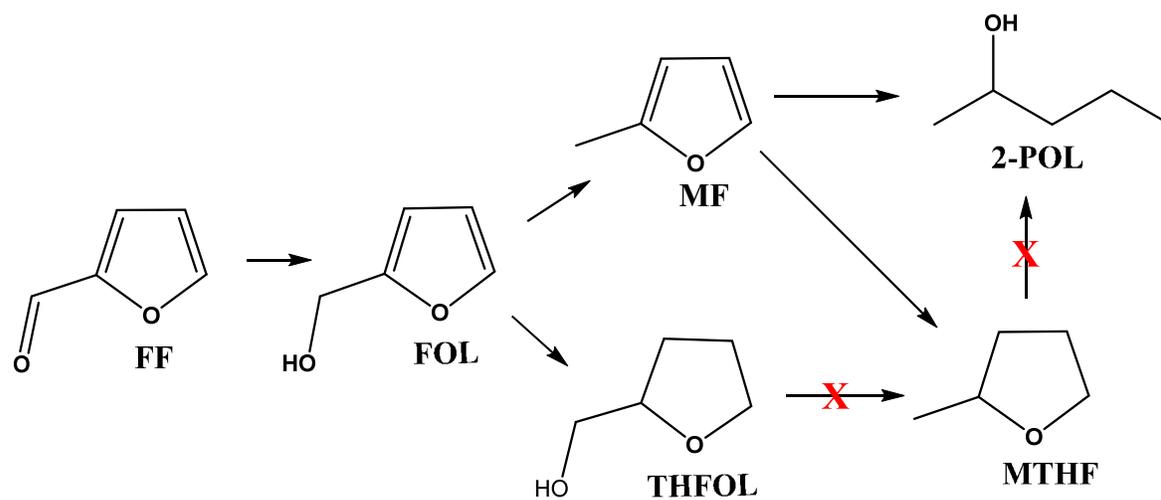
Graphical Abstract: Catalytic conversion of furfural to 2-pentanol over Co-Cu/Al$_2$O$_3$ catalysts