



Preparation of Ga₂O₃-modified sulfated zirconia mesopore and its application on cellobiose hydrolysis

Addy RACHMAT^{1,*}, Rizki DWIFAHMI¹, Nova YULIASARI¹, Ady MARA¹, and Desnelli DESNELLI¹

¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Sriwijaya, Jl. Palembang-Prabumulih KM-35, Inderalaya 30662, South Sumatera, Indonesia

*Corresponding author e-mail: addy_rachmat@unsri.ac.id

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Abstract

Heterogeneous catalyst plays vital role in biomass processing due to slow rate of biological and naturally pathway processes. Solid acid sulfated zirconia (SZ) is a promising catalyst with properties that can be tuned up. Sulfated zirconia was successfully modified by 2%, 5% and 10% (wt.) Ga₂O₃ (xGa-SZ; x = 2, 5 and 10) via template-assisted sol-gel method. The catalysts were characterized through various method (XRD, SEM-EDS and Gas Sorption analysis) and applied on hydrolysis of cellobiose, a model compound of cellulose. Diffraction pattern showed xGa-SZ formed completely tetragonal phase whereas un-promoted SZ contains mixed phase of monoclinic and tetragonal. Acidity evaluation via gravimetric method using ammonia as probe molecule indicates the Ga₂O₃ promoted sulfated zirconia has larger acidity. The SEM-EDS results confirmed the presence of Gallium element on the surface of promoted xGa-SZ. Gas sorption analysis shows specific surface area is improved (83 m²·g⁻¹ to 123 m²·g⁻¹) and increased pore radii (36 Å to 56 Å). The adsorption-desorption isotherm displayed pattern of meso-porosity material. At higher T and longer time, SZ yield more glucose than xGa-SZ. However, at shorter time, 2Ga-SZ and 10Ga-SZ show better hydrolysis performance. The solid acid 10Ga-SZ shows potential performance as heterogeneous catalyst for cellobiose conversion in modest conditions.

1. Introduction

The use of renewable feedstock in producing chemical or energy resource is one of 12 principles in green chemistry [1]. Cellulosic biomass, which produced by all of crops as side product and solid waste is a renewable source for chemicals as well as energy resource. Cellulose is known as a persistent polymer that not easily break down in chemical way. To gain better understanding on cellulose decomposition, model compound is often used as initial effort before the real one. Chemical process required catalyst with specific properties and morphology. Solid acid catalyst has a wide variety of applications in the processing of materials into chemicals and other feedstock. The need for such catalyst tends to increase, which lead to inevitable development for catalyst with better efficiency and activity. Tuning up a catalyst properties is necessary to fulfill various requirement by particular reaction for instance isomerization, alkylation, hydrolysis, hydro-cracking and esterification [2-5]. Among various materials used as solid acid catalyst namely sulfated metal oxide, sulfonated carbon, resin, and heteropoly acid, only metal oxides that show a high potential being recovered from the reaction mixture in a relatively simple treatment process [6].

Metal oxide-based solid acid such as sulfated zirconia has been reported as easily acid tuned up catalyst in addition to thermal resistance and large surface area and porosity [7,8]. Preparation method for sulfated zirconia has been developed to achieve a better acidity,

larger surface area and porosity as well as phase stabilization toward more active structure i.e. tetragonal phase [5,9]. Supporting sulfated zirconia on a host material reduce catalyst acidity later catalytic activity [10]. Modification of sulfated zirconia through surfactant-assisted route followed by Gallium sulphate impregnation had been reported by Hwang & Mou (2009) [11]. Surfactant used as structure-directing agent such as N-cetyl-N,N,N-trimethylammonium bromide/CTAB and Pluronic P-123 Triblock copolymer had been widely used by some authors. Large surface area and pore diameter obtained from the as-prepared catalyst (pore size 2 nm to 50 nm) known as mesoporous materials. Such catalyst provides lot of active site on its surfaces and shows high catalytic activity in n-butane isomerization. Another sulfated zirconia modification through Gallium oxide impregnation was reported by other author although it was prepared without using surfactant-assisted route. As a result, the catalyst has relatively low specific surface area, which reported between 94 m²·g⁻¹ to 113 m²·g⁻¹, nevertheless the catalysts show good activity toward isomerization reaction due to its excellent acidity [7].

The application of Ga-promoter sulfated zirconia in hydrolysis of cellobiose reported in limited publication. The majority of publication employed sulfated zirconia for esterification and used without metal promoter [2,12-14]. Excellent acidity combined originated from Lewis and Brønsted acid provide Ga-promoted sulfated zirconia as perfect solid acid catalyst suitable for hydrolysis of cellobiose. The presence of gallium oxide on the surface of sulfated zirconia affect Brønsted

acidity by weakening the M – OH bond, which make proton release more easily [15]. Hwang & Mou (2009) reported Ga-promoted sulfated zirconia showed catalytic activity on *n*-butane isomerization nearly twice Al-promoted sulfated zirconia although both has similar surface area specific and acidity. Previously, Cerrato *et al.* (2006) reported Ga-promoted sulfated zirconia and confirmed its excellent acidity both Lewis and Brønsted as well as high catalytic activity towards *n*-butane isomerization.

Here, we reported a series of Ga-promoted sulfated zirconia along with its material characterization and its application on hydrolysis of cellobiose in mild condition, which is relatively low temperature and pressure. Cellobiose was chosen as representative compound of cellulose due to its β -1,4 glycosidic bond, which similar to cellulose. To the best of our knowledge, no article has been reported on this matter. The catalysts were prepared through template-assisted sol-gel method and gallium sulphated was added via incipient wetness impregnation.

2. Experimental

Chemicals used in this experiment were purchased from Sigma-Aldrich: $ZrOCl_2 \cdot 8H_2O$ (99.0%), Ammonia solution 25%, N-cetyl-N,N,N-trimethylammonium bromide/CTAB (99%), $Ga_2(SO_4)_3 \cdot xH_2O$ (99.99%), Hydrochloric acid 32% Ajax Finechem. All materials used without further purification or treatment. The preparation method was adopted from Sun *et al.* (2004) with modification i.e. using different template and calcination condition [16].

2.1 Preparation of Ga_2O_3 promoted-sulfated zirconia

Sulfated zirconia was prepared by dissolving zirconyl oxychloride (0.081 mol) in distilled water along with hydrochloric acid and CTAB (0.024 mol) on a hot plate magnetic stirrer at 60°C for 5 h. Zirconium hydroxide formed by adding NH_3 dropwise into the mixture to form white precipitation. The gel was separated from liquid part and placed into Teflon-lined autoclave in a hydrothermal condition followed by heating for 24 h at 100°C. Solid zirconia amorphous collected through vacuum filtration and was sulfated by 10 mL $(NH_4)_2SO_4$ 0.5 M through immersion and gently stirred for 30 mins. Ga_2O_3 impregnation was carried out by using $Ga_2(SO_4)_3$ precursor through wetness impregnation method. The amount of promoter was setup to achieve 2 wt%, 5 wt%, and 10 wt% of Ga_2O_3 . Calcination carried out at 600°C in Memmert furnace, at heating rate $5^\circ \cdot min^{-1}$, and held for 5 h. Catalysts produced in this stage were sulfated zirconia without Ga_2O_3 promoter (SZ), and sulfated zirconia with 2%, 5% and 10% Ga_2O_3 labelled as 2Ga-SZ, 5Ga-SZ, 10Ga-Z.

2.2 Catalyst characterization

Diffraction pattern of samples was obtained by powder XRD instrument Rigaku Miniflex (Cu $K\alpha = 1.54 \text{ \AA}$) X-ray 30 kV, 10 mA, scan speed $10 \text{ deg} \cdot \text{min}^{-1}$, range 5° to 80° at scanning rate 0.02° . The morphological feature was determined by JEOL JSM-6510 SEM-EDS using accelerating voltage 20 kV, magnification 3000 \times . The specific surface area was calculated by BET formula using data from adsorption-

desorption isotherm measured by Nova instrument Quantachrome NovaWin using N_2 gas adsorbate, bath temperature 77.3 K and outgas temperature 300°C. Diffraction and microscopy techniques conducted without repetition. Ammonia adsorption used in acidity measurement by gravimetry method. The weight of ammonia adsorbed was used in the calculation to determine acidity using following formula:

$$A = \frac{w_a}{w_c \times M_a} \times 1000 \frac{\text{mmol}}{\text{g}}$$

where A is acidity, w_a is the weight of ammonia adsorbed (g), w_c is the weight of catalyst, and M_a is molecular weight of ammonia (17.007 $\text{g} \cdot \text{mol}^{-1}$).

2.3 Catalytic activity test

Hydrolysis of cellobiose conducted hydrothermally in Teflon-line autoclave. Initially, 0.2 g cellobiose added to 0.1 g prepared catalysts and 20 mL distilled water. The reaction condition was varied in two different temperature (160°C and 175°C) and three different reaction time (60, 90 and 120 min). The catalysts employ were SZ, 2Ga-SZ, 5-Ga-SZ and 10Ga-SZ. At the end of reaction, the liquid product separated and collected through centrifuge and the resulting product was confirmed by HPLC Shimadzu using UV detector. All of activity tests and product characterization carried out without repetition.

3. Results and discussion

3.1 Crystallinity and phase type of the catalysts

The XRD pattern reveals that the resulting materials shows diffraction patterns of tetragonal (Figure 1(b-d)) and monoclinic phase (Figure 1(a)). Diffraction pattern of SZ (Figure 1(a)) has more peaks compared other samples, which confirmed to be monoclinic phase of zirconia crystalline (JCPDS no. 37-1484). Diffraction pattern shows another peak, which can be attributed to tetragonal phase in small amount within the material. The Ga-promoted SZ in contrary, only possess diffraction pattern that match with tetragonal phase (JCPDS no. 17-923). Four peaks as shown by Figure 1(b) through 1.d at 30° , 35° , 51° and 60° confirmed their crystalline type.

The presence of Ga_2O_3 within zirconium hydroxide during the impregnation process, followed by calcination at 600°C favored the formation of tetragonal upon crystallization. Previous report by Moreno *et al.*, (2001) confirmed the formation of tetragonal phase upon addition of Al and Ga into zirconia. Rabee *et al.*, (2019) also publicized the formation of tetragonal zirconia after adding Al and Mg ions into the precursor of sulfated zirconia preparation [17]. Tetragonal zirconia generally made by doping of metal such as Yttrium during the material preparation [18]. Lately, various metal oxide including Al, Fe, Ga, and Mg has been reported can also triggered tetragonal phase formation on zirconia. Zirconia catalytic performance has been reported correlates with the existence of oxygen vacancies on surface structure. The vacancy promotes zirconia on trapping electron of conduction band hence enhance its catalytic performance. Recently Xia *et al.*, (2022) reported that tetragonal zirconia has the lowest oxygen vacancy formation energy compared to monoclinic and cubic phase [19].

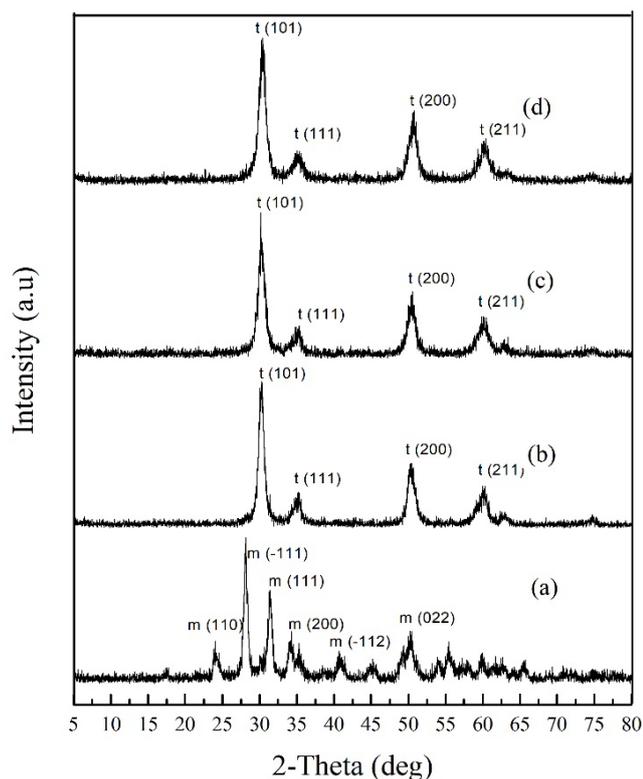


Figure 1. XRD pattern of material prepared (a) SZ, (b) 2Ga-SZ, (c) 5Ga-SZ, and (d) 10Ga-SZ.

In addition to metal promoters, sulfate group triggered tetragonal phase as well. Sulfate was added to the catalyst approximately 2 wt% to 3 wt%. The effect of Sulphur on sulfated zirconia both on structure and activity is obvious as reported by several authors [20,21]. The sulfate attached on zirconia surface indicated by FTIR spectrum at 1126 cm⁻¹, which was reported on our previous work [4]. According to Temvtutirojn, C. *et al.*, [21], this spectra correspond to the bidentate sulfate.

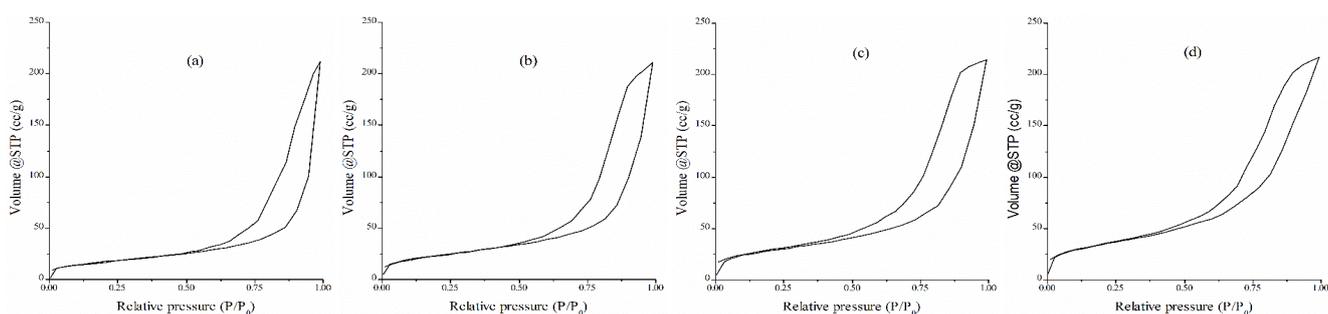


Figure 2. Isotherm adsorption-desorption of (a) SZ, (b) 2Ga-SZ, (c) 5Ga-SZ, and (d) 10Ga-SZ.

Table 1. The porosity of sulfated zirconia with and without Ga-promoter.

Catalyst	Specific surface area (m ² ·g ⁻¹)	Pore volume (cc·g ⁻¹)	Pore radii (Å)
SZ	62.5	0.345	48.1
2Ga-SZ	83.9	0.344	56.9
5Ga-SZ	100.6	0.347	48.2
10Ga-SZ	123.2	0.346	36.7

3.2 Porosity and surface area properties

Material with large surface area and exhibit porosity tends to adsorb more substances on its surface. Such properties are important for materials used as catalyst and adsorbent. Gas sorption analysis shows porosity by the catalyst prepared. The isotherm adsorption-desorption display curvature shape typical for mesopore material. Figure 2 shows a slight difference between SZ and Ga-promoted SZ especially at high P/P₀.

Isotherm adsorption-desorption of SZ shows hysteresis loop without plateau at high relative pressure whereas Ga-promoted SZ has it. The hysteresis closure occurred at rather higher relative pressure hence the shape of hysteresis loop considered as type H2 [22]. The relative pressure at which the closure occurred between 0.3 to 0.5 is typical for porous material of type mesopore (2 nm to 50 nm pore radii). Table 1 resumed the calculation result according to multi-point BET and BJH-desorption to determined specific surface area, pore volume, and pore radii of the zirconia catalysts.

Enhanced porosity of a material can be achieved by using template such as surfactant-assisted as reported by several authors [23,24]. Impregnating Ga₂O₃ into sulfated zirconia, furthermore, increased its specific surface area up to 123.2 m²·g⁻¹ as confirmed by Table 1. This high surface area accompanied by large pore radii, which is obtained at upper limit of mesopore type ~50 nm. Catalytic activity of a material influenced by several factors. Textural property, which include specific surface area and porosity believed to affect the activity [25].

At acidity test using gravimetric method, it is confirmed that 10Ga-SZ adsorbed more ammonia than other catalysts (1.87 mmol·g⁻¹). The method aimed to evaluate material ability to adsorb base molecule i.e., NH₃. The interaction of ammonia and catalyst surface possibly occurred through physisorption type. The sulfate group bonded on the surface might interact with ammonia chemically. Catalyst with the lowest surface (SZ) as expected gave less amount of ammonia adsorption (5.8 × 10⁻² mmol·g⁻¹).

3.3 Surface morphology of Ga-promoted and unpromoted SZ

Surface morphology of materials can be altered by combining with another material during the synthesis. Sulfated zirconia as discussed in the previous section, shows porosity change after Ga-impregnation. SEM image depicts at 3000 magnify at Figure 3 show slight morphology changing especially at 2% and 10% Ga₂O₃. It has small particles distributed at the surface. By using EDS method, the presence of metal on the surface can be identified and quantified according to energy loss of electrons that transmitted during the measurement, which suffered inelastic scattering.

The EDS result gave a more accurate result if the metal detected distributed uniformly on the surface being measured. Table 2 shows the EDS result of all catalyst prepared. The Ga content seems inaccurate especially for 2Ga-SZ due to low content of Ga₂O₃ impregnated hardly distributed on surface by wetness-impregnation method. Table 2 at least provide an overview of the existence Ga₂O₃ on the sulfated zirconia. The unpromoted SZ shows no Ga content in accordance with the preparation process. There is carbon content among all catalyst, possibly came from incomplete decomposition of CTAB template or it originated from embedding medium.

3.4 Catalytic activity of catalysts in hydrolysis of cellobiose

Hydrolysis of cellobiose is a water-mediated reaction assisted by acid catalyst. The effort to substitute homogeneous catalyst such as H₂SO₄ has been conducted ever since the existence of solid acid is known. Here, we studied the activity of Ga₂O₃-impregnated sulfated zirconia on hydrolysis of cellobiose. The catalysts have properties that support this function such as large surface area and proper acidity. The result of batch-mode reaction of cellobiose hydrolysis displays on Table 3.

To obtain glucose product, hydrolysis reaction must be carefully chosen between some affecting variables particularly time and temperature. High temperature required to overcome the energy barrier of chemical bond breaking. Table 3 shows the hydrolysis of cellobiose tend to produce more glucose at longer reaction time. Some authors reported the reaction temperature that achieved optimum yield of glucose (32%) at 160°C in 90 min by using combined oxide WO₃/ZrO₂ catalyst [26], whereas other reported using sulfated zirconia impregnated on SBA at same temperature reaction yields ~50% [27]. Several types of catalyst might require different optimal condition to achieve good catalytic performance. Catalyst 10Ga-SZ shows higher glucose yields particularly at 90 min and 120 min might attributed to

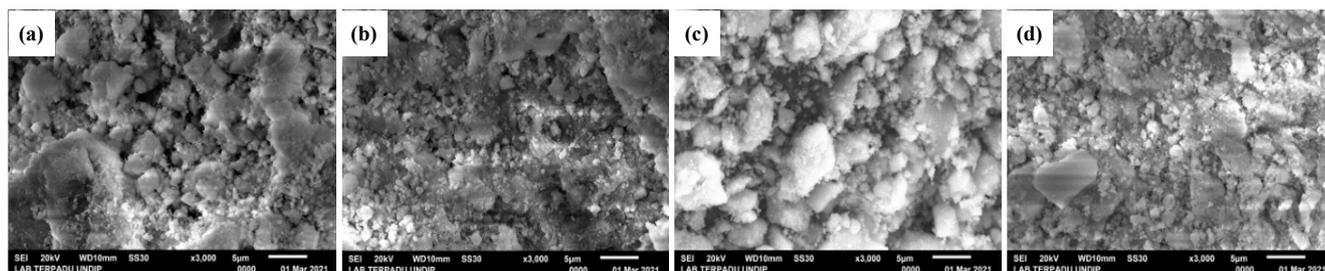


Figure 3. SEM images of sulfated zirconias (a) SZ, (b) 2Ga-SZ, (c) 5Ga-SZ, and (d) 10Ga-SZ.

Table 2. The composition of catalyst prepared based on EDS measurements.

Element (%)	SZ	2Ga-SZ	5Ga-SZ	10Ga-SZ
Zr	82.72	80.17	67.76	72.85
Ga	0	6.69	7.1	8.66
C	16.09	13.14	17.24	17.95

Table 3. Result of cellobiose hydrolysis over Ga₂O₃ promoted and unpromoted sulfated zirconia.

Catalyst	Reaction time (min)	Glucose Yield (%)	
		160°C	175°C
SZ	60	1.379	4.163
	90	1.401	4.146
	120	1.407	4.367
2Ga-SZ	60	1.428	1.375
	90	1.369	1.441
	120	1.330	1.461
5Ga-SZ	60	1.256	1.396
	90	1.552	1.343
	120	1.451	1.465
10Ga-SZ	60	1.414	3.978
	90	1.250	4.335
	120	1.446	4.197

its large surface area and high acidity possessed. Reaction on catalyst surface strongly supported by active sites available as provided by acidity and surface area available. This result however, shows not much different from SZ catalyst. 10Ga-SZ although has more acidity, but in water-medium reaction suffer from sulfate leaching, which might reduce its activity at significant point.

According to Carlier & Hermans, Cellobiose hydrolysis has at least two different pathways that can be occurred [28]. Brönsted acid was preferred then Lewis on acid-catalyzed hydrolysis, but combined effect of both Brönsted and Lewis acids was also reported by other authors in acid catalyst reaction. Azar suggested that the better interaction between catalyst and substrate might increase the desired product [29]. Metal oxide such as zirconia however, shows low interactions due to physical character difference.

4. Conclusions

Modification of zirconia is successfully conducted by sulfate and impregnation of Ga₂O₃ promoter. The resulting material shows improved properties in term of acidity, surface morphology and specific surface area namely 10Ga-SZ, which was impregnated with 10% Ga₂O₃. Increased Ga₂O₃ promoter shows linear improved in the properties mentioned. The porosity of catalysts display size in the range of mesopore, which support for assisting reaction with large molecular size. The catalytic performance towards cellobiose hydrolysis however, need further investigation at on reaction parameters to obtain optimum result of glucose.

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