Sol-gel Sulfated Silica as a Catalyst for Glycerol Acetylation with Acetic Acid

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Abstract

This paper reports on the impact of sol-gel sulphated silica (SS), used as a solid acid catalyst in the esterification of glycerol with acetic acid. The effects of time, temperature, and molar ratio of acetic acid to glycerol were evaluated in order to optimize the reaction conditions for achieving a high monoacetin yield. A series of catalysts were prepared, with different loading percentages from 5 to 20 wt%. The obtained sulphated silica had high specific surface area in the range of 330-720 m^2g^{-1}. The results indicated that the catalytic activity (acidic properties) increased with the amount of sulphuric acid loaded into the silica. In fact, the SS20 showed the highest catalytic activity when using a reaction temperature of 50°C and a glycerol to acetic acid mole ratio of 6 in 6h. All the catalysts also showed a favorable selectivity to monoacetin.

Keywords: glycerol; acetylation; sulphated silica; monoacetin; sol-gel

1. INTRODUCTION

Glycerol is the main by-product of oil transesterification with methanol and ethanol in biodiesel production. The increasing production of biodiesel is causing a huge amount of glycerol. Therefore, alternatives to overcome this issue and make biodiesel generation more economical have been considered [1,2,3]. Recently, many researches have concentrated on the catalytic conversion of bioglycerol into useful compounds, such as 1, 2-propandiol, 1, 3-propanediol, acrolein, glyceric acid, esters of glycerol, etc. Esterification of glycerol with short chain carboxylic acid (e.g., acetic acid) has been applied to convert glycerol to value-added chemical acetins (i.e., monoacetin, diacetin, and triacetin). This study aims to achieve monoacetin with a high percentage compared to two other main products. Monoacetin is widely used as a raw material in the production of biodegradable polyesters. Moreover it has been used as solvent, plasticizer, softening agent and many other industrial applications [4,5,6,7].

Acetylation is an acid catalysed reaction. Traditionally, mineral acid catalysts e.g., sulphuric acid, phosphoric acid, or organic sulfonic acids, such as Twitchell-type reagents, were used as catalysts in spite of their environmental problems and the large amount of salts that mightbe generated during the neutralization process [8]. In resolving these drawbacks, solid acid catalysts such as zeolite, amberlyst-15, heteropolyacids (tungstophosphoric acid, TPA), and sulphated zirconia were substituted for Bronsted acid [4, 9,10,11]. Zirconia based catalyst showed 80% selectivity to triacetin [5], heteropolyacids (HPAs) encaged in USY zeolite catalyst showed up to 60% selectivity to diacetin, with approximately 70% glycerol conversion [10], Sncl$_2$ catalyst was used in glycerol acetylation and the dominant products were monoacetin (55%) and diacetin (45%) [6], and sulphated zirconia (SZ), on the other hand, showed the significant selectivity to monoacetin in mild condition [7].

As inorganic materials functionalized with sulphuric acid have attracted much attention for acid catalysed esterification reaction, the focus of this study is on preparation of sulphated silica (SS) solid acid heterogeneous catalysts by using sol-gel method to obtain catalysts with large surface area and good anchoring of sulphur species [12]. It is common that silica is an inert material, in which the use of anions such as SO_4^{2-}, PO_4^{3-} ... have been found to boost the acidity and some specific physico-chemical behavior of silica, containing thermal stability and mesoporosity [13, 14]. In comparison to other types of solid acid catalysts, sulphated silica makes the acetylation reaction more selective to monoacetin in mild reaction conditions (i.e., shorter times and lower temperatures) [7]. In this study, the catalytic performance of sulphated silica with different sulphur loading percentages (5, 10, 15, and 20) will be investigated in glycerol esterification with acetic acid. In addition, the

effect of several parameters such as temperature, time, and catalyst weight on conversion and selectivity will be examined.

2.   MATERIALS AND METHODS

2.1   Preparation of Sulphated Silica using a Sol-Gel Method

The catalysts were synthesized by sol-gel method [12]. Tetraethoxysilane (TEOS, 98% Aldrich), used as a precursor for silica, was added to the mixture of 1-butanol and water, with the mole ratios of 10:1 and water to tetraethoxysilane with the mole ratio of 10:1 under vigorous stirring, at room temperature. Sulphuric acid was added drop-wise to the solution; both as the sulphating agent and as the catalyst of the polycondensation of the gel. The obtained hydrogel was dried slowly at 100 °C for 3 h and then refluxed with methanol over 72 h. The resulting gel was annealed at 800 °C for 4 h in air. The catalysts were prepared at different loading percentage of sulphuric acid (5, 10, 15, and 20%) and were denoted as SS (Sulphated Silica).

2.2   Characterization

The infrared (IR) spectra of catalysts were recorded at room temperature in KBr pellets, using a Perkin Elmer Paragon 2000 FTIR spectrometer, over the range 500–4000 cm^{-1}, under atmospheric conditions. The surface area of the catalyst was measured using the Brunauer-Emmett-Teller (BET) method (N_2 adsorption) with a Gemini apparatus (Micromeritics Instrument Corporation). The surface analysis was conducted using X-ray Photoelectron Spectroscopy (XPS), with an XPS type ultra from Kratos, equipped with monochromatic Al Kα radiation. Samples were analysed at 3×10^{-9} torr. The binding energies were referenced to the C 1s line at 284.6 eV to correct possible deviations caused by the charging effect of the samples. Ammonia Temperature Programmed Desorption (NH_3-TPD) was used to estimate the number and strength of acid sites. Samples, calcined at 800°C in air for 4 h, were fluxed with a He flow (Linde UHP, 99.999%) at up to 550°C, and were maintained for 60 min at this temperature. Next, the samples were allowed to cool to room temperature and were exposed to flowing NH_3 (20% in He) for 30 min. Then, the system was purged for 30 min with helium to eliminate any excess NH_3 gas. The temperature of the samples was raised linearly (at 10 °C /min) from room temperature to 650 °C. The desorbed NH_3 was monitored using a thermal conductivity detector and quantified by comparing the areas under the curve of the respective thermograms with those obtained from previous calibrations using known amounts of NH_3. The NH_3-TPD analysis was carried out in an AMI-3 apparatus from Altamira Instruments.

2.3   Catalyst Activity Measurements

The esterification reactions were carried out under vacuum using different temperatures in the range of 50-110°C with two different molar ratio of acetic acid to glycerol (3 and 6) in a stirred batch reactor equipped with reflux system. A Dean-Stark trap was attached to the 50 ml round bottom flask to extract the produced water which deactivates the catalyst and causes reversibility of the reaction. In a typical experiment, 0.2 g of the catalyst was loaded into the well miscible solution of reactants in the container. The stirring speed was maintained at 500 rpm. After cooling, the catalyst was separated from the solution mixture by centrifugation and washing with water. The products were analysed using a gas chromatography (GC-Hewlett Packard Model 6890N) equipped with a flame ionization detector (FID) and HP-5 as column. 1-hexanol as an internal standard was used for quantification measurements.

3.   RESULTS AND DISCUSSION

3.1   Catalyst Characterization

Figure 1 depicts the FTIR transmittance spectra of sulphated silica annealed at 400, 600, and 800 °C. A broad band between 3300 and 3500 cm^{-1} is assigned to O-H stretching in H-bonded water. This band can be confirmed through the band at about 1635 cm^{-1}, due to the scissor bending vibration of the molecular water. The intensity of these bands clearly declines in higher temperatures of calcination. The symmetric vibration of Si-O appears at 800 cm^{-1} and the peak at around 1100 cm^{-1} is attributed to the asymmetric vibration of silicon atoms in siloxane (Si-O-Si), which are overlapped or partially overlapped with the S-OH stretching vibration from the HSO_4^- ion. These results suggest that the sulphate group is bonded to the silicon atom as a mono-coordinated group [15].
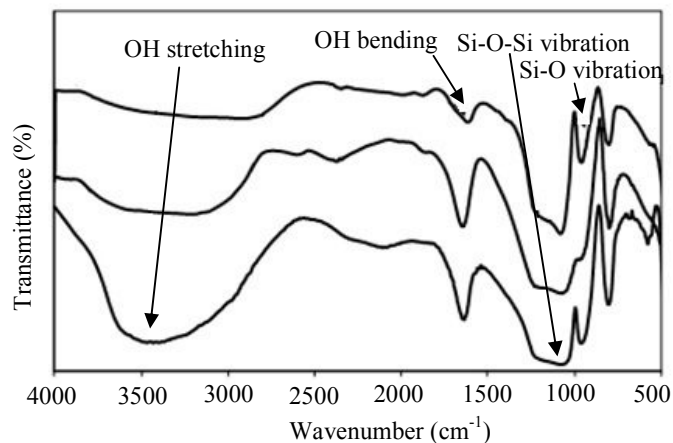
Figure: 1: FTIR transmittance spectrum of $SO_4^{2-}.SiO_2$ at different annealing temperatures, (a) 800, (b) 600, (c) 400 °C.

The textural properties of the catalysts calcined at 800°C, obtained from the nitrogen adsorption isotherms, are summarized in Table 1.

Table 1: Textural properties of SS samples

Sample	% H_2SO_4	BET surface area (m/g)	Pore volume (cm^3/g)	Pore size (nm)
SS-0	0	722	0.021	6.9
SS-5	5	642	0.017	2.2
SS-10	10	448	0.011	3.6
SS-15	15	330	0.009	4.9
SS-20	20		0.004	7.5

The physico-chemical properties of silica and supported sulphate catalysts are shown in Table 1. All synthesized solids show a very high specific surface area and mesoporous texture. BET analysis showed that there was a strong correlation between the textural properties and the sulphur content of the catalysts. Immobilization of sulphuric acid into the silica matrix led to a continuous decrease of the surface area and pore volume, which might have been due to the pores blockage by the active nonporous species that were formed. However, no typical mode was observed in terms of catalysts pore size distribution.

Table 2: Total acidity from TPD of ammonia

Sample	% H_2SO_4	Temperature at maximum		Total NH_3 desorbed (mmol.gr^{-1})	
		peak 1	peak 2	peak 1	peak 2
SS-0	0	-	450	-	250
SS-5	5	271	453	140.	280
SS-10	10	280	531	334	388
SS-15	15	277	539	409	465
SS-20	20	247	550	436	479

The NH_3-TPD profiles of catalysts are shown in Figure 2. TPD profile of silica has been included for the sake of comparison. Desorption peaks in maximum temperature ranges of 180–250, 280–330, and 380–500 °C are normally attributed to NH_3 chemisorbed on weak, medium, and strong acid sites, respectively [16]. In all supported catalysts with different sulphate loading percentage, two desorption peaks (centered at 280 and 550 °C) were observed which attributed to the presence of moderate and strong acid sites. The total acidity of catalysts is listed in Table 2.

SS-20 exhibited the largest proportion of medium and strong acid sites by 436 and 479 mmol.g^{-1}, respectively. The peak broadening in samples is attributed to the strong interaction between the acid sites and the adsorbed NH_3. It is observed that the level of sulphate ion determined the amount of NH_3 desorbed. The higher the amount of sulphate ion resulted in the higher amount of desorbed NH_3 and consequently the higher acidic activity of the catalysts.
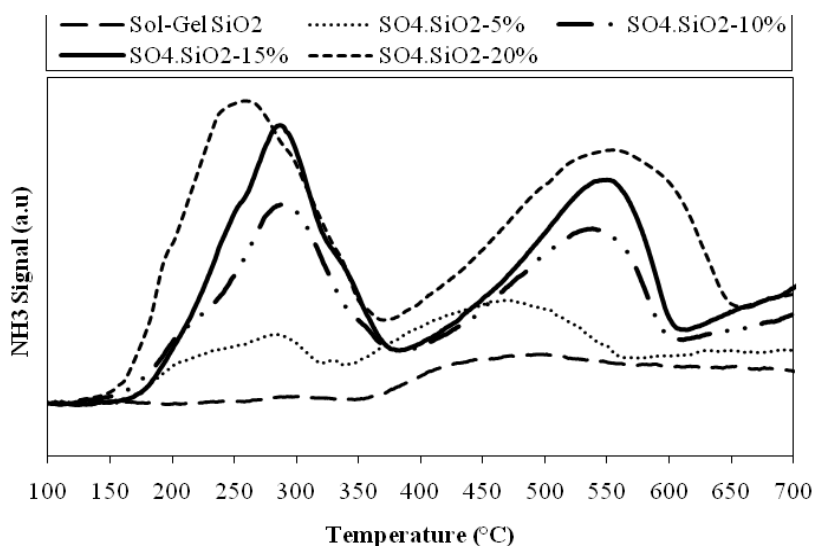

Figure 2: NH_3 temperature-programmed-desorption profiles of Sol-gel SiO_2 and SS (5, 10, 15, 20%w)

The X-ray photoelectron spectra of SS were applied to verify the presence of sulphate species and identify the chemical state of the sulphated surface of the silica. As was expected, the only contamination existing in the XPS results was designated to the carbon element, which was originated from the analysis itself. The C1s peak was set at 284.6 eV to offset the electron charging effect for all spectra. The XPS results of the SS surface are shown in Figure 3. The binding energy for $S2P_{3/2}$ at 169 eV is attributed to S-O bonds in SO_4^{2-} species, indicating that the oxidation state of sulphur in the sample is hexavalent (S^{6+}) [17]. The absence of a peak at around 163-164 eV reveals that there is no elemental sulphur or Si-S type species in the sample [18]. The binding energy of $S2P_{3/2}$ at 167.5 eV is due to the presence of SO_3^{2-} species. Therefore, the absence of this peak in the SS catalyst leads to the absence of sulphite groups in this sample. The presence of free sulphate ions in the sample would be unlikely, because they were absorbed by the acid solution and thus, this explains the anchoring of the sulphates onto the surface of the silica. In addition, the S2p spectrum was never intense due to the low intrinsic sensitivity factor of this element. The spectral region corresponding to the O1s shows the main signal assigned to oxygen bonded to silicon atoms as Si–O–Si at the 533.1 eV, whilst the binding energy at about 533.8 eV was related to Si-O-S or Si-OH or chemisorbed water and a lower energy signal appearing close to 532.5 eV was assigned to the sulphate ion SO_4^{2-}. From the XPS results, the binding energy of the Si2p in silica and SS were 103.4 and 103.8 eV, respectively. Shifting to a higher binding energy in O1s and Si2p indicates the electron interaction between the sulphate anion and the Si cation on the surface of the silica species [19].
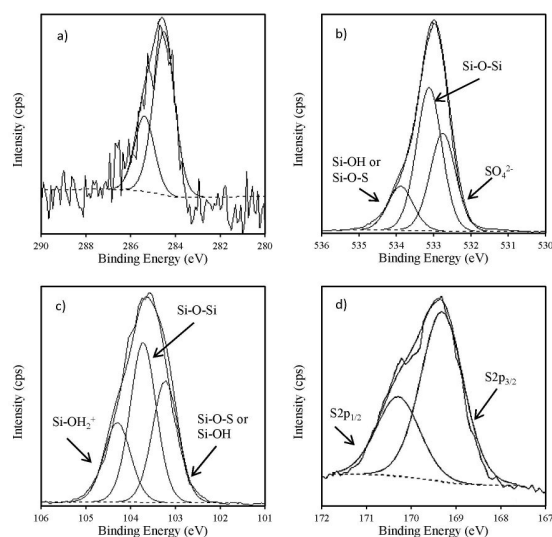

Figure 3: XPS spectra of the a) C1s, b) O1s, c) Si2p and d) S2p of Sulphated Silica (SS)

3.2 Catalyst Experiments

The products of esterification of glycerol with acetic acid over sulphated silica include monoacetin, diacetin, and triacetin, which were analysed by GC-FID and capillary column of HP-5 [20]. Table 3 shows the glycerol conversion and selectivity of the products over different loading percentages of sulphated silica during 6h of the experiment. It has also exhibited the influence of the acetic acid molar ratio to glycerol on selectivity to mono-, di- and triacetin, and glycerol conversion over SS catalysts. As expected, an increase in molar ratio of AcOH to Gly led to an increase in reaction yield. It was observed that all catalysts showed high catalytic activity in a high molar ratio of acetic acid to glycerol. The highest selectivity to monoacetin (i.e., desired product) was observed in lower molar ratio of AcOH to Gly, whereas an increase in molar ratio resulted in diacetin and triacetin production predominantly. SS-10 showed the most selectivity to monoacetin in a molar ratio of 3 compared to other catalysts, while SS-20 exhibited the most activity due to strong acidic sites as verified by the TPD results.

Table 3: Catalyst activity in glycerol esterification. (Reaction conditions: catalyst amount= 0.2 g; reaction temperature= 50 ^{o}C; reaction time= 2 h)

Catalyst	Mole ratio AcOH/Gly	Selectivity (%)			Conversion (%)
		Monoacetin	Diacetin	Triacetin	
SS-5	6	56.40	42.05	1.50	84.28
SS-10	6	75.25	22.31	2.40	87.32
SS-15	6	64.49	30.78	4.62	93.42
SS-20	6	51.90	45.27	2.11	96.88
SS-5	3	65.32	32.45	1.69	78.68
SS-10	3	81.12	18.32	Traces	81.63
SS-15	3	69.47	25.85	4.52	88.94
SS-20	3	58.83	37.10	3.24	90.12

As SS-10 showed the highest selectivity to monoacetin in molar ratio of 3, we considered this catalyst for optimization process.

Different experiments were carried out in order to evaluate the effect of reaction time. The reaction time varied from 2 to 8 h, and the results are shown in Figure 4. As expected in the beginning of the reaction, the selectivity towards monoacetin was high; however, as the reaction continued, the selectivity towards di and triacetin increased due to the expense of monoacetin. This increase in selectivity to di and triacetin over time is mainly corresponded to the further acetylation of monoacetin, as the glycerol conversion is being completed from 2 to 8 h. Therefore, SS-10 is a highly selective catalyst for producing monoacetin in lower reaction times.
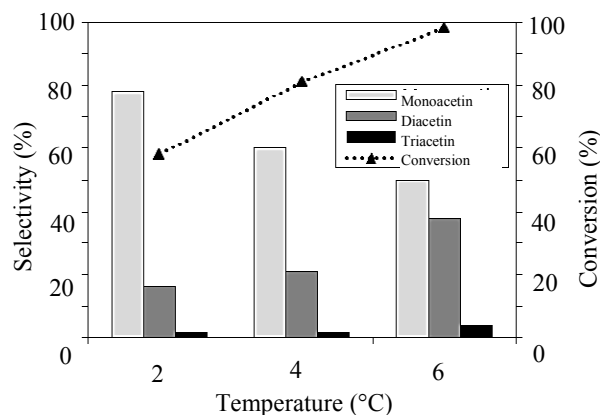
Figure 4: Effect of reaction time during glycerol acetylation over SS-10 as a catalyst (Reaction conditions: reaction temperature: 50 ^{o}C; catalyst weight: 200 mg; AcOH/Gly mole ratio: 3)

The effect of reaction temperature was examined and the results are shown in Figure 5. Glycerol conversion and selectivity depend on both the nature of the catalyst and the temperature of the reaction. The conversion of glycerol increased slightly with an increase in reaction temperature. That should be due to the fact that as the reaction temperature increased from 50 to 110 ^{o}C, the formation of diacetin and triacetin was predominant, whereas the monoacetin production was preferred in lower reaction temperatures. Similar selectivities and activities were achieved by using dodecatungstophosphoric acid, immobilized into silica matrix at 120 ^{o}C [21].
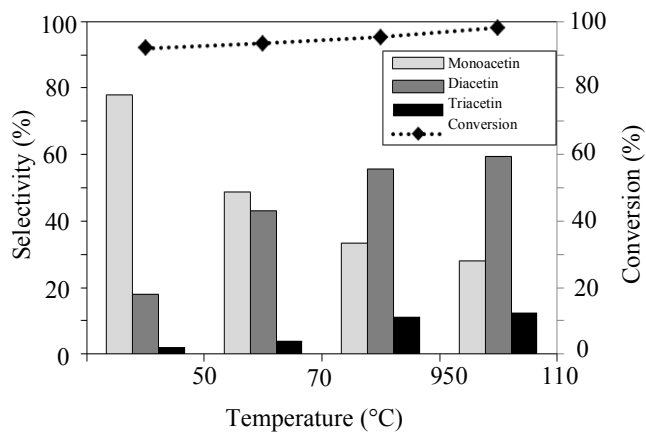

Figure 5: Influence of reaction temperature during glycerol acetylation over SS 10 as a catalyst (Reaction conditions: reaction time: 2 h; catalyst weight: 200mg; AcOH/Gly mole ratio: 3)

The effect of catalyst loading on the glycerol acetylation was also investigated. The range of 0.2-0.8 g of catalyst was selected, while the reaction temperature was maintained at 50 ^{o}C for 6 h. Figure 6 represents a slight increase in glycerol conversion with an increase in catalyst amount from 0.2 to 0.8 g whereas the selectivity to monoacetin declined by catalyst amount increased. In case of diacetin and triacetin the selectivity improved when the catalyst amount increased. It is worthwhile to mention that in higher weight of catalyst, the selectivity was less influenced by the catalysts amount. It can be concluded from the above discussion that monoacetin is predominantly formed by adding 0.2 g of catalyst to the mixture of reactants.
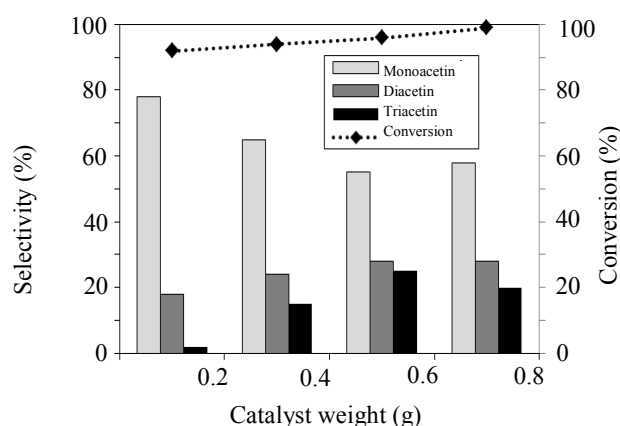

Figure 6: Effect of catalyst weight on glycerol acetylation over SS-10 as a catalyst (Reaction conditions: reaction time: 2 h; temperature: 50 ^{o}C; AcOH/Gly mole ratio: 3)

4. CONCLUSION

The acetylation of glycerol with acetic acid over a series of sulphated silica as solid acid catalyst was studied. All reaction parameters (temperature, time, catalyst loading, and glycerol to acetic acid molar ratio) have been optimized to obtain the highest selectivity to monoacetin. The study indicates that glycerol conversion and selectivity to monoacetin depends, not only on the above factors but also can be influenced by the acidic property of the catalyst (sulphate content).

Acknowledgement

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