Esterification of Fatty Acid Catalyzed by Ga_2O_3-Impregnated Sulfated Zirconia Mesopore

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Abstract. Heterogeneous catalysts are considered as valuable materials in enhancing many chemical reactions to obtain specific products. Solid acid catalyst such as sulfated zirconia (SZ) exhibits an adjustable morphology and acidity properties making it suitable catalyst. In this research, we utilize the mesoporous sulfated zirconia modified by impregnation of gallium oxide by 2, 5, and 10% (wt) Ga_2O_3 (xGa-SZ) that were prepared by template-assisted sol-gel method as catalyst for the esterification of lauric acid. GC-MS analysis results reveal that 5Ga-SZ and 10Ga-SZ were able to catalyze the esterification of lauric acid into methyl laurate, while 2Ga-SZ were inactive due to insufficient surface area and/or acidity. Thus, the solid acid xGa-SZ has potential to be used as heterogeneous catalyst for production of biodiesel.

Keywords: Sulfated zirconia, gallium oxide, solid acid catalyst, esterification

1 Introduction

Solid acid catalysts are utilized in a diverse range of applications for processing materials into valuable chemicals. The demand for such catalysts continues to grow, driving the development of more efficient and active catalysts. It is crucial to fine-tune the properties of catalyst materials to meet specific requirements for particular reactions, such as isomerization, alkylation, hydrolysis, hydrocracking, and esterification [1–4]. While such reactions commonly utilize homogeneous catalysts, heterogeneous acid catalysts such as sulfated metal oxides, sulfonated carbons, resins, and heteropoly acids, can be easily recovered from the reaction mixture in a relatively straightforward process [5].

Metal oxide, such as sulfated zirconia (SZ), are known for their easily adjustable acidity, thermal resistance, and large surface area and porosity [6,7]. To achieve better performance in acidity, surface area and pore size, and stabilization towards a more active structure, such as the tetragonal phase, various methods have been developed regarding this metal [4,8]. However, impregnating sulfated zirconia on other material can decrease its acidity hence its activity [9].

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In a study by Hwang & Mou, sulfated zirconia was modified using a surfactant-template technique, followed by gallium sulfate impregnation. The resulting catalyst had a large surface area and pore diameter, and showed high catalytic activity in n-butane isomerization. However, the researchers did not report on the catalyst's activity in other reactions, such as esterification, which is important for producing biodiesel [10]. Another study reported modification of sulfated zirconia through gallium oxide impregnation without using a surfactant-assisted route. The resulting catalyst had a relatively low specific surface area, ranging between 94 to 113 m^2/g. However, the catalysts showed good activity towards isomerization reactions due to its excellent acidity [6]. Overall, while sulfated zirconia has many beneficial properties as a solid acid catalyst, its activity can be affected by factors such as support material and modification methods. Further research is needed to fully understand the optimal conditions for utilizing sulfated zirconia in various catalytic reactions.

Limited publications have reported on Ga-promoter SZ catalysis in biodiesel production. While the majority of publications employed sulfated zirconia without a metal promoter [1,11–13], Ga-promoted sulfated zirconia has a high potential to be used as catalyst for esterification due to its excellent acidity combined with couple Lewis and Brønsted acid. The addition of Ga_2O_3 on the surface of SZ, weaken M-OH bond and affects Brønsted acidity, which makes proton release easier (14). Hwang & Mou reported that Ga_2O_3-promoted SZ has catalytic activity twice as high as on n-butane isomerization compare to Al_2O_3-promoted SZ, even though both have similar specific surface area and acidity. Cerrato et al. also published a report on Ga_2O_3-promoted SZ and reveals exceptional acid properties both Lewis and Brønsted in addition to great catalytic activity on n-butane isomerization [6].

In our previous publication, we reported a series of Ga_2O_3-promoted SZ used in hydrolysis of cellobiose [15]. In this study, we explore the ability of the aforementioned acid catalyst for the esterification of lauric acid in low-temperature conditions. The catalysts prepared through the sol-gel method, template-assisted, and Ga-sulfate was added via incipient wetness impregnation.

2 Research Methodology

Chemicals used in this research were purchased from Sigma-Aldrich, except where noted. Zirconium(IV) oxychloride octahydrate, distilled water (self-made), 37% hydrochloric acid, cetyltrimethylammonium bromide/CTAB, ammonia, ammonium sulfate, gallium sulfate, lauric acid (Emery Oleochemicals Sdn. Bhd.), methanol, and sulfuric acid were used without further purification or treatment.

2.1 Preparation of Sulfated Zirconia Catalyst

Sulfated zirconia was prepared using a method that we reported in our previous publication [15], adapted from Sun et al. [16]. 5.99 g of zirconium(IV) oxychloride octahydrate, 20.5 mL 37% hydrochloric acid, and 2.5 g CTAB were dissolved in 115 mL distilled water. The mixture was then stirred on a hot plate magnetic stirrer at 60 °C for 5 hours. Subsequently, ammonia was added dropwise to form white precipitate of zirconium hydroxide. The gel-like substance was separated from the liquid part and placed into a Teflon-lined autoclave under hydrothermal conditions, and then heated at 100 °C for 24 hours. The solid amorphous zirconia was then washed and collected using vacuum filtration.

Non-promoted sulfated zirconia (SZ) was prepared by immersing amorphous zirconia in 0.5 M ammonium sulfate solution while gently stirred for 30 minutes. The obtained sulfated zirconia was then dried in an oven at 100 °C for 24 hours. Lastly, the catalyst was calcinated at 600 °C for 20 hours.

Ga-promoted sulfated zirconia (xGa-SZ) was prepared from amorphous zirconia using gallium sulfate as precursor. 0.2 g, 0.5 g, and 1.0 g of gallium sulfate were dissolved in 75% ethanol and then added dropwise into 9.8 g (2Ga-SZ; 2% w/w of Ga-promotor), 9.5 g (5Ga-SZ; 5% w/w of Ga-promotor), and 9.0 g (10Ga-SZ; 10% w/w of Ga-promotor) of amorphous zirconia respectively. The mixtures were then stirred for 5 hours and then dried in an oven at 100 °C for 24 hours. Finally, the catalysts were calcinated at 600 °C for 20 hours.

2.2 Catalyst Characterization

Diffraction pattern was obtained using Rigaku Miniflex powder X-ray diffractometer (Cu Kα = 1.54 Å using operation condition reported previously). The surface morphology features were recorded by JEOL JSM-6510 SEM-EDS using accelerating voltage of 20 kV and at 3,000× magnification. The specific surface area was calculated by using Brunauer–Emmett–Teller (BET) formula on the data obtained from adsorption-desorption isotherm measured using Nova Instrument Quantachrome NovaWin using N_2 gas adsorbate.

2.3 Catalyst Acidity Test

The acidity of the catalysts was determined by gravimetric analysis. 0.5 g of sulfated zirconia catalyst were added into a crucible with known weight, and then heated at 100 °C in an oven for 1 hour. After heating, the crucible was cooled down to room temperature in a desiccator and subsequently weighed. The crucible was then put into a vacuum desiccator and the atmosphere was removed. After that, 5 mL of ammonia was inserted into the vacuum desiccator and the system was left standing for 24 hours. Afterwards, the crucible was weighed and the weight before and after adsorption was compared.

2.4 Catalytic Activity Test

Esterification of lauric acid was conducted in a reflux system using oil bath and hotplate magnetic stirrer. 15 mmol of lauric acid were mixed with 225 mmol of methanol in the presence of the catalyst prepared (5% w/v of xGa-SZ). As comparison, the esterification was also carried out using sulfuric acid (10% w/v) as catalyst. Reaction mixture was heated at 75 °C for 12 hours, followed by 1 hour heating without cooling condenser to remove excess methanol. Methyl laurate product was detected using Thermo Scientific Trace^{TM} 1300 Gas Chromatograph-Mass Spectrometer (GC-MS), and the peaks were detected by mass spectrometry using external standard.

3 Results and Discussion

3.1 Synthesis and Characterization of xGa-SZ

Sulfated zirconia catalysts with 0, 2, 5, and 10 percent weight of gallium oxide were successfully synthesized and characterized with powder XRD, SEM-EDS, surface adsorption-desorption isotherm, and gravimetric analysis of acidity as we have reported in our previous publication. It was found that the impregnation of gallium oxide into sulfated zirconia changed the structure of the solid from monoclinic to tetragonal, increased its specific surface area, and increased its total acidity. [15] It was also confirmed that the pore radii of the synthesized solid catalysts were still within range to be classified as mesoporous material, i.e. 2–50 nm or 20–500 Å [17]. Table 1 summarizes the characterization of the acid catalysts.

Table 1. Summary of the characterization of xGa-SZ [15]

Catalyst	**SZ**	**2Ga-SZ**	**5Ga-SZ**	**10Ga-SZ**
Zr (%)	82.72	80.17	67.76	72.85
Ga (%)	0.00	6.69	7.10	8.66
Structure	Monoclinic	Tetragonal	Tetragonal	Tetragonal
Specific surface area ($m^2 \cdot g^{-1}$)	62.5	83.9	100.6	123.2
Increase of surface area	1.00×	1.34×	1.61×	1.97×
Pore volume ($cm^3 \cdot g^{-1}$)	0.345	0.344	0.347	0.346
Pore radii (Å)	48.1	56.9	48.2	36.7
Total acidity ($\times 10^{-5}$ $mol \cdot g^{-1}$)	5.8	61.0	75.1	186.7
Increase of acidity	1.0×	10.5×	12.9×	32.2×

Surface area and acidity are two important aspects that affects the performance of esterification reaction using heterogeneous catalysts. Catalysts with high surface area provide more active sites for the reaction, while acidity of the catalyst (which corresponds to the amount of ammonia adsorbed by the catalyst in the characterization) relates to the amount of Brønsted (Zr–OH, S–OH, and Ga–OH moieties) and/or Lewis acid sites (Zr^{4+} and Ga^{3+} moieties) on its surface. The addition of gallium oxide to sulfated zirconia was proven to increase both the catalyst's surface area up to almost two times and also its acidity up to 32 times higher than the non-promoted catalyst.

Satyarthi, et al. reported that pore volume and pore radii could affect the catalytic performance of heterogeneous catalysts in the esterification of fatty acid. They found that when comparing the esterification reaction over mesoporous and microporous solid catalyst, the mesoporous catalyst (which have larger pore radii and pore volume) had better turnover frequency than the microporous catalyst [18]. However, in the context of this research, we expect that pore volume and pore radii to have no significant impact on the reaction as these parameters are similar across all of the prepared catalyst.

3.2 Catalytic Activity of xGa-SZ

As seen on Table 1, it was found that the acidity of xGa-SZ is correlated with the concentration of gallium impregnated into the zirconia. Thus, it could be expected that 10Ga-SZ would be the most active catalyst in this study. In order to investigate the catalytic activity, the obtained gallium-promoted sulfated zirconia were used to catalyze the esterification reaction of lauric acid ($C_{11}H_{23}COOH$, $M_r = 200$) into methyl laurate ($C_{11}H_{23}COOCH_3$, $M_r = 214$) and their performances were compared against sulfuric acid. Lauric acid was chosen in this study because it is the main fatty acid contained in coconut oil and palm kernel oil (48.91% and 48.07% respectively), which are potential biomass sources for biofuel or chemical production [19]. The result of GC-MS analysis is shown on Table 2.

Table 2. GC-MS data of the reaction mixture

Catalyst	Mass	Compound	Retention Time (minutes)	% Peak Area
H_2SO_4	214	Methyl laurate	8.61	31.02
	200	Lauric acid	9.00	68.98
2Ga-SZ	214	Methyl laurate	–	–
	200	Lauric acid	8.59	74.32
5Ga-SZ	214	Methyl laurate	8.58	31.97
	200	Lauric acid	8.79	68.03
10Ga-SZ	214	Methyl laurate	8.38	30.42
	200	Lauric acid	8.59	44.46

Previous report on the esterification using non-promoted sulfated zirconia shows that the conversion of lauric acid reached 100%, while the yield of methyl laurate was as high as 90% [3]. Thus, it was expected that Ga-modified catalyst would be able to outperform the non-promoted sulfated zirconia. It was found that 5Ga-SZ and 10-GaSZ were able to convert lauric acid into methyl laurate, while 2Ga-SZ could not, as proven by the lack of peaks observed for methyl laurate. Despite the increased surface area and acidity from the non-promoted SZ, 2Ga-SZ may not have big enough surface area and/or high enough acidity to catalyze the esterification reaction. Alternatively, the inactivity of 2Ga-SZ could also be caused by imperfect preparation.

Due to the qualitative nature of the methods used in this study, the yield of the reaction could not be properly calculated. However, as the GC-MS data between the esterification catalyzed by sulfuric acid and solid acid catalysts were similar, xGa-SZ may have high conversion rate (80–90%) akin to the reported results with sulfuric acid as catalyst [20]. Further studies are needed to quantitatively confirm the effectivity of gallium-promoted sulfated zirconia as catalyst for esterification reaction and to find ways to improve the catalytic performance.

4 Conclusions

Gallium-promoted sulfated zirconia with 0%, 2%, 5%, and 10% w/w of Ga were successfully synthesized and characterized. Addition of gallium oxide into sulfated zirconia increased the acidity of the sulfated zirconia by a factor of 10.5 (2Ga-SZ), 12.9 (5Ga-SZ), and 32.2 (10Ga-SZ). The solid acid catalysts 5Ga-SZ and 10Ga-SZ were found to be active as catalyst for esterification of lauric acid into methyl laurate.

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