Supporting information

Selective regression design for rapid upgrading of raw sugar into 5-HMF bio-fuel additive under sustainable/reusable system

Panya Maneechakr a,*, Irwan Kurnia b, Asep Bayu c, Obie Farobie d, Chanatip Samart e, Suwadee Kongparakul e, Guoqing Guan f, Surachai Karnjanakom a,*

a Department of Chemistry, Faculty of Science, Rangsit University, Pathumthani 12000, Thailand
b Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung – Sumedang KM. 21 Jatinangor, Sumedang 45363, Indonesia
c Research Center for Biotechnology, Indonesian Institute of Sciences (LIPI), Bogor, West Java, Indonesia
d Department of Mechanical and Biosystem Engineering, Faculty of Agricultural Engineering and Technology, IPB University (Bogor Agricultural University), IPB Darmaga Campus, Bogor, West Java 16002, Indonesia
e Department of Chemistry, Faculty of Science and Technology, Thammasat University, Pathumthani 12120, Thailand
f Energy Conversion Engineering Laboratory, Institute of Regional Innovation (IRI), Hirosaki University, Aomori 030-0813, Japan

*Corresponding Author
E-mail: panya.m@rsu.ac.th (P. Maneechakr) and surachai.ka@rsu.ac.th (S. Karnjanakom)
Experimental

Catalyst characterization

(I) The textural properties of catalyst such as surface area, pore volume and pore size were investigated by N\textsubscript{2} adsorption-desorption isotherms using a Quantachrome Autosorb 1 gas analyzer. Prior measurement, the moisture in catalyst structure was removed by heating at 150 °C for 2 h. Here, surface area and porosity of catalyst were defined by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Hallenda (BJH) methods, respectively.

(II) The XRD patterns of crystal structures in catalyst were recorded using an X-ray diffractometer (Rigaku TTRAX III) in 2 theta range of 10-70° with a scanning step of 0.02° at each point using Cu Kα (λ=0.15418 nm) radiation at 40 kV and 20 mA. The existence of each functional group on adsorbent surface was verified by Fourier transform infrared spectrometry (FT-IR) using a PerkinElmer Spectrum 100 FT-IR spectrometer under ATR technique absorption mode in the range of wavenumber between 4000 and 400 cm\textsuperscript{-1}.

(III) The surface morphology (3D) of catalyst and the presence of Fe and S elements on catalyst were observed by a scanning electron microscope (SEM S-4800; Hitachi) equipped with energy dispersive spectroscopy (EDS).

(IV) The magnetic characteristics of catalyst were tested using a vibrating sample magnetometer (VSM, Quantum design, DMS model 1660) under an applied field range of ±10 kOe. The surface electronic states of catalyst were investigated by X-ray photoelectron spectroscopy (XPS, Thermo VG ESCALAB250 using AlKα radiation). Prior to the XPS measurements, the samples were treated in a 10 vol% H\textsubscript{2}/Ar flow at 200 °C for 4 h. The XPS data were internally calibrated, fixing the binding energy of C 1s at 284.6 eV.
(V) Thermal stability of sulfonic group functionalized on catalyst and humins amount adsorbed on spent catalyst were investigated using a Thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851). Analysis process was conducted from temperatures of 100-700 °C using air gas at a flow rate 10 ml/min with a heating rate 5 °C/min.

(VI) The catalyst acidity was determined by NH$_3$-Temperature-programmed desorption (NH$_3$-TPD) using a BEL-CAT analyzer (BEL, Japan). Before measurement, the catalyst powder was preheated at 200 °C for 6 h under He flow (50 ml/min). For NH$_3$ adsorption procedure, the NH$_3$ gas (5% of NH$_3$/He) was adsorbed on catalyst at 40 °C for 1 h with a flow rate of 50 ml/min until it was saturated. Thereafter, NH$_3$ desorption process was carried out by increasing of temperature with a heating rate of 3 °C/min. Here, the adsorbed NH$_3$ concentration was quantified from the peak area by calibration using the standard gas.

(VII) The existence of Lewis and Brønsted acid sites on catalysts were analyzed by pyridine-probed Fourier transformed infrared (Py-FTIR) spectroscopy under resolution of 2 cm$^{-1}$ in wavenumber of the 4000 and 500 cm$^{-1}$ range. Before pyridine adsorption test, the catalysts were preheated at 200°C for 1 h in a vacuum system in order to remove water or some impurities adsorbed on the surface structure, and then cooled down to ambient temperature. Afterwards, the solid wafer was exposed to pyridine, by breaking a capillary containing 50 mL of liquid pyridine inside the spectrometer cell. The IR spectra were recorded at various conditions by increasing the cell temperature from 50 to 200 °C. The determination of Lewis and Brønsted acid sites was made with respect to the area range of the adsorption band at 1600 to 1400 cm$^{-1}$, respectively. The acid strength was determined with respect to the variation of the number of Lewis and Brønsted acid sites as a function of temperature.
Results and discussion

The results of VSM with their hysteresis loops are provided in Fig. S2. Here, the saturated magnetization values of S0@Fe-Cu-C and S2@Fe-Cu-C were 10.6 and 5.5 emu/g, respectively. The decreasing in saturated magnetization value should be generally resulted from functionalization of sulfonic groups on catalyst support [1]. It should be remarked here that the time about 40-60 s were required for separating out of S2@Fe-Cu-C from reaction system, depending on viscosity of mixture solution. The thermal decomposition ranges of sulfonic group studied by TG-DTG technique are provided in Fig. S3. It is distinctly found that S2@C and S2@Fe-Cu-C exhibited thermal decomposition range of sulfonic group under different temperatures at 315 and 340 °C, respectively. This demonstrates that the higher stability and lower leaching possibility of sulfonic groups on catalyst were well supported when S2@Fe-Cu-C was applied for catalytic reaction in this study.

The plausible mechanism and reusable system for catalytic conversion of CS into 5-HMF and other products over DES integration in the presence of ChCl+MeCN+S@Fe-Cu-C are shown in Fig. S5. During hot condition, CS molecule was interacted with ChCl (nucleophile site) via electrostatic mechanism, resulting further transformation into intermediate chemicals over S@Fe-Cu-C catalyst. During the reactions, ChCl could mainly serve as the H-bond acceptor for stabilizing the H-bond donor from –SO3H and -COOH groups on S@Fe-Cu-C, resulting in well enhancement of 5-HMF product selectivity with suppression of humins formation. Meanwhile, MeCN could be also protonated by proton transfer from Brønsted acid sites of –SO3H and -COOH on S@Fe-Cu-C catalyst [2,3]. During this way, hydroxyl group or glycosidic bond the anomeric center of CS structure would interact at electrophilic position of protonated MeCN, leading to the generation of covalent bond at oxygen and sulfur atoms. Due to the stable interactions between
DES (ChCl+MeCN+S@Fe-Cu-C) with CS molecules, higher reactivity for CS hydrolysis into glucose and fructose should be occurred. Furthermore, the existence of hydrogen bonding with electrostatic interaction on C-H and/or C-O bonds of intermediates could promote for further dehydration of fructose into 5-HMF product. Here, glucose molecule was isomerized into fructose via Lewis-acid site in S@Fe-Cu-C catalyst. For the contribution of surface oxygen-containing functional groups, 5-HMF production could well promote by nature of Brønsted acid sites. Herein, sulfonic groups promoted critical way for hydrolysis and dehydration reactions. Meanwhile, carboxylic, phenolic and lactonic groups easily formed on S@Fe-Cu-C structure under incomplete carbonization and pyrolysis processes were applied as the supporters for improving the catalytic performance of sulfonic nature, resulting in better catalytic activity when compared with other types of catalysts. In addition, the possibility to be applied in practical process for reusable system could be truly focused under the presence of DES (ChCl+MeCN+S@Fe-Cu-C) vi in-situ extraction procedure. For instance, (I) S-MAC could be conveniently separated using external magnetic field, and well reused without significant reduction of catalytic activity, (II) spent ChCl could be facilely recrystallized and recovered for several times, and (III) the mixture between 5-HMF and MeCN could be easily separated based on different principle of boiling point between 5-HMF (~82 °C) and MeCN (~115°C). In addition, to avoided some contamination after recycling of spent catalyst and spent ChCl without regeneration process and to approach for sustainable/reusable system in practical process, lower loading of substrates (~3.3 wt.%) are required for their complete conversion into chemical products in each condition [4].
References


Fig. S1. Synthesis procedures of S@Fe-Cu-C catalyst in each step.
Fig. S2. Magnetization curves of (A) S0@Fe-Cu-C and (B) S2@Fe-Cu-C.
Fig. S3. DTG plots of (A) S0@Fe-Cu-C and (B) S2@Fe-Cu-C.
Fig. S4. Schematic illustration of the catalytic pathways from CS conversion into 5-HMF and humins.
Fig. S5. Turnover rate (TOR) for catalytic production of 5-HMF from CS conversion using different catalysts.
**Table S1** Catalytic comparison of different acid catalysts for 5-HMF production from sucrose conversion.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Conditions</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-Fn-AC</td>
<td>MIBK</td>
<td>120 °C, 80 min</td>
<td>30.0</td>
<td>[44]</td>
</tr>
<tr>
<td>CrCl$_3$.6H$_2$O</td>
<td>DMSO</td>
<td>120 °C, 90 min</td>
<td>54.8</td>
<td>[45]</td>
</tr>
<tr>
<td>NiCl$_2$.6H$_2$O</td>
<td>TetraEG(mim)$_2$][OMs]$_2$</td>
<td>120 °C, 40 min</td>
<td>62.2</td>
<td>[46]</td>
</tr>
<tr>
<td>COP-SO$_2$H/SB</td>
<td>DMSO</td>
<td>100 °C, 120 min</td>
<td>45.0</td>
<td>[47]</td>
</tr>
<tr>
<td>STrzDBTH</td>
<td>DMSO</td>
<td>140 °C, 20 min</td>
<td>56.3</td>
<td>[48]</td>
</tr>
<tr>
<td>S@Fe-Cu-C</td>
<td>MeCN+ChCl</td>
<td>105 °C, 60 min</td>
<td>86.7</td>
<td>This work</td>
</tr>
</tbody>
</table>