

Synthesis of Fuel Intermediates from HMF/Fructose

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Abstract Alkylation of toluene, anisole and mesitylene with HMF and fructose is reported using $Glu-Fe_3O_4-SO_3H$ solid acid catalyst. HMF was found to alkylate toluene, anisole and mesitylene in high yields and high selectivity under solvent free conditions. Polyalkylation and self etherification of HMF was not observed. The alkylated product on

hydrodeoxygenation forms liquid alkanes of different chain lengths which have properties of transportation fuels or diesel fuels. The catalyst was easily recoverable and reusable minimum 5 times to achieve good yields and high selectivity of alkylated product.

Graphical Abstract



Keywords 5-Hydroxymethylfurfural · Alkylation · Hydrodeoxygenation · Diesel fuels

1 Introduction

5-Hydroxymethylfurfural (HMF) is a building block for production of petroleum derived diesel fuels i.e. mixture of long chain alkanes [1]. Hydrodeoxygenation of HMF gives rise to short carbon chain lengths which are not found to be suitable as transportation fuels as they have low boiling point and low specific energy density. Hence HMF has to be coupled with other reactive intermediates. Typically for such type of conversions a C–C bond formation is necessary. C–C bond formation is used to obtain the intermediate oxygenated molecules, which are subsequently converted into alkanes with excellent

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diesel properties through a hydrodeoxygenation step. Dumesic et al. reported formation of liquid biofuels using aldol condensation of furfural or 5-hydroxymethylfurfural with ketones which involves carbon-carbon bond formation and which upon subsequent hydrodeoxygenation produced liquid alkanes [2, 3]. However, in this case there are drawbacks of self and cross condensation products which leads to lower selectivity of the product formed. Zhang et al. reported the synthesis of C₁₀ or C₁₁ branched alkanes from the aldol condensation of MIBK with furfural followed by hydrodeoxygenation process [4]. Dumesic et al. have developed a process to produce higher alkanes from sorbitol [5]. Corma et al. have developed a process to convert 2-methylfuran into 6-alkyl undecanes [6]. Sutton et al. used Pd/H₂, lanthanum triflate in presence of glacial acetic acid for hydrodeoxygenation process to produce alkanes [7]. Recently, Wang et al. used Pt/NbOPO₄ catalyst for direct hydrodeoxygenation of biomass to liquid alkanes [8]. Iborra et al. studied alkylation of toluene with HMF using various heterogeneous catalysts like H Beta, USY, mordenite, zeolites and mesoporous aluminosilicates [9]. In all the cases, monoalkylated products of 5-(o-, m- and p-methyl) benzylfuran-2-carbaldehyde were formed along with -OBMF coming from self etherification of HMF as the undesired product. 5-(o-, m- and p-methyl) benzylfuran-2-carbaldehyde was then transformed into a mixture of alkanes and hydrophobic molecules which can be blended with kerosene or diesel using hydrogenation conditions in the presence of mixture of catalyst Pt/C-Pt/TiO₂ [10]. Generally catalysts used for Freidel-Crafts alkylation are FeCl₃, p-TSA, HCOOH [11]. But certain drawbacks associated with homogeneous catalyst are it requires a neutralization step and tedious workup procedures. Thus recovery and reuse of catalyst is not possible. Also solvents required for the reaction are expensive, volatile and toxic. Therefore there is a need to develop a heterogeneous catalytic process which can avoid competitive reactions such as polyalkylations and self etherification of HMF, and maximizing alkylation of aromatics with HMF. Heterogeneous catalyst can also be easily recoverable and reusable. Use of toxic solvents for alkylations should also be avoided. This will definitely give rise to new opportunities in the field of biofuels and chemicals. In this article, we studied our previously synthesized Glu-Fe₃O₄-SO₃H catalyst for selective Freidel Crafts reaction of HMF/fructose using different arenes like toluene, anisole and mesitylene [12].

2 Experimental

2.1 Experimental Procedure

2.1.1 General Methods

All commercially available reagents were used without further purification unless otherwise stated. All reactions were carried out under an argon atmosphere in flame-dried glassware under positive pressure of argon with magnetic stirring. Column chromatography was performed on silica gel (100–200 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker spectrometer using TMS as an internal standard. NMR data are reported as follows: chemical shift, multiplicity (bs=broad singlet, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant (Hz), and integration. GC was recorded on Agilent 6890N. GC-MS was performed on Agilent 7890A. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) with a time-of-flight mass analyzer.

2.1.2 Catalyst Preparation

5.0 g of glucose and 276 mL of FeCl₃ solution with a concentration of 100 mmol/L were mixed in a flask and stirred for 5 h at rt. Then, the water in the mixture was evaporated, and the solid residue was dried at 378 K overnight and sieved again to collect the particles with a size smaller than 120 mesh to obtain the Fe preloaded glucose. Fe preloaded glucose was then stirred with *p*-TSA (5 eq) at 140 °C for 24 h under argon atmosphere. The mixture was then cooled to rt, and then slowly added to a beaker containing 500 mL deionised water. The suspension mixture was then filtered off and washed repeatedly with deionised water to remove all the sulfate ions (SO₄^{2–}). The solid was further washed with absolute ethanol to remove the water, and then dried at 353 K overnight to get a black magnetic material (Glu–Fe₃O₄–SO₃H).

2.1.3 Synthesis of 5-(-o, -m and -p substituted) Benzylfuran-2-carbaldehyde

A mixture of HMF (1 equiv)/fructose (1 equiv), the corresponding arene (10 equiv) and solid acid catalyst (15 wt%) was heated at respective temperature and for respected time under nitrogen atmosphere using an oil bath. After completion of the reaction the catalyst was removed using a magnet and the resulting residue was purified by flash column chromatography using ethyl acetate/pet ether (2:3) as eluent to afford the desired compound.

2.2 Experimental Data

2.2.1 5-(-o, and -p-methyl) Benzylfuran-2-carbaldehyde

¹H NMR (400 MHz, CDCl₃): δ 9.54 (s, 2H), 7.20 (s, 2H), 7.15–7.19 (m, 8H), 6.18 (d, *J*=3.4 Hz, 1H), 6.07 (d, *J*=2.4 Hz, 1H), 4.06 (s, 2H), 4.02 (s, 2H), 2.34 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 177.6, 177.1, 162.3, 161.7, 157.1, 136.6, 136.4, 134.3, 132.9, 130.5, 129.7, 129.4, 128.7, 127.3, 126.3, 123.1, 109.7, 109.6, 34.7, 34.4, 32.6,

21.0, 19.3; GC-MS: m/z 200.1, 185, 171.1, 128.1, 115.1, 91.0; HRMS (ESI) m/z calcd for $[C_{13}H_{12}NaO_2]$ 223.0730 found 223.0735.

2.2.2 5-(-o, and -p-methoxy) Benzylfuran-2-carbaldehyde

¹H NMR (400 MHz, CDCl₃): δ 9.45 (s, 2H), 7.15–6.23 (m, 2H), 7.06–7.12 (m, 4H), 6.77–6.88 (m, 4H), 6.05–6.09 (m, 2H), 3.99 (s, 4H), 3.24 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 177.2, 162.4, 157.3, 151.9, 130.5, 130. 0, 128.5, 124.6, 123.3, 120.7, 114.2, 110.6, 109.6, 55.4, 55.3, 34.1, 29.7, 27.2; HRMS (ESI) m/z calcd for $[C_{13}H_{12}NaO_3]$ 239.0679 found 239.0684.

2.2.3 5-(mesityl) Furan-2-carbaldehyde

¹H NMR (400 MHz, CDCl₃) δ 9.53 (s, 1H), 7.11 (d, J=3.4 Hz, 1H), 6.90 (s, 2H), 5.92 (d, J=3.4 Hz, 1H), 4.05 (s, 2H), 2.29 (s, 3H), 2.28 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 177.0, 161.9, 152.1, 136.8, 136.6, 129.6, 129.1 (s), 109.1, 28.0, 20.8, 19.9 (s); GC-MS: m/z 228, 213, 182.1, 167.1, 156.1, 143.1, 105.1, 91.1, 77.1; HRMS (ESI) m/z calcd for [C₁₅H₁₆NaO₂] 251.1043 found 251.1048.

3 Results and Discussions

3.1 Characterization of the Catalyst

Due to our continuous interest in this field, we have synthesized a magnetic carbonaceous solid acid catalyst Glu- Fe_3O_4 -SO₃H. For preparation of this catalyst, we choose readily available D-glucose as a carbon precursor, Fe was preloaded on glucose using FeCl₃ and p-TSA was used as a sulphonating agent to create active acidic sites. Initially Fe was preloaded on glucose using FeCl₃. The free -OH groups in glucose easily coordinated with adsorbed Fe (III) ions and then evaporation of solvent and drying gave black Fe (III) based complex. This complex was then pyrolysed and sulfonated simultaneously using p-TSA at 140 °C under nitrogen. The Fe preloaded on glucose was partly hydrolysed to FeO(OH) during drying. FeO(OH) was further reduced to Fe₃O₄ by reducing components like H₂, CO₂ and CO which are formed during carbonation process. Pyrolysis and sulfonation in-situ leads to formation of a polycylic aromatic structure embedded with active Fe₃O₄, -SO₃H, -COOH and -OH sites.

The catalyst thus obtained was characterized with FT-IR (Spectrum 400), PXRD (Panalytical X'Pert Pro), Elemental analysis from EDAX (Nova Nano SEM 450), SEM (Quanta[™] Scanning Electron Microscope), XPS (Prevac Ambient Pressure Photo Electron Spectroscopy) and BET surface area (Quantachrome ASiQwin). The acid densities were measured by acid base titration. FT-IR spectrum (Fig. 1a) showed characteristic peaks at 1012 and 1040 cm^{-1} which are attributed to O=S=O stretching vibrations in -SO₃H groups and peak at 1127 cm⁻¹ for SO₂H stretching. This indicates that the sulfonic acid groups have been successively incorporated on the catalyst surface. Peaks at 1645 cm^{-1} attributed for C=C stretching vibrations in aromatic carbons and peak at 1670 cm⁻¹ attributed for C=O stretching. Peak at 1714 cm^{-1} attributed to presence of C=O stretching vibration of -COOH group. Bands at 2925 cm⁻¹ attributed for C-H stretching band. Bands due to O-H stretching were observed at 3410 cm⁻¹. The PXRD (Fig. 1b) showed a weak but broad peak of 2θ at 15° – 30° , indicating formation of amorphous carbon having aromatic carbon sheets oriented in a random fashion. The sharp peaks seen indicates the formation of Fe_3O_4 crystallite in the pyrolysis process. The energy dispersive X-ray analysis (Fig. 1c) confirms that the catalyst surfaces are composed mainly of C, O, Fe and S. Composition of S and Fe is found to be 7.4 and 7.7% respectively from EDAX. The elemental analysis showed composition of C to be 50%, H to be 4% and S to be 9%. SEM (Fig. 1d) image shows formation of porous nature of the catalyst. The surface composition of Glu–Fe₃O₄–SO₃H was analysed by XPS (Fig. 1e). The C 1s spectrum includes six peaks with different binding energy values. The peaks could be assigned to the carbon atoms in the forms of C-S (283.5 eV), C-C (284 and 284.5 eV), C-O (285 eV), C=O (285.5 eV), O=C-O (286 eV). The S 2p spectrum showed three different peaks that can be assigned to S-C (186.5), S-O (169 eV) and S=O (169.5 eV). O 1s spectrum shows peaks in the range 530-535 eV indicating the presence of Fe-O and C-O-Fe groups suggesting the linkage of Fe₃O₄ with porous carbon. BET surface area, pore size and pore volume was calculated using the standard Brunauer-Emmett-Teller (BET) equation and was found to be 3.38 m²/g, 9.53 Å and 6.07 m³/g respectively. The total acid density and the sulphonic acid density of Glu-Fe₃O₄-SO₃H based on acid base titration was found to be 2.87 and 1.46 mmol/g respectively.

3.2 Alkylation of Toluene with HMF/Fructose in Various Solvents

To start with, HMF and fructose were screened for various solvents for the alkylation reaction with arenes in presence of $Glu-Fe_3O_4-SO_3H$ catalyst (Table 1). Toluene was used as a model aromatic compound for studying the alkylation reaction with HMF. In case of alkylation of arenes with HMF and fructose, solvents like isopropanol, acetonitrile, DMSO, DMF, nitromethane gave formation of corresponding mono alkylated product, a mixture of



Fig. 1 a FT-IR of Glu–Fe₃O₄–SO₃H. b PXRD of Glu–Fe₃O₄–SO₃H. c EDAX of Glu–Fe₃O₄–SO₃H. d SEM image of Glu–Fe₃O₄–SO₃H. e XPS of Glu–Fe₃O₄–SO₃H. f FT-IR of reused Glu–Fe₃O₄–SO₃H. g SEM image of reused Glu–Fe₃O₄–SO₃H.

isomers of 5-(*o*-, *m*- and *p*-methyl) benzylfuran-2-carbaldehyde in good yields, whereas solvents like THF, DCM, water, methanol, ethanol, and sulpholane did not show formation of any alkylated product at all. Of all the solvents that were screened, HMF showed complete conversion and the highest yield of alkylated HMF under solvent free conditions at 100 °C. GC analysis of crude reaction mixture after completion of the reaction showed formation of isomers of 5-(o-, m- and p-methyl) benzyl-furan-2-carbaldehyde. The isomers in the alkylated product 5-(o-, m- and p-methyl) benzyl-furan-2-carbaldehyde were formed in the ratio of 45:49:6 (o: p: m). No traces

Table 1 Alkylation of HMF/fructose with toluene



Sr. No	Starting	Solvent	Temp (°C)	Time (h)	% Yield HMF	% Yield alkylated HMF	o:p:m ratio of alkylated HMF
1	HMF	IPA	80	30	_	65	40:55:5
2	HMF	CH ₃ CN	80	32	_	53	38:56:6
3	HMF	DMSO	140	33	_	46	34:58:8
4	HMF	DMF	100	32	_	41	36:58:6
5	HMF	CH ₃ NO ₂	100	30	_	68	45:46:9
6	HMF	Neat	100	30	_	70	45:49:6
7	Fructose	IPA	80	30	23	65	37:56:7
8	Fructose	CH ₃ CN	80	32	36	51	36:59:5
9	Fructose	DMSO	140	33	40	44	34:58:8
10	Fructose	DMF	100	36	41	31	34:57:7
11	Fructose	CH ₃ NO ₂	100	36	30	58	46:48:6
12	Fructose	Neat	100	38	21	70	45:46:9

of any other side products were observed indicating complete conversion and 100% selectivity. No side products arising from self etherification of HMF, polyalkylated oligomers and hydrooxyalkylation of aromatic rings were observed indicating good efficiency of the catalyst. The GC mass of all the three peaks that were observed in GC showed the same mass, indicating that all the three peaks are of -ortho, -meta and -para isomer of 5-methylbenzyl-furan-2-carbaldehyde. ¹H NMR showed -ortho and -para isomers as the major products formed in the ratio 44:55. Meta isomer being minor was not observed in the ¹H NMR spectrum of the product. Fructose conversion was also studied in the presence of Glu-Fe₃O₄-SO₃H catalyst under neat reaction conditions. Fructose was completely converted to 70% of alkylated HMF and 21 % of HMF was isolated after 38 h at 100 °C. The reaction when carried out without using Glu-Fe₃O₄-SO₃H

Table 2 Study of catalyst concentration in formation of alkylated $\ensuremath{\mathsf{HMF}}$

Sr. No.	Starting	Catalyst conc. (wt%)	% Yield HMF	% Yield alkyl- ated HMF
1	HMF	5	_	52
2	HMF	10	-	54
3	HMF	15	_	70
4	Fructose	5	46	31
5	Fructose	10	40	43
6	Fructose	15	30	58

catalyst, no alkylation of HMF was observed indicating that $Glu-Fe_3O_4-SO_3H$ acts as an acidic catalyst for alkylation reaction.

3.3 Study of Effect of Catalyst Concentration in Alkylation Reaction

Effect of catalyst concentration was studied on the reaction of HMF/fructose with arenes using 5, 10 and 15 wt% of Glu– Fe₃O₄–SO₃H catalyst under neat reaction conditions at 100 °C (Table 2).The yields were found to increase with increasing catalyst concentration from 5 to 15 wt%. Highest yield of the product was observed using 15 wt% of the catalyst. Further increasing the catalyst concentration to 20 wt% did not have any significant impact on the yield of the product. Similarly in case of fructose, 15 wt% of catalyst gave highest yield of 58% of alkylated HMF along with 30% of HMF that was isolated. Thus, 15 wt% was considered as the optimum catalyst concentration for studying alkylation reaction.

3.4 Alkylation of Anisole and Mesitylene with HMF/ Fructose

After optimisation of solvent condition and catalyst concentration, different arenes were studied for the alkylation reaction with HMF/fructose. Anisole and mesitylene were also studied for alkylation reaction and the results are described in Table 3. Alkylation of anisole with HMF gave highest yield of 70% of alkylated HMF under solvent free conditions giving 100% selectivity. GC analysis showed that the *ortho, para* and *meta* isomers in alkylated product 5-(*o*-, *m*- and

Table 3 Alkylation of HMF/fructose with anisole and mesitylene



Sr. No	Starting	Arene	Solvent	Temp (°C)	Time (h)	% Yield HMF	% Yield alkylated HMF	<i>o:p:m</i> ratio of alkylated HMF
1	HMF	Anisole	IPA	80	32	_	62	40:55:5
2	HMF	Anisole	CH ₃ CN	80	34	_	57	38:56:6
3	HMF	Anisole	DMSO	140	36		46	34:58:8
4	HMF	Anisole	DMF	100	30	_	28	36:58:6
5	HMF	Anisole	CH_3NO_2	100	33	_	67	45:47:8
6	HMF	Anisole	Neat	100	32	_	70	45:50:5
7	HMF	Mesitylene	IPA	80	15	_	49	-
8	HMF	Mesitylene	CH ₃ CN	80	18	_	45	-
9	HMF	Mesitylene	DMSO	140	20	_	41	-
10	HMF	Mesitylene	DMF	100	20	_	27	-
11	HMF	Mesitylene	CH ₃ NO ₂	100	16	_	55	-
12	HMF	Mesitylene	Neat	100	15	_	60	-
13	Fructose	Anisole	IPA	80	30	24	63	37:58:5
14	Fructose	Anisole	CH ₃ CN	80	34	35	53	43:52:5
15	Fructose	Anisole	DMSO	140	36	30	39	34:58:8
16	Fructose	Anisole	DMF	100	38	33	29	34:60:6
17	Fructose	Anisole	CH ₃ NO ₂	100	30	26	50	44:50:6
18	Fructose	Anisole	Neat	100	30	31	66	45:50:5
19	Fructose	Mesitylene	IPA	80	15	34	55	-
20	Fructose	Mesitylene	CH ₃ CN	80	16	40	43	-
21	Fructose	Mesitylene	DMSO	140	20	30	38	-
22	Fructose	Mesitylene	DMF	100	20	33	39	-
23	Fructose	Mesitylene	CH_3NO_2	100	18	19	42	-
24	Fructose	Mesitylene	Neat	100	15	35	61	_

p-methoxy) benzyl-furan-2-carbaldehyde was formed in the ratio = 45:50:5 (*o*: *p*: *m*). GC mass showed same mass for all the three isomers that were observed in GC. ¹H NMR showed only the *ortho* and *para* isomers formed in the ratio 44:56. *Meta* isomer was not observed in the ¹H NMR as it was formed in very minor amount. Isopropanol and nitromethane also gave complete conversion of

Table 4 Comparison of Glu–Fe $_3\mathrm{O}_4\text{--}\mathrm{SO}_3\mathrm{H}$ catalyst for alkylation of HMF

Sr. No	Catalyst	Starting	Arene	% Yield alkylated HMF	% Yield OBMF
1	FeCl ₃	HMF	o-xylene	37	_
2	<i>p</i> -TSA	HMF	Toluene	95	5
3	Mordenite	HMF	Toluene	11	9
4	Hβ- zeolite	HMF	Toluene	54	15
5	Glu–Fe ₃ O ₄ – SO ₃ H	HMF	Toluene	70	Not observed

HMF to alkylated product in good yield and selectivity. Whereas, alkylation of anisole with fructose gave 66% yield of alkylated HMF and 31% of HMF was isolated under neat reaction conditions. Alkylation of mesitylene with HMF gave 60% yield of alkylated product under neat reaction conditions. GC and ¹H NMR spectrum showed single product formation for alkylation of mesitylene with HMF under neat reaction conditions. GC mass further confirmed the product formation. In case of alkylation of fructose with mesitylene highest yield of 61% of alkylated product was obtained along with 35% of HMF isolated. The HMF thus isolated in each step could readily be reused for alkylation reactions.

The mechanism of this reaction could be described as follows. Fructose in the presence of acidic catalyst gets converted into HMF. The solid acid catalyst then enables the formation of methyfurfural cation from HMF and this cation then reacts with the aromatic compound giving the desired alkylated product. Also, there are chances that the

Table 5 Reusability of $Giu - Fe_3O_4 - SO_3H$ cataly
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Sr. No.	Run	% Yield	
1	1st	70	
2	2nd	70	
3	3rd	69	
4	4th	68	
5	5th	68	

methylfurfural cation may react with another molecule of HMF giving the corresponding –*O*BMF ether formation.

3.5 Comparison of Known Catalyst with Glu–Fe₃O₄– SO₃H Catalyst for Alkylation Reaction

Till date very few catalyst are studied for alkylation of HMF with arenes and the comparision of $Glu-Fe_3O_4-$ SO₃H catalyst with various reported homogeneous and heterogeneous catalyst is given in Table 4. FeCl₂ catalyzed alkylation of o-xylene with HMF gave only 37% yield of alkylated product [13]. p-TSA is a common catalyst used for alkylation reaction giving 95% yield of alkylated HMF along with 5% of -OBMF formation [10]. Mordenite and H- β zeolite heterogeneous catalyst when used as a catalyst gave formation of 11 and 54% alkylated product HMF along with 9 and 15% of OBMF respectively [10]. Whereas, alkylation of HMF with toluene using Glu-Fe₃O₄-SO₃H catalyst showed complete conversion of HMF and gave about 70% yield of alkylated HMF with 100% selectivity. No traces of other side products were obtained in the reaction. Also the Glu-Fe₃O₄-SO₃H catalyst was easily seperable and recyclable.

3.6 Reusability of Glu–Fe₃O₄–SO₃H Catalyst

After the reaction the catalyst could be easily separated magnetically. It was dried in the oven at 100 °C for 2–3 h and then was reused in alkylation reaction of toluene with HMF under solvent free conditions at 100 °C (Table 5). The catalyst showed consistent yields and selectivity even after five runs indicating good stability and efficiency in reuse experiments. FT-IR (Fig. 1f) of the Glu–Fe₃O₄–SO₃H catalyst after five repeated experiments showed no change in the IR spectrum of spent and fresh catalyst. SEM image

(Fig. 1g) after five runs also did not show any significant difference in surface morphology compared to that of the fresh catalyst.

4 Conclusion

In conclusion, the Glu–Fe₃O₄–SO₃H catalyst was found to selectively alkylate HMF and fructose with toluene, anisole and mesitylene giving high yields under solvent free conditions. Solvents isopropanol and nitromethane also gave significant yields of alkylated products. No side products were observed during the reaction. HMF isolated from fructose alkylation reaction could be reused for further alkylation. The alkylated products can be further converted to diesel fuels using hydrodeoxygenation step. The catalyst could be easily recovered and reused minimum five times without any significant loss in yield of the products.

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