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Carbonate-Catalyzed Room-Temperature Selective Reduction of Biomass-Derived 5-Hydroxymethylfurfural into 2,5-Bis(hydroxymethyl)furan

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Abstract: Catalytic reduction of 5-hydroxymethylfurfural (HMF), deemed as one of the key bio-based platform compounds, is a very promising pathway for the upgrading of biomass to biofuels and value-added chemicals. Conventional hydrogenation of HMF is mainly conducted over precious metal catalysts with high-pressure hydrogen. Here, a highly active, sustainable, and facile catalytic system composed of K₂CO₃, Ph₂SiH₂, and bio-based solvent 2-methyltetrahydrofuran (MTHF) was developed to be efficient for the reduction of HMF. At a low temperature of 25 °C, HMF could be completely converted to 2,5-bis(hydroxymethyl)furan (BHMF) in a good yield of 94% after 2 h. Moreover, a plausible reaction mechanism was speculated, where siloxane in situ formed via hydrosilylation was found to be the key species responsible for the high reactivity.

Keywords: biomass conversion; biofuels; hydrogenation; green chemistry; sustainable catalysis

1. Introduction

As the depletion of traditional energy resources such as coal and petroleum continues, the efficient synthesis of fuels and value-added molecules from biomass is becoming both urgent and essential [1–6]. Among the biomass derivatives, 5-hydroxymethylfurfural (HMF), which can be obtained from sugars (e.g., fructose [7–10] and glucose [11–13]) via dehydration, is hailed as a key platform molecule for producing a variety of valuable products, see Figure 1 [14,15]. For example, catalytic oxidation of HMF can be converted to 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), 2-formyl-5-furancarboxylic acid (FFCA), and 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) [14–17]. On the other hand, HMF can be hydrogenated to 2,5-bis(hydroxymethyl)- furan (BHMF), 1,6-hexanediol, 5-methylfurfural (MF), 2,5-dimethylfuran (DMF), 2,5-dimethoxytetrahydrofuran (DMTHF), and 2,5-dihydroxymethyl-tetrahydrofuran (DHMTHF) using various metals (e.g., Pt, Ru, Pd, Cu, Zr) on different supports (e.g., C, SiO₂, Co₃O₄) [17–22]. As one of promising bio-based downstream products, BHMF can be applied in the preparation of various functional materials (e.g., polymers, resins, crown ethers, and artificial fibers), and used as versatile scaffolds in the preparation of medicines and relevant bioactive compounds [23].



Figure 1. Schematic illustration for upgrading bio-based HMF to value-added products. (HMF: 5-hydroxymethylfurfural, BHMF: 2,5-bis(hydroxymethyl)-furan, FDCA: 2,5-furandicarboxylic acid, DFF: 2,5-diformylfuran, FFCA: 2-formyl-5-furancarboxylic acid, DMF: 2,5-dimethylfuran, HMFCA: 5-hydroxymethyl-2-furancarboxylic acid, DHMTHF: 2,5-dihydroxymethyl-tetrahydrofuran, DMTHF: 2,5-dimethoxytetrahydrofuran, MF: 5-methylfurfural).

In most cases, the efficient catalytic hydrogenation of HMF into BHMF mainly occurs over precious metals (e.g., Ru, Pd) [20,24], or transition metals (e.g., Cu) [25–28] under a relatively high pressure of H₂ (1-10 MPa), see Table 1. The employed metallic catalysts are typically expensive, with relatively harsh reaction conditions [20,25]. Likewise, transfer hydrogenation using alcohol (e.g., ethanol, 2-propanol) or formic acid as the liquid hydrogen source has also attracted much attention from many researchers [21,25,29–32]. However, the use of formic acid may lead to the corrosion of the equipment and metal leaching, while the alcohol can further react with BHMF by etherification to reduce its selectivity [33]. Thereby, it is still essential to explore cheap and green alternative catalytic systems for the reduction of HMF to BHMF in high efficiencies.

Table 1. Activity comparison with previously reported results of HMF-to-BHMF hydrogenation.

Entry	Catalyst	Temperature (°C)	Time (h)	Mole/Pressure of H-Donor	Yield (%)	Conversion (%)	Reference
1	Pd/C	80	20	10 MPa H ₂	82	97	[19]
2	Ru/CeO_x	130	2	2.7 MPa H_2	81	100	[23]
3	Ru-Mg–Zr	130	2	2.72 MPa H_2	94		[23]
4	Cu/C	180	8	5 MPa H_2	53.3	70	[24]
5	Ru/CoNi-LDO	180	4	1 MPa H_2^-	49.9	100	[27]
6	Cu(50)-SiO ₂	100	4	1.5 MPa H_2	93	95	[28]
7	$ZrO(OH)_2$	150	2.5	ethanol	83.7	94.1	[29]
8	ZrBa(3)-SBA	150	2.5	isopropanol	55.4	58.8	[30]
9	Cu/AlO_x	220	CF ^a	1,4-butanediol	93	94	[25]
10	Ru/Co_3O_4	190	6	isopropanol	82.8	100	[20]
11	Cm*Ru(HTsDPEN)	40	2	formic acid	99	100	[31]
12	Pd/C	70	4	formic acid	94	-	[32]
13	K ₂ CO ₃	25	2	Ph ₂ SiH ₂	94	100	This work
^a CF: Continuous flow.							

Hydrosilylation of carbonyl compounds to siloxanes shows great potential in the selective synthesis of alcohols [34,35]. This type of conversion process is very attractive because the used silanes are a water- and air-stable hydrogen source, which is able to be stimulated by metal-containing

catalysts under mild conditions [22,36–40]. In addition, the strongly basic solvent used was proposed to facilitate its coordination with the catalytically active species (e.g., carbonate) [41], which is favorable for the reaction with silane to release hydride. In this regard, 2-methyltetrahydrofuran (MTHF) with relatively strong Lewis basicity [42], which is derivable from renewable lignocellulosic biomass [43], may have the superior capability to promote the hydrogenation of carboxides using hydrosilanes and is also preferable to protect the environment [44–46]. These features make MTHF a very attractive solvent for organic reactions, potentially in the efficient synthesis of BHMF from HMF.

In the present work, potassium carbonate, an abundant, readily available, and cost-effective salt, is developed to be highly efficient for chemoselective hydrogenation of HMF into BHMF at room temperature employing Ph_2SiH_2 and MTHF as the hydrogen source and solvent, respectively. The effects of different experimental parameters, including various catalysts, solvent type, reaction time, catalyst dosage, and hydrosilane amount on the reaction activity were studied. In addition, the reaction mechanism was also elucidated.

2. Results and Discussions

2.1. Effect of Different Catalysts

The reactivity of various catalysts on the synthesis of BHMF from HMF was first studied using Ph₂SiH₂ as an H-donor at room temperature in MTHF. Without a catalyst, no reaction took place, see Table 2, entry 1, indicating that the reaction was chemically stable at examined conditions (room temperature for 2 h). The presence of K_2CO_3 was found to be highly efficient for the hydrogenation of HMF (100% conversion) under identical conditions, giving BHMF in 70.1% yield, see Table 2, entry 2. Gratifyingly, after post-treatment with methanol, a much higher BHMF yield (94.2%) was obtained, see Table 2, entry 3. The relatively lower selectivity toward BHMF without methanol treatment was due to the formation of the siloxane intermediate, as identified by LC-MS, see Figure S1, while the addition of methanol could facilitate the breakage of the siloxane bond to give BHMF in high selectivity. By comparison, almost no reaction occurred when employing Li₂CO₃, Na₂CO₃, KCl, CaCO₃, or SrCO₃ as a catalyst (entries 6–10), while KHCO₃ and CH₃COOK gave no more than 40% BHMF yield at an HMF conversion of around 50% (entries 4 and 5). These results indicated that both cations and anions played a crucial role in the reaction. With the increase of the cation radius, the salt ionic property increased, thus showing enhanced solubility [47]. Among the alkali/alkaline earth metals, K⁺ (with a relatively larger ionic radius) allows the paired carbonate to be more freely available to contact the hydrosilane and substrate. Apart from the cation, the influence of the anion on the reaction is not negligible, mainly with respect to its basicity that has a positive correlation with nucleophilicity. In this regard, carbonate with good accessibility and relatively high nucleophilicity is more prone to attack and activate the silane, Ph_2SiH_2 , to release hydride [47]. In view of the superior BHMF yield, K_2CO_3 was chosen as the optimized catalyst for the reduction process.

Entry	Catalyst	Yield (%)	Conversion (%)
1	none	0	0
2	K_2CO_3	70.1	100
3 a	K_2CO_3	94.2	100
4	KHCO ₃	40.0	53.1
5	CH ₃ COOK	35.0	50.2
6	Li ₂ CO ₃	0	<1
7	Na ₂ CO ₃	0	<1
8	KCl	0	0
9	CaCO ₃	0	0
10	SrCO ₃	0	<1

Table 2. The results for reduction of HMF to BHMF over difference catalysts.

Reaction conditions: HMF (0.5 mmol), catalyst (0.1 mmol), Ph_2SiH_2 (1.4 mmol H⁻), MTHF (2 mL), 25 °C, and 2 h. ^a After the reaction, 3 mL methanol was added into the resulting mixture, followed by stirring under ambient conditions for 30 min.

2.2. Influence of Reaction Time

In the assistance of the optimized catalyst, K_2CO_3 , the influence of the reaction time on the hydrogenation of HMF to BHMF was studied. All experiments were conducted at 25 °C with the reaction time of 0.5–6 h and the results are displayed in Figure 2. Both the yield of BHMF and the conversion of HMF increased with prolonging the time-course from 0.5 h to 2 h, demonstrating that a comparatively longer reaction time could promote the formation of BHMF. However, the BHMF selectivity decreased as the time was extended to 4 h, possibly due to generating cross-linked siloxanes. These results obviously revealed that the hydrogenation of HMF to BHMF employing this facile and benign catalytic system was extremely selective and active, in comparison with other previous ones utilizing H₂, alcohol, or formic acid as the hydrogen source, see Table 1. Therefore, 2 h and 25 °C were chosen to be the optimized reaction time and temperature, respectively, with K_2CO_3 as the catalyst for the subsequent study.



Figure 2. The effect of reaction time on the reduction of HMF into BHMF. (Reaction conditions: HMF (0.5 mmol), K₂CO₃ (0.1 mmol), Ph₂SiH₂ (1.4 mmol H⁻), MTHF (2 mL), and 25 °C; After the reaction, 3 mL methanol was added into the resulting mixture, followed by stirring under ambient conditions for 30 min.)

2.3. Influence of Various Solvents

The effect of the used solvents in the reduction reaction was also investigated. MTHF, an aprotic solvent, with relatively high polarity, displayed high HMF conversion (100%) and satisfactory BHMF yield (94%), see Figure 3. In contrast, the solvents (e.g., DCM, 1,4-dioxane, CH₃CN, THF, and GVL) with relatively low polarity exhibited inferior performance, affording BHMF in yields of 20.1%, 25.2%, 60.0%, 67.1%, and 70%, respectively. A solvent with moderate polarity could affect the solvent–reactant interactions [48,49], where the increased interaction of HMF and solvent might promote the formation of BHMF. On the other hand, the solubility of Ph₂SiH₂ can also be enhanced by compatible polarity of the solvent, thereby facilitating the interaction of Ph₂SiH₂ with the catalyst to release H⁻. Overall, the appropriate interaction between the solvent, hydrosilane, and catalyst can facilitate the release of hydride to attack HMF, thus giving BHMF in a good yield.



Figure 3. Effect of solvent type on reduction of HMF into BHMF. (Reaction conditions: HMF (0.5 mmol), K_2CO_3 (0.1 mmol), Ph_2SiH_2 (1.4 mmol H⁻), solvent (2 mL), 25 °C, and 2 h; After the reaction, 3 mL methanol was added into the resulting mixture, followed by stirring under ambient conditions for 30 min.)

2.4. Influence of Different Hydrosilanes

The influence of various hydrosilanes on the catalytic reduction of HMF into BHMF was studied by using K₂CO₃ as the catalyst, see Table S1. Among the employed simple silanes, phenylsilane (PhSiH₃) and diphenylsilane (Ph₂SiH₂), see Table S1, entries 5 and 6, revealed relatively higher yields of BHMF, which might be due to their superior hydride-donating capability [50]. Although the conversion of HMF reached 100% with PMHS as an H-donor, the obtained BMHF yield was relatively low (66.0%). The possible reason is that PMHS might react with products and substrates, forming insoluble PMHS-derived resin in a relatively large molecular weight under alkaline conditions, see Figure S2B. Even after adding methanol, the formed solid was not completely dissolved, see Figure S2C, indicating the relatively stable resin structure. It can be speculated that some of the formed silicon–oxygen bonds could not be cleaved during the post-treatment with methanol, thus impeding the formation of BHMF with a high selectivity. In view of the superior BHMF yield, Ph₂SiH₂ as a comparatively cheap hydrogen source was screened out for further optimization of HMF hydrogenation.

2.5. Influence of Ph₂SiH₂ Dosage

The Ph₂SiH₂ dosage was found to have a significant effect on BHMF synthesis, as shown in Figure 4. As the dosage of Ph₂SiH₂ rose from 0.05 to 0.7 mmol, the yield of BHMF was observed to increase from 20.0 to 94.2%, accordingly. Nevertheless, when the PMHS dosage was more than 0.7 mmol, the BHMF yield was decreased despite constant HMF conversion. The decline in the yield of BHMF was most likely caused by the reaction of excessive Ph₂SiH₂ with potassium carbonate and BHMF to form cross-linked siloxanes that are too stable to hydrolyze even proceeding post-treatment with methanol. In a word, the use of 0.7 mmol Ph₂SiH₂ was favorable to attain the highest BMHF yield at 25 °C for 2 h in MTHF.



Figure 4. Effect of H⁻ dosage of Ph₂SiH₂ on the reduction of HMF into BHMF. (Reaction conditions: HMF (0.5 mmol), K₂CO₃ (0.1 mmol), MTHF (2 mL), 25 °C, and 2 h; After the reaction, 3 mL methanol was added into the resulting mixture, followed by stirring under ambient conditions for 30 min.)

2.6. Influence of Catalyst Dosage

The effect of the K₂CO₃ dosage on the production of BHMF from HMF under the optimal conditions was further investigated at 25 °C over a period of 2 h, see Figure 5. When the K₂CO₃ dosage increased from 0 to 0.1 mmol, the conversion of the HMF and BHMF yield rose to 100% and 94.2%, respectively. However, as the catalyst dosage was beyond 0.1 mmol, the yield of BHMF displayed a remarkable reduction, which could be attributed to BHMF adsorption onto the surface of solid K₂CO₃, thus inhibiting the alcoholysis of the siloxane intermediate to release the product BHMF [32]. In addition, the fast depletion of Ph₂SiH₂ was most likely to occur by forming pentavalent silicate species ((Ph₂SiH₂)-CO₃) with carbonate [51]. Although the pentavalent silicate species were active for hydrogenating carboxides [52], serious polymerization was prone to happen due to utilizing superfluous K₂CO₃ (e.g., 0.25 mmol), hence possibly decreasing the catalyst activity.



Figure 5. Influence of K_2CO_3 dosage on synthesis of BHMF from HMF. (Reaction conditions: HMF (0.5 mmol), Ph₂SiH₂ (1.4 mmol H⁻), MTHF (2 mL), 25 °C, and 2 h; After the reaction, 3 mL methanol was added into the resulting mixture, followed by stirring under ambient conditions for 30 min.)

2.7. Reaction Mechanism for HMF-to-BHMF Hydrogenation

To explicitly interpret the reaction mechanism for hydrogenating HMF to BHMF, ex situ ¹H NMR spectra were recorded at 25 °C in the time course of 0.5–2 h, see Figure 6. The aldehydic proton **1a** of HMF gradually disappeared, while the protons of hydroxyl **2c** and methine of the furan ring **2a** of BHMF were also detected and significantly enlarged by further extending the reaction duration. The mechanism for the hydrogenation of aldehydes or ketones catalyzed by K₂CO₃ was thus proposed to be very similar to the reduction process of amides [53], where Ph₂SiH₂ might act as an H-donor to promote the reduction of HMF to BHMF, as demonstrated by in situ NMR in our previous study [39]. The possible reaction mechanism of the hydrogenation of HMF to BHMF is shown in Scheme **1**. Initially, the interaction of a Lewis base (carbonate) and Ph₂SiH₂ forms a high-valency silicate species, which is a nucleophile in nature [54] and can activate the aldehyde group by hydride transfer to afford the siloxane intermediate, followed by hydrolysis to give BHMF. This catalytic system is simple to operate and does not produce observable byproducts during the reduction process, compared with other previous reaction systems [26,27].

To make our process more promising for real application, relatively stable sugar like fructose has been used as the starting material instead of unstable HMF. It was found that a moderate yield of BHMF (66%) could be obtained via a one-pot two-step reaction process separately catalyzed by Amberlyst-15 and K_2CO_3 . This sequential process makes the biomass derivative HMF a promising platform molecule for the production of value-added chemicals.



Figure 6. Ex situ ¹H NMR spectra of hydrogenating HMF to BHMF at 25 °C in 0.5–2 h. (Reaction conditions: HMF (0.5 mmol), Ph_2SiH_2 (1.4 mmol H⁻), K_2CO_3 (0.1 mmol), and MTHF (2.0 mL); After the reaction proceeded for 2 h, 3 mL CD₃OD was added into the resulting mixture, followed by stirring under ambient conditions for 30 min.)



Scheme 1. Plausible reaction pathway for the HMF-to-BHMF reduction.

3. Materials and Experiments

3.1. Materials

5-hydroxymethylfurfural (HMF, 99%), 2,5-bis(hydroxymethyl)furan (BHMF, 99%), phenylsilane (97%), polymethylhydrosiloxane (PMHS, 99%), triethoxysilane (97%), diphenylsilane (97%), deuterated dimethyl sulfoxide (DMSO- d_6 , 99.8 at.% D), deuterated methanol (CD₃OD, 99.8 at.% D), 1,4-dioxane (99%), potassium carbonate (K₂CO₃, 99%), gamma-valerolactone (GVL, 99%), naphthalene (99%), methanol (99%), triethylsilane (99%), trimethoxysilane (99%), Amberlyst-15 (>99%), fructose (>99%), and 1,1,3,3-tetramethyldisiloxane (97%) were bought from Innochem Technology Co., Ltd. (Beijing, China). Tetrahydrofuran (THF, 99%) was bought from Shanghai TCI Develop. Co., Ltd. (Shanghai, China). Lithium carbonate (Li₂CO₃, 99%) and sodium carbonate (Na₂CO₃, 99%) were purchased from Aladdin Ind. Inc. (Shanghai, China). Potassium bicarbonate (KHCO₃, 99%), potassium chloride (KCl, 98%), acetonitrile (MeCN, 99%), 2-methyltetrahydrofuran (MTHF, 99%), and dichloromethane (DCM, 99%) were bought from Sigma-Aldrich Co. LLC. (Shanghai, China). Other used chemicals were of analytical grade without further purification, unless stated otherwise.

3.2. Procedures for Catalytic Reduction of HMF into BHMF

The tested reactions were all conducted in Ace pressure tubes (15 mL). In a general reaction process, 0.5 mmol HMF, 0.1 mmol K_2CO_3 , 2.0 mL MTHF, and 0.7 mmol Ph₂SiH₂ were added into the reactor and sealed. Afterwards, the tube was moved into an oil-bath under magnetic stirring at 400 rpm for a certain period. The zero time was established when the reactor was placed in the bath (25 °C). Upon completion, methanol (3 mL) was added into the resulting mixture, followed by stirring under ambient conditions for 30 min to proceed alcoholysis of the siloxane intermediate. Then, the resulting reaction solution was filtered to remove solid particles, while the yield of BHMF was quantified by GC and the conversion of HMF was analyzed by HPLC. When fructose (0.5 mmol) instead of HMF was used as the substrate, an additional reaction process under otherwise identical reaction conditions. All the reactions were repeated three times, and the obtained results were the average values of three individual experiments, with a standard deviation (σ) of 0.5–4.2%.

3.3. Analytical Methods 1100 (Agilent Technologies) system

HMF conversion was analyzed by HPLC (1100 series, Agilent Technologies Inc., CA, USA) equipped with a refractive index detector, an ultraviolet detector (λ = 284 nm), and an Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA, USA). The column temperature was set at 25 °C, and the mobile phase used was acetonitrile/0.1 wt.% acetic acid aqueous solution (30:70, *v*/*v*) at a flow rate of 1.0 mL min⁻¹ (HMF retention time: 3.7 min). BHMF was quantitatively analyzed by an Agilent 7890B GC (Agilent Technologies Inc., Santa Clara, CA, USA) fitted with a flame ionization detector and an HP-5 column. Analysis conditions were optimized as 1 µL injection volume, 0.7 mL/min nitrogen

carrier gas, 75:1 split ratio, with injector and detector temperatures of 240 and 280 °C, respectively; oven temperature programmed from 60 °C (keeping for 1 min) to 100 °C at a rate of 5 °C/min, then raised to 270 °C (keeping for 2 min) at a rate of 10 °C/min (BHMF retention time: 14.7 min). Naphthalene (10 mg) was used as an internal standard. The products were quantified based on the standard curves of the corresponding commercial reagents ($R^2 \ge 0.9997$). In addition, liquid products were identified by GC-MS (6890N GC/5973 MS, Agilent Technologies Inc., CA, USA), while a siloxane intermediate was identified by liquid chromatography/mass spectrometry (LC-MS) (Ultimate 3000 LC/Q Exactive MS, Thermo Fisher Scientific, San Jose, CA, USA).

3.4. Reaction Time-Course Study

For the time-course study of the reaction with NMR, after the reaction had proceeded for a specific time (0.5–2 h), 3 mL deuterated methanol was added into the reaction solution, followed by stirring under ambient conditions for 30 min, and then 0.5 mL of the reaction solution was taken. ¹H NMR spectra of the reaction mixtures were performed using an NMR spectrometer (JEOL-ECX 500, JEOL, Tokyo, Japan).

4. Conclusions

In this work, a benign and efficient catalytic protocol was developed for selective hydrogenation of HMF into BHMF in good yields (ca. 94%) at room temperature for 2 h, using abundant, readily available, and cost-effective K₂CO₃ as the catalyst, eco-friendly Ph₂SiH₂ as the hydrogen source, and green and renewable MTHF as the solvent. The developed silane-mediated catalytic system was extremely active and selective, in comparison with previous reports that use noble or transition metals as a catalyst while H₂, formic acid, or alcohol as the hydrogen source. The mechanistic study illustrated the reaction proceeded via the hydrosilylation process with a high-valency silicate species as the key hydride species formed by the activation of Ph₂SiH₂ with carbonate, which can greatly facilitate the hydride transfer toward the aldehyde group to afford the siloxane intermediate. Subsequently, BHMF is obtained by the in situ hydrolysis of the siloxane intermediate, which can be significantly promoted by post-treatment with methanol. Moreover, this catalytic system is simple to operate and produces fewer byproducts during the process, exhibiting great promise for biomass upgrading.

Supplementary Materials: The Supplementary Materials are available online at http://www.mdpi.com/2073-4344/8/12/633/s1. Figure S1. LC-MS spectrum of the siloxane intermediate obtained in the hydrogenation of HMF to BHMF; Figure S2. Images of the K₂CO₃-catalyzed hydrogenation of HMF to BHMF using PMHS as H-donor; Figure S3. GC-MS spectrum of BMHF obtained from hydrogenation of HMF; Figure S4. GC-MS spectrum of dimethoxydiphenylsilane obtained from the interaction of Ph₂SiH₂ and MeOH; Table S1. Effect of different hydrosilanes on the hydrogenation of HMF to BHMF.

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Conflicts of Interest: There are no conflicts to declare.

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