



Short Communication

Carbocatalyst in biorefinery: Selective etherification of 5-hydroxymethylfurfural to 5,5'-(oxy-bis(methylene))bis-2-furfural over graphene oxide



Hongliang Wang^{a,b}, Yinxiong Wang^a, Tiansheng Deng^a, Chengmeng Chen^a, Yulei Zhu^{a,c}, Xianglin Hou^{a,*}

^a Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, People's Republic of China

^b Graduate University of Chinese Academy of Sciences, Beijing, People's Republic of China

^c State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, People's Republic of China

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ABSTRACT

Hydroxymethylfurfural (HMF) is an important biomass based building block which can be efficiently produced from carbohydrates, while the utility of HMF warrants further exploration. Herein, we explored a green method for the transformation of HMF into a symmetrical ether named 5'-oxy(bis-methylene)-2-furfaldehyde (OBMF) promoted by graphene oxide (GO). HMF conversion in no-polar solvents was obviously higher than that in polar solvents. Water existed in the reaction system could significantly decrease the OBMF yield. Moreover, the high catalytic performance of GO was closely related to oxygen containing groups on GO. A maximum OBMF yield of 86% was obtained under optimized conditions.

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1. Introduction

The preparation of chemicals from bioresources rather than steadily depleting fossil resources has become a vital necessity for the sustainable chemical industry [1–3]. In this respect, one of the most widely envisioned approaches is to develop efficient processes, especially efficient and no-toxic catalysts, to transform biomass into some platform molecules and further converse these platform molecules into various chemicals [4–6]. 5-Hydroxymethylfurfural (HMF), which can be produced from dehydration of hexose, has been considered as a vital platform molecule in biorefinery processes [7,8]. It can be used to synthesize a broad range of furan derivatives with great potential used in the production of fuels, pharmaceuticals and polymers [9,10]. The synthesis of 5'-oxy(bis-methylene)-2-furfaldehyde (OBMF) from etherification of two HMF molecules is of much interest due to the versatile applications of OBMF. OBMF can not only be used as a monomer for the preparation of some imine-based polymers with high thermal and electrical conductivity [11], but also can be used for the synthesis of heterocyclic ligands and hepatitis antiviral precursors [12].

Homogeneous organic acids, especially para-toluenesulfonic acid (*p*-TSA), were used for the conventional synthesis of OBMF. For example, Musau and Munavu reported 58% yield of OBMF could be

obtained through etherification of HMF over *p*-TSA catalysis under Dean–Stark conditions in toluene [13]. Besides, treatment of HMF and 5-chloro-methyl-2-furfural under Williamson reaction condition can also yield OBMF. However, large amounts of residues and by-products were generated when homogeneous acids or bases were used. Solid acids were studied with the aim of improving the OBMF yield. In this respect, Corma and co-workers introduced structured micro- and mesoporous aluminosilicates as solid acids for the etherification of HMF to OBMF. They found that Al-MCM-41 exhibited an excellent performance owing to its suitable acidity, small diffusion constraint and good adsorption property [14]. Recently, nanocarbons especially graphene and its derivatives have attracted tremendous interest for the development of advanced green catalysts [15,16]. Graphene oxide (GO) functioned as a precursor to produce graphene can be readily prepared through the oxidative exfoliation of graphite. The existence of various oxygen-containing functionalities (e.g. alcohols, epoxides, carboxylates, sulfate groups) in GO suggests that it has good adsorption property and suitable acidity. Moreover, the specific two-dimensional structure of GO can minimize the diffusional constraints. There were already some studies that introduced GO as a green acid catalyst for organic synthesis reactions [17,18]. Yu et al. reported GO as a promising catalyst for the dehydrative etherification of benzyl alcohol to dibenzyl ether [18]. They found that GO exhibited high catalytic activity and good selectivity in the reaction, and the maximum dibenzyl ether yield can be reached to 85.4%.

* Corresponding authors. Tel.: +86 351 4049501; fax: +86 351 4041153.
E-mail address: houlx@sxicc.ac.cn (X. Hou).

In this work, we present the use of GO as an efficient heterogeneous catalyst for the synthesis of OBMF from HMF under mild reaction conditions, see Scheme 1. The effects of solvent, catalyst loading, water removal, reaction time and temperature on the yield of OBMF have been carefully studied.

2. Materials and methods

2.1. Materials

HMF (99%) was purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China) and organic solvents (analytical grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received and without further purification. Graphene oxide (GO) was prepared by a modified Hummers' method [19], see supplementary information.

2.2. Catalytic experiments

HMF etherification reaction was carried out in a 10 mL stainless steel micro-autoclave with a Teflon lining and sealed by a screw cap or in a 25 mL round bottom flask reactor equipped with an inverse Dean–Stark trap. A thermostatic oil bath was used as heating source. The mixture was stirred by a small magnetic bar during the reaction. After the reaction, GO was separated by filtration and washed with water and 95% ethanol for several times before reusing. The detailed analysis method was giving in the supplementary information.

3. Results and discussion

3.1. Effect of the reaction medium on HMF conversion and OBMF selectivity

Yu et al. used GO for the catalytic etherification of benzyl alcohol to dibenzyl ether in a solvent-free environment, and good results have been achieved [18]. Thus, the etherification of HMF to OBMF was initially carried out without using any solvent. As listed in Table 1, in an optimized experiment, when 63 mg HMF mixed with 20 mg GO and reacted at 130 °C for 8 h in a sealed micro-autoclave, the HMF conversion and OBMF selectivity were detected to be 61% and 68%, respectively. Next, different polar and non-polar solvents were employed with the aim to improve the yield of OBMF. Both the conversion of HMF and the selectivity of OBMF were found to be improved when 0.5 mL dichloromethane (CH₂Cl₂) was added. Besides, it was discovered that the conversion of HMF in polar solvents (water, DMSO, DMF) was obviously lower than that in non-polar solvents (CH₂Cl₂, toluene). It is known that the coupling of alcohols to ethers on the surface of solid catalysts usually proceeds via S_N2 reactions [20]. It involves the in situ formation of an oxonium ion at the surface of catalyst followed by a nucleophilic bimolecular substitution [21]. Solvents have strong effects on the activation free energy of S_N2 reactions. Dimethylsulfoxide (DMSO) and dimethylformamide (DMF) are polar aprotic solvents with high dielectric constant and rich lone pair electrons, and they are not in favor of oxonium ion formation. However, the formation of an oxonium ion is

Table 1

Etherification of HMF into OBMF with graphene oxide as an acid catalyst.^a

Entry	Solvent	GO loading (mg)	HMF conversion (%)	OBMF selectivity (%)
1	–	20	61	68
2	Water	20	34	15
3	DMSO	20	27	12
4	CH ₂ Cl ₂	20	74	83
5	Toluene	20	81	34
6	4-Chlorotoluene	20	71	68
7	DMF	20	51	27
8	CH ₂ Cl ₂	0	–	–
9	CH ₂ Cl ₂	10	56	86
10	CH ₂ Cl ₂	30	83	69
11 ^b	CH ₂ Cl ₂	20	98	88
12 ^b	Toluene	20	98	61

^a Reaction conditions: 63 mg HMF was dissolved in 0.5 mL solvent and reacted at 130 °C for 8 h in a micro-autoclave.

^b Reaction conditions: 63 mg HMF was dissolved in 0.5 mL solvent and reacted at 100 °C for 8 h in a round-bottomed flask with water removal trap.

the key process in the dehydration of alcohols to ether over solid catalysts, and it is usually facilitated by electron withdrawing solvents.

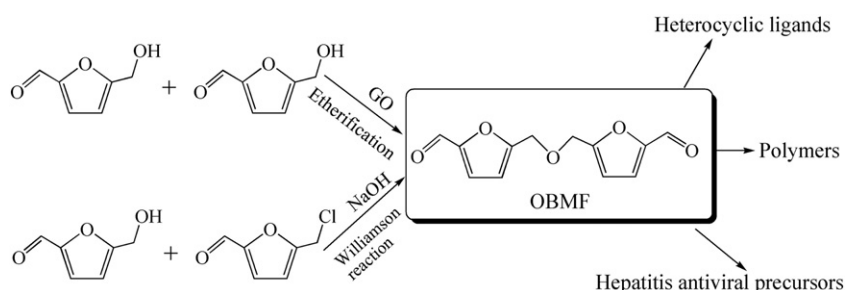
Water is not an effective solvent for this reaction, since it can induce serious side reactions such as HMF rehydration and polymerization which are also promoted by acid catalysts. Besides, water is a main product of the etherification reaction, and thus it is not favorable for the equilibrium shift to the side of OBMF production. When toluene was used as the solvent, the conversion of HMF was high, while the selectivity of OBMF was rather low. This result is probably due to that toluene with an activated aromatic ring can aroused serious alkylation reaction [11]. When 4-chlorotoluene, a deactivated aromatic solvent, was used for the replacement of toluene in the reaction, it was discovered that the conversion of HMF had a little drop (71%) but the selectivity of OBMF had a significant improvement (68%). Thus it can be concluded that solvents with a deactivated aromatic ring and adequate polarity are suitable for this reaction.

3.2. Effect of the catalyst loading on HMF conversion and OBMF selectivity

The GO loading has an obvious effect on the reaction. No conversion of HMF to OBMF was observed without adding any catalyst. The HMF conversion decreased from 74% to 63% when the GO loading was decreased from 20 mg to 10 mg, while the OBMF selectivity had a slight improvement from 83% to 86%. The low conversion of the reactant can be attributed to the insufficiency of catalytic active sites. On the contrary, when the GO loading was increased to 30 mg, the HMF conversion was improved to 83%, however the OBMF selectivity was decreased to 69%. Thus, the optimal GO loading was to be 20 mg for the reaction.

3.3. Effect of water removal on the HMF etherification reaction

As was described above, the conversion of HMF was relatively low, even if in an optimized experiment it was no more than 85%. Since water was produced during the etherification reaction, it may had



Scheme 1. Synthesis and applications of OBMF.

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