Solid Acid Catalyst Mesoporous Sulfated Zirconia with Metal Oxide Promoter and Its Application on Hydrolysis of Cellulose into Fermentable Glucose

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Received: 24.07.2023 Accepted:03.09.2023

Abstract- Sulfated zirconia mesopore was synthesized via template-assisted sol-gel method followed by impregnation of metal oxide (Al and Fe) as promoters in various amount. These solid acids were applied on cellulose hydrolysis at several condition and seek glucose yield as the desired product. The resulting catalysts were characterized by using XRD, gas sorption analyzer, FTIR, SEM-EDS and TEM. Sulfated zirconia impregnated with Al_2O_3 and Fe_2O_3 show tetragonal phase based on five peaks (2θ at 30.4°, 35.3°, 50.3°, 60.5° and 63.2°) that appear for both, which are closely referred to (111), (200), (220), (311) and (222) reflections of tetragonal ZrO_2. FTIR spectra reveals S=O stretching vibrations between 1300 and 1450 cm^{-1} which is identified as sulfate group whereas sulfate bonds to zirconia surface is identified at wavenumber 900-1150 cm^{-1}. The porosity property of Al5-MZS and Fe5-MZS are enhanced as represent by large surface area (170 and 180 m^2/g). The as prepared catalysts display active catalytic at long hydrolysis time (16–24 h). The catalyst show promising potential future use in glucose production from cellulose hydrolysis.

Keywords Sulfated zirconia mesopore, cellulose, hydrolysis, Al_2O_3 and Fe_2O_3 promoter.

1. Introduction

Various alternative energy resources have been explored through intense research with unsatisfactory result due to inability to completely replace oil dependency. The most promising alternative combustible energy resources so far is biofuel namely biodiesel and bioethanol. Sustainability, environmental friendly and its renewability in addition to physicochemical properties are advantages to be considered as oil replacement [1]–[4]. Biodiesel can be converted into shorter chain hydrocarbon through hydrocracking process [5]–[8]. The high temperature required made fatty acid methyl ester (FAME) produced from esterification as well as transesterification are preferred [9], [10].

Another biofuel resource in form of oxygenated compounds has attain concern and consider as third generation of energy resource. Instead of converting edible oil into combustible compounds, cellulosic biomass can be converted via hydrolysis assisted with acid catalyst to produce fermentable glucose and other oxygenated compounds [11], [12]. The main problem of cellulosic biomass to be converted into other compounds is it persistent character against conventional chemical reaction [13]. Additional step to disrupt the massive H-bond that formed 3D polymer structure of cellulose is obligatory. Recently, ionic liquids (ILs) begin to use widely for cellulose pre-treatment. ILs has ionic bond which able to disrupted H-bond

and made cellulose structure more vulnerable to chemical reaction [14], [15].

Various catalysts had been evaluated for cellulose hydrolysis including sulfated zirconia (ZrS) tungstated zirconia (ZrW), tungstated alumina and heteropoly acids [16], [17]. Other catalyst such as sulfonated carbonaceous based acids [18]–[20], carbon mesopore [21], [22], zeolite [23], magnetic solid acids [24] were also reported. Whereas some catalyst produced very low of glucose yield, high amount of glucose yields was reported in cellulose hydrolysis by using sulfonated carbonaceous catalyst [18]. Carbonaceous catalyst can be obtained from carbonization of biomass or its products such as sucrose and glucose [25] and lignin [26]. The complexity of biomass structure and composition particularly on partial hydrolysis product and solid residue requires the separation of carbonaceous catalyst from reaction mixture must be carefully thought out. Such situation might hamper the recovery of catalyst [27].

Sulfated zirconia (SZ) prepared in form of mesoporous materials and enhanced acidity exhibit a promising material for hydrolysis catalyst. SZ catalyst can be easily prepared from organic or inorganic precursors with the addition of structure directing agents such as *N*-cetyl-*N,N,N*-trimethylammonium bromide (CTAB) it can provide large surface area and mesopore diameter. Soaking zirconia with $(NH_4)_2SO_4$ enhances solid acidity which according to some authors produced a highly solid acid material [28]. To increase sulfate retention in SZ, additional promoter can be added such as Alumina (Al_2O_3). Early report by Canton *et al*. showed that acidity of SZ with alumina promoter reached maximum steady state activity at 9.3 mmol g-1 h-1 compare to non-promoted SZ at only 3 mmol g-1 h-1 [29]. The advance properties of mesopore SZ in acidity and porosity suit its utilization for cellulose hydrolysis. To increase glucose product, well-prepared catalyst as well as cellulose pretreatment is needed. The latest step is necessary to overcome the massive hydrogen bonding in cellulose structure.

Here, we report cellulose pretreated with 1-Buthyl-3-methylimidazoilum Bromide ([BMIM]Br) which then hydrolyzed using sulfated zirconia mesopore catalyst with promoter Al_2O_3 and Fe_2O_3. Sulfated zirconia mesopore with promoter Al_2O_3 and Fe_2O_3 had been proved as excellent solid acid catalyst for iso-butane isomerization, fatty acid esterification and other acid catalysis reactions. The sulfated zirconia had been used in cellulose hydrolysis without pretreatment as well as enhancement on its acidity and porosity hence resulted in unsatisfactory yield. The combined effort in both catalyst and cellulose treatment will give more effective catalysis and better reactant accessibility towards reaction condition.

2. Materials and Methods

2.1. Materials

Zirconyl oxychloride ($ZrOCl_2{\cdot}8H_2O$) was purchased from Sigma Aldrich as well as *N*-cetyl-*N,N,N*-trimethylammonium bromide (CTAB), cellulose microcrystalline and 1-Buthyl-3-methylimidazoilum Bromide ([BMIM]Br). The same supplier also provided $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$. Ammonia 25% (NH_3) and Ammonium sulphate ($(NH_4)_2SO_4$ were purchased from Merck Millipore.

2.2. Preparation of Sulfated Zirconia with Template Assisted CTAB

Zirconia was prepared by mixing $ZrOCl_2{\cdot}8H_2O$ and CTAB in 3:1 mol ratio using distilled water in proportional amount [4], [30]. The mixture was stirred at 50 °C for 5 h by using hotplate and magnetic stirrer. After 5 h, the pH of resulting solution was adjusted by ammonia addition into the mixture dropwise until pH became 10. Zirconium hydroxide precipitated in form of white gel that then filtered, placed in autoclave and aged at 100 °C overnight. Zirconium hydroxide product washed thoroughly to remove remaining chloride ions. Prior calcination, zirconium hydroxide was sulfated by soaking in $(NH_4)_2SO_4$ 0.5 M for half an hour. The solid was calcined at 600 °C for 5 h in heating rate 5°/minute. Zirconia produced was labeled as MZS. Zirconia also prepared from similar precursor without the addition of CTAB and $(NH_4)_2SO_4$ soaking and marked as Z.

2.3. Preparation of Sulfated Zirconia Template Assisted with Promoter Al_2O_3 and Fe_2O_3

The Al_2O_3 and Fe_2O_3 promoted sulfated zirconia prepared in same procedure until zirconium hydroxide was obtained. Zirconium hydroxide prior calcined was impregnated by $Al_2(SO_4)_3$ via incipient wetness method. $Al_2(SO_4)_3$ was impregnated in various amount i.e. 1, 2 and 5 wt% (w/w). The Fe_2O_3 promoted sulfated zirconia was prepared in similar step except $Fe_2(SO_4)_3$ used as precursor. The resulting catalyst obtained by these procedures were marked as Al1-MZS, Al2-MZS, Al5-MZS as for Fe-promoter were marked as Fe1-MZS, Fe2-MZS and Fe5-MZS.

2.4. Catalysts Characterization

The crystallinity and phase's formed were examined using diffractometer powder of Rigaku XRD setting operation condition at 30 kV, 10 mA, scan speed and range at 10°/min and 3–90°. Surface area and porosity were evaluated using Quantachrome instruments in which the data obtained was calculated according to multipoint BET (specific surface area and adsorption-desorption isotherm) and BJH method (pore size of desorption and pore volume). Sulphate group was identified using FTIR spectrophotometry Shimadzu scanned from wavenumber 4000 cm^{-1} to 400 cm^{-1}. The acidity provide by sulphate group was confirmed by measuring ammonia adsorption which was calculated gravimetrically. Surface morphology and particle size and shape distribution were observed using SEM Energy Dispersive Spectroscopy and Jeol JEM 1400 Transmission Electron Microscope. Characterization also conducted to identified crystallinity change of cellulose before and after [BMIM]Br treatment by using Diffractometer Rigaku XRD.

2.5. Hydrolysis of Cellulose over Sulfated Zirconia Impregnated with Al_2O_3 and Fe_2O_3

Cellulose was pretreated by [BMIM]Br prior used in hydrolysis reaction. The ionic liquids and cellulose were mixed in 20:1 weight ratio. Mixture placed in oil bath, heated and stirred on hotplate and magnetic stirrer at 90 °C for 4 h. Thick and clear solution was formed after one hour stirring. Cellulose was then separated by adding distilled water into the solution. After filtration, washing and drying in oven, cellulose obtained in coarse solid particles.

Teflon-line autoclave was used in this work. In a typical experiment, catalyst and cellulose were weighted in 1:2 weight ratio. Distilled water added in proportional amount to cellulose to ensure that it available in excess. Heating carried out in an oven at two different temperatures (130 and 150 °C) for several duration times (3, 5, 16 and 24 h). After duration time required was achieved, the reaction mixture was centrifuged, and liquid supernatant was collected for glucose analysis. Analysis of glucose was carried out by HPLC method in Metacharb 87C column using H_2O eluent, flow rate 0.5 mL/min, temperature 85 °C equipped with RID detector. Experiments were performed for all Al and Fe-MZS catalyst as well as zirconia without promoter (MZS and Z).

3. Results and Discussion

3.2. Characterization of the Prepared Catalysts: Crystallinity and Acidity

The crystalline structure and phase form of prepared catalysts were ascertained by diffraction pattern obtained from XRD-powder. All catalysts exhibited ZrO_2 crystalline with tetragonal phase as dominant structure (Fig. 1). Z catalyst however, exhibited small amount of monoclinic phase. Five distinctly diffraction peaks (2θ at 30.4°, 35.3°, 50.3°, 60.5° and 63.2°) appear for all of them, which are closely referred to (111), (200), (220), (311) and (222) reflections of tetragonal ZrO_2 as described in reference code 017-0923. A slightly peak shifting is observed among diffraction pattern towards larger angle of 2θ. Based on Bragg's law, it is apparent that peak shifts to larger angle is correspond to smaller distance on d-spacing. Tetragonal structure of zirconia stabilized by the presence of sulfate group as reported by Shi *et al.* [31]. These authors suggest that sulfate groups create bridge towards zirconium atoms which upon calcination tends to form crystal in tetragonal phase below temperature of sulfate untreated zirconia.

Impregnation by Al_2O_3 and Fe_2O_3 has no effect on diffraction pattern of prepared catalysts. Metal impregnation at 5 wt% however, reduce the crystallinity of zirconia as display in Fig. 1. The intensity and sharpness of pattern markedly decrease compare to 1 and 2 wt% promoter. Retardation of phase transition in zirconia during calcination is stronger when metal promoter added in significant amount. This explain why zirconia with 5 wt% Al_2O_3 and Fe_2O_3 promoter appears to be less crystalline compare to 1 and 2 wt% promoter.

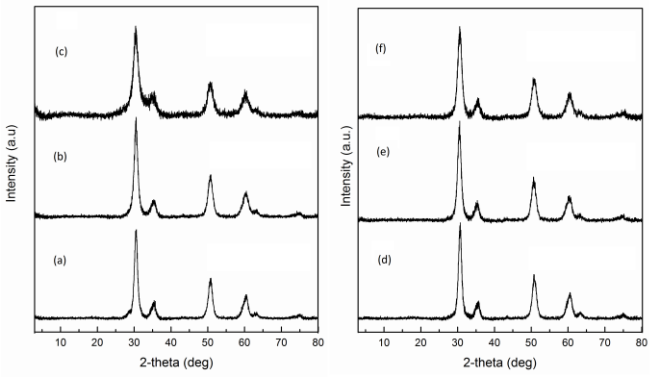


Fig. 1. Diffraction pattern of sulfated zirconia impregnated and calcined at 600 °C for 5 h with metal promoter (a) Al1-MZS, (b) Al2-MZS, (c) Al5-MZS, (d) Fe1-MZS, (e) Fe2-MZS and (f) Fe5-MZS.

Fig. 1 as mentioned earlier, confirmed that all prepared catalysts with Al_2O_3 and Fe_2O_3 promoter have tetragonal structure. The Z catalyst however, displays small portion of monoclinic phase in its crystal structure. Our previous work on this material also informed that zirconia prepared with template assisted but without sulfate treatment contain portion of monoclinic phase. In catalyst application, tetragonal phase is preferred because it is more active catalytic.

Tetragonal phase is not the only thing zirconia needed to be an efficient catalyst, acid properties which available as Lewis or Brønsted acid are also important issue. FTIR analysis of S=O stretching vibrations between 1300 and 1450 cm^{-1} can be identified belongs to sulfate group. Sulfate bonds to zirconia surface is identified from bands at 900-1150 cm^{-1} of type S–O [32]. According to Fig. 2, no peak reveals at 1400 cm^{-1}. Lack of peak at this wavenumber possibly because the existence of partial ionic character and hydrated condition of sulfate group on the zirconia surface [33]. Several pioneer authors have proposed sulfated zirconia structure. One of them suggested that the origin of Lewis acid comes from zirconium bonded with sulfate oxygen, which tends to positively charge due to electron density more attracted to the oxygen. Brønsted acid sites was formed when sulfated zirconia is exposed to water. The positively charge zirconium forms a bond with water and create induced polar which turn one of the hydrogen atom to be more positive. The Al2-MZS, Al5-MZS, Fe2-MZS and Fe5-MZS have similar FTIR spectrum. During incipient wetness impregnation, increase amount of metal promoter precursor is accompanied by increase amount of sulfate adsorbed.

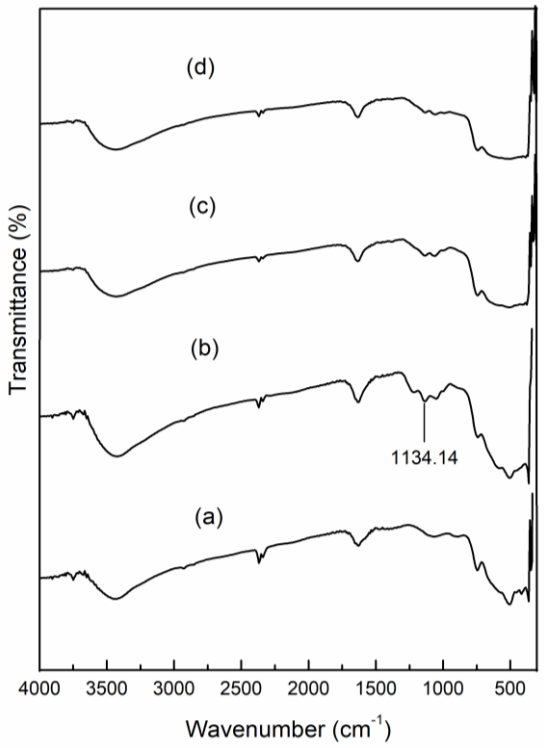


Fig. 2. FTIR spectra of prepared catalysts represent by (a) Z, (b) MZS, (c) Al1-MZS and (d) Fe1-MZS.

The addition of metal promoter into sulfated zirconia alters the balance of Lewis and Brønsted acid sites of zirconia. Acidity measurement based on ammonia adsorption follow by gravimetry analysis confirmed that total acidity of Al_2O_3 and Fe_2O_3 promoted sulfated zirconia is increased. Zirconia without metal impregnation (Z and MZS) as shown on Table 1 has total acidity 0-3.35 mmol/g, whereas sulfated zirconia impregnated with Al_2O_3 and Fe_2O_3 has total acidity 6.99-10.52 mmol/g.

Table 1. Acidity of prepared catalysts calculated by ammonia Gravimetric

No.	Catalyst	Acidity (mmol g^{-1})
1	Al1-MZS	6.99
2	Al2-MZS	8.90
3	Al5-MZS	10.53
4	Fe1-MZS	8.92
5	Fe2-MZS	8.45
6	Fe5-MZS	9.74
7	MZS	3.34
8	Z	1.5

The sulfated zirconia with promoter Al_2O_3 and Fe_2O_3 has the acidity required for its application especially in solid acids catalyst reaction such as esterification and hydrolysis of cellulose.

3.3. The Porosity and Textural Properties of Catalysts

Gas sorption analysis was conducted to ascertain prepared catalyst has large specific surface area and pore of mesopore type. The isotherm adsorption-desorption exhibits hysteresis type IV categorized by IUPAC. This type of hysteresis concludes that sulfated zirconia with Al and Fe promoter is indeed porous materials. Examination further on the shape of hysteresis suggest that the pore type contained is H1, a cylindrical-like pore or H2 type, pore with irregular shape and size.

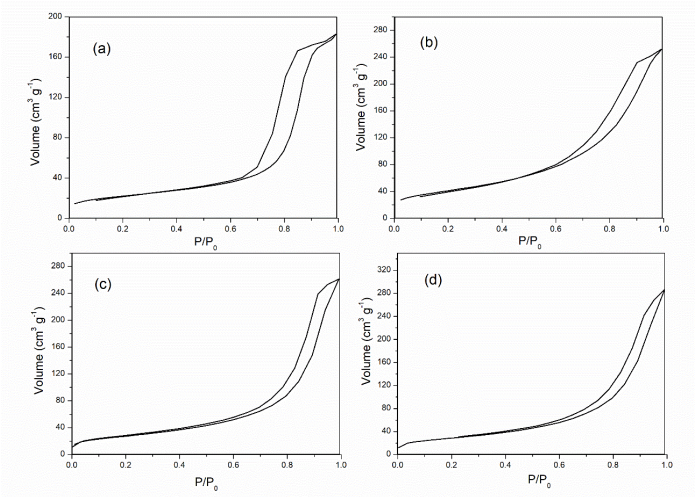


Fig. 3. Isotherm adsorption-desorption of (a) Z, (b) MZS, (c) Al1-MZS and (d) Fe1-MZS.

By comparing the isotherm adsorption-desorption between sulfated and impregnated zirconia with zirconia un-treated, it is identified that the slope become smaller, but the amount of volume adsorbed is bigger. From this point of view, sulfated and impregnated zirconia can be expected to have larger surface area compare to Z (Table 2).

Among the metal impregnated sulfated zirconia, Al1-MZS shows slightly smaller area but larger pore size on its surface. Result from t-plot analysis confirmed it has no micropores type. Fe5-MZS displays remarkable surface area between all metal impregnated sulfated zirconia. Being calcined in the same temperature (600 °C) there is no evidence of wall collapse, which can reduce pore size due to high temperature heating. No micropores was found according to calculation by t-plot methods. The surface area and pore size obtained in this work is in accordance with previous works by other authors [34], [35].

Large surface area with porous characteristics changes the textural properties of materials. Fig. 4 depicted the appearance of TEM image of sulfated zirconia impregnated with Al_2O_3 and Fe_2O_3.

Table 2. Specific surface area and pore radii of prepared catalysts

Catalyst	Specific surface area (m^2 g^{-1})[a]	Pore radii (nm)[b]	Pore volume (cm^3 g^{-1})[b]	Metal content (wt%)[c]
Al1-MZS	98.062	7.1	0.416	0.85
Al2-MZS	135.973	4.5	0.401	1.65
Al5-MZS	170.045	3.79	0.392	3.64
Fe1-MZS	102.843	5.51	0.460	0.34
Fe2-MZS	141.175	5.53	0.422	1.32
Fe5-MZS	180.739	2.00	0.559	4.27
Z	76.729	4.85	0.310	NA
MZS	147.508	3.30	0.396	NA

Calculated by [a]Multi-point BET, [b]BJH Desorption, [c]SEM-EDS

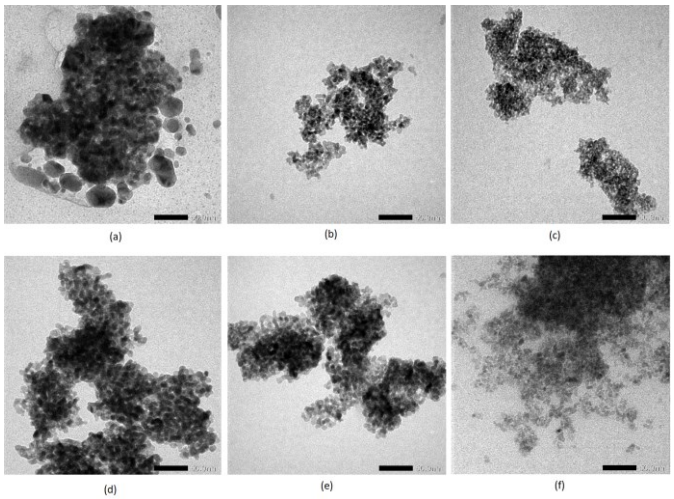


Fig. 4. TEM image of prepared catalysts (a) Al1-MZS, (b) Al2-MZS, (c) Al5-MZS, (d) Fe1-MZS, (e) Fe2-MZS and (f) Fe5-MZS.

From the Fig. 4., it can be discerned that the particle size of sulfated zirconia becomes smaller as the amount of metal promoter impregnated increased. The presence of sulfate and metal promoter during calcination of zirconia may affects zirconia crystal growth and how it becomes particle of porous materials. Some authors correlated Al promoter with increased of thermal stability, sulfate retention and acids densities caused by altering balanced distribution of acids site strength [36], [37]. The amount of metal impregnated indicates by SEM-EDS as written on Table 2. The interaction between metal sulfate used and $Zr(OH)_4$ surely affected by particle size, possibility of blocked pore and the stirring process during incipient wetness impregnation.

3.4. Hydrolysis of pre-treated cellulose with [BMIM]Br over sulfated zirconia

Prior hydrolysis, cellulose was treated with [BMIM]Br in 1:20 ratio. The aimed of this treatment is to weaken massive hydrogen bonds, which connected cellulose chain into 3D network structure. Diffraction pattern of cellulose before and after treatment is displayed in Fig. 5.

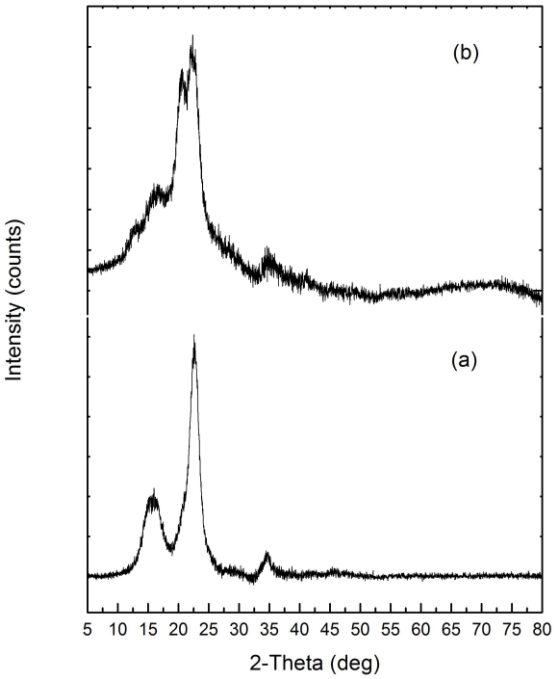


Fig. 5. XRD pattern of cellulose (a) before and (b) after pre-treatment with [BMIM]Br.

Fig. 5 exhibits how cellulose after IL's treatment become more amorphous. The diffraction pattern lost its sharpness and the peak broadening was observed. Ionic liquids possess high dipolarity, large dispersion force and hydrogen bonds, which during its interaction with cellulose could disrupt 3D network structure of cellulose. The mechanism of disruption includes removing Hydroxyl groups of cellulose via π–π interaction and forming Hydrogen bond between IL's and cellulose-OH [26].

The treated cellulose was subjected to hydrolysis experiment by using sulfated zirconia catalysts. Teflon-line autoclave was used without stirring and the result is shown in Table 3.

Table 3. Glucose product of cellulose hydrolysis by using sulfated zirconia at various temperature (T/°C) and duration (h)

Catalyst	130 °C				150 °C			
	3 h	5 h	16 h	24 h	3 h	5 h	16 h	24 h
Al1-MZS	n.d.	n.d.	0.06	0.077	n.d.	150.3	2048.7	1796
Al2-MZS	0.01	n.d.	0.5	0.878	n.d.	3658.9	2357.1	1511.3
Al5-MZS	n.d.	0.065	n.d.	1.528	234.6	2870.1	1362.7	1127.8
Fe1-MZS	n.d.	n.d.	0.239	0.381	38.2	294.4	691.1	2053.9
Fe2-MZS	n.d.	n.d.	2.189	0.423	83.9	259.8	1579.1	2814.7
Fe5-MZS	0.04	0.389	1.24	1.25	863.6	3446.1	2208.1	5024.7
Z	n.d.	n.d.	NA	0.2	n.d.	n.d.	69.5	321.8
MZS	0.01	n.d.	0.227	1.489	1069.8	n.d.	4341	6774.3
H_2SO_4 1 wt%	0.36	4.89	18.37	18.31	1421.5	7.55% (b/v)	1810.8	6825.8
No catalyst	n.d.	n.d.	n.d.	0.02	n.d.	663.9	1049.6	1658.1

Note: Experimental condition: temperature 130 °C and catalyst to substrate ratio 1:2, all numbers in μg/mL except stated specifically, n.d. means not detected, NA means not available.

The persistent character of cellulose against chemical decomposition i.e. hydrolysis is well known and become obstacle for its utilization. Table 3 reveals that at 130 °C, glucose yield is resulted in a small amount. Catalysts Al2-MZS and Fe5-MZS are the only prepared catalysts that able to give result after 3 h (0.01 and 0.04%) while at 5 h duration time, Al5-MZS and Fe5-MZS gave glucose yield although in low amount (0.065 and 0.389%). The prepared catalysts however, show increase its activity in longer duration time. At 16 and 24 h duration time, Al5-MZS, Fe2-MZS and Fe5-MZS exhibit significant catalytic activity. Hydrolysis at 150 °C give more glucose product as it detected in significant amount particularly for hydrolysis reaction after 5, 16 and 24 hours. Compare to homogeneous catalyst, result from solid catalysis hydrolysis is incomparably small especially at short duration time. Longer reaction time however, shows a comparable result from catalysts Fe5-MZS and MZS to the H_2SO_4 catalyst.

Mild reaction condition is chosen to avoid product decomposition due to high temperature and long duration. As it has been noticed by some authors, factors that have to be compromised are configuration of reactor, mild condition reaction and solid acid catalyst suited for hydrothermal condition with high re-usability [38]. Choosing the condition of reaction is not an easy task, Table 3 displays how sulphuric acid used as catalyst can only achieve yield 18.3 ppm at 130 °C. This result is increased markedly at 150 °C to 7.55% after 5 hours. Early report suggest that hydrolysis of cellulose in sulphuric acids 0.5% able to obtained 87.6% conversion at 219 °C in 7 min [39] while other reported 13.7% glucose yield by using 0.04 M sulphuric acids at 160 °C for 2 h [40]. Our result is obtained at lower temperature. Furthermore, solid acid catalyst appears to need more duration time to attain good accessibility into cellulose matrix. Wang *et al*., reported to attained 9% yield of glucose by using ZrO_2. This slightly higher result comes from lower ratio of cellulose to catalyst 0.05:0.15 at 160 °C for 12 h [41]. We used ratio of cellulose to catalyst 2:1 at 150 °C and the highest glucose yield is 5024 ppm (0.5%) over Fe5-MZS and 6774.3 ppm (0.67%) over MZS catalysts. This condition considered as moderate ratio between excessive use of catalyst and too small amount of it to be catalytically active.

Sulfated zirconia prepared in this research however, displays good potential from the material development point of view. Fe5-MZS showed distinctive result compare to un-promoted sulfated zirconia. It exhibited more active catalytic in duration time 3, 5 and 16 h compare to MZS. As metal impregnated increase, it appears that the catalyst is more active catalytic as indicate from glucose result at 24 h hydrolysis hence can be considered as hydrothermally stable. The Fe5-MZS catalyst has the possibility to improve its performance in elevated temperature and high autogenous pressure created by hydrothermal condition.

4. Conclusion

The sulfated zirconia successfully synthesized with improved character by adding CTAB in the precursor and impregnated with metal promoter. Its better porosity and acidity however, is not strong enough to break down cellulose in hydrolysis reaction. Mild condition must be accompanied by stouter pre-treatment cellulose and hydrothermal atmosphere. Fe5-MZS shows the most potential among prepared catalyst for further evaluation on hydrolysis of cellulose.

Acknowledgment

Gratefully thanks are addressed to Universitas Sriwijaya for providing research funding through Unggulan Kompetitif 2021 no. DIPA-023.17.2.677515/2021 and laboratory instruments needed to accomplish the project. This

publication served as additional research outcome of the project.

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