



Catalytic synthesis of 2,5-bis-methoxymethylfuran: A promising cetane number improver for diesel

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ABSTRACT

Efficient hydrogenation of 5-hydroxymethylfurfural (HMF) into 2,5-bis-hydroxymethylfuran (BHMF) was performed using a Cu/SiO₂ catalyst, obtaining as high as 97% BHMF yield. In the presence of acidic ZSM-5 zeolite (HZSM-5), the synthesized BHMF further reacted with methanol, leading to 70% yield of corresponding 2,5-bis-methoxymethylfuran (BMMF). The target product BMMF was an excellent cetane number improver for diesel, proved by its cetane number of 80 (much higher than that of the commercial diesel), high flash point (90 °C) and low cold filter plugging point (<−37 °C).

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1. Introduction

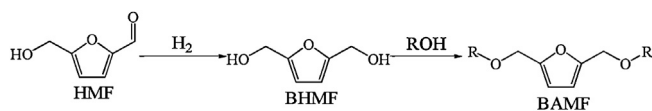
Modern energy supplies are mainly based on fossil resources, including petroleum, coal and natural gas, which are rapidly depleted due to growing fuel consumption. Therefore, scientists are keen to convert the abundant biomass feedstock into liquid fuels or fuel additives from the perspective of sustainable chemistry [1]. 5-Hydroxymethylfurfural (HMF), a high boiling point furanic compound produced from the dehydration of biomass-derived carbohydrates, is viewed as a key intermediate [2]. Plentiful work has already been carried out on conversion of HMF into fuels and chemicals [3]. As HMF itself is oxygen-rich and non-volatile, it is necessary to lower the polarity and the boiling point to obtain liquid fuels or fuel additives derived from HMF. Several potential fuel products such as 2,5-dimethyl-furan (DMF), 2,5-dimethyl-tetrahydrofuran (DMTHF), methyl levulinate (LM) and γ -valerolactone (GVL) have been obtained from HMF [4–9].

Recently, another group of HMF derivatives, 2,5-bis-alkoxymethylfurans (BAMF), has attracted attention and they are regarded as potential bio-diesel candidates [9,10–12]. As shown in Scheme 1, BAMF is synthesized from HMF hydrogenation into 2,5-bis-hydroxymethylfuran (BHMF) and subsequent etherification of BHMF with different alcohols. Among those, methanol and ethanol are both ideal choices. Methanol is the cheapest monohydric alcohol at present for its easy access from syngas and ethanol can be readily gained from the fermentation of renewable cellulose or starch with its price reasonable to be used as a liquid fuel. The synthesis of fuels from methanol and ethanol has already been reported in previous studies. As reported in the literature, PtSn/Al₂O₃ and Amberlyst-15 catalysts can convert HMF into 2,5-bis-(ethoxymethyl)-furans (BEMF) [10] and such a catalytic system may even be applicable to 2,5-bis-(methoxymethyl)-furans (BMMF) synthesis. Despite that, PtSn/Al₂O₃ hydrogenation catalyst can only achieve about 80% selectivity in converting HMF into BHMF with over 10% by-products produced. Whether Amberlyst-15 is the best choice among the solid acid catalysts for the etherification of BHMF with methanol still remains to be further investigated. Moreover, the physical properties especially the cetane number that makes BAMF suitable to be used as a diesel additive have not been investigated yet.

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Scheme 1. Reaction pathways for the synthesis of BAMF from HMF.

In this work, a novel catalytic system to convert HMF into BMMF was developed. A low-cost supported Cu/SiO₂ catalyst is employed in the efficient hydrogenation of HMF into BHMF. Then in the presence of HZSM-5, the synthesized BHMF further reacts with methanol to produce 2,5-bis-methoxymethyl-furan (BMMF). The physical properties of BMMF such as its cetane number, flash point and cold filter plugging point are presented.

2. Experimental

2.1. Materials

5-Hydroxymethylfurfural (HMF, ≥99%) was obtained from WujiangYingChuang Chemical Reagent Co., Ltd. Methanol was purchased from Guangzhou Jinhua Chemical Reagent Co., Ltd. Cu/SiO₂ hydrogenation catalyst was from Liaoning Haitai Scientific and Technological Development Co., Ltd and was used without pre-reduction. Acidic β-zeolite molecular sieve (Si/Al = 25), acidic ZSM-5 zeolite (Si/Al = 25, 38, 300) were all from the Catalyst Plant of Nankai University. No. 0 diesel was obtained from the local gas station. No. 3: A molecular sieve was from Shanghai Hengye Chemical Engineering Co., Ltd. Amberlyst-15 (600–850 μm) was from Sigma-Aldrich.

2.2. Typical experimental procedures

Hydrogenation of HMF was carried out in a 250 mL autoclave. 0.5 g Cu/SiO₂ catalyst and 10 g HMF pre-dissolved in 50 mL methanol were charged into the autoclave, which was purged three times and then pressurized to 2.5 MPa with H₂. Zero time and mechanical stirring started after the autoclave was heated to 100 °C. After the reaction had proceeded for 8 h, the autoclave was cooled down to room temperature. The Cu/SiO₂ catalyst and methanol were removed by filtration and vacuum distillation, respectively. The remaining solid product was dried in vacuum, weighed and then analyzed by NMR and element analysis. The solid product diluted with acetone to 5 g/L was further analyzed by high-resolution mass spectrometer. The recovered Cu/SiO₂ catalyst after being washed by methanol was then used for the next run.

Etherification of BHMF with methanol was performed in a 100 mL autoclave vessel lined with teflon. In a typical reaction, 4 g BHMF, 40 mL methanol and 1 g acidic ZSM-5 zeolite (Si/Al = 25) were charged into the vessel, which was heated in an oil bath preset at 100 °C with magnetic stirring for 12 h and then cooled down to room temperature. After removal of the catalyst and methanol by filtration and vacuum distillation, respectively, the left-over liquid was dried in vacuum to further remove the volatile components and then heated under highly reduced pressure to evaporate the product 2,5-bis-methoxymethylfuran (BMMF), which was weighed and then analyzed by NMR and element analysis. The recovered BMMF diluted with acetone to 5 g/L was further analyzed by high-resolution mass spectrometry.

The one pot conversion of HMF into BMMF was carried out in a 100 mL autoclave. 5 g HMF pre-dissolved in 50 mL methanol, 0.5 g Cu/SiO₂ catalyst and 0.5 g HZSM-5 (Si/Al = 25) were charged into the autoclave, which was purged three times and then pressurized to 2.5 MPa with H₂. Zero time and mechanical stirring started after the autoclave was heated to 120 °C. When the reaction proceeded for 12 h, the autoclave was cooled down to room temperature.

The Cu/SiO₂, HZSM-5 and methanol were removed by filtration and vacuum distillation. The left-over liquid was dried in vacuum to further remove the volatile components and then heated under highly reduced pressure to evaporate the product 2,5-bis-methoxymethylfuran (BMMF). Under the same reaction conditions above, the one-pot synthesis of BMMF from HMF was successfully scaled up to 500 g HMF in 10 L autoclave. Approximately 1 kg BMMF was produced in this way for the measurement of its cetane number using 1.2 kg HMF as substrate after three pots reaction where 500 g, 500 g and 200 g HMF were used as reactants.

3. Results and discussion

3.1. Hydrogenation of HMF into BHMF

Hydrogenation of HMF into BHMF is relatively easy through selective reduction of aldehyde to hydroxymethyl group. However, during hydrotreatment, the two hydroxymethyl groups of BHMF could be further converted into methyl or CH₄ [4,5,13]. With CuRu/C [4] and RhCl₃ [5] as catalysts, HMF is hydrogenated into 2,5-dimethyl-furan (DMF) and 2,5-dimethyl-tetrahydrofuran (DMTHF), respectively. The effects of Pd/C, Pt/C and Ru/C on the hydrogenation of HMF in ionic liquids have also been investigated and six principal products including 5-methylfurfural (MF), BHMF, 5-methylfurfuryl alcohol (MFA), DMF, 5-methyltetrahydrofurfuryl alcohol (MTHFA), and 2,5-hexadione (HD) were reported [13]. Using supported Ru or Raney Ni catalysts, HMF was efficiently hydrogenated into 2,5-di-hydroxy-methyl-tetrahydrofuran (DHMTHF) [3,14]. As previously analyzed, in the presence of PtSn/Al₂O₃, approximately 80% BHMF selectivity was obtained from hydrogenation of HMF in ethanol. By now, highly selective hydrogenation of HMF into BHMF has not been reported. As we know, the chemical structure of HMF is similar to that of furfural. Efficient hydrogenation of furfural into furfuryl alcohol has already been achieved over carbon-supported copper catalyst [15]. Hence, an inexpensive Cu/SiO₂ catalyst was investigated in the conversion of HMF. The catalyst (0.5 g) was added to 50 mL methanol containing 10 g of dissolved HMF. The reaction lasted 8 h at 100 °C. During that period, the hydrogen pressure decreased in the first 5 h and then maintained constant in the last 3 h. After the reaction, the catalyst, methanol and other volatile components were removed by filtration and vacuum distillation. The remaining 9.8 g solid (97% yield) was then characterized by high resolution mass spectrometry, NMR and elemental analysis (Figs. S1 and S2 and Table S2). The characterization demonstrated the formation of BHMF product. As a furan derivative, BHMF itself is regarded as a valuable polymer monomer [2b]. The recovered Cu/SiO₂ catalyst was recycled for the next run, and the catalyst did not lose its activity at all even after being recycled for four times, as testified by the hydrogen pressure drop rate. Almost the same time duration was needed to achieve the same hydrogen pressure drop. Only 0.04% of Cu species drained into methanol, suggesting a long-term use of the catalyst. Compared with the literature [10], Cu/SiO₂ achieved a more BHMF selectivity (97%) than the reported PtSn/Al₂O₃ catalyst (80%) in the same time (5 h). In addition, Cu/SiO₂ is much cheaper than PtSn/Al₂O₃ and more practical in commercialization. The conversion may also be realized if the conditions such as temperature, hydrogen pressure and substrate loading alter, which is not the focus of this work.

3.2. Conversion of BHMF into BMMF

The efficient hydrogenation of HMF provided us with adequate amount of BHMF as precursor to the acid-catalyzed synthesis of 2,5-bis-methoxymethylfuran (BMMF). The reactivity of BHMF with methanol was first tested using HZSM-5 (Si/Al = 25) as catalyst

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