

Effects of Water on the Copper-Catalyzed Conversion of Hydroxymethylfurfural in Tetrahydrofuran

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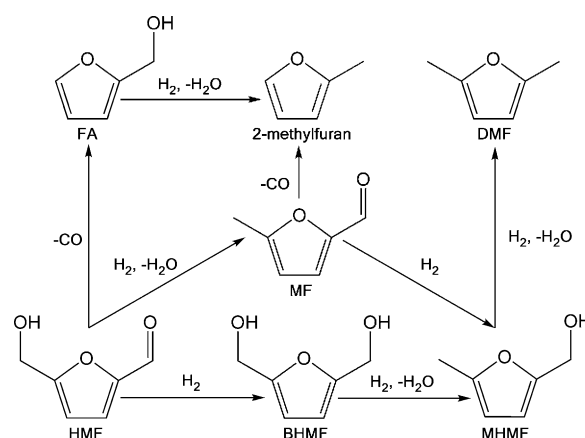
Reaction kinetics were studied to quantify the effects of water on the conversion of hydroxymethylfurfural (HMF) in THF over Cu/ γ -Al₂O₃ at 448 K using molecular H₂ as the hydrogen source. We show that low concentrations of water (5 wt%) in the THF solvent significantly alter reaction rates and selectivities for the formation of reaction products by hydrogenation and hydrogenolysis processes. In the absence of water, HMF was converted primarily to hydrogenolysis products 2-methyl-5-hydroxymethylfuran (MHMF) and 2,5-dimethylfuran (DMF), whereas reactions carried out in THF–H₂O mixtures (THF/H₂O = 95:5 w/w) led to the selective production of the hydrogenation product 2,5-bis(hydroxymethyl)furan (BHMF) and inhibition of HMF hydrogenolysis.

Cellulosic biomass-derived chemicals, such as hydroxymethylfurfural (HMF) and furfural, are precursors for the production of sustainable biofuels and biochemicals. For example, HMF is derived from glucose and can be converted into various fuel molecules and valuable industrial chemicals.^[1–3] One such molecule is 2,5-dimethylfuran (DMF), which is produced by the metal-catalyzed hydrogenolysis of HMF. DMF is considered to be a promising liquid transportation fuel additive owing to its high energy density of 30 MJ L⁻¹. Furthermore, DMF has a higher research octane number (i.e., 119) as well as lower volatility and lower solubility in water compared to ethanol.^[4] The production of DMF from HMF hydrogenolysis in organic solvents was studied by means of catalytic transfer hydrogenation and also using molecular hydrogen, achieving high selectivity and yield.^[5–15] For example, 81% DMF yield was achieved at full HMF conversion using Ru/C in isopropanol solutions.^[7] Furthermore, bifunctional catalysts, such as Ru/Co₃O₄, were shown to achieve >90% DMF yield from HMF in tetrahydrofuran (THF) at moderate temperatures (e.g., 403 K).^[10] Moreover, nearly quantitative DMF yields (i.e., 98%) from HMF were obtained using PtCo bimetallic catalysts in butanol through transfer hydrogenation.^[9] Notably, Román-Leshkov et al. reported 71% yield of DMF starting from concentrated fructose solutions in 1-butanol using bimetallic CuRu/C.^[3]

To date, experimental studies primarily focus on obtaining high yields of DMF using low concentrations of HMF and precious metal catalysts, but studies addressing the scale-up chal-

lenges of DMF production from HMF hydrogenation are limited at present. Biomass conversion inevitably produces considerable amounts of water and reaction byproducts, and therefore, inexpensive and robust water-tolerant catalysts are of interest for economical industrial processes. Cu-based catalysts were previously reported to exhibit good reaction performance for HMF hydrogenolysis to DMF and furfural to 2-methylfuran, without excessive hydrogenation of the furan ring or ring opening.^[3] Herein, based on reaction kinetics studies, we report the effects of water on HMF hydrogenation and hydrogenolysis reactions over a Cu/ γ -Al₂O₃ catalyst in THF solvent using molecular H₂ as the hydrogen source.

The reaction pathways for HMF hydrogenation and hydrogenolysis to DMF were extensively studied in the literature.^[3,7,11,12,15–18] Scheme 1^[7] displays a typical reaction scheme



Scheme 1. Reaction network for HMF hydrogenation (modified from [7]).

for HMF hydrogenation, where DMF is obtained by either first hydrogenating HMF to 2,5-bis(hydroxymethyl)furan (BHMF) or by hydrogenolysis of HMF to 5-methylfurfural (MF). The furanic compounds can undergo ring hydrogenation and decarbonylation to generate byproducts that are not converted to DMF, such as 2,5-dimethyltetrahydrofuran (DMTHF) and furfuryl alcohol (FA).

We performed studies on HMF conversion reactions in both pure THF and a THF–H₂O mixture to probe the aforementioned reaction scheme as well as to understand the temporal evolution of products formed during HMF hydrogenation over a Cu-based catalyst. Figure 1 displays the concentration profiles of products obtained in both pure THF and THF–H₂O (THF/H₂O = 95:5 w/w) at 448 K using molecular H₂ as the hydrogen source. In the absence of water (i.e., pure THF solvent), HMF hydrogenation led to the hydrogenolysis products DMF, 2-methyl-5-hy-

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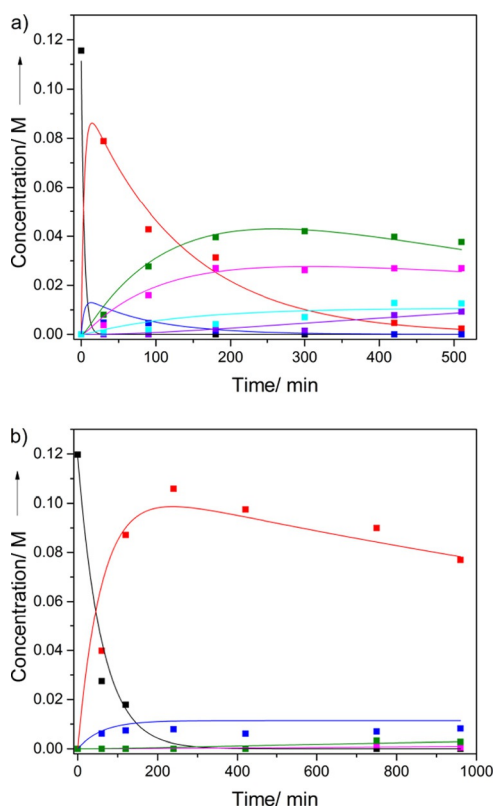


Figure 1. Concentration profiles of HMF, reaction intermediates, and products in (a) pure THF solvent and (b) THF–H₂O mixture (THF/H₂O = 95:5 w/w) at 300 psi H₂ pressure, 448 K, 550 rpm stirring speed, and with Cu/γ-Al₂O₃ catalyst (200 mg in pure THF and 500 mg in THF–H₂O). Data points and lines represent experimental data and model, respectively. The compounds quantified are as follows: HMF (■, —), BHMf (■, —), MF (■, —), MhMF (■, —), DMF (■, —), 12HD (■, —), DMTHF (■, —).

droxymethylfuran (MhMF), and DMTHF, as well as the ring-opened compounds 1,2-hexanediol (12HD) and 2,5-hexanediol (25HD). Key features of the concentration profiles in Figure 1 were then assessed in an attempt to construct a simplified reaction scheme for purposes of reaction kinetics modeling. The primary intermediates formed from HMF were BHMf and MF, which are one-step hydrogenation and hydrogenolysis products from HMF. Further conversions of BHMf and MF to MhMF exhibit the rise and fall of an intermediate concentration profile in a consecutive reaction. In contrast, neither the MhMF profile nor the DMF profile versus time behave as BHMf and MF in consecutive reactions. Instead, they embody the characteristics of being parallel reactions. Specifically, in pure THF solvent the concentration of DMF is always greater than that of MhMF, indicating that DMF is not solely produced from MhMF, as proposed for noble metal catalysts. Therefore, we suggest that over the Cu/γ-Al₂O₃ catalyst used in this study, DMF can also be produced from BHMf. In support of this perspective, the evolution of the selectivity profile is provided in Figure S1 (in the Supporting Information). Furthermore, significant DMTHF production by furan ring hydrogenation was not observed over our Cu-based catalyst in pure THF solvent, whereas DMTHF production from HMF is prevalent with noble metals, such as Pd or Pt^{19,19}. To further explore the absence of

ring hydrogenation over Cu/γ-Al₂O₃, the conversion was carried out with 2 wt% DMF in pure THF solvent to yield 4% of DMTHF after 17 h at the same reaction conditions, demonstrating that Cu is not active for furan ring hydrogenation. Hence, we propose a pathway for DMTHF formation from BHMf.

Our studies of HMF conversion in the THF–H₂O solvent (THF/H₂O = 95:5 w/w) over Cu/γ-Al₂O₃, show that BHMf and MF are the primary products formed, whereas the concentrations of DMF and MhMF remained relatively low throughout the reaction process. The products DMTHF, 12HD, and 25HD were undetected. Previous studies of HMF hydrogenation in biphasic 1-butanol–H₂O reaction systems and in monophasic THF–H₂O reaction systems suggest that degradation product formation originates from BHMf.^[20] The overall selectivity to unidentified products increased when the solvent system was changed from 1-butanol–H₂O to water or to THF–H₂O mixtures, suggesting the involvement of water in degradation reactions for HMF hydrogenation reactions.

Based on previous literature studies as well as our experimental observations for HMF conversion in THF, we suggest that Scheme S1 is initially a reaction network to describe our reaction system. Accordingly, we have used this reaction scheme to build a kinetic model to quantify the reaction kinetics for HMF conversion processes. We then use sensitivity analyses and the Akaike information criterion (see the Supporting Information) to identify the key aspects of this reaction scheme for HMF conversion over the Cu/γ-Al₂O₃ catalyst. After a series of refinements to Scheme S1, we find that the more simplified Scheme 2 achieves the best model fit with the highest number of products and the least number of reaction pathways. Scheme 2 still preserves the aforementioned characteristics of parallel versus consecutive reactions. MhMF hydrogenolysis to DMF (*k*₈), although mechanistically feasible, has a small effect on DMF production compared to BHMf hydrogenolysis to DMF (*k*₄). The rate of 25HD production (*k*₁₁) is combined with the DMF decomposition step (*k*₁₀), because the small amount of 25HD that is produced throughout the reaction does not affect the overall concentration profiles.

The kinetic model developed for describing Scheme 2 is summarized in Equations (1)–(7).

$$r_{\text{HMF}} = -((k_1 + k_2)[\text{HMF}]) \times n \quad (1)$$

$$r_{\text{BHMf}} = (k_1[\text{HMF}] - (k_3 + k_4 + k_5 + k_6)[\text{BHMf}]) \times n \quad (2)$$

$$r_{\text{MF}} = (k_2[\text{HMF}] - k_7[\text{MF}]) \times n \quad (3)$$

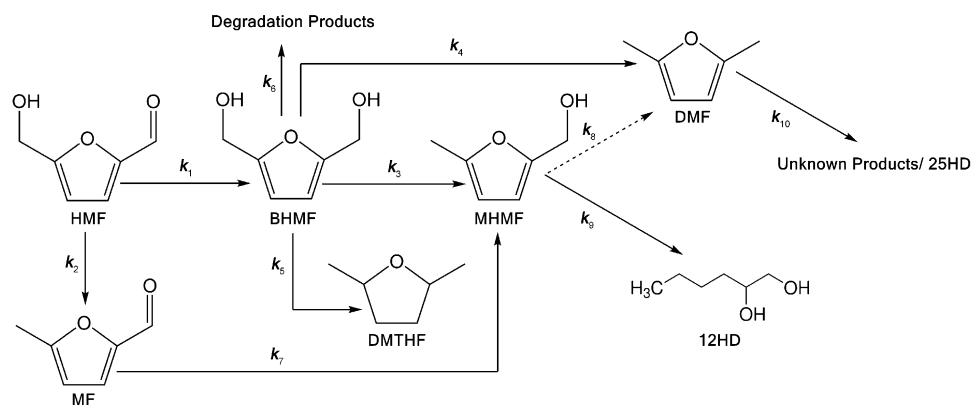
$$r_{\text{DMTHF}} = k_5[\text{BHMf}] \times n \quad (4)$$

$$r_{\text{MhMF}} = (k_3[\text{BHMf}] - k_9[\text{MhMF}]) \times n \quad (5)$$

$$r_{\text{DMF}} = (k_4[\text{BHMf}] - k_{10}[\text{DMF}]) \times n \quad (6)$$

$$r_{12\text{HD}} = k_9[\text{MhMF}] \times n \quad (7)$$

where *r_i* represents the rate of consumption of species *i*, *n* is the number of moles of active sites of the catalyst, [*i*] is the concentration of species *i*, and *k_x* is the apparent reaction rate constant for reaction step *x* in Scheme 2. A first-order rate de-



Scheme 2. Proposed reaction pathway for the hydrogenation of HMF in THF and THF-H₂O mixture catalyzed by Cu/ γ -Al₂O₃.

whereas adsorbed MHMF can undergo a second, consecutive hydrogenation step, converting BHMF to DMF. Furthermore, the product-like reaction profile of MHMF suggests that the re-adsorption of MHMF on the catalyst surface is negligible, possibly owing to the competitive adsorption of BHMF and other reaction products, which is in accord with the results of the sensitivity analyses showing that MHMF hydrogenolysis to DMF (k_8) has a minor effect on the

pendence on reactant concentration was assumed for each step in the reaction network. The information content of the data set is not sufficient to explore the scenario of using different reaction orders for different steps. The application of the Weisz–Prater Criterion (see the Supporting Information) verified the absence of intraparticle mass-transfer limitations.^[21] The dependence of the rate on the gas-phase partial pressure of H₂ was found to be half-order; therefore, the reaction rate is not expected to be dependent on the liquid-phase H₂ concentration, as shown previously (see the Supporting Information).^[22] The H₂ pressure terms were neglected from the rate equations because reactions were carried out at constant pressure.

The simplified reaction kinetics model was used to fit the experimental data (Figure 1) by optimizing the rate constants (k_1 – k_{10}) using nonlinear least squares regression in MATLAB (nlinfit function). Confidence intervals are reported as the 95% confidence level (nlinpci function). Figure 1 demonstrates the ability of the model to describe the experimental data. The optimized rate constants are reported in Table 1. The rate constants were normalized by the total number of surface copper sites of the Cu/ γ -Al₂O₃ catalyst, as measured by N₂O titration, obtaining a surface site density value of $190 \pm 21 \mu\text{mol g}^{-1}$.

Based on the results from our reaction kinetics model using the simplified reaction network (Scheme 2), the rate constant for BHMF hydrogenolysis to DMF (k_4) is more than two orders of magnitude larger than the rate constant for MHMF hydrogenolysis to DMF (k_8). To explore the possibility that deactivation of the Cu/ γ -Al₂O₃ catalyst is responsible for the slow rate of MHMF hydrogenolysis to DMF, a two-step experiment was performed starting with 2 wt% HMF in pure THF and fresh copper catalyst at 448 K and 300 psi H₂ pressure. After 3 h of reaction, the catalyst was removed, fresh catalyst was added to the reactor, and the reactor was heated at 448 K for an additional 2 h. The resulting concentrations of MHMF and DMF remained similar after the addition of fresh catalyst and subsequent reaction, indicating that the suppression of MHMF hydrogenolysis to DMF is not a result of catalyst deactivation. Hence, we propose that BHMF is first adsorbed on the catalyst surface and hydrogenated to MHMF. A portion of the MHMF can desorb,

Table 1. Optimized rate constants (k) for HMF hydrogenation and hydrogenolysis in pure THF and THF-H₂O (THF/H₂O = 95:5 w/w) over Cu/ γ -Al₂O₃.^[a]

Rate constant ^[b]	Pure THF	THF/H ₂ O = 95:5 w/w
k_1	$9.4 \pm 0.9 \times 10^1$	2.6 ± 0.7
k_2	$1.5 \pm 0.6 \times 10^1$	$2.8 \pm 1.5 \times 10^{-1}$
k_3	$6.9 \pm 0.3 \times 10^{-1}$	$2.0 \pm 2.0 \times 10^{-3}$
k_4	2.3 ± 0.3	$6.0 \pm 6.0 \times 10^{-3}$
k_5	$3.7 \pm 1.1 \times 10^{-1}$	$(0-1.0 \times 10^{-2})^{[c]}$
k_6	0	$5.3 \pm 4.3 \times 10^{-2}$
k_7	5.0 ± 3.4	$(0-1.9 \times 10^{-1})^{[d]}$
(k_8)	$(0-8.9 \times 10^{-2})^{[e]}$	(insensitive) ^[e]
k_9	$3.2 \pm 1.5 \times 10^{-1}$	(insensitive) ^[c]
k_{10}	$7.3 \pm 1.9 \times 10^{-1}$	$(0-2.2)^{[c]}$

[a] The values in parentheses indicate results from insensitive reaction pathways (see the Supporting Information for details). As a result, these pathways are not involved in the model fit of Figure 1. [b] The unit for k is (moles of sites)⁻¹ s⁻¹. [c] Insensitivity arises from the lack of product formation. [d] The insensitivity is induced by the minimal amount of MHMF formed. [e] Insensitive pathways arise when compared to more favorable pathways in forming the same products.

production of DMF. An experiment using 1 wt% MHMF in THF under the same reaction conditions was performed to eliminate the possibility of a resulting effect from the low reactivity of MHMF. The selectivity of DMF was 25% after 90 min, suggesting that MHMF hydrogenolysis can proceed without the presence of BHMF and in turn supporting the hypothesis of negligible re-adsorption of MHMF. Similarly, the concentration profile in Figure 1a for BHMF conversion to DMTHF supports our suggestion that several subsequent BHMF hydrogenations occur on the catalyst surface.

The presence of water (i.e., THF/H₂O 95:5 w/w) has significant effects on the reaction rates of HMF hydrogenation and hydrogenolysis. For example, the rate of HMF hydrogenation to BHMF (k_1) and the rate of HMF hydrogenolysis to MF (k_2) decrease by approximately one order of magnitude compared to the reaction in pure THF. Furthermore, the rates of BHMF hydrogenolysis to MHMF (k_3) and DMF (k_4) are both reduced by two orders of magnitude compared to reaction in pure THF. This lower rate of hydrogenolysis compared to hydrogenation

leads to the selective production of BHMF by hydrogenation, while inhibiting DMF production in THF–H₂O solvent mixtures. Moreover, BHMF degradation reactions (k_d) become more significant in the presence of water.

Based on the above results, we suggest that the observed decreases in the rate constants for hydrogenation and hydrogenolysis stem from inhibition of the active sites on Cu/ γ -Al₂O₃ by adsorption of water. The active sites for this reaction system under reducing conditions (i.e., in excess H₂) are likely to be Cu⁰, in view of the active sites reported for furfural hydrogenation and MHMF hydrogenolysis to DMF over copper chromite catalysts.^[23,24] A similar effect was reported for furfural hydrogenation and hydrogenolysis to FA and 2-methylfuran, respectively, over Cu/SiO₂.^[25] The conversion of furfural was reported to be lower after addition of water in the reaction solution owing to the competitive adsorption of water on the Cu surface, leading to decreased rates of furfural conversion. This behavior would be observed if the heat of adsorption of water is comparable to that of furfural and higher than that of FA and 2-methylfuran. Sitthisa et al. reported that the adsorption of furfural proceeds through the strong interaction between the carbonyl oxygen and Cu. The heat of adsorption of furfural on Cu is approximately two or three times higher than that of FA and 2-methylfuran.^[25] The higher heat of adsorption of carbonyl-containing molecules compared to hydroxyl-containing molecules suggests that HMF will be most likely adsorbed on Cu through the carbonyl group as well, behaving similar to furfural.

In summary, the effect of water on HMF hydrogenation and hydrogenolysis was studied over a Cu/Al₂O₃ catalyst using molecular H₂ as the hydrogen source. Based on modeling of the reaction kinetics data, we have found that the addition of 5 wt% water in the THF solvent results in significant decreases in the rates of BHMF formation through HMF hydrogenation and DMF formation through hydrogenolysis. This study demonstrates that the presence of water can result in the delay of the DMF production through HMF hydrogenolysis owing to water coverage on active sites of Cu/ γ -Al₂O₃. This negative effect of water could become particularly important when DMF production processes are scaled up, as biomass conversion in general is accompanied by water production in large quantities.

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