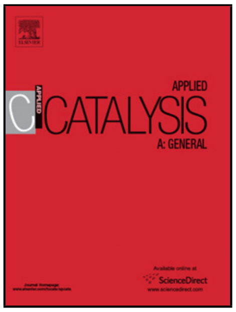


Title: Remarkable catalytic synergism of alumina, metal salt and solvent for conversion of biomass sugars to furan compounds

Author: <ce:author id="aut0005" author-id="S0926860X17300042-5b29e22ecd27983e97f4c142065b00ed"> Gajula Sampath<ce:author id="aut0010" author-id="S0926860X17300042-f0344fb6d9fe5054403f82ca768a8c63"> Kannan Srinivasan

PII: S0926-860X(17)30004-2
DOI: http://dx.doi.org/doi:10.1016/j.apcata.2017.01.004
Reference: APCATA 16115

To appear in: *Applied Catalysis A: General*

Received date: 26-10-2016
Revised date: 24-12-2016
Accepted date: 6-1-2017

Please cite this article as: Gajula Sampath, Kannan Srinivasan, Remarkable catalytic synergism of alumina, metal salt and solvent for conversion of biomass sugars to furan compounds, Applied Catalysis A, General http://dx.doi.org/10.1016/j.apcata.2017.01.004

Remarkable catalytic synergism of alumina, metal salt and solvent for conversion of biomass sugars to furan compounds

Gajula Sampath and Kannan Srinivasan*

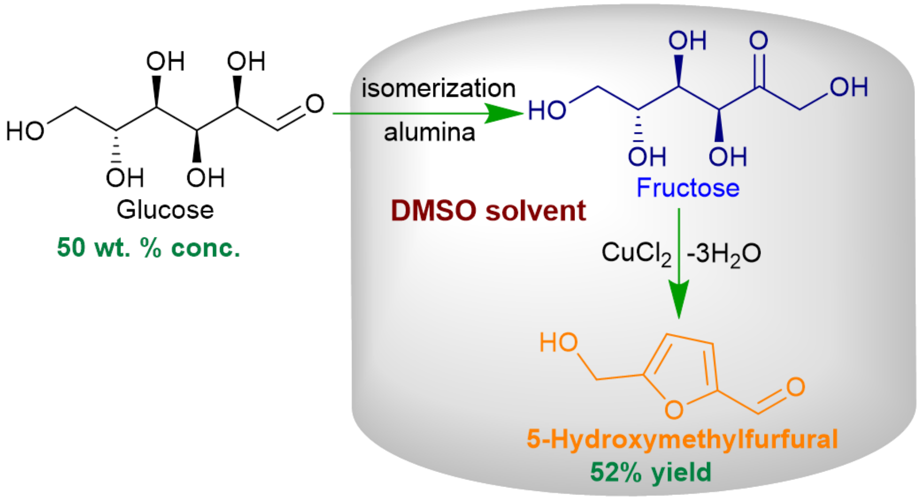
Inorganic Materials and Catalysis Division, CSIR-Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), GB Marg, Bhavnagar - 364 002, India

Academy of Scientific and Innovative Research, Central Salt and Marine Chemicals Research Institute, GB Marg, Bhavnagar-364 002, India

***Manuscript Correspondence**:

Prof. Dr. Kannan Srinivasan
Inorganic Materials and Catalysis Division
CSIR-Central Salt and Marine Chemicals Research Institute
Council of Scientific and Industrial Research (CSIR)
Bhavnagar - 364 002
India
Tel: +91-278-2567760 Ext. 7030
FAX: +91-278-2567562
E-mail: skannan@csmcri.org ; kanhem1@yahoo.com

Graphical abstract



Highlights:

- Metal salt, alumina, and DMSO together synergistically converted glucose to HMF
- Alumina isomerizes glucose to fructose, and $CuCl_2$ & DMSO convert fructose to HMF
- The system can work for up to 50 wt% concentrations and for different sugars
- System can tolerate water, and promises the use of industrial sugar syrups

Abstract

Catalytic conversion of sugars to furan compounds has become an important field in the research area of chemicals production from biomass. Here, a remarkable synergism of transition metal salt, alumina and solvent effectively converted glucose to 5-hydroxymethylfurfural (HMF). Studies showed that the alumina participates in glucose to fructose isomerization, while metal salt and DMSO solvent promote fructose dehydration to HMF. This system can work for upto 50 wt% concentration of substrate giving 52% HMF yield. This system can also convert different hexose (including disaccharides and starch) sugars to HMF and pentose sugars to furfural. In terms of HMF yield and stability, this system showed tolerance to the presence of water (upto 15 wt%). Further, oxidized products of HMF showed high solubility in DMSO (45 wt% for 2,5-diformylfuran and 55 wt% for 2,5-furandicarboxylic acid), and they were precipitated out when water was added. These studies promise this sytem as efficient for production of HMF and its further conversions.

Keywords

5-Hydroxymethylfurfural, Dimethylsulphoxide, Synergism, Alumina, Isomerization, Dehydration

1. Introduction

With diminishing petroleum resources and increasing concerns on its utilization, it became necessary to look for alternative renewable sources. Besides considering renewables like solar, wind and H_2, "biomass" has its own potential for the production of organic chemicals that are necessary for our daily life [1]. Among the various platform molecules derivable from biomass, 5-hydroxymethylfurfural (HMF) is a promising intermediate obtained by acid-catalyzed dehydration of sugar part of the biomass like cellulose and starch. HMF has diverse applications, as a raw material, such as solvents (e.g. 2,5-dimethylfuran and 2,5-dimethyltetrahydrofuran), polymer precursors (2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF)), fuel additives and for several value-added chemicals [2].

For HMF production, the mostly used substrate is fructose owing to its ease of selective conversion. However, for practical application, it is necessary to use abundant glucose as a substrate which can be produced commercially with more than 90% yield by acid or enzymatic hydrolysis of starch and cellulose which is the most abundant organic material on Earth. It is worth mentioning here that most of the catalysts used for fructose dehydration to HMF did not work efficiently for glucose [3]. This was also evidenced when sucrose was used as substrate wherein only the fructose part was converted to HMF leaving behind the unconverted glucose [4].

Recently direct conversion of glucose to HMF using chromium salts in ionic liquid systems (ILs) was reported [5]. The inhibition in HMF selectivity by other metal salts was due to lack of glucose to fructose isomerization that led to multiple paths forming other products including mannose, 1,6-anhydroglucose, etc. Many other catalytic systems were also tried like combination of solid catalysts (Amberlyst-15 as Brønsted acid and hydrotalcite as Brønsted base catalysts in N,N-dimethylformamide (DMF) with 3 wt% glucose concentration [6], Amberlyst-70 Brønsted acid Sn-based materials as Lewis acid with 2 wt% glucose), and as well as bifunctional catalysts (SO_4^{2-}/ZrO_2-TiO_2 in a biphasic solvent and $SO_4^{2-}/ZrO_2-Al_2O_3$ in dimethylsulphoxide (DMSO) (5 wt% glucose, 423 K) [7]. Recently, updated reviews covered many catalysts and solvent systems used in the production of HMF and other furan derivatives [8-10]. In overall, carbohydrate processing to HMF with current systems is expected to be expensive, have limitations on working at higher concentration of sugars and devoid of green quotient due to the proficient use of toxic and corrosive catalysts. It is also necessary that additional processes and catalysts are needed for the subsequent valorisation of HMF through cascade operations that demand the avoidance of separation and purification problems [11]. Hence, integrated multistep reaction systems with components that work at high substrate concentration, low cost, less toxic, easy-to-handle catalysts and solvents which can be used for subsequent steps without the necessity of separation are desirable.

Normally in chemical reactions, solvents play some important roles. In literature, DMSO was used as a co-solvent along with ionic liquids or water to improve the HMF yield [12]. It was observed that it can acts as a promoter or catalyst in the conversion of sugars

[13]. Further, it interacts strongly with HMF through solvation, and thereby restricts the contact of HMF with intermediates and water molecules, preventing the undesired side reactions [14]. Also, owing to its high solubility for sugars including starch, and the product HMF, it is possible to conduct reaction even at high substrate concentrations.

In ILs, only Cr-salts showed good selectivity to HMF from glucose, whereas other salts which gave similar yields from fructose were non-selective when glucose was used at similar conversions [5]. In another study, various metal salts were tested wherein $CuCl_2$ showed higher selectivity of HMF from fructose while very little selectivity from glucose compared to $CrCl_2$ while $FeCl_3$ did not show any conversion of glucose [15]. However, it would be advantageous if Cu and Fe compounds are used which are less toxic, abundant and also would assist in further steps like oxidation or reduction [16-18]. Lewis acid catalysts are known for catalysing the isomerization, and Al-based catalysts were reported for isomerization of glucose to fructose [19]. Among them alumina is a cheap, abundant and heterogeneous Lewis acid catalyst.

With a hypothesis on the cooperative activity of transition metal salts ($FeCl_3$ or $CuCl_2$), Al_2O_3 and DMSO, we combined them with an endeavour for the selective conversion of glucose to HMF, studied the reactions for up to 50 wt% of substrate concentration.

2. Experimental

2.1 Materials

Alumina (active neutral-150mesh), L-Rhamnose (monohydrate), D-(-)-Arabinose, [BMIM]Cl (>98%), furfural (>99%) and HMF (>98%) were purchased from Sigma-Aldrich. D-(+)-Cellobiose (>98%), D-(+)-Galactose (>98%) and D-(+)-Xylose (>98%) were purchased from Alfa-Aesar. Sucrose (AR), Glucose (Dextrose anhydrous), DMSO (AR), and DMF (AR) were purchased from sd-fine Chemicals, India.

2.2 Reaction procedure

Reactions were carried out in a 25 ml round bottomed screw cap tube with magnetic stirring in a preheated oil bath (on Schott hot plate) set at reaction temperature. For a typical reaction, first 3 g of solvent was taken in a reactor tube and was pre-heated until the desired reaction temperature was achieved. Then 0.9 g of substrate (30wt%), and catalysts were added and stirred at 800 rpm for a specified reaction time. The weight percentage of substrate indicated is with respect to the amount of solvent [(substrate/solvent) x 100]. After the reaction, tube was taken out and cooled to room temperature. The reaction mixture samples were stored in a refrigerator at 4 °C before the analysis.

2.3 Analytical methods

Quantification of reactant and products was done with X-bridge amide column using UHPLC (Shimadzu-Nexera) system linearly connected to Photo diode array (PDA) and evaporative light scattering detector (ELSD) detectors. Sample for analysis was prepared by diluting the reaction mixture in water, followed by filtering through a 0.25 µm pore-size syringe filter. Acetonitrile-water mixture of 0.2 wt% triethylamine was used as mobile phase at 1 ml/min flow rate and keeping the column temperature at 35 °C. The method was set with constant change of the mobile phase mixture from 80:20 to 60:40 that reached in 13 min and then a constant ratio of 80:20 was maintained for 7 min to stabilize to the initial ratio for the analysis of the next sample. The sugars were quantified using ELSD (conditions: spray chamber (SC) temperature 20 °C, drift tube (DT) temperature 45 °C and N_2 carrier pressure 50 psi). HMF and furfural were quantified by PDA detector at 284 and 260 nm respectively. Quantification was done based on calibration method using standards.

For all the compounds, standard solutions were made and calibration graphs were drawn for computing the conversion and yield. After plotting the calibration graphs, and getting the amount of substance, the following equations were used for calculation.

$$\text{Conversion (\%)} = 100 - \left[\frac{\text{moles of reactant remained}}{\text{initial moles of reactant}} \text{ X } 100\right]$$

$$\text{Yield (\%)} = \frac{\text{moles of product formed}}{\text{initial moles of reactant}} \text{ X } 100$$

2.4 Catalyst characterization

Recyclability of alumina was checked by separating the alumina after reaction by centrifugation, then washing twice with DMSO and used for the reaction by taking fresh DMSO, $CuCl_2$ and substrate. After 4th use, alumina was calcined at 550 °C for 6 h and used for next cycle.

For determination of carbon content on used alumina after each use, the alumina was washed two times with 2 ml of DMSO, and then 3 times with 5 ml of MeOH, followed by drying in oven. Carbon content was determined by CHNS elemental analysis using Elementor’s Vario Microcube instrument.

To analyse the acid sites on alumina of both fresh and the calcined form of used catalyst, pyridine adsorption followed by Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic technique analysis was carried out and compared with literature data [20, 21]. Alumina samples of study were first taken on a watch glass along with 25 ml of pyridine in a beaker, together were put in a vacuum desiccator, applied vacuum and kept for 1 h. Then pyridine was removed and the physically adsorbed pyridine on sample was removed by applying vacuum two times. Then DRIFT analysis of the pyridine-adsorbed samples was conducted using DRIFT spectroscopic investigations were carried out using a Nicolet 5PC spectrometer equipped with a COLLECTOR II diffuse reflectance mirror system and a high-temperature DRIFT spectroscopic cell (Spectra-Tech Inc.) at various temperatures (25, 150, 250, 350 and 450 ^{o}C). The data received at 150 ^{o}C showed clear bands, hence the acidity of all the samples was compared by using this data.

For the determination of pore volume of alumina samples, the washed sample was first dried in oven at 100 ^{o}C for 2 h. After cooling to room temperature, water was slowly added dropwise until the powder becomes completely wet by capillary action through the pores. The pore volume was determined by measuring the increase in the weight of the sample.

3. Results and discussion

3.1 Catalytic synergism

Initially reactions were studied at 80 $^{\circ}$C with 30 wt% glucose in DMSO solvent using $CuCl_2$ and alumina as catalysts separately. As shown in Table 1, independently both the catalysts did not give any HMF yield from glucose, and on the contrary the combination of these two catalysts formed HMF. It was also observed that in the presence of only alumina, formation of fructose from glucose was observed, whereas it was not observed in the absence of alumina or in the presence of $CuCl_2$. It indicates that the alumina is participating in glucose to fructose isomerization. Mechanistically, both, the ring opening of cyclic form of glucose (glucopyranose) and the ring-closing of the open-chain form of fructose into fructofuranose form in the process of isomerization are caused by the hydrogen shift, a reversible reaction as reported in literature [22]. The individual roles of DMSO and $CuCl_2$ in the conversion of glucose to HMF were checked by comparing their activity by taking both glucose and fructose as substrate individually (Table 1). The results indicate that, unlike from glucose, HMF is formed from fructose in presence of DMSO without any catalyst added. However, In the presence of $CuCl_2$, the yield of HMF increased further. But in the presence of alumina, both the conversion of fructose and yield of HMF decreased, which may be due to the reversible isomerization of fructose to glucose. But when $CuCl_2$ is added along with alumina, conversion of both glucose and fructose increased, which indicates that $CuCl_2$ is promoting the conversion of sugar towards dehydration step. It was also observed that $CuCl_2$ is promoting the conversion of fructose towards HMF formation. Thus, the synergic effect of both $CuCl_2$ and Al_2O_3 plays a significant role in the conversion of glucose to HMF (Scheme 1).

The yield of HMF from glucose further increased to 56% within short period of time (3 h) by increasing the reaction temperature to 120 ^{o}C (Table 2, entry 3). In literature, hydrotalcites were reported for the isomerization of glucose to fructose and was also used in combination with Amberlyst-15 for direct one-pot conversion of glucose to HMF where Amberlyst-15 participates in fructose dehydration to HMF [6]. Along this line, Lewis acidic $CuCl_2$ was combined with Brønsted basic hydrotalcite (MgAl3-CO_3-HT); however, this combination did not show any synergism (Table 2, entry 2). The role of alumina was further confirmed by conducting the reaction in water medium at similar conditions which resulted in glucose to fructose isomerization only. In water, although conversion is low (11%), the selectivity to fructose is very high (>95%) with alumina compared to many other isomerization catalysts reported [19].

Variation in anion of metal salt was checked by taking Cu^{II} salts of different anions (SO_4^{2-}, NO_3^- and Cl^-). A slightly higher yield was observed with chloride salt (Figure 1), which is due to the additional influence of chloride ion as reported in literature [23]. The chlorides of different transition metals with alumina were tested and the activity order is $Cu^{II} > Fe^{III} \approx Cr^{III} > Ni^{II} > Co^{II} > Zn^{II}$ (Table 2). Cu, Fe, and Cr salts showed similarly activity. The combination of $CuCl_2$ and alumina was tested for the reaction in other solvents which are commonly reported for this reaction. [BMIm]Cl supported this catalytic combination similar to the DMSO for the yield of HMF (Figure 2). But water and DMF solvents were inactive for HMF yield.

DMSO or IL, alumina, and metal salt are all together synergistically working as a catalytic system, and in the absence of any one of these components, the yield of HMF is poor.

3.2 HMF synthesis from other substrates

The combination of $CuCl_2$, alumina, and DMSO was applied for other sugar substrates also. This catalytic system successfully converted fructose, galactose, cellobiose and sucrose into HMF (Table 3). Also, it converted pentose sugars to furfural. As this system is non-Brønsted acidic in nature, it did not hydrolyze the starch polymer to glucose and hence no further conversion to HMF was observed (Table 3, entry 6). However, by adding small amount of Brønsted acid (0.02 mmol H_2SO_4), the reaction was initiated upon glucan polymer hydrolysis and 26% yield of HMF was achieved (Table 3, entry 7). The added acid alone was ineffective to produce HMF (Table 3, entry 8). On the other hand, without adding any acid, disaccharides (sucrose and cellobiose) were converted into HMF with similar yields as that of their monomers (Table 3, entry 4 and 5).

3.3 Reaction kinetics and stability of HMF

Kinetic experiments under similar conditions revealed that, upon increasing the reaction temperature from 100 to 120 °C, the required time to get maximum HMF yield decreased by 6 times, and by increasing from 120 to 140 °C the required time decreased by 3 times. However, irrespective of the temperature, the maximum achievable yield was same (56±2%). The reaction was scaled up to 10 times of substrate, solvent and catalysts (9 g glucose, 30 g DMSO, 3 g alumina, 0.5 mmol $CuCl_2$) under the similar conditions as mentioned in Table 2, Entry 3 (120 °C, 3 h), and no change in HMF yield (56%) was observed. Reaction at higher glucose concentration (50 wt% with respect to DMSO) was carried out at 140 °C. The HMF yield is 52% indicating no significant loss in the efficiency this catalytic system even at high substrate concentration. The lesser yields for this reaction, in particular at high sugar concentration, are common due to unidentified side-products [5], humins and soluble polymers formation by reaction intermediates [24]. We propose that the yields can be further improved by using appropriate co-solvents.

Normally, the presence of water decreases the HMF yield as HMF is less stable at higher temperatures and in aqueous medium [25]. To examine the negative influence, deliberate addition of water to the solvent was performed. Yield of HMF from glucose did not decrease with up to 15 wt% of water in DMSO (Table 3, Entry 1). This may be due to the holding of water molecules by DMSO to a certain limit (here 15 wt%) to avoid the contact of water with intermediates and products. This result is encouraging as this catalytic system is amenable when the real industrial aqueous sugar syrups are used. Here, the stability of HMF in the reaction system was assessed by first taking 100 mg of HMF in 3 g DMSO and stirred at 120 °C for 3 h. To that, 200 μL water was added and stirred for 2 h. After that 0.3 g alumina and 0.1 mmol $CuCl_2$ were added and stirred for another 2 h. No variation in HMF content was noted in all these cases indicating its stability under the reaction conditions. The stability HMF is due to its strong interaction with DMSO that further avoids the contact of HMF with reactant, intermediates, and water as reported in literature [14]. In literature it was also was reported that metal salts enhance the stability of HMF [5]. The limit in maximum yield of HMF may be due to high reactivity of HMF with reaction intermediates which leads to polymerization [24].

3.4 Recyclability of alumina

After the reaction, the alumina was recovered by centrifugation and tested for its recycle efficiency by adding along with fresh $CuCl_2$ under the optimized conditions (120 ^{o}C using 30 wt% glucose). A gradual decrease in the yield of HMF with reuse of alumina was observed over four cycles (Table 4). It is due to blocking of active sites of alumina by condensed polymers formed during the reaction. This reason was supported by the increase in the intensity of brown color as supported from carbon content on the alumina with recycles (3.2 to 3.5 from 1st to 4th use) measured by CHNS analysis and the color change of alumina from white to brown after first use and gradual increase in intensity of brown color upon recycles (Table 4). DMSO or MeOH washings could not remove the adsorbed polymers; however, upon calcination at 550 °C for 6 h turned the color to white indicating the removal of polymers, and the catalytic activity was nearly restored, giving 48% yield.

Pyridine adsorption studies with DRIFT spectroscopy analysis was carried out for both fresh alumina, alumina used up to 4th cycle, and calcined form of used alumina samples. Fresh alumina showed the bands at 1542, 1650 and 1485 cm^{-1} which indicate Bronsted acidity and a band at 1446cm^{-1} region which indicates Lewis acidity (Fig. 3). On the contrary, used alumina showed no such bands indicating the acid sites were blocked due to deposition of polymeric products. However, upon calcination of the used alumina, the corresponding bands of the acid sites reappeared indicating that the catalytic sites were regained by the removal of polymers. The absence of shift in these bands for both the samples indicates that there is no change in nature and strength of acid sites. However when the bands corresponding to the Lewis and Bronsted acid sites were compared, a change in the ratio of these sites upon calcination was observed. This could probably due to a decrease in number of hydroxyl groups upon calcination. This change is probably be responsible for the variation in the HMF yield.

The pore volume analysis was assessed for the alumina samples to see any textural variations occur upon reuses or calcination. All the samples showed similar pore volume in the range of 0.73±0.02 ml/g (Table 4) which showed insignificant change in structural porosity upon recycles and upon calcination, suggesting that the porosity is not a factor for this variation in activity.

3.5 Scope for the conversion of HMF to DFF or FDCA

It was reported that the solubility of FDCA and DFF in both water and acetic acid medium was very low (around 0.1 wt%) [26]. Although, FDCA solubility can be improved in aqueous basic medium, it involves neutralization of acid groups on FDCA. Here, we checked separately the solubility of these compounds in DMSO, and it showed a significant solubility for both FDCA (55 wt%) and DFF (45 wt%). It is worth mentioning here that DMSO is explored as a solvent for the oxidation of HMF to DFF and FDCA in literature [16]. Further we checked the separation possibility of these compounds from DMSO by adding water to the product mixture. Just by adding small amount of water (20 wt%), both DFF and FDCA precipitated out from solvent as white solid (Figure 4). Thus, albeit having the problem in separating HMF from DMSO [27], the very high solubility of FDCA and DFF in DMSO and separation (by adding water) will allow one to use this solvent for further reactions of HMF at high concentrations.

The factors like, high stability of HMF, separation possibility for oxidized furan derivatives from DMSO, redox catalytic nature of metal compounds and cooperative nature of alumina create newer opportunities to study subsequent reactions in one-pot leading to commercially useful products [28]. We believe this system can be improved further through detailed investigations like using co-solvents & co-catalysts, reaction optimization, chemical engineering, modification of catalysts, etc.

4. Conclusions

The synergism of a metal salt, alumina and DMSO was observed for the efficient conversion of glucose to HMF in high yields even at high glucose concentration (52% HMF yield at 50 wt% concentration of glucose in DMSO solvent with combination of $CuCl_2$ and alumina). The activity studies showed that the alumina participates in glucose to fructose isomerization, while $CuCl_2$ & DMSO involve in fructose dehydration to HMF. This catalytic system can convert various hexose and pentose sugars to HMF and furfural respectively. The tolerance of this system to the presence of water for up to 15% allows the use of industrial sugar solutions. The high solubility of FDCA (55 wt%) and DFF (45 wt%) in DMSO and their precipitation by adding water gives an opportunity for this system to be used for further conversions of HMF. Further investigations of the system might assist in improving the performance of this system.

Acknowledgements

CSIR-CSMCRI Communication No. 028/2015. Authors thank CSIR, New Delhi for financial support under the project OLP-0031. G.S. thanks University Grants Commission, New Delhi for a Senior Research Fellowship. The authors thank Analytical Division and Centralized Instrument Facility for instrumental support.

References

[1] P.N.R. Vennestrøm, C.M. Osmundsen, C.H. Christensen, E. Taarning, Angew. Chem. Int. Ed. 50 (2011) 10502-10509.

[2] C. Moreaua, M. N. Belgacemb, A. Gandini, Topics Catal. 27 (2004) 1-4.

[3] A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, Green Chem. 13 (2011) 754-793.

[4] C. Carlini, M. Giuttari, A.M.R. Galletti, G. Sbrana, T. Armaroli, G. Busca, Appl. Catal. A: Gen. 183 (1999) 295-302.

[5] H. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science 316 (2007) 1597-1600.

[6] J. Tuteja, S. Nishimura, K. Ebitani, Bull. Chem. Soc. Japan 85 (2012) 275-281.

[7] J. Zhang, L. Lin, S. Liu, Energy Fuels 26 (2012) 4560-4567.

[8] R.J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Chem. rev. 113 (2013) 1499-1597.

[9] T. Wang, M.W. Nolte, B.H. Shanks, Green Chem. 16 (2014) 548-572.

[10] S.P. Teong, G. Yi, Y. Zhang, Green Chem. 16 (2014) 2015-2026.

[11] A.I. Torres, P. Daoutidis, M. Tsapatsis, Energy Environ. Sci. 3 (2010) 1560-1572.

[12] Q. Bao, K. Qiao, D. Tomida, C. Yokoyama, Catal. Commun. 9 (2008) 1383-1388.

[13] A.S. Amarasekara, L.D. Williams, C.C. Ebede, Carbohydr. Res. 343 (2008) 3021-3024.

[14] G. Tsilomelekis, T.R. Josephson, V. Nikolakis, S. Caratzoulas, ChemSusChem 7 (2014) 117-126.

[15] E.A. Pidko, V. Degirmenci, E.J.M. Hensen, ChemCatChem 4 (2012) 1263-1271.

[16] G.A. Halliday, R.J. Young, V.V. Grushin, Org. Lett., 5 (2003) 2003-2005.

[17] L. Ngoc-Thuc, P. Lakshmanan, K. Cho, Y. Han, H. Kim, Appl. Catal. A:Gen, 464 (2013) 305-312.

[18] Y. Liu, M.A. Mellmer, D.M. Alonso, J.A. Dumesic, ChemSusChem 8 (2015) 3983-3986.

[19] A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis, A.A. Lappas, ChemCatChem 8 (2016) 1100-1110.

[20] E.P. Parry, J. Catal. 2 (1963) 371-379.

[21] C.B. J. Billingham, J. Yarwood, Clay Minerals 31 (1996) 513-522.

[22] V. Choudhary, A.B. Pinar, R.F. Lobo, D.G. Vlachos, S.I. Sandler, ChemSusChem 6 (2013) 2369-2376.

[23] J.B. Binder, R.T. Raines, J. Am. Chem. Soc. 131 (2009) 1979–1985.

[24] X. Hu, S. Kadarwati, S. Wang, Y. Song, M.D.M. Hasan, C.Z. Li, Fuel Process. Technol. 137 (2015) 212-219.

[25] G. Tsilomelekis, M.J. Orella, Z. Lin, Z. Cheng, W. Zheng, V. Nikolakis, D.G. Vlachos, Green Chem. 18 (2016) 1983-1993.

[26] M.A. Lilga, R.T. Hallen, M. Gray, Topics Catal. 53 (2010) 1264-1269.

[27] J. Wang, J. Ren, X. Liu, G. Lu, Y. Wang, Aiche Journal 59 (2013) 2558-2566.

[28] Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Nature 447 (2007) 982-985.

Figure Captions:

Figure 1 Anion variation study of Cu^{II} salts with alumina (0.9 g glucose (30 wt%), 0.3 g Al_2O_3, 0.05 mmol copper salt, 3 g DMSO, 120 °C, and 3 h)

Figure 2 Solvent variation study (0.9 g glucose (30 wt%), 0.3 g Al_2O_3, 0.05 mmol $CuCl_2$, 3 g solvent, 120 °C, and 3 h)

Figure 3 Pyridine adsorption DRIFT-IR spectra of fresh alumina and calcined used alumina

Figure 4 The separation of FDCA or DFF from DMSO

Scheme 1 Conversion of glucose to HMF in DMSO with alumina and metal salt

Fig.1

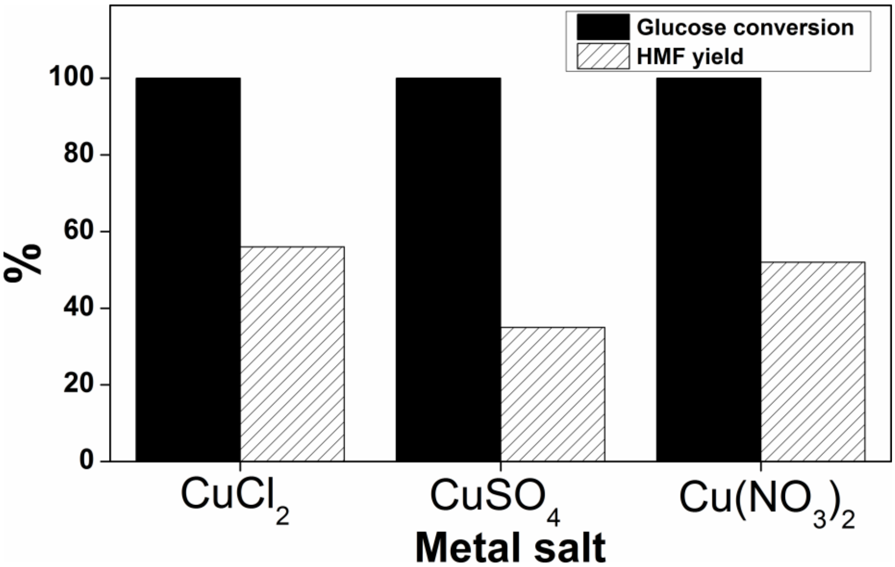

Glucose conversion
HMF yield
100
80
60
40
20
0
%
$CuCl_2$
$CuSO_4$
$Cu(NO_3)_2$
Metal salt

Fig.2

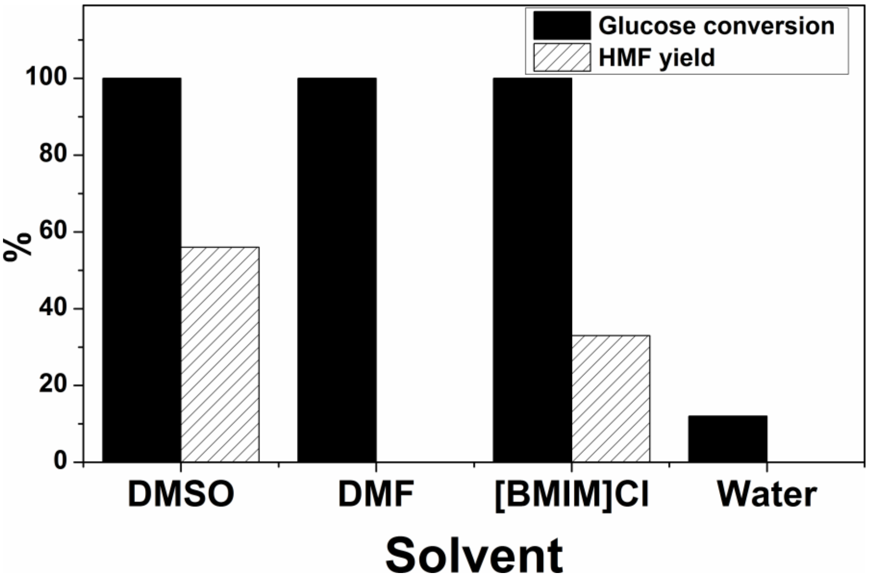

Glucose conversion
HMF yield
%
0
20
40
60
80
100
DMSO
DMF
[BMIM]Cl
Water
Solvent

Fig.3

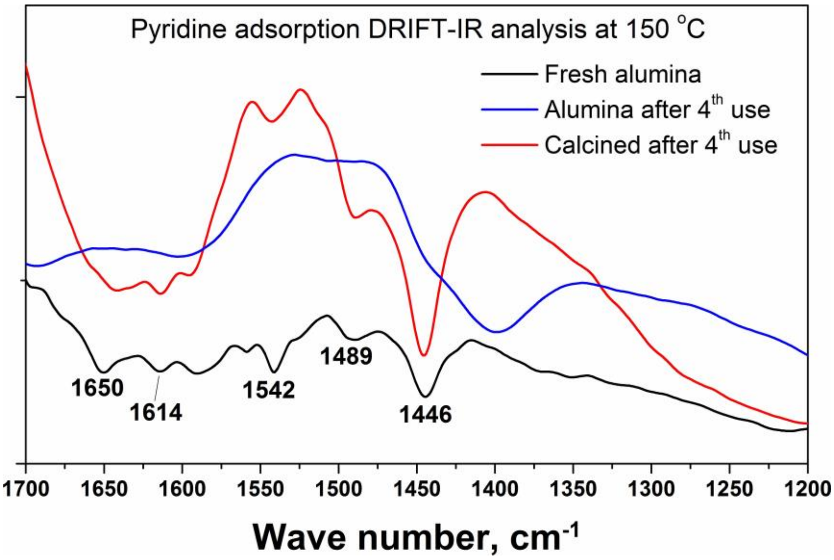
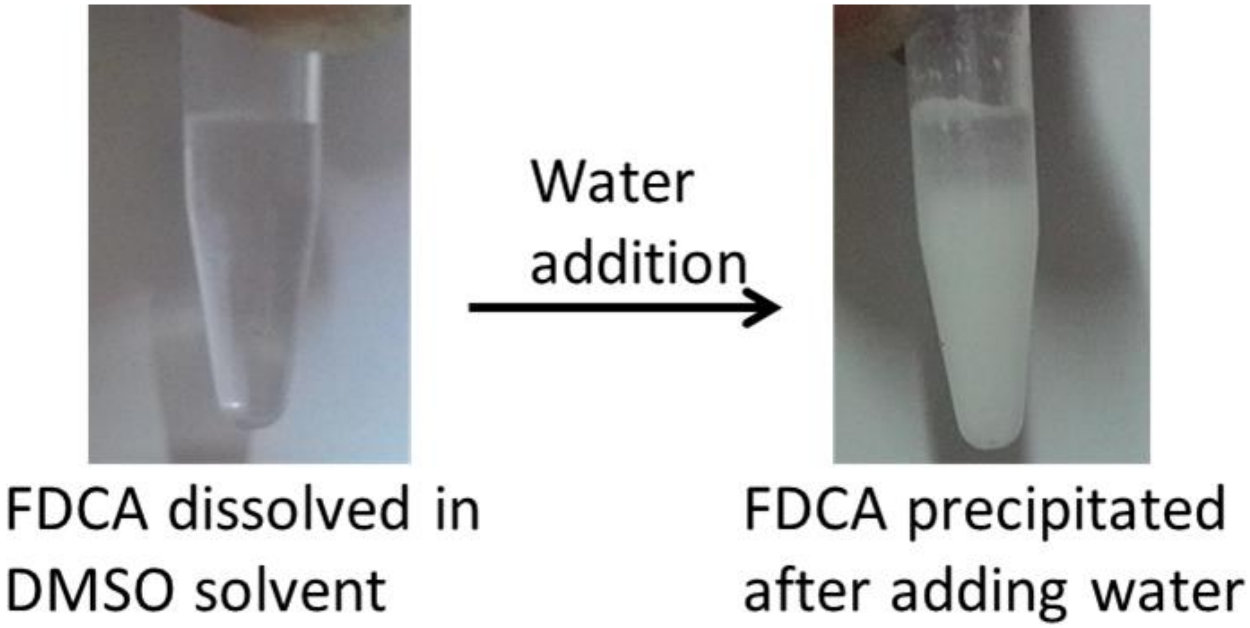

Pyridine adsorption DRIFT-IR analysis at 150 °C
Fresh alumina
Alumina after 4th use
Calcined after 4th use
1650
1614
1542
1489
1446
1700
1650
1600
1550
1500
1450
1400
1350
1300
1250
1200
Wave number, cm-1

Fig.4


Water
addition
FDCA dissolved in
DMSO solvent
FDCA precipitated
after adding water

Scheme.1

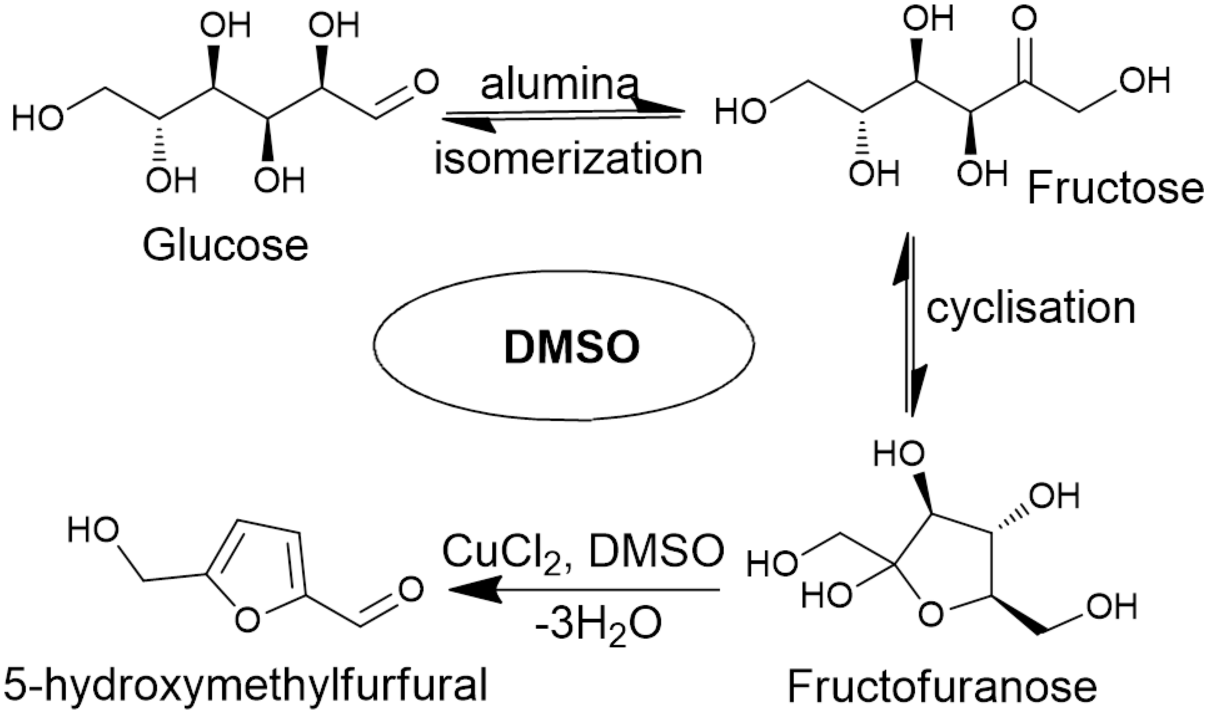

OH
OH
HO
O
OH
OH
Glucose
alumina
isomerization
OH
O
HO
OH
OH
OH
Fructose
cyclisation
DMSO
HO
OH
HO
HO
O
OH
Fructofuranose
CuCl$_2$, DMSO
-3H$_2$O
HO
O
O
5-hydroxymethylfurfural

Table 1 Glucose/fructose conversion to HMF with different catalyst components

Catalyst	**Glucose conv.**	**HMF yield**	**Fructose yield**
No catalyst	5	0	0
$CuCl_2$	72	0	0
Al_2O_3	19	0	9
$CuCl_2$+Al_2O_3	62	20	0
	Fructose conv.	**HMF yield**	**Glucose yield**
Blank	72	38	0
$CuCl_2$	100	61	0
Al_2O_3	30	0	0
$CuCl_2$+Al_2O_3	83	42	0

0.9 g substrate (30 wt%), 3 g solvent, 80 ^{o}C, 18 h; Amount of Al_2O_3 is 0.3 g, $CuCl_2$ is 0.05 mmol

Table 2 Glucose to HMF over different catalytic combinations

Entry	**Metal salt (0.1mmol)**	**2nd catalyst (0.3 g)**	**HMF yield (%)**
1	$CuCl_2$[a]	-	09
2	$CuCl_2$	Hydrotalcite	0
3	$CuCl_2$	Al_2O_3	56
4	$FeCl_3$	Al_2O_3	51
5	$CrCl_3$	Al_2O_3	49
6	$NiCl_2$	Al_2O_3	35
7	$CoCl_2$	Al_2O_3	30
8	$MnCl_2$	Al_2O_3	21
9	$ZnCl_2$	Al_2O_3	13

0.9 g glucose (30 wt%), 3 g DMSO solvent, 120 $^{\circ}$C, 3 h. [a]higher amount of $CuCl_2$ (0.6 mmol) was used

Table 3 Production of HMF and furfural from different substrates[a]

Entry	Substrate	HMF yield
1	Glucose[b]	57
2	Fructose	67
3	Galactose	33
4	Cellobiose	52
5	Sucrose	64
6	Starch[c]	0
7	Starch[d]	26
8	Starch[d][e]	3
	Pentoses	**Furfural yield**
9	Rhamnose	31
10	Xylose	20
11	Arabinose	21

[a]0.9 g substrate (30 wt%), 0.3 g Al_2O_3, 0.05 mmol $CuCl_2$, 3 g DMSO, 120 ˚C, 3 h; [b]0.45 g water was added; [c]20 mg water was added to initiate hydrolysis; [d]20 μL 1M H_2SO_4 (0.02 mmol of H_2SO_4) was added; [e]without Al_2O_3 and $CuCl_2$ added

Table 4 Recyclability of alumina

Reuse of alumina	Glucose conversion	HMF yield (%)	Alumina after use	Carbon content on alumina after use (wt%)	Pore volume (ml/g)
Fresh alumina					0.74
1st use	100	59		3.2	0.75
2nd use	90	21		3.3	0.75
3rd use	88	15		3.4	0.70
4th use	89	08		3.5	0.71
After calcination	100	48			0.74

0.9 g glucose (30 wt%), 0.3 g alumina, 0.05 mmol $CuCl_2$, 3 g DMSO solvent, 120 ˚C, 5 h.