

**Etherification and reductive etherification of 5-(hydroxymethyl)furfural:
5-(alkoxymethyl)furfurals and 2,5-bis(alkoxymethyl)furans as potential bio-diesel
candidates**

*Madhesan Balakrishnan, Eric R. Sacia and Alexis T. Bell**

Energy Biosciences Institute
and
Department of Chemical and Biomolecular Engineering
University of California, Berkeley
Berkeley, CA 94720, USA

bell@cchem.berkeley.edu

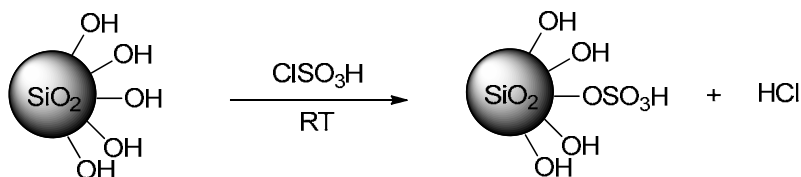
Supporting Information

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1. Preparation of silica sulfuric acid¹



A 500 mL suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube was charged with silica gel (30 g). Chlorosulfonic acid (11.65 g, 0.1 mol) was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After the addition was complete the mixture was shaken 30 min. The white solid obtained was washed with EtOH (4×60 mL) using a fritted funnel and dried at 100 °C for 12h to give silica sulfuric acid (38 g, 2.63 mmol/g acid loading).

2. Preparation of Pt/Sn bimetallic catalysts on alumina²

Synthesis of platinum/tin catalysts supported on γ -alumina involved the following steps:

- (i) The support (γ -alumina with a BET surface area of 70-100 m²g⁻¹) was dried in a vacuum oven (25 mm Hg) at 100 °C for 12 h.
- (ii) Catalysts were prepared by impregnation of the above γ -alumina with solutions of H₂PtCl₆·6H₂O and SnCl₂ in 0.6 M HCl, with appropriate wt% loadings. Typically, one gram of γ -alumina was impregnated with the following solutions.

For **Pt₁Sn_{0.25}/Al₂O₃** – H₂PtCl₆·6H₂O (26.5 mg, 0.051 mmol) and SnCl₂ (4.8 mg, 0.021 mmol) in 0.6 M HCl (0.5 mL)

For **Pt₁Sn_{0.5}/Al₂O₃** – H₂PtCl₆·6H₂O (26.5 mg, 0.051 mmol) and SnCl₂ (9.5 mg, 0.042 mmol) in 0.6 M HCl (0.5 mL)

For **Pt₁Sn₁/Al₂O₃** – H₂PtCl₆·6H₂O (26.5 mg, 0.051 mmol) and SnCl₂ (19 mg, 0.084 mmol) in 0.6 M HCl (0.5 mL)

(iii) The catalysts were dried at 120 °C for 12 h.

(iv) The solids were reduced by hydrogen at 500 °C for 12 h before use.

3. Syntheses of key compounds for the GC quantification studies

3(a). 5-(Ethoxymethyl)furfural (EMF, 2a) and 5-(ethoxymethyl)furfural diethylacetal (EMFDEA, 4a)

A solution of 5-(hydroxymethyl)furfural (**1**, 0.252 g, 2 mmol) in ethanol (4 g) was added with Amberlyst-15 (5 mol%) to a 8 mL screw-cap vial equipped with a magnetic spin bar. The reaction mixture was sealed, stirred (250 rpm) and heated at 75 °C on the deck of the Symyx Core Module for 24 h before cooling to ambient temperature. The reaction mixture was then passed through a small pad of silica gel by washing with ethyl acetate (3×10 mL) to remove catalyst particles, after which the solvents were evaporated at reduced pressure to produce a crude reaction mixture which was purified by column chromatography (silica gel, 100-200 mesh). Initially, elution of the column with ethyl acetate/hexanes (1:19) gave pure EMFDEA (0.123 g, 27%). Further, the elution with ethyl acetate/hexanes (1:5) gave EMF. The pure fractions identified by GC were collected together and concentrated and vacuum dried (0.160 g, 52%).

EMF (**2a**), ¹H NMR (400 MHz, CDCl₃), δ 1.21 (t, *J* = 8.2 Hz, 3H), 3.57 (q, *J* = 6.67 Hz, 2H), 4.51 (s, 2H), 6.50 (d, *J* = 4 Hz, 1H), 7.19 (d, *J* = 4 Hz, 1H), 9.59 (s, 1H).

EMFDEA (**4a**), ¹H NMR (400 MHz, CDCl₃), δ 1.21 (t, *J* = 8.2 Hz, 9H), 3.50-3.73 (m, 6H), 4.42 (s, 2H), 5.50 (s, 1H), 6.27 (d, *J* = 4 Hz, 1H), 6.36 (d, *J* = 4 Hz, 1H).

3(b). 5-(Hydroxymethyl)furfural diethylacetal (HMFDEA, 6a)

A solution of 5-(hydroxymethyl)furfural (**1**, 0.126 g, 1 mmol) in ethanol (2 g) was added with Amberlyst-15 (5 mol%) to a 4 mL screw-cap vial equipped with a magnetic spin bar. The reaction mixture was sealed, stirred (250 rpm) and heated at 75 °C on the deck of the Symyx Core Module for 2.5 h. Then the reaction mixture was then passed through a small pad of silica gel by washing with ethyl acetate (3×5 mL) to get rid of catalyst particles, after which the solvents were evaporated and the crude reaction mixture was purified by column chromatography (silica gel, 100-200 mesh) by eluting the column with ethyl acetate/hexanes (1:3) gave HMFDEA (0.112 g, 56%).

HMFDEA (**6a**), ¹H NMR (400 MHz, CDCl₃), δ 1.23 (t, *J* = 8.2 Hz, 6H), 1.66 (bs, 1H), 3.56-3.74 (m, 4H), 4.59 (bs, 2H), 5.49 (s, 1H), 6.25 (m, 2H).

3(c). 2,5-Bis(hydroxymethyl)furan (BHMF, 7)

A methanolic solution of 5-(hydroxymethyl)furfural (**1**, 0.5 g, 3.97 mmol in 10 mL) was cooled to 0 °C. Sodium borohydride (0.6 g, 15.87 mmol) was then slowly added with stirring.

The reaction mixture was allowed to warm to 25 °C over 3h and stirred overnight at room temperature. The reaction was carefully quenched with sat. aq. sodium chloride solution (10 mL) and stirred for a further 6h. The methanol in the reaction mixture was evaporated and it was extracted with ethyl acetate (3×10 mL). The organic layers were combined and washed with brine (15 mL) and dried (Na₂SO₄). The solvents were evaporated and the crude mixture was recrystallized in chloroform to yield pure **7** (0.47 g, 93%).

BHMF (**7**), ¹H NMR (400 MHz, D₂O), δ 4.56 (s, 4H), 6.36 (s, 2H).

3(d). 2,5-Bis(ethoxymethyl)furan (BEMF, **8a**)

A solution of 2,5-bis(hydroxymethyl)furan (**7**, 0.128 g, 1 mmol) in ethanol (2 g) was added with Amberlyst-15 (5 mol%) to a 4 mL screw-cap vial equipped with a magnetic spin bar. The reaction mixture was sealed, stirred (250 rpm) and heated at 60 °C on the deck of the Symyx Core Module for 5 h. The reaction mixture was then passed through a small pad of silica gel by washing with ethyl acetate (3×10 mL) to get rid of catalyst particles. After which the solvents were evaporated and the crude reaction mixture was purified by column chromatography (silica gel, 100-200 mesh) by eluting the column with ethyl acetate/hexanes (1:19) gave BEMF (0.127 g, 69%).

BEMF (**8a**), ¹H NMR (400 MHz, CDCl₃), δ 1.22 (t, *J* = 8.2 Hz, 6H), 3.54 (q, *J* = 6.67Hz, 4H), 4.42 (s, 4H), 6.25 (s, 2H).

3(e). 5-(Ethoxymethyl)Furfuryl alcohol (EMFA, **9a**)

An ethanolic solution of 5-(ethoxymethyl)furfural (**2a**, 0.5 g, 3.25 mmol in 10mL) was cooled to 0 °C. Sodium borohydride (0.5 g, 13 mmol) was then slowly added with stirring. The reaction mixture was allowed to warm to 25 °C over 3h and stirred for overnight at room temperature. The reaction was carefully quenched with brine solution (10 mL) and stirred for another 6h. The ethanol was evaporated and the reaction mixture was extracted with ethyl acetate (3×10 mL). The organic layers were combined and washed with brine (15 mL) and dried (Na₂SO₄). The crude reaction mixture was purified by column chromatography (silica gel, 100-200 mesh) using ethyl acetate/hexanes (1:5) as elution solvents, giving pure EMFA (0.451 g, 89%).

EMFA (**9a**), ¹H NMR (400 MHz, CDCl₃), δ 1.22 (t, *J* = 8.2 Hz, 3H), 1.90 (bs, 1H), 3.54 (q, *J* = 6.67Hz, 2H), 4.42 (s, 2H), 4.58 (s, 2H), 6.25 (dd, *J* = 8.1, 3.9Hz, 2H).

4. References:-

1. (a) Zolfigol, M. A.; Bamoniri, A. *Synlett* **2002**, 1621, (b) Zolfigol, M. A. *Tetrahedron* **2001**, 57, 9509.
2. Beltramini, J.; Trimm, D. L. *Applied Catalysis* **1987**, 31, 113.

5. ^1H NMR Spectra of key products

