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Dual Acidic Titania Carbocatalyst for Cascade Reaction of Sugar to

Etherified Fuel Additives

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Abstract

An inexpensive carbocatalyst containing Brønsted acidic sulfonic acid group and Lewis acidic Ti^{4+} is found to be effective for cascade conversion of C₆ sugar to 5ethoxymethylfurfural (EMF) via sequential dehydration, and etherification reactions. HMF and fructose conversions at mild conditions achieved 91% and 64% EMF yields, respectively. The results indicate that the two acid sites interplay synergistically for high EMF yield and minimal ring-opened product ethyl levulinate (EL), another promising biofuel additive. Etherification of 2,5-bis(hydroxymethyl)furan (BHMF) with alcohols of varying carbon lengths formed alkoxymethylfurans (AMF) with high yields. The catalyst retained good activity upon recycling. The nature and strength of the acid sites are elucidated.

Keywords: Etherification, Titanium dioxide, Lewis acid, carbocatalyst, 5alkoxymethylfuran, 5-ethoxymethyluran

1. Introduction

The awareness of climate change and high market volatility of conventional fuels, owing to demand-supply imbalance, necessitates to the development of renewable alternatives and sustainable technologies to meet the growing energy demand for future generations [1]. The catalytic conversion of non-food biomass or cellulosic sugars into liquid fuels, e.g., 2,5-dimethylfuran (DMF) [2], 5-ethoxymethylfurtural (EMF) [3, 4] and high carbon alkanes (diesel, gasoline, jet fuel) [5-7] has been reported. However, poor process economics is the major challenge towards commercialization. Thus, production of low oxygenated EMF and analogous alkoxymethylfurans (AMF) via cascade catalysis of cellulosic sugars or etherification of sugar derived 5-hydroxymethylfurfural (HMF) can be economically more competitive.

EMF has a similar energy density (8.7 kWhL⁻¹) as standard gasoline (8.8 kWhL⁻¹) and diesel (9.7 kWhL⁻¹) and has superior energy density than ethanol (energy density = 6.1 kWhL⁻¹) [8, 9]. Its high boiling point (274 °C) is another advantage. Avantium has tested 20% EMF blended diesel in passenger vehicle engine. They found EMF can reduce SO_x emission, solid particulate contamination, and soot formation [10]. In addition, the engine ran smoothly for many hours using EMF blended fuel [11]. EMF can also be used as a flavor and aroma ingredient in wine and beers [12]. Homogeneous and heterogeneous catalytic systems [13] have been reported for the production of such fuel additives. Homogeneous catalysts, e.g., mineral acids, inorganic salts [14, 15], ionic liquids [16, 17], organic acids [18, 19], have offered moderate to high catalytic performance. The major challenge in homogeneous catalysis is the separation of the catalysts for recycling.

Therefore, solid acid catalysts are promising from economic and environmental standpoint. Zeolites, sulfonated metal oxides, modified mesoporous silica and ion-exchange resins including Amberlyst-15 [20-23] have been used for EMF synthesis. Antunes et al. have

used sulfonated graphene oxide for the etherification of HMF, which produced a mixture of EMF (42%), ethyl levulinate (EL) (43%) (another high octane fuel additive) and EMFdiethyl acetal (9%) at 140 °C for 24 h [9]. The catalytic systems containing Lewis and Brønsted acid sites have been reported to be more selective for EMF synthesis. Thus, mesoporous silicas containing Lewis acidic AI^{3+} achieved 68% EMF yield from HMF at 140 °C for 5 h [24]. A significant amount of non-fuel by-products, e.g., ethyl 4-oxopentanoate and 1,1-diethoxy ethane (DE) were formed, which posed a separation challenge and products purification. A one-pot approach of macro-algae derived agar conversion to a mixture of EMF and EL (5:2) using a $-SO_3H$ functionalized Dowex 50WX8 catalyst in the presence of CrCl₂ or 1-ethyl-3-methylimidazolium chloride ([EMIM]CI) has been reported, [25], but poor yield (30%) was the main drawback.

Recently, we have reported the synthesis of a sulfonated carbocatalyst containing Brønsted acidic sulfonic acid group and Lewis acidic Ti^{4+} (hereto referred as Glu-TsOH-Ti) via a one-pot hydrothermal method [26]. This dual acidic carbocatalyst exhibited excellent catalytic performance for dehydration of glucose and xylose to HMF and furfural, respectively [26], consistent with another report in which a hydrothermally prepared sulfonated carbocatalyst has been reported to be performed better over commercial zeolites, niobic acid or Amberlyst-15 for cellulosic biofuels production [27]. Usually sulfonated carbonaceous materials are synthesized by two-step processes involving preparation of carbonaceous materials in the first step followed by incorporation of $-SO_3H$ group under harsh oxidation conditions using concentrated sulfuric acid [28]. To avoid harsh reaction conditions, we reported a one-pot method by heating a homogeneous mixture of glucose (Glu) and *p*-toluenesulfonic acid (TsOH) and titanium(IV) isopropoxide in a sealed autoclave at 180 °C for 24 h. The ratio of Brønsted to Lewis acid density in the carbocatalyst was 1.2 [26]. In addition, the acid sites were more accessible for cascade isomerization and

dehydration of sugars [26]. Herein, we report that the Glu-TsOH-Ti catalyst is effective for the etherification of HMF and 2,5-bis(hydroxymethyl)furan (BHMF) to their corresponding etherified fuel additives.

2. Experimental section

Materials, detailed instrumentation and catalysis methods, and products analysis and quantification procedures are described in the supporting information. In short, the catalyst was synthesized and characterized following our reported methods [26]. Dehydration and etherification reactions were carried out in a 50-mL round bottom flask. NMR spectra of various isolated products are shown in the supporting information. This includes ¹H and ¹³C NMR spectra of bis-hydroxymethylfuran (BHMF) (Figures S1-S2), ¹H NMR spectrum of isolated EMF (Figure S3), ¹H and ¹³C NMR spectra of EMF obtained from fructose (Figures S4-S5), ¹H and ¹³C NMR spectra of 2,5-bis(ethoxymethyl)furan (BEMF; Figure S6 –S7), ¹H and ¹³C NMR spectra of 2,5-bis(methoxymethyl)furan (BMMF; Figures S8 – S9), ¹H NMR of 2,5-bis(propoxymethyl)furan (BPMF; Figure ¹H NMR S10), of 2,5-¹H and ¹³C spectra of bis(butoxymethyl)furan (BBMF; Figure S11), and 2.5bis(isopentoxymethyl)furan (BIPMF; Figure S12-S13).

3.0 Results and Discussions

3.1 Material characterization. The dual acidic Glu-TsOH-Ti catalyst was characterized by powder XRD, FTIR, NH₃-TPD, pyridine-FTIR, FE-SEM, HR-TEM, N₂-sorption, AAS, and ICP-OES techniques [26]. FTIR spectrum showed peaks at v=1010 cm⁻¹, 1035 cm⁻¹, and ~1115 cm⁻¹ for $-SO_3H$ groups (Figure S14). Pyridine-FTIR spectrum also confirmed the presence of Brønsted and Lewis acid sites (Figure S15). The wide-angle XRD pattern showed three major crystalline peaks at 2 θ = 25.3°, 37.8, and 48.08°, corresponding to the (101),

(004) and (200) crystal planes of anatase TiO₂ (Figure 1a), (JCPDS File Card No. 21-1272). XPS analysis revealed two Ti 2p peaks at 457.8 eV for ${}^{2}p_{3/2}$ and 463.4 eV for ${}^{2}p_{1/2}$ (Figure 1b) [29]. Detailed XPS data are in the supporting information (Figure S18). Higher binding energies for Ti 2p peaks of Glu-TsOH-Ti than that of pure TiO₂ lattice could be attributed to the electronic interaction of Ti with $-SO_3H$; thus, TiO₂ in Glu-TsOH-Ti could be considerably modified as reported earlier [30]. TEM and HRTEM (Figures 1c and 1d) images show plate-like TiO₂ particles of dimensions of 10–20 nm that are self-assembled (loosely assembled). Calculation of d-spacing value (d=0.35 nm) from the HRTEM analysis (Figure



Figure 1: Characterization of Glu-TsOH-Ti: Powder-XRD (a), XPS-spectra of Ti 2p (b) TEM, HR-TEM (c) and (d). TiO₂ particles in the TEM image are indexed.

1d) suggests that TiO_2 exists in anatase form. The HRTEM data also correlated with FESEM image showing the material is composed of nanoparticles of approximately 20 nm size that

are aggregated to form larger particles in some part of the image (Figures S16 and S17). Elemental mapping by energy dispersive X-ray spectroscopy (EDS) in SEM also confirmed the presence of both titanium and sulfur atoms in the material. Further analysis by AAS suggested the presence of 3.2 wt% titanium. EDS-SEM data showed that the material contained 76% and 9.1 wt% C and O, respectively. The BET surface area of Glu-TsOH-Ti is $42.5 \text{ m}^2\text{g}^{-1}$ with a pore volume of 0.0543 cm³g⁻¹ (N₂ adsorption-desorption plot, Figure S19). NH₃-TPD showed three desorption peaks for ammonia at 194.7 °C, 297.9 °C and 298.8 °C with a total acid density of 1.03 mmolg⁻¹. Total Brønsted acid density, as determined from the amount of sulfur content by ICP-OES method, was measured as 0.56 mmol g⁻¹. Thus, the ratio of Brønsted to Lewis acid density in the catalyst is 1.2.

3.2 Catalysis

3.2.1 HMF to EMF. Initial experiments were conducted using pure HMF as the starting substrate. HMF (1 mmol) etherification with ethanol (5 mL) in the presence of 50 mg catalyst achieved 91% EMF yield at 90 °C for 6 h. The ¹H NMR spectrum (Figure S3) showed no signals for unreacted HMF. A blank experiment without the catalyst yields only 3% EMF, which confirms the true effectiveness of Glu-TsOH-Ti. A previous report using mesoporous silica catalysts containing Lewis acidic Al³⁺ (Al-MCM-41 (50)) claimed 68% EMF yield from HMF at 140 °C for 5 h [31]. Although the total acidity of Al-MCM-41 (50) was not reported, a comparison of the catalytic performance of Glu-TsOH-Ti and Al-MCM-41 (50) suggests the superior activity of Glu-TsOH-Ti (91% EMF at 90 °C) than that of Al-MCM-41 (50) (68% EMF at 140 °C). The effectiveness of Glu-TsOH-Ti for EMF synthesis was then compared with other reported heterogeneous catalysts (Ar-SO₃H-SBA-15, Ar-CMSs-SO₃H, OMC-SO₃H and Glu-TsOH-Ti) in Table S1. Sulfonated carbon materials and Glu-TsOH-Ti are the most effective, in terms of EMF yield, although a direct comparison of these two

catalysts is difficult because of differences in the reaction conditions. Higher activity of Glu-TsOH-Ti in our earlier publication [26], is attributed to better accessibility of its acid sites and dual acidity, consistent with a prior report claiming Lewis acidic AI^{3+} in extra-framework zeolite facilitated HMF etherification to EMF [24]. It was proposed that HMF forms an oxonium by the Lewis acid sites upon adsorption on the surface, which then reacts with ethanol.

The reaction profile (Figure 2) reveals the formation of the ring-opening product, EL, upon conducting the reaction for a prolonged time. Because of ring-opening of EMF, its yield decreased and EL formed. The ring-opening of EMF is likely occurring by the Brønsted acid sites (0.56 mmol g⁻¹). A prior report explained that Brønsted acidic catalysts (H₂SO₄, Amberlyst[®] and Al-MCM-41 (25) favored the ring-rehydration and etherification, while the Lewis acid sites in the catalysts (ZrO₂-SBA-15, Al³⁺ isolated sites in extra-framework Al-MCM-41 (50)) acted synergistically to form EMF selectively.[24] Another paper reported that a SO₄²⁻/TiO₂ catalyst exhibited better catalytic performance and selectivity to methyl levulinate[32] from glucose when compared the results with TiO₂, Zr₃(PO₄)₄, H-mordenite and ZSM-5 catalysts. It is likely due to the higher acid density of SO₄²⁻/TiO₂ (0.63 mmol/g) than those of SO₄²⁻/ZrO₂ (0.57 mmol/g) and Zr₃(PO₄)₄ (0.30 mmol/g) [32]. The Lewis acidity of Tr⁴⁺ in SO₄²⁻/TiO₂ also likely facilitated isomerization of glucose to fructose, a key step to form HMF and then EMF.



Figure 2. The reaction profile of HMF etherification with the Glu-TsOH-Ti catalyst at 90 °C.

3.2.2 BHMF to 2,5-Bis(alkoxymethyl)furan. The etherification of BHMF was conducted with ethanol, methanol, n-propanol, n-butanol, and isoamyl alcohol to synthesize the corresponding AMF products (Table 1). The reaction temperatures with different alcohols were adjusted to keep the temperatures before their boiling points; however, it didn't change the yield of the corresponding etherified products significantly. A reaction with high catalyst loading showed a little effect on the yield (entry 5). The reaction time was found to have a profound effect on the yield and the nature of the etherified product. It was found that –OH groups of BHMF etherified with ethanol. First, 5-(ethoxymethyl)furan alcohol (EMFA) and BEMF are formed in 4 h (entry 2). When the reaction continued for 8 h, EMFA is fully converted to BEMF as the sole product with 92% yield and 100% selectivity (entry 3). The etherification of BHMF with ethanol was conducted using varying amounts of Glu-TsOH-Ti (Figure S20). It shows the catalytic performance enhanced with increasing the catalyst amount from 5 mg to 20 mg. Higher loadings (>20 mg) showed no pronounced effect, which is likely due to the mass transport limitation of the catalyst.

Entry	Alcohols	Т	Yield	Etherified products	
		(°C)	(%)	Ethernhed products	
1	МеОН	70	89	O BMMF	
2 ^a	EtOH	80	51		
				32% EMFA 51% BEMF	
3	EtOH	80	92		
4	nPrOH	100	90	O O O O O O O O O O O O O O O O O O O	
5 ^b	nBuOH	120	93		
6	Isoamyl	120	88	BIPMF	

Table 1. Etherification of BHMF with different alcohols.

Reaction conditions: BHMF = 1 mmol; alcohols = 5 mL, Glu-TsOH-Ti = 20 mg and 8 h reaction time. ^a reaction time = 4 h; ^b Glu-TsOH-Ti = 40 mg.

3.2.3 Fructose to HMF. The effectiveness of the Glu-TsOH-Ti catalyst was further evaluated for one-pot conversion of fructose to EMF, where dehydration and etherification take place sequentially. A preliminary reaction yielded 60% HMF, 29% EMF and 6% EL for 6 h at the quantitative conversion of fructose (entry 1, Table 2). The yield of EMF improved to 64% upon conducting the reaction for a prolonged time (24 h; entry 2, Table 2). EL (13%) and HMF (21%) accounted for the remaining carbon balance. Ring-opening of EMF to EL was observed for a 48 h reaction (entries 3 and 4, Table 2). The color of the product solutions turned darker for carrying out the reaction for longer times, indicating some amount of

humins could be formed [26]. A blank experiment without the catalyst showed no fructose conversion. Another reaction using glucose as the starting substrate gave low EMF and EL yields (entry 5, Table 2). A prior study reported that a sulfonated silica-carbon catalyst was effective for the conversion of fructose to EL and EMF, giving up to 80% total yield [13]. However, this catalyst was ineffective for glucose isomerization to fructose, resulting in poor yields of EL (7%) and EMF (4%). A similar observation was noted in another report for glucose conversion to EL/EMF using a sulfonic acid functionalized carbocatalyst [33]. In contrast, our carbocatalyst gives a slightly higher yield of EMF in comparison with the results of the sulfonated silica-carbon catalyst [13], due to high HMF yield via glucose isomerization and dehydration by the Lewis and Brønsted acid sites, as noted in our previous study [26]. HMF is then etherified to EMF by the Bronsted acid sites. The ring-opening of EMF occurs by the Brønsted sites when the reaction is prolonged.

			Fructose or	Yield (mol%)		
Entries	Time (h)	Glu-TSOH-Ti	glucose	HMF	EMF	EL
		(ing)	Conv. (%)			
1	6	50	100	60	29	6
2	24	50	100	21	64	13
3	30	50	100	nd	66	18
4	48	50	100	nd	43	36
5	24	25	nd	24	19	7
6 ^a	24	50	87	nd	17	4
7	24	cycle 2	100	26	61	10
8	24	cycle 5	100	24	59	9
9	24	cycle 6	100	25	58	7

Table 2. Fructose or glucose conversions to etherified products.

Other reaction conditions: Ethanol = 5 mL, temperature = $120 \, ^{\circ}\text{C}$. ^aglucose as the starting substrate. Entries 7-9 show the catalyst recyclability results. Nd = not determined.

The catalyst recyclability studies show (entries 7-9, Table 2) a slight decrease in the etherified and ring-opened products in the 6^{th} cycle, which could be due to the loss of the catalyst mass during recovery. The hot-filtration test of the catalyst for HMF etherification indicates no leaching of its Brønsted acid sites (Figure S21).

4.0 Conclusions

We reported a dual acidic carbocatalyst, containing titania as Lewis acid and sulfonated groups as Bronsted acid sites, is effective for HMF etherification to high octane fuel additives with maximum yield of up to 93%. The Lewis and Brønsted acid sites act synergistically to enable higher yield of furan ring containing products and minimal ring-opened side products. The two acid sites also enhanced the catalyst's performance and products selectivity in one-pot conversion of fructose via sequential dehydration and etherification reactions.

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6.0 References

[1] J. Goldemberg, Ethanol for a Sustainable Energy Future, Science, 315 (2007) 808-810.

[2] Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates, Nature, 447 (2007) 982-985.

[3] Z. Zhang, Y. Wang, Z. Fang, B. Liu, Synthesis of 5-Ethoxymethylfurfural from Fructose and Inulin Catalyzed by a Magnetically Recoverable Acid Catalyst, ChemPlusChem, 79 (2014) 233-240.

[4] J.G. Pereira, S.C.A. Sousa, A.C. Fernandes, Direct Conversion of Carbohydrates into 5-Ethoxymethylfurfural (EMF) and 5-Hydroxymethylfurfural (HMF) catalyzed by Oxomolybdenum complexes, ChemistrySelect, 2 (2017) 4516-4521.

[5] S. Dutta, B. Saha, Hydrodeoxygenation of Furylmethane Oxygenates to Jet and Diesel Range Fuels: Probing the Reaction Network with Supported Palladium Catalyst and Hafnium Triflate Promoter, ACS Catalysis, 7 (2017) 5491-5499.

[6] S. Dutta, A. Bohre, W. Zheng, G.R. Jenness, M. NuÌ □nÌ*f*ez, B. Saha, D.G. Vlachos, Solventless C–C Coupling of Low Carbon Furanics to High Carbon Fuel Precursors Using an Improved Graphene Oxide Carbocatalyst, ACS Catalysis, 7 (2017) 3905-3915.

7

[7] B. Saha, S. Liu, S. Dutta, W. Zheng, N.S. Gould, Z. Cheng, B. Xu, D.G. Vlachos, Catalytic Hydrodeoxygenation of High Carbon Furylmethanes to Renewable Jet―fuel Ranged Alkanes over a Rhenium Modified Iridium Catalyst, ChemSusChem, (2017).

[8] M. Mascal, E.B. Nikitin, Towards the Efficient, Total Glycan Utilization of Biomass, ChemSusChem, 2 (2009) 423-426.

[9] M.M. Antunes, P.A. Russo, P.V. Wiper, J.M. Veiga, M. Pillinger, L. Mafra, D.V. Evtuguin, N. Pinna, A.A. Valente, Sulfonated Graphene Oxide as Effective Catalyst for Conversion of 5-(Hydroxymethyl)-2-furfural into Biofuels, ChemSusChem, 7 (2014) 804-812.

[10] J. Yanowitz, E. Christensen, R. McCormick, Utilization of Renewable Oxygenates as Gasoline Blending Components, National Renewable Energy Laboratory (NREL), Golden, CO., 2011.

[11] A. Bohre, S. Dutta, B. Saha, M.M. Abu-Omar, Upgrading Furfurals to Drop-in Biofuels: An Overview, Acs Sustainable Chemistry & Engineering, 3 (2015) 1263-1277.

[12] B.A.V.B.A.N.H.A.C.S.A.V.K.J.A.V.H.A.D.G. Vanderhaegen, Evolution of chemical and sensory properties during aging of top-fermented beer, Journal of agricultural and food chemistry, v. 51 (2003) pp. 6782-6790-2003 v.6751 no.6723.

[13] R. Zhong, F. Yu, W. Schutyser, Y. Liao, F. de Clippel, L. Peng, B.F. Sels, Acidic mesostructured silica-carbon nanocomposite catalysts for biofuels and chemicals synthesis from sugars in alcoholic solutions, Applied Catalysis B: Environmental, 206 (2017) 74-88.

[14] S. Dutta, S. De, M.I. Alam, M.M. Abu-Omar, B. Saha, Direct conversion of cellulose and lignocellulosic biomass into chemicals and biofuel with metal chloride catalysts, Journal of Catalysis, 288 (2012) 8-15.

[15] B. Liu, Z. Zhang, K. Huang, Z. Fang, Efficient conversion of carbohydrates into 5ethoxymethylfurfural in ethanol catalyzed by AlCl3, Fuel, 113 (2013) 625-631.

[16] M. Imteyaz Alam, S. De, S. Dutta, B. Saha, Solid-acid and ionic-liquid catalyzed onepot transformation of biorenewable substrates into a platform chemical and a promising biofuel, RSC Advances, 2 (2012) 6890-6896.

[17] S. Saravanamurugan, O. Nguyen Van Buu, A. Riisager, Conversion of Mono- and Disaccharides to Ethyl Levulinate and Ethyl Pyranoside with Sulfonic Acid-Functionalized Ionic Liquids, ChemSusChem, 4 (2011) 723-726.

[18] K.S. Arias, S.I. Al-Resayes, M.J. Climent, A. Corma, S. Iborra, From Biomass to Chemicals: Synthesis of Precursors of Biodegradable Surfactants from 5-Hydroxymethylfurfural, ChemSusChem, 6 (2013) 123-131.

[19] L. Bing, Z. Zhang, K. Deng, Efficient One-Pot Synthesis of 5-(Ethoxymethyl)furfural from Fructose Catalyzed by a Novel Solid Catalyst, Industrial & Engineering Chemistry Research, 51 (2012) 15331-15336.

[20] P. Che, F. Lu, J. Zhang, Y. Huang, X. Nie, J. Gao, J. Xu, Catalytic selective etherification of hydroxyl groups in 5-hydroxymethylfurfural over H 4 SiW 12 O 40/MCM-41 nanospheres for liquid fuel production, Bioresource technology, 119 (2012) 433-436.

[21] L. Bing, Z. Zhang, K. Deng, Efficient one-pot synthesis of 5-(ethoxymethyl) furfural from fructose catalyzed by a novel solid catalyst, Industrial & Engineering Chemistry Research, 51 (2012) 15331-15336.

[22] S. Saravanamurugan, A. Riisager, Solid acid catalysed formation of ethyl levulinate and ethyl glucopyranoside from mono-and disaccharides, Catalysis Communications, 17 (2012) 71-75.

[23] Z. Yuan, Z. Zhang, J. Zheng, J. Lin, Efficient synthesis of promising liquid fuels 5ethoxymethylfurfural from carbohydrates, Fuel, 150 (2015) 236-242.

[24] P. Lanzafame, D.M. Temi, S. Perathoner, G. Centi, A. Macario, A. Aloise, G. Giordano, Etherification of 5-hydroxymethyl-2-furfural (HMF) with ethanol to biodiesel components using mesoporous solid acidic catalysts, Catalysis Today, 175 (2011) 435-441.

[25] J.-P. Lange, W.D. van de Graaf, R.J. Haan, Conversion of Furfuryl Alcohol into Ethyl Levulinate using Solid Acid Catalysts, ChemSusChem, 2 (2009) 437-441.

[26] M.G. Mazzotta, D. Gupta, B. Saha, A.K. Patra, A. Bhaumik, M.M. Abu-Omar, Efficient Solid Acid Catalyst Containing Lewis and Brønsted Acid Sites for the Production of Furfurals, ChemSusChem, 7 (2014) 2342-2350.

[27] P.A. Russo, M.M. Antunes, P. Neves, P.V. Wiper, E. Fazio, F. Neri, F. Barreca, L. Mafra, M. Pillinger, N. Pinna, A.A. Valente, Solid acids with SO3H groups and tunable

surface properties: versatile catalysts for biomass conversion, Journal of Materials Chemistry A, 2 (2014) 11813-11824.

[28] V.L. Budarin, J.H. Clark, R. Luque, D.J. Macquarrie, Versatile mesoporous carbonaceous materials for acid catalysis, Chemical Communications, (2007) 634-636.

[29] M. Sathish, B. Viswanathan, R.P. Viswanath, C.S. Gopinath, Synthesis, Characterization, Electronic Structure, and Photocatalytic Activity of Nitrogen-Doped TiO2 Nanocatalyst, Chem. Mater., 17 (2005) 6349-6353.

[30] D. Gupta, K.K. Pant, B. Saha, Titania nanoparticles embedded in functionalized carbon for the aqueous phase oxidation of 5-hydroxymethylfurfural, Molecular Catalysis, 435 (2017) 182-188.

[31] G. Morales, M. Paniagua, J.A. Melero, J. Iglesias, Efficient production of 5ethoxymethylfurfural from fructose by sulfonic mesostructured silica using DMSO as cosolvent, Catalysis Today, 279 (2017) 305-316.

[32] L. Peng, L. Lin, H. Li, Q. Yang, Conversion of carbohydrates biomass into levulinate esters using heterogeneous catalysts, Applied Energy, 88 (2011) 4590-4596.

[33] J. Wang, Z. Zhang, S. Jin, X. Shen, Efficient conversion of carbohydrates into 5hydroxylmethylfurfan and 5-ethoxymethylfurfural over sufonic acid-functionalized mesoporous carbon catalyst, Fuel, 192 (2017) 102-107.



Highlight

- HMF etherified fuel additives of different carbon lengths are synthesized with high yields
- Furan rings retained in the etherified products with minimal ring-opening
- A dual acidic carbocatalyst acts synergistically to achieve products with high selectivity
- A cascade of conversion of fructose to etherified products is achieved

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