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Article

Influence of supports for selective production of 2,5-dimethylfuran via bimetallic copper-cobalt catalyzed 5-hydroxymethylfurfural hydrogenolysis

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ABSTRACT

The hydrogenolysis of carbon–oxygen bonds is an important model reaction in upgrading biomass-derived furanic compounds to transportation fuels. One of these model reactions, namely conversion of 5-hydroxymethylfurfural (HMF) to the gasoline additive 2,5-dimethylfuran (DMF), is especially attractive. In this study, bimetallic Cu-Co catalysts supported on CeO₂, ZrO₂, and Al₂O₃ were used for the selective hydrogenolysis of HMF to DMF. The structures of the fresh and used catalysts were studied using X-ray diffraction, the Brunauer-Emmett-Teller method, transmission electron microscopy, temperature-programmed reduction by H₂, temperature-programmed desorption of NH₃, and CHNS analysis. The structures were correlated with the catalytic activities. The Cu-Co/CeO₂ catalyst produced mainly 2,5-bis(hydroxymethyl)furan via reduction of C=O bonds on large Cu particles. The Cu-Co/Al₂O₃ catalyst gave the best selectivity for DMF, as a result of a combination of highly dispersed Cu, mixed copper-cobalt oxides, and suitable weak acidic sites. Cu-Co/ZrO₂ had low selectivity for DMF and produced a combination of various over-hydrogenolysis products, including 2,5-dimethyltetrahydrofuran and 5,5-oxybis(methylene)-bis(2-methylfuran), because of the presence of strong acidic sites. The reaction pathways and effects of various operating parameters, namely temperature, H₂ pressure, and time, were studied to enable optimization of the selective conversion of HMF to DMF over the Cu-Co/Al₂O₃ catalyst.

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1. Introduction

Energy crises, depletion of fossil fuel reserves, and global warming have increased interest in the production of biobased materials [1]. In confronting these challenges, biorefined materials have emerged as an alternative to industrial carbon. In biorefining, lignocellulosic biomass is transformed into value-added chemicals and fuels [2]. The hydrogenation/hydrogenolysis of furans such as furfural (FAL) and 5-hydroxymethylfurfural (HMF) has been widely studied for the production of biobased fuels such as 2-methylfuran (2-MF),

2-methyltetrahydrofuran, pentane, and 2,5-dimethylfuran (DMF) [3–6]. HMF is a valuable chemical because it can be converted to a variety of chemicals such as 2,5-bis(hydroxymethyl)furan (BHMF), 2-hydroxymethyl-5-methylfuran (5-MFOL), DMF, and 2,5-dimethyltetrahydrofuran (DMTHF) (Scheme 1) [7–9]. DMF is an important compound because it has potential use in gasoline blends and can be converted to *p*-xylene through a Diels-Alder reaction with ethylene [10–12].

Precious metals, i.e. Pt, Pd, Rh, Ru, and Au, are the main metals with potential uses in the hydrogenation of HMF to

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DMF; Pd and Ru have been reported to give the best selectivities for DMF [9,13–17]. The first reported catalyst for hydrogenation of HMF to DMF was CuRu/C, which gave 71% yields of DMF from two different starting materials [9,18]. It was reported that the activity of this catalyst gradually decreased because of deactivation of active centres and/or the presence of chloride ions [9]. Thananattananachon and Rauchfuss reported the conversion of HMF to DMF using Pd/C as a catalyst and formic acid as an additive [8]. An excellent yield, i.e. 93%, with 99% HMF conversion was achieved, but only when formic acid and H₂SO₄ were used. However, because of their highly corrosive nature and environmental concerns, the use of both formic acid and H₂SO₄ is restricted. Luijckx et al. [19] used a combination of Pd/C and HCl to reduce HMF to DMF; The results were similar to those reported by Rauchfuss et al. [8]. Zu et al. [15] used Ru/Co₃O₄ as a catalyst for the selective conversion of HMF to DMF at 130 °C and 0.7 MPa; they clearly identified the roles of Ru and CoO_x, which are responsible for reduction and hydrogenolysis of carbonyl and hydroxyl groups, respectively.

Because of the high cost of noble metals, research on precious-metal-free catalysts which can effectively convert HMF to DMF is needed. Yang et al. [20] obtained a 76% yield of DMF over Ni/Co₃O₄ catalysts; the roles of Ni and CoO_x were similar to those reported for Ru and CoO_x by Zu et al. [15]. Cu/ZnO, Cu–Zn alloy, Cu/MgO/Al₂O₃, Ru-modified Cu/MgO/Al₂O₃, and Cu–PMO catalysts have been examined in the hydrogenation of HMF to DHMF and DMF [21–23]. However, the development of low-cost and environmentally benign robust catalytic systems for this reaction is still in progress.

Recently, supported bimetallic Cu–Co nanoclusters have emerged as versatile catalytic systems for hydrogenation/hydrogenolysis reactions because of the presence of Cu(0), CoO_x species, and mixed oxide phases [24–34]. It has been reported that early-transition-metal oxides such as CoO_x, ReO_x, and MoO_x can effectively split C–O and O–H bonds [15,19,35,36]. A combination of Cu metal and CoO_x could

therefore be effective in the production of DMF by hydrogenation/hydrogenolysis of HMF. In our previous work, we hydrogenated FAL to 2-MF over bimetallic Cu–Co catalysts supported on SiO₂, H-ZSM-5, and Al₂O₃ [29]. Cu–Co/Al₂O₃ was the best hydrogenolysis catalyst because of the presence of small Cu particles and Cu–Co_x mixed phases, and synergies among Cu, Co, and Al₂O₃.

The present work was undertaken based on the background described above. In this study, instead of using SiO₂ and H-ZSM-5 as supports, materials which stabilize metal dispersion and improve oxygen storage (e.g. CeO₂ and ZrO₂) were examined and compared with Al₂O₃ as supports for Cu–Co bimetallic catalysts. The structures of these synthesized catalysts were studied using X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET) method, transmission electron microscopy (TEM), temperature-programmed desorption of NH₃ (NH₃-TPD), temperature-programmed reduction by H₂ (H₂-TPR), and CHNS analysis. The activities and selectivities of these catalysts in the hydrogenolysis of HMF to DMF were investigated. Cu–Co/Al₂O₃ catalysts were best for the hydrogenolysis of biomass-derived HMF to DMF; DMF was selectively obtained in 78% yield under mild conditions. The HMF conversion and DMF selectivity were optimized based on the reaction pathways and effects of the reaction parameters, namely temperature, H₂ pressure, and time.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF), HMF, and all the products shown in Scheme 1 (all GC grade) were purchased from Sigma-Aldrich, Mumbai, India. The supports, i.e. CeO₂, ZrO₂, and Al₂O₃ (purity 99%), were purchased from Sterling Chemical Pvt., Ltd., Surat, India. Bimetallic Cu–Co catalysts with Cu:Co molar ratios of 1, 2, and 4 were synthesized on CeO₂, ZrO₂, and Al₂O₃ at fixed Cu

Scheme 1. Reaction pathway in DMF synthesis from HMF.

loadings of 10 wt% by impregnation with aqueous solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Details of the synthesis and characterization of the supported bimetallic Cu-Co catalysts are available elsewhere [29].

2.2. Catalytic activity study

Hydrogenation of HMF was performed in a 100-mL autoclave reactor (Amar Equipment Pvt., Ltd., Mumbai, India). Briefly, the catalyst (0.5 g) was reduced at $280 \pm 2^\circ\text{C}$ in a H_2 flow at 1 MPa for 3 h. The reactor was cooled to room temperature and flushed with N_2 . The reactor was charged with HMF (2.5 mmol) in THF (20 mL). The catalytic activities of the prepared catalysts were investigated at 160–230 $^\circ\text{C}$ under a H_2 pressure of 3.0 MPa with stirring at 1000 r/min. The reproducibility of each reaction was checked by repeating it twice. Product samples were analysed using a Sigma GC system with a flame ionization detector (FID). An AB-5 capillary column of dimensions 30 m $\times$ 0.25 mm $\times$ 0.5 μm was used. In a typical procedure, the initial oven temperature was held at 50 $^\circ\text{C}$ for 2 min and increased to 300 $^\circ\text{C}$ at a ramping rate of 10 $^\circ\text{C}/\text{min}$ and held for 2 min. The product suspension (1 μL) was injected into the capillary column using a 20:1 split ratio, with N_2 as the carrier gas. The carbon balance was calculated in each run by measuring the carbon in the liquid phase using GC-FID; it was found to be >92% in each run because of unidentified products. The unidentified products were quantified by subtracting the overall carbon balance at each step from 100%. The following equation was used to determine the amount of carbon in the reaction mixture: carbon balance (%) = moles of carbon after reaction (reactant and products)/moles of carbon before reaction (reactant) $\times$ 100.

3. Results and discussion

3.1. Catalyst structure

3.1.1. XRD results

The effects of the support on the crystalline phases of the bimetallic Cu-Co (Cu/Co = 1) catalysts were investigated using XRD. The XRD patterns of the calcined and reduced catalysts are shown in Figs. 1–3. The XRD patterns of the ZrO_2 and CeO_2 catalysts show the presence of face-centred cubic (fcc) ZrO_2 and (fcc) CeO_2 crystalline structures (Fig. 1), based on the JCPDS files [JCPDS 83-0936 and JCPDS 81-0792] [37]. However, no (fcc) structure was observed for Al_2O_3 ; only a weak diffraction peak at $2\theta = 67^\circ$ indicated the presence of Al_2O_3 . To gain further insights into the effects of the supports on active site formation in the bimetallic catalysts, we examined the XRD patterns of monometallic Cu (10 wt%) and Co (10 wt%) on all three supports and compared them with the patterns of the bimetallic counterparts (Fig. 1). The intensities of the diffraction peaks from all three supports decreased after doping with 10 wt% Cu and 10 wt% Co in the monometallic catalysts. The intensities decreased further after doping simultaneously with Cu and Co. This implies that the crystallinities of the supports decreased as a result of high metal loadings. The diffraction

Fig. 1. Wide angle XRD patterns of supports CeO_2 , ZrO_2 , Al_2O_3 , monometallic Cu (10 wt%) (a, c, e) and Co (10wt%) (b, d, f) supported on CeO_2 , ZrO_2 and Al_2O_3 respectively, and bimetallic Cu-Co (Cu/Co = 1) (g, h i) catalysts supported on CeO_2 , ZrO_2 and Al_2O_3 respectively, calcined at 450 $^\circ\text{C}$.

patterns of the monometallic Cu and Co catalysts over all three supports showed diffraction peaks from CuO at $2\theta = 35.5^\circ$ and 38.7° , which are assigned to the (111) and (111) planes of monoclinic copper oxide [JCPDS 80-1917 and 45-0937], and from Co_3O_4 at $2\theta = 37^\circ$, 44° , and 56° [JCPDS 43-1003] [28,29].

Specific XRD patterns were observed for doped Cu-Co over all three supports (Fig. 1). For the calcined catalysts, either segregated CuO or a spinel oxide consisting of $\text{Co}_3\text{O}_4/\text{CuCo}_2\text{O}_4$ was clearly observed. Because of their similar cubic frameworks and unit cell parameters (Co_3O_4 , $a = 8.177 \text{ \AA}$ and CuCo_2O_4 , $a = 8.122 \text{ \AA}$), Co_3O_4 and CuCo_2O_4 are not easily distinguishable based on their XRD patterns [29]. The Cu-Co/ CeO_2 and Cu-Co/ ZrO_2 catalysts showed weak but clear diffraction peaks at $2\theta = 35.5^\circ$ and 38.7° , which are assigned to the (111) and (111) planes of monoclinic copper oxide [JCPDS 80-1917 and 45-0937], and diffraction peaks attributed to Co_3O_4 at $2\theta = 37^\circ$, 44° , and 56° [JCPDS 43-1003]. For Cu-Co/ Al_2O_3 , the weak diffraction peaks at $2\theta = 35.5^\circ$ and 38.7° are attributed to highly dispersed Cu on porous Al_2O_3 [28,29]. The full-widths at half-maximum (FWHM) of the diffraction peak at $2\theta = 37^\circ$, which is attributed to CuCo_2O_4 , increased in the order $\text{CeO}_2 < \text{ZrO}_2 < \text{Al}_2\text{O}_3$; this is because Cu-Co/ Al_2O_3 has the smallest crystals.

In the case of the reduced catalysts (Fig. 2), Cu-Co/ ZrO_2 showed weak diffraction peaks from (fcc) Cu metal and Cu_2O . However, diffraction peaks from (fcc) Cu_2O were not observed for the other two catalysts, i.e., Cu-Co/ CeO_2 and Cu-Co/ Al_2O_3 ; they only displayed diffraction peaks from (fcc) Cu metal. The FWHMs of the strongest peak, at $2\theta = 44.3^\circ$, decreased in the order of $\text{CeO}_2 < \text{ZrO}_2 < \text{Al}_2\text{O}_3$. This confirms that the metal particles in Cu-Co/ Al_2O_3 are smaller than those in the other two catalysts. The sizes of the Cu metal crystallites in the reduced

Fig. 2. Wide angle XRD patterns of Cu-Co (Cu/Co = 1) catalysts supported on CeO₂, ZrO₂ and Al₂O₃ reduced at 280 °C.

catalysts were calculated using the Scherrer formula, based on the Cu (111) peak at $2\theta = 44.3^\circ$. The CeO₂-supported catalyst had the largest Cu particles, of average size 25 nm; the average Cu particle size for the Al₂O₃-supported catalyst was 15 nm. The differences among the phases and crystallite sizes obtained with different supports can be attributed to the nature of the supports and/or metal-support interactions. The oxide supports used in this study interact weakly with Cu and Co, and the order of the interaction strengths is CeO₂ > ZrO₂ > Al₂O₃ [38]. The stronger interactions between both the metals and CeO₂ produced large segregated CuO and Co₃O₄ phases, whereas the strong interactions between copper and cobalt oxides and their weaker interactions with Al₂O₃ promoted formation of mixed copper-cobalt oxides. To understand the synergy between Cu and Co over Al₂O₃, the reduced bimetallic Cu-Co (Cu/Co = 1) catalyst was compared with its monometallic counterparts, i.e. Cu (10 wt%)/Al₂O₃ and Co (10 wt%)/Al₂O₃ (reduced at 280 °C), as shown in Fig. 3. The monometallic Cu catalyst contained large Cu crystals but the monometallic Co catalyst contained both oxide and metallic forms because of the reducing conditions used in this study. Monometallic Co₃O₄ is reduced at or above 450 °C. In contrast to the monometallic catalysts, bimetallic Cu-Co/Al₂O₃ (Cu/Co = 1) gave diffraction peaks from Cu and/or Co metal and partially reduced CoO_x. The low intensities of the diffraction peaks from Cu metal suggest that co-doping of Co and Cu on porous Al₂O₃ significantly decreased the size of the metal crystallites. The particle size of monometallic Cu, based on the peak at 44.3° , was 25–30 nm. However, as reported earlier, the corresponding size was 15 nm for bimetallic Cu-Co/Al₂O₃ (Cu/Co = 1). These observations are in good agreement with previously reported results for Cu-Co catalysts [24–34].

3.1.2. Textural properties

The textural properties of the supports and the Cu-Co catalysts supported by CeO₂, ZrO₂, and Al₂O₃ are summarized in Table 1. Because of its ordered porous structure, Al₂O₃ had the highest BET surface area, i.e. 166 m²/g, and a pore volume of 0.54 cm³/g. CeO₂ had the lowest BET surface area, (112 m²/g) and pore volume, (0.28 cm³/g). The decreases in the surface

Fig. 3. Wide angle XRD patterns of Al₂O₃ supported mono (Cu & Co, 10wt%) and bimetallic Cu-Co (Cu/Co = 1) reduced at 280 °C for comparison.

area, pore volume, and pore size of CeO₂ after doping with Cu and Co were smaller than those for the other two supports; Al₂O₃ showed the largest reductions in surface area, pore volume, and pore size. The differences among the textural properties of the synthesized catalysts can be attributed to the nature of the supports and their interactions with both metals. The small decline in the pore volume and pore size of CeO₂ after doping could be the result of deposition of metal particles on the external surface of the support rather than in the pores. However, the Al₂O₃-supported catalyst showed large reductions in pore volume and pore size; this can be attributed to deposition of metal particles on the surface and in the pores. It can be assumed that CeO₂ can stabilize metal particles on the surface because it has strong interactions with both the metals used in this study. However, compared with CeO₂, Al₂O₃ has weak interaction with Cu and Co, and this may result in highly dispersed metal particles. These results are in agreement with those reported by Wang et al. [39], who suggested that strong interactions between Cu and Co and weaker interactions with Al₂O₃ lead to highly dispersed metal particles on porous Al₂O₃. This may result in a high surface area compared with those of the other two catalysts.

3.1.3. Morphology

TEM images of freshly reduced Cu-Co (Cu/Co = 1) on different supports are shown in Fig. 4. The dispersion and mor-

Table 1

Textural and structural characteristics of supports and supported Cu-Co catalysts.

Samples	Cu:Co ^a (wt%)	Cu:Co ^b (wt%)	S _{BET} (m ² /g)	V _p (mL/g)	D _p (nm)	d _p (nm)	Ref.
CeO ₂			112	0.28	3.2		
ZrO ₂			132	0.38	4.6		
Al ₂ O ₃			166.1	0.54	6.6		[29]
Cu-Co/ CeO ₂	10:10	9.2:8.4	82.6	0.18	2.6	25	
Cu-Co/ ZrO ₂	10:10	10.6:10.2	94.4	0.24	3.4	20	
Cu-Co/ Al ₂ O ₃	10:10	10.4:9.9	113.5	0.32	4.6	15	[29]

^a Loading ratio used in the synthesis.

^b Evaluated by EDX analysis.

Fig. 4. TEM micrographs of Cu-Co (Cu/Co = 1) catalysts supported on CeO₂ (a), ZrO₂ (b) and Al₂O₃ (c).

phology/ordering of the Cu-Co nanoparticles on different supports vary depending on the nature of the support and the discrete interactions between the support and both Cu and Co. Agglomerated large metal crystallites (25–30 nm) were observed in the CeO₂-supported catalyst because of the strong interactions between CeO₂ and the metal particles. Similar-sized but segregated, non-uniformly distributed Cu-Co nanoparticles were observed on ZrO₂. Cu-Co/Al₂O₃ had well dispersed, ordered, uniformly spherical small nanoparticles. The metal particles in Cu-Co/Al₂O₃ were mainly of uniform size about 20 nm. This morphology/ordering of Cu-Co nanoparticles on CeO₂, ZrO₂, and Al₂O₃ can be explained based on a combination of a porous structure and metal-support interactions.

The more uniform distributions of Cu-Co particles on the Al₂O₃ support can be ascribed to the interactions between uniformly porous Al₂O₃ and both Cu and Co species being weaker than the metal-support interactions in the other cases [29].

3.1.4. Reductive properties

The reductive properties of Cu-Co/CeO₂, Cu-Co/ZrO₂, and Cu-Co/Al₂O₃ were investigated using H₂-TPR. Metal-support interactions play a vital role in stabilizing and reducing metal oxides to metallic sites. In particular, for bimetallic catalytic systems, the interactions between each metal component and the support significantly affects the chemical environment of the metals and/or the reduction temperature. Weakly interacting metal oxide species are easily reduced to the metallic state [38]. Conversely, if the metal oxides are strongly adsorbed on the support, they are difficult to reduce, and this leads to incomplete reduction and formation of low-valence metals [37,38]. The reductive properties of the Cu-Co (Cu/Co = 1) catalysts supported on CeO₂ and ZrO₂ were determined using H₂-TPR and the profiles were compared with that of Cu-Co/Al₂O₃ [29] (Fig. 5). The nature of the support significantly affected the reducibility of the bimetallic catalysts. The differences among the reduction temperatures showed that the CeO₂ (broad hump at 220–370 °C) support had stronger interaction with both metals. Al₂O₃ and ZrO₂ showed broad humps which were deconvoluted to several peaks. The TPR profile of the ZrO₂-supported catalyst showed three major reduction peaks. The first peak, at 200 °C, is attributed to the reduction of small CuO particles, which interact weakly with ZrO₂. The second peak, at 250–370 °C, is ascribed to the reduction of larger CuO particles, which are strongly attached to ZrO₂. The third

peak, at around 400 °C, is attributed to the reduction of Co₃O₄ species on the ZrO₂ surface.

The TPR profile for Cu-Co/Al₂O₃ was different from those for the other two catalysts, and reduction occurred at a lower temperature; this is ascribed to the reduction of mixed copper-cobalt oxides and small Cu particles. These observations are supported by the XRD and TEM results. The presence of multiple reduction peaks indicates two-step reduction of Cu and partial reduction of CuCo₂O₄/Co₃O₄ [16,35]. Among the three supports, Al₂O₃ has the weakest interactions with the copper-cobalt oxide phases and this enhances the reducibility of the copper oxides and mixed CuCo₂O₄, which increases the number of Cu–CoO_x sites in Cu-Co/Al₂O₃. To clarify the effect of synergy between Cu and Co on the reductive properties, the reduction profiles of monometallic Cu (10 wt%)/Al₂O₃ and Co (10 wt%)/Al₂O₃ were also obtained (Fig. 5), and compared with those of their bimetallic counterparts. The differences among these reductive behaviours were discussed at length in our previous work [29]. Table 2 shows the experimental H₂ consumptions during TPR. It can be deduced that Co and Cu are both essentially completely reduced by 400 °C on all three supports, with Cu-Co/CeO₂ being slightly less reduced (82%) compared with the other two (88% and 96%).

3.1.5. Surface acidity

The surface acidities of the bimetallic Cu-Co (Cu/Co = 1) catalysts supported on CeO₂ and ZrO₂ were determined using

Fig. 5. H₂-TPR patterns of Cu-Co (Cu/Co = 1) catalysts supported on CeO₂, ZrO₂ and Al₂O₃ calcined at 450 °C.

Table 2

Quantitative Hydrogen consumption during TPR.

Samples	Cu/Co ^a (wt%/wt%)	H ₂ consumption (mmol/g.cat)	Metal re- duced (%)	Ref.
Cu-Co/CeO ₂	1	32.6	82	—
Cu-Co/ZrO ₂	1	44.3	88	—
Cu-Co/Al ₂ O ₃	1	53.8	96	[29]

^a Loading ratio used in the synthesis.

NH₃-TPD and the results were compared with those for Cu-Co/Al₂O₃ (Fig. 6 and Table 3). Generally, the strengths of the acidic sites, based on the NH₃ desorption temperature, can be classified as weak (< 250 °C), medium (250–400 °C), and strong (> 400 °C) acidic sites. The overall acidity of a catalyst can be calculated from the relative peak areas in the NH₃-desorption curves [29]. Cu-Co/CeO₂ (Cu/Co = 1) had few weak and strong acidic sites, and had only medium acidity. Cu-Co/Al₂O₃ (Cu/Co = 1) showed three peaks (at 145, 335, and 555 °C), which can be ascribed to NH₃ desorption from weak, medium, and strong acidic sites. Cu-Co/ZrO₂ (Cu/Co = 1) showed two peaks (minor 100–250 °C, major 350–550 °C), which can be ascribed to NH₃ desorption by weak and strong acidic sites (Fig. 6 and Table 3). A comparison of the results for the three catalysts shows that Cu-Co/Al₂O₃ (Cu/Co = 1) had the maximum acidity, i.e. 0.49 mmol/g cat. The order of the total acidities was Al₂O₃ > ZrO₂ > CeO₂. It is worth noting that five different types of OH groups are present on the surface of γ -Al₂O₃, giving a net electric charge (σ), depending on the number of Al neighbours and Al coordination [40,41]. The removal of OH groups during high-temperature treatment (calcination) creates unsaturated surface cations, with mainly tetrahedrally [Al(IV)] and octahedrally [Al(VI)] coordinated Al [42,43]. Both Lewis and Brønsted acidic sites may therefore be present on Al₂O₃, depending on the degree of dehydration.

3.2. Catalytic activity

3.2.1. Catalyst screening for HMF hydrogenation to DMF

We previously reported a liquid-phase hydrogenation of FAL to 2-MF using a highly efficient non-noble metal, environmentally benign, bimetallic Cu-Co catalyst [29]. The advantage of this catalytic system, which was prepared using an impregnation method, over other Cu-based catalysts has been thoroughly discussed. In our previous work, we found that SiO₂ and H-ZSM-5 supports gave low selectivities for C–O hydrogenolysis. In this study, we therefore used materials which can stabilize metal dispersion and improve oxygen storage, i.e. CeO₂ and ZrO₂, as supports for Cu-Co (Cu/Co = 1) and compared the per-

Fig. 6. NH₃-TPD patterns of Cu-Co (Cu/Co=1) catalysts supported on CeO₂, ZrO₂ and Al₂O₃ calcined at 450 °C.

formance of these catalysts with that of Cu-Co/Al₂O₃ (Cu/Co = 1) in the hydrogenation/hydrogenolysis of HMF to DMF at 200 °C and 3.0 MPa (Fig. 7). The support plays a significant role in the selective hydrogenation/hydrogenolysis of HMF to DMF. Cu-Co/CeO₂ showed the lowest catalytic activity (78% conversion) and Cu-Co/Al₂O₃ showed the highest catalytic activity (98% conversion) in HMF hydrogenation. The order of the catalytic activities was CeO₂ < ZrO₂ < Al₂O₃. HMF contains three functional groups, namely C=O, O–H, and the furan ring (Scheme 1). Over Cu catalysts, HMF hydrogenation proceeds by reduction of the C=O bond to give the diol intermediate BHMF. Further hydrogenolysis of BHMF leads to the formation of DMF via another intermediate, i.e. 5-MFOL [20–23]. Nagaraja et al. [44] proposed that the presence of a larger amount of metallic Cu than of CuO promoted reduction of the C=O bond in FAL to give furfuryl alcohol. In our previous work, we also observed that the conversion of FAL to furfuryl alcohol via C=O reduction increased with increasing amount of surface metallic Cu [27]. The activities of all three catalysts used in this study can therefore be explained based on (1) the degree of reduction, i.e. the amount of surface metallic Cu species, indicated by H₂ consumption during TPR, and (2) the number of copper-cobalt mixed oxide sites available. Cu-Co/CeO₂ gave the lowest H₂ consumption, and Cu-Co/Al₂O₃ consumed the highest volume of H₂.

In terms of product selectivity, the main compounds identified in the liquid reaction products were BHMF, 5-MF, 5-MFOL, and DMF, over all three catalysts. However, the selectivity for the desired product (DMF) is affected by the support, the second metal, or both. For example, Cu-Co/CeO₂ gave the highest

Table 3Acidity of bi-metallic Cu-Co catalysts supported on CeO₂, ZrO₂, and Al₂O₃, using ammonia-TPD method.

Samples	Cu/Co [*] (wt%/wt%)	Amount of ammonia desorbed (mmol/g.cat)			Total Acidity (mmol/g.cat)	Ref.
		<200 °C	250–450 °C	>450 °C		
Cu-Co/CeO ₂	1	0.03	0.18	0.04	0.25	—
Cu-Co/ZrO ₂	1	0.08	0.04	0.28	0.40	—
Cu-Co/Al ₂ O ₃	1	0.13	0.21	0.14	0.49	[29]

^{*} Loading ratio used in the synthesis.

Fig. 7. Catalytic activity for hydrogenolysis of HMF over supported bi-metallic copper-cobalt catalyst. Reaction conditions: 200 °C, 3.0 MPa, 8 h, Catalyst 0.5 g, HMF 2.5 mmol, THF 20 mL. I—5-Methylfurfural (5-MF), II—bis(hydroxymethyl-furan) (BHMf), III—5-methylfurfuryl alcohol (5-MFOL), IV—5,5-oxybis(methylene)bis(2-methylfuran), V—2,5-dimethylfuran (DMF), VI—2,5-dimethyltetrahydrofuran (DMTHF), Oth = FOL, MF and few of unknown products.

selectivity for BHMf because of preferential reduction of the C=O bond in HMF. Small amounts of hydrogenolysis products such as 5-MF, 5-MFOL, and DMF, and small amounts of the products FOL and MF, which were produced by decarbonylation followed by hydrogenolysis, were also detected. Cu-Co/Al₂O₃ was the most active in polarizing O–H and C–O bonds, resulting in DMF production via sequential hydrogenation/hydrogenolysis of HMF. These results show that Cu effectively promotes hydrogenation and moderately promotes hydrogenolysis. In addition, Cu can break the C=O bond during hydrogenation of FAL and HMF [21,28,44]. It has also been reported that Cu metal gives selective production of propylene glycol via glycerol hydrogenolysis [43]. Sithisa et al. [44] proposed that aldehydes were preferentially adsorbed in the $\eta^1(\text{O})$ configuration on Cu metal, which allows interactions between surface Cu and the oxygen of the FAL carbonyl group, to yield furfuryl alcohol. It has also been reported that surface Cu can induce O–H bond scission to form stable alkoxide (CH_3O) intermediates during methanol decomposition [45].

The above findings suggest that the increased selectivity of Cu-Co/Al₂O₃ for DMF production via C–O and O–H hydrogenolysis can be attributed to synergy between surface metallic Cu sites and partially reduced CoO_x sites. The XRD and TPR results show that Cu-Co/Al₂O₃ has the maximum amounts of surface metallic Cu and mixed oxide phases, resulting in an increased rate of hydrogenolysis [29]. It has been reported that the reduced forms of spinel CuCoO₄ catalysts involve metallic Cu dispersed on CoO_x [34,35]. It has also been reported that early-transition-metal oxides such as ReO_x, MoO_x, and CoO_x are effective catalysts in the hydrogenolysis of biomass-derived components [35,36]. Previous studies [47,48] have shown that dissociative adsorption of H₂ on Cu(0) has a low activation energy [49]. Similar effects have been observed for promotion of Cu catalysts with noble metals [50]. Recently, our group reported that an increase in the Co loading increased Cu disper-

sion because of the strong interactions between Cu and Co. A combination of Cu–CoO_x was found to be effective in the one-step hydrogenation of FAL to 2-MF via reduction of the C=O bond followed by C–O hydrogenolysis [29]. These previous reports and the present experimental findings suggest that the improved dispersion of Cu in the presence of Co and the synergy between Cu and CoO_x species as a result of strong interactions between Cu and Co facilitate the hydrogenolysis of HMF to DMF. This is supported by the XRD, BET, and H₂-TPR results. Metallic Cu and mixed Cu–Co particles can therefore activate H₂ to enable partial reduction of Co₃O₄, which is difficult to reduce at low temperatures. This reducibility of the bimetallic catalysts is responsible for the enhanced activity of the Cu–Co/Al₂O₃ catalyst.

Cu-Co/ZrO₂ had low selectivity for DMF (about 40%) and produced a combination of ring-saturation and over-hydrogenolysis products such as DMTHF and other by-products. The properties of ZrO₂ and the presence of strong acidic sites may be responsible for this behaviour; the strong acidic sites may cause side reactions such as ring opening or ring saturation. Bui et al. [51] reported that ring opening by hydrolytic cleavage of the furanic C–O bond was usually promoted by Brønsted acidic sites in acidic materials. In addition, traces of 5,5-oxybis(methylene)bis(2-methylfuran), formed by dehydration of 5-MOL, were also observed with Cu-Co/ZrO₂. This is in agreement with a previous report [15].

We studied the hydrogenolysis of 5-methylfurfural (5-MF) over the same catalysts and under the same reaction conditions (Fig. 8) to explore the reaction pathways and clarify the reasons for the superior hydrogenolysis activities of some of the catalysts. The hydrogenolysis activity of Cu-Co/CeO₂ was inferior to those of the other two catalysts. About 86% 5-MF was converted over Cu-Co/CeO₂, with 32% selectivity for DMF. The major product selectivity was for 5-MFOL (48%), formed via reduction of the C=O bond in 5-MF. Following the trend observed for HMF hydrogenation, Cu-Co/Al₂O₃ showed excellent hydrogenolysis activity and produced about 82% DMF with

Fig. 8. Catalytic activity for hydrogenolysis of 5-methylfurfural over supported bi-metallic copper-cobalt catalysts. Reaction conditions: 200 °C, 3.0 MPa, 8 h, Catalyst 0.5 g, 5-MF 2.5 mmol, THF 20 mL. Oth=5,5-oxybis(methylene)bis(2-methylfuran), 2,5-dimethyltetrahydrofuran (DMTHF), FOL, MF and few of unknown products.

99% conversion of 5-MF. However, although 99% conversion of 5-MF was achieved over Cu-Co/ZrO₂, the selectivity for DMF (56%) was low and large amounts of ring-saturation and ring-opening products were obtained. These results are in agreement with those obtained for one-step hydrogenolysis of HMF to DMF.

3.2.2. Effects of Cu/Co molar ratio on HMF hydrogenolysis

The effect of the Cu/Co molar ratio on the catalytic activity of bimetallic Cu-Co/Al₂O₃ was investigated by studying catalysts with various molar ratio (Cu/Co = 1, 2, and 4) at 200 °C and 3.0 MPa. The results were compared with those for the monometallic Cu (10 wt%)/Al₂O₃ and Co (10 wt%)/Al₂O₃ counterparts (Table 4). The catalytic activity of Co (10 wt%)/Al₂O₃ was low, which confirms that Co₃O₄ species alone have little effect on HMF hydrogenolysis under the present conditions. This result is in agreement with that reported by Zu et al. [15], who found that Co₃O₄ had low catalytic activity in HMF hydrogenation. When 10 wt% Cu/Al₂O₃ was used, BHMF, formed via activation of the carbonyl group, was the major product (45.5%). However, the bimetallic catalysts gave lower selectivities for BHMF and increased selectivities for DMF; the DMF selectivity reached a maximum of about 68.4% over Cu-Co/Al₂O₃ (Cu/Co = 1). BHMF was the main intermediate formed over all the catalysts, and it was converted to DMF via 5-MF and MFOL by subsequent hydrogenation and hydrogenolysis under the present conditions [22–26]. It can be deduced that hydrogenation of the C=O bond followed by hydrogenolysis of C–O and O–H bonds in HMF is favoured at higher temperatures because of activation of the C–O and O–H bonds, which results in formation of DMF as the major product and BHMF, MFA, and MFOL as minor products over bimetallic Cu-Co catalysts [46]. These results can be explained based on previously reported XRD, H₂-TPR, and X-ray absorption near-edge structure studies, which showed that the amounts of surface metallic Cu and mixed Cu-Co phases increased with increasing Co loading; this is responsible for the enhanced hydrogenolysis activity of the bimetallic catalysts [29].

We then studied the effects of temperature, H₂ pressure, and time on reactions using the Cu-Co/Al₂O₃ (Cu/Co = 1) catalyst to improve the DMF yield.

3.3. Effects of operating parameters

Table 4

Effect of Cu/Co molar ratio on hydrogenolysis of HMF.

Catalyst	Cu/Co * (wt%/wt%)	HMF Conversion (%)	Selectivity (%)				
			DMF	BHMF	5-MF	5-MFOL	Oth
Cu/Al ₂ O ₃	—	92.7	38.5	45.5	3.5	2.5	10.0
Cu-Co/Al ₂ O ₃	1	99.9	68.4	5.4	8.6	12.8	4.8
Cu-Co/Al ₂ O ₃	2	98.4	56.6	16.2	10.4	12.2	4.6
Cu-Co/Al ₂ O ₃	4	98.2	43.0	35.0	10.0	3.5	8.5
Co/Al ₂ O ₃	—	42.7	10.5	35.0	8.5	6.5	39.5

* Loading ratio used in the synthesis.

Reaction conditions: 200 °C, 3.0 MPa, 8 h, Catalyst 0.5 g, HMF 2.5 mmol, THF 20 mL.

HMF: 5-hydroxymethylfuran; DMF: 2,5-dimethylfuran; BHMF: 2,5-bis hydroxymethylfuran; 5-MF: 5-methylfurfural; 5-MFOL: 5-methylfurfuryl alcohol; Oth: FOL, MF and few of unknown.

Fig. 9. Effect of temperature on the conversion of HMF to DMF over Cu-Co/Al₂O₃ (Cu/Co = 1). Reaction conditions: 3.0 MPa, 8 h, Catalyst 0.5g, HMF 2.5 mmol, THF 20 mL.

3.3.1. Effects of temperature

The effect of temperature on the selective hydrogenolysis of HMF to DMF was studied over the temperature range 160–230 °C at a constant H₂ pressure of 3.0 MPa (Fig. 9). The HMF conversion was low (68%) at 160 °C, but increased with increasing temperature. It reached the maximum, i.e. 100% at 220 °C, and remained constant with further temperature increases to 230 °C. These results can be attributed to an increase in the reaction rate because of facilitation of C=O bond breaking over metallic Cu, resulting in increased activation of molecular H₂ in the reaction mixture [22,23]. Hydrogenation of the C=C bond (bond energy = 615 kJ/mol) is easier than C=O bond (bond energy = 715 kJ/mol) hydrogenation [45]. However, the presence of the conjugated furan ring makes hydrogenation of the C=O bond easier than C=C bond hydrogenation in the selective hydrogenation of HMF to DMF, which is generally promoted at higher temperatures [46]. At 160 °C the selectivity for DMF was low (40.6%), with formation of by-products such as BHMF, 5-MF, and 5-MFOL. However, with increasing temperature, the selectivity for DMF improved significantly and reached a maximum of 78% at 220 °C. It is worth noting that hydrogenation of the C=O bond in HMF was favoured at low temperatures over Cu catalysts because of the higher activation energies of C–O and O–H, resulting in the formation of BHMF as a major product. However, higher temperatures promote C–O and O–H hydrogenolysis, which results in further conversion of BHMF to DMF.

A high temperature is therefore important for C–O and O–H hydrogenolysis of the intermediates BHMF, 5-MF, and/or 5-MFOL. Further increases in temperature resulted in over-hydrogenolysis products and the yield of DMF dropped. This suggests that the conversion of HMF to DMF had reached a maximum at 220 °C, and the effect of further increases in the reaction temperature was insignificant. A reaction temperature of 220 °C was therefore used in subsequent experiments.

3.3.2. Effects of H_2 pressure

In hydrogenation/hydrogenolysis reactions, the solubility of H_2 , as well as other parameters (temperature and time), is important. A high H_2 pressure is needed to accelerate the hydrogenation of biobased molecules [22]. The optimum H_2 pressure for selective hydrogenation of HMF to DMF was identified by performing reactions at 220 °C and various pressures in the range 10–40 bar (Fig. 10). The conversion and selectivity both increased with increasing pressure up to 30 bar, and reached 100% and 78%, respectively. The HMF conversion did not change significantly with further increases in pressure. The conversion of HMF to DMF increased with increasing H_2 pressure up to 3.0 MPa because of the increasing solubility of H_2 in the reaction mixture. However, pressures above 3.0 MPa did not significantly change the HMF conversion because of the larger amount of chemisorbed hydrogen (H_{ads}) on the catalyst, which became saturated. However, above 3.0 MPa, a slight decrease in DMF selectivity was observed. This can be attributed to further opening and hydrogenation of the furan ring. A H_2 pressure of 3.0 MPa was therefore chosen for subsequent experiments.

3.3.3. Effects of time

The effects of time on the HMF conversion and the selectivity for DMF were investigated over the range 2–10 h at 220 °C and 3.0 MPa. Fig. 11 shows that only 21% conversion of HMF and 5.6% selectivity for DMF were achieved in 2 h. When the reaction time was prolonged from 2 to 8 h, the conversion reached 100% and the selectivity increased to 78%. The increased selectivity for DMF with time corresponds to conversion of increasing amounts of intermediates such as BHMF,

Fig. 10. Effect of hydrogen pressure on the conversion of HMF to DMF over Cu-Co/ Al_2O_3 (Cu/Co = 1). Reaction conditions: 220 °C, 8 h, Catalyst 0.5 g, HMF 2.5 mmol, THF 20 mL.

Fig. 11. Effect of time on the conversion of HMF to DMF over Cu-Co/ Al_2O_3 (Cu/Co = 1). Reaction conditions: 3.0 MPa, 220 °C, Catalyst 0.5 g, HMF 2.5 mmol, THF 20 mL.

5-MF, and 5-MFOL to DMF. When the reaction time was further increased to 10 h, the HMF conversion remained constant at 100%; however, the selectivity for DMF decreased slightly. This can be attributed to the formation of increasing amounts of by-products when the reaction time increased beyond a certain value. A reaction time of 8 h was therefore used in subsequent experiments. The transformation of HMF to DMF proceeds via the intermediates BHMF or 5-MF, and then 5-MFOL. Conversion of both intermediates to DMF is considered to be slow and requires more time over Cu-based catalysts.

3.4. Stability of catalysts in HMF hydrogenolysis

The Cu-Co/ Al_2O_3 catalyst, which gave the best catalytic performance, was recycled twice to evaluate its stability. The HMF conversion and selectivity for DMF dropped from 100% to 62% and 78% to 42%, respectively, in the second run (Table 5). The decrease in the catalytic activity was investigated by examining the differences between the structures of the spent and freshly reduced catalysts using TEM and CHNS analysis. TEM and CHNS analysis showed the presence of carbon after use. The TEM results showed that carbon was deposited on the active sites and the particle size increased after the second cycle; these factors could cause the significant drop in the activity of the catalyst. These observations agree with our previous work on FAL hydrogenation, in which coke formation was observed [29]. To confirm the reasons for the loss of catalytic activity, the

Table 5

Reusability of Cu-Co/ Al_2O_3 (Cu/Co=1) catalyst toward hydrogenolysis of HMF to DMF.

Catalysts	Conversion of HMF (%)	Selectivity of DMF (%)
Cu-Co/ Al_2O_3 (Fresh)	100	78.0
^a Cu-Co/ Al_2O_3 1 st cycle	78.4	54.0
^a Cu-Co/ Al_2O_3 2 nd cycle	62.4	42.6
^b Cu-Co/ Al_2O_3 1 st cycle	94.6	72.2

^a Without calcinations. ^b With calcinations.

Reaction Conditions: 220 °C, 3.0 MPa, Catalyst 0.5 g, HMF 2.5 mmol, THF 20 mL, 8 h.

used catalyst (Cu-Co/Al₂O₃ after the second cycle) was calcined at 500 °C and activated in situ at 280 °C to remove deposits, and then tested under same reaction conditions. As expected, the conversion of HMF and selectivity for DMF both increased, to 94% and 72%, respectively. It can therefore be concluded that the catalyst lost activity because coke formed during HMF hydrogenation covered the active sites on the catalyst.

4. Conclusions

Three supported bimetallic catalysts, i.e. Cu-Co/CeO₂, Cu-Co/ZrO₂, and Cu-Co/Al₂O₃, with Cu/Co molar ratios of 1, 2, and 4 were used in the hydrogenolysis of HMF to DMF. The intrinsic properties of the carriers and the strong interactions between Cu and Co significantly affected the catalytic performances of the Cu-based bimetallic catalysts. The activity of Cu-Co/CeO₂ in C–O bond breakage was modest because of its large Cu particles and low acidity. Cu-Co/Al₂O₃ was much more active in hydrogenation/hydrogenolysis of HMF because of the presence of metallic Cu and mixed copper-cobalt oxides, and appropriate acidic sites. Cu-Co/ZrO₂ showed similar activity but different product selectivity because of morphological differences and the presence of strong acidic sites. The catalytic activity of Cu-Co/Al₂O₃ in the conversion of HMF to DMF increased with increasing Co loading and the activities of the bimetallic catalysts were higher than those of their monometallic counterparts. The catalyst with the highest loading (Co = Cu = 10 wt%) gave an excellent catalytic performance; this is attributed to the presence of mixed copper-cobalt oxide species on porous Al₂O₃. Time and temperature were important parameters in the selective conversion of HMF to DMF. Based on

these promising results, further studies will focus on the reaction mechanism and kinetics of HMF conversion.

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Graphical Abstract

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Influence of supports for selective production of 2,5-dimethylfuran via bimetallic copper-cobalt catalyzed 5-hydroxymethylfurfural hydrogenolysis

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The present study explored the use of non-noble, environmentally benign, bimetallic copper-cobalt catalysts in the selective production of 2,5-dimethylfuran via 5-hydroxymethylfurfural hydrogenolysis.

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载体对其负载的Cu-Co双金属催化剂上5-羟甲基糠醛氢解选择性生成2,5-二甲基呋喃的影响

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摘要: 碳-氧键氢解是生物质呋喃基化合物制备交通燃料常见的模型反应, 其中5-羟甲基糠醛(HMF)转化为汽油添加剂2,5-二甲基呋喃(DMF)尤为引人关注. 本文采用CeO₂, ZrO₂和Al₂O₃负载的Cu-Co双金属催化剂用于HMF选择性氢解制DMF的反应中. 采用X射线衍射、N₂吸附-脱附、投射电镜、H₂-程序升温还原、氨-程序升温脱附和元素分析表征了新鲜的和使用过催化剂的结构, 并将其与催化活性相关联. Cu-Co/CeO₂催化剂通过在大的Cu颗粒上还原C=O键生成了最多的2,5-二(羟甲基)呋喃(BHMF). 但Cu-Co/Al₂O₃催化剂具有高度分散的Cu, Cu-Co复合氧化物和大量的弱酸位, 因而生成DMF的选择性最高. Cu-Co/ZrO₂催化剂则由于存在强酸位, DMF选择性较低, 生成了各种过度氢解产物, 如2,5-二(亚甲基)呋喃和5,5-二(亚甲基)呋喃. 因此, 考察了Cu-Co/Al₂O₃催化剂上的反应路径, 以及温度、氢气压力和时间等操作条件的影响, 使其具有较优的HMF转化率和DMF选择性.

关键词: 5-羟甲基糠醛; 加氢; 氢解; 铜-钴; 双金属; 生物燃料

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