Synthesis and characterization of supported sugar catalyst by dip coating method

J Janaun, N J Siambun, N N Safie
1Universiti Malaysia Sabah, Jalan UMS 88400 Kota Kinabalu, Sabah, Malaysia

E-mail: jidon@ums.edu.my

Abstract
Sugar catalyst is a novel solid acid catalyst with reactivity comparable to that of sulphuric acid in biodiesel production. However, the fine powder form of sugar catalyst with the non-porous structure might cause large pressure drop in a packed bed reactor due to low bed porosity, affecting the reaction conversion especially in gas phase reaction. Furthermore, higher pressure drop requires higher electrical energy to drive the fluid through. Increasing the particle size is anticipated to be able to overcome the pressure drop matter. Hence, a deposition of sugar catalyst on larger particle materials was studied. Three types of materials were used for this investigation namely aluminum, silica and clay. The deposition was done via dip-coating method. The materials were characterized for their total acidity, thermal stability, functional groups, surface area, and element composition. The total acidity for SCDCAl, SCDCSi, and SCDCCl were 0.9 mmol/g, 0.2 mmol/g, and 0.4 mmol/g, respectively. The ratio of char deposited on SCDCAl, SCDCSi and SCDCCl were 0.9 g of support/g of carbon, 0.040 g of support/g of carbon, and 0.014 g of support/g of carbon respectively. FTIR and EDX analyses were carried out to determine the presence of active sites of the catalysis by identifying the functional groups such as –COOH, -OH, -SO₃H. The results showed that –SO₃H was detected on the surface of synthesized catalysts, except for SCDCCl. The pore size of SCDCAl, SCDCSi and SCDCCl were classified as macropores because the average diameter were greater than 50nm. The catalysts were stable up to 400 °C. The results showed that the dip-coating method could deposit sugar catalyst on aluminum, silica, and clay at low total acidity concentration.

1. Introduction
Recently, the research on biodiesel and related catalyst have attracted attention due to its potential as an alternative renewable energy and its ability to mitigate environmental pollution. Biodiesel, or known as fatty acid methyl ester (FAME), is an alternative diesel fuel that is derived from the renewable biomass that contains free fatty acids (FFA) or triglycerides, such as vegetable oils, animal fats, waste oils and waste greases [1]. Transesterifying such inexpensive feedstock with homogeneous acid catalysts is not susceptible to high FFA contents but require expensive equipment[2]. Basic homogeneous catalyst is however, not suitable as it yields bad side effect such as soap formation which require excessive water for its removal from the final products. Heterogeneous catalyzed process is widely favored compared to the other catalytic processes as it is easily separated and

1 To whom any correspondence should be addressed.

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purified. In addition to that, it reduces energy consumption, more environmentally benign and it is economically competitive due to the low total capital investment and manufacturing cost. West et al.,[3] showed through simulation that solid-acid catalyzed process is more economical compared to supercritical processes, homogeneous acid, and alkali catalysis processes.

A novel heterogeneous acid catalyst known as sugar catalyst or carbon-based solid acid catalyst was discovered by Toda et al.,[4] derived from the incomplete carbonization of D-glucose followed by sulfonating the pyrolyzed char with concentrated or fuming sulphuric acid. These types of catalyst were reported to show excellent catalytic performance in biodiesel synthesis especially for low quality feedstock due to the presence of polycyclic aromatic hydrocarbon containing –SO₃H groups and phenolic –OH and –COOH groups [5]. Furthermore, the sugar catalyst afforded a high yield of above 90 % [6] that is comparable with sulphuric acid [7].

Fine powder of sugar catalyst is non-porous and has low specific surface area (<1 m²g⁻¹) resulting in lack of usability in industrial operation which typically require large catalysts size. According to Melero et al.,[8], catalytic reactions are sensitive to the catalysts structure, surface atomic arrangement and coordination, which can be well controlled by tuning the specific composition, morphology and the size of catalyst. Hence, increasing the specific surface areas and its particle size are expected to overcome the limitation of sugar catalyst. The size increase can be achieved by depositing the powdered form of sugar catalyst onto supports which are industrially usable such as metal, ceramics, and glass. Chemical pretreatment known as wet-etching pretreatment is reported in this paper. It is proved to increase the adherence of the catalytic layer and forming an oxide layer by creating an anchor sites for deposition of catalyst to occur [9]. Further explanation by Reymond [10], the HCl treatment is often used to clean the metallic surfaces and helps forming a pseudo-layer accessible to chemisorption of small charged particles [11]. In this research, dip coating method with wet-etching pretreatment is reported for the coating of sugar catalyst on various commercially available supports namely aluminum, glass and clay to synthesize novel supported sugar catalyst. The aim is to evaluate the sugar catalyst deposition on the support, and subsequently chemically and physically characterized.

2. Methodology

2.1 Material
D-glucose (carbon precursor) (Systerm, D (+)-Glucose-monohydrate), Fuming Sulphuric acid (Across Organics; Extra Pure 20-30 % free SO₃), Fuming Hydrochloric acid 37 % (Merck), Fuming Nitric Acid, 65 % (System), Sodium Hydroxide (Systerm pellets) were used as received. Commercial aluminum plate, low-cost microscope borosilicate glass slides (Sail Brand; typical composition: 80 % SiO₂, 14 % B₂O₃, 4 % Na₂O, and 2 % Al₂O₃)[12], and commercial clay (typical composition : 28.6 % Si, 15.1 % Al, 0.66 % Fe, 0.3 % Ti, 1.69 % K, 7.07 % loss of ignition) [13] were used as supports.

2.2 Preparation of supported sugar catalyst by dip coating on aluminium, silica and clay
The synthesis of supported sugar catalyst comprised of few important steps namely; (i) pretreatment of support, (ii) pretreatment of carbon precursor, (iii) pyrolysis of supported D-glucose on aluminum, glass and clay, and lastly (iv) sulphonation using fuming sulphuric acid. The steps are summarized in Figure 1.

Figure 1. Schematic diagram of synthesis route of supported sugar catalyst on aluminium, silica and clay
Initially the supports were cut into smaller pieces. Aluminum supports were cut into rectangular shape size of 1.0 cm x 0.5 cm, silica supports were cut into size of 1.0 cm x 1.0 cm using glass cutter, clay support were crushed to irregular shapes and sizes larger than 4 mm. About 30 g of supports underwent a wet-acid etching pretreatments with 37 % fuming hydrochloric acid, HCl and 65 % fuming nitric acid, HNO₃. Supports were immersed in 20 mL of 37 % fuming HCl solutions at retention time of 2-3 minutes to improve superficial roughness, and subsequently in 20 mL of 65 % fuming HNO₃ solutions at 80 °C for 5 minutes. After drying in oven at temperature of 120 °C that is higher than boiling point of hydrochloric acid (83 °C) and nitric acid (110 °C), for 1 hour to remove the unreacted nitrate and chloride ions, the support was immersed in a solution contained 85 g of D-glucose and 25 g of deionized water. The supported D-glucose was dried in the oven at 104 °C to remove water. The pyrolysis was then conducted in a tube furnace at 400 °C for 4 hours under N₂ atmosphere at heating rate of 10 °C/min. Multiple vapor phase sulfonation was done accordingly [14]. In the multiple vapor phase sulfonation process, -SO₃H group was introduced into the framework of carbon char through heating of concentrated sulfuric acid in the two neck round bottom flask at 150 °C for 6 hours, the sulfuric acid vapor produced is then diffused and absorbed onto the external surfaces and the pores of char particles. The sulfonation was repeated three times. The supported sugar catalyst was named as supported sugar catalyst on aluminum (SCDCAl), supported sugar catalyst glass (SCDCSi) and supported sugar catalyst clay (SCDCCI) accordingly.

2.3 Characterization of supported sugar catalyst
Total acidity was determined using a back-titration method. A mass of 0.1 g of sample was poured in a beaker containing 60 mL of 0.008 M NaOH, and stirred for 30 minutes at room temperature. The NaOH solution as the analyte was titrated using 0.02 M HCl as the titrant. Phenolphthalein was used as indicator to detect the end point at pH 7. The functional groups of synthesis catalysts were determined by using Fourier Transform Infrared Spectrometry (FTIR) with the scan range of 650 cm⁻¹ to 4000 cm⁻¹. The pore size and surface area of catalysts were determined by using Automated Mercury Porosimeter, Pascal 440 series via mercury intrusion at density temperature of 25 °C and pressure at 200 MPa. The SEM-EDX analyses were carried out at Electro High Tension (EHT) = 5.00 kV, Working Distance (WD) = 5 - 7 mm, vacuum mode = variable pressure with the magnification power of 100x for support and 1000x for supported sugar catalyst, while signal VPSE was chosen for the non-conductive samples. The structure of carbon material was analyzed using X-Ray Diffraction (XRD) Philips Xpert Pro. The XRD patterns were analyzed under Cu Ka1 radiation (λ = 1.541 nm) and Ka2 radiation (λ = 1.541 nm). The determination of thermal stability of the catalysts was carried out using Thermal Gravimetric Analysis (Perkin-Elmer) in nitrogen atmosphere with flowrate of 20 mL/min and the temperature rate was set at 10 °C/min to 400 °C.

3. Results and discussion

3.1 Total char coated and total acidity of sugar catalyst deposited on different supports
As shown in Table 1, the ratio of char deposited on aluminum has the highest value of 0.9 (g_c/g_s), followed by clay with 0.4 (g_c/g_s), and silica with 0.2 (g_c/g_s). During the wet-etching treatment, only aluminum reacted vigorously which promoted its roughness compared to clay and silica. At the surface of the coating the chemical reactivity and the roughness must be considered in addition to the shear strength [15]. The roughness of the surface creates a better grip for the char, compared to the smooth surface; reducing the gliding of the carbon char from the surface. This suggested that the roughness of the aluminum support, increased its shear strength and resulted in high amount of char coated. As denoted in Table 1, SCDCAl, SCDCSi and SCDCCI possessed lower total acidity compared to the powdered sugar catalyst that has 3.05 mmolg⁻¹ [14]. This indicated that, the sulphonic ions were loosely bonded to the support that easily washed away during washing process, instead of forming a
hydrogen bonding with the carbon char \[16\]. The SCDCAl has the highest total acidity, confirming higher char deposits gives higher total acidity.

**Table 1.** Amount of char successfully coated on three different supports with respective total acidity

| Sample  | Type of support | Char coating (g) | Ratio of char deposited on the support, weight of char, \( g_c \) /weight of support, \( g_s \), \((g_c/g_s)\) | Total acidity, TA (mmol/g) |
|---------|-----------------|------------------|-------------------------------------------------------------------------------------------------|-----------------------------|
| SCDCAl  | Aluminum        | 49.74            | 4.97                                                                                           | 0.9                         |
| SCDCSi  | Silica          | 1.04             | 0.04                                                                                           | 0.2                         |
| SCDCCI  | Clay            | 0.43             | 0.01                                                                                           | 0.4                         |

3.2 FT-IR

![FT-IR spectra](image)

**Figure 2.** FT-IR spectra of supported sugar catalyst on aluminium, silica and clay

Figure 2 shows the FT-IR analysis of SCDCAl, SCDCSi and SCDCCI. SCDCCl and SCDCSi exhibit peak at 1050 cm\(^{-1}\) which indicated a presence of –SO\(_3\)H groups \[4\]. The same peak observed in SCDCAl but with broader and weaker peak. SCDCAl and SCDCSi exhibit peak at 1600 cm\(^{-1}\) due to the C=C stretching \[17\]. The bands at 756 cm\(^{-1}\) observed for all supported catalyst were related to the out of plane blending modes of C-H bonds of aromatic and heterotopic compounds \[18\]. A strong stretching band at 1020 cm\(^{-1}\) to 1250 cm\(^{-1}\) indicated a presence of C-O bond. The band at 1251 cm\(^{-1}\) was related to Ar-OH stretching or aromatic acidic groups \[20\]. The FT-IR spectra coupled with EDX data which confirmed that SCDCAl and SCDCSi contained large amount of oxygen, the carbon deposited consist of polycyclic aromatic carbon sheets containing –SO\(_3\)H, –COOH, and –OH moieties which also in agreement Peng et al., \[21\] for the sugar catalyst.

3.3 Surface area

Based on Table 2, the surface area of aluminum and silica have increased by 63 % and 30 % respectively after catalyst deposition, whereas it has decreased 22 % for clay. The surface are in clay decreased due to the presence of sugar catalyst that cause blockage of pores of the clay thus reducing of surface SCDCAl, the pores mainly come from the surface area of the deposited sugar catalyst. The
increase of surface area of SCDCAl and SCDCSi compared to their original support can be associated with the surface area of the deposited sugar catalyst. This is because Aluminum and Silica used were non-porous. The pore size of SCDCAl, SCDCSi and SCDCCl could be classified as macropores because the average diameters were greater than 50nm.

Table 2. Surface area and total porosity (%) of support and supported sugar catalyst obtained from Automated Mercury Porosimeter, Pascal 440 series, 200MPa, 25 °C

| Parameters                        | Support     |     | Supported Catalyst                      |
|----------------------------------|-------------|-----|----------------------------------------|
|                                  | Aluminum    | Silica | Clay | SCDCAl | SCDCSi | SCDCCl |
| Total specific surface area (m²/g)| 1.24        | 0.71  | 6.29 | 3.38   | 1.02   | 4.91   |
| Average pore diameter (nm)       | 587.70      | 4051.25 | 1612.01 | 3844.73 | 116.79 | 1442.22 |
| Total porosity (%)               | 4.68        | 1.90  | 58.86 | 6.81   | 0.3339 | 15.57  |

3.4 EDX analysis
The EDX analysis showed that the weight percentage of sulphur was the highest for SCDCSi with 0.06 wt. %, followed by SCDCAl with 0.04 wt. %, sulphur was not detected in SCDCCl. SCDCAl had slightly lower composition of element C, S, and O compared to SCDCSi. Table 1 shows clay composed of the lowest ratio of char, that less sites available for sulphonic ions, -SO₃H to attach during sulphonation. Despite of that, SCDCCl possessed the highest amount of oxygen. This was likely due to the nature of support that consisted of closely packed oxygen and hydroxyls in octahedral and tetrahedrons arrangements [23]. This data is in agreement with the total acidity analysis where SCDCCl composed of higher acidity compared to silica, due to presence of oxygen containing moieties such as hydroxyl and carboxylic acid groups.

Table 3. EDX analysis of supported sugar catalyst

| Catalyst | Composition (wt. %) |
|----------|---------------------|
|          | C       | S        | O       |
| SCDCAl   | 8.44    | 0.04     | 2.31    |
| SCDCSi   | 8.90    | 0.06     | 3.03    |
| SCDCCl   | 8.64    | 0.00     | 3.89    |

3.5 SEM analysis
Figs. 4 (a) to (c) depicted the morphology of supports via SEM images. The supports had different morphologies, due to the variation in elements that present. Based on SEM images, the surface of glass is smooth compares to aluminum and clay.

Figure 3. SEM Images (a) aluminum support (b) silica support (c) clay support at magnification 100x
As indicated in Table 1, the aluminum support attached most sugar catalyst. As shown in Fig 5(a), obvious layers of sugar catalyst with many pores is visible. On the other hand, only one layer of sugar catalyst was attached to the silica. Correspondingly, sugar catalyst attached on clay is less obvious due to its morphology explained by Nayak and Singh [23], that clay materials possess a layered structure. However, it can attach higher content of sugar catalyst compared to silica because according to Alkan et al., [24] clay sorption properties come from their high surface area and high porosity.

![Figure 4](image)

**Figure 4.** SEM Images (a) SCDCAl at magnification 100x (b) SCDCSi at magnification 1000x (c) SCDCCl at magnification 1000x.

### 3.6 XRD

As shown in Figure 6, X-ray diffraction (XRD) of SCDCAl and SCDCSi displayed a broad diffraction peak (2θ = 10 - 30°) and a weak diffraction peak (2θ = 35 - 50°) which can be assigned to amorphous carbon, composed of aromatic carbon sheets oriented in a considerably random fashion [16]. Meanwhile the SCDCCl has different diffraction patterns due to the least carbon contained. The weak diffraction peak (2θ = 70°) could be associated with titanium [13].

![Figure 5](image)

**Figure 5.** XRD patterns of supported sugar catalysts

### 3.7 TGA

The thermal stability of supported sugar shows that the supported sugar catalysts underwent two stages of weight loss from room temperature to 400 °C. The first weight loss occurred at 70 °C for SCDCAl, 50 °C for SCDCSi and 45 °C for SCDCCl. This is possibly due to the loss of low molecular weight compounds such as water. From 70 °C to 200 °C there is major decline of weight due to the hydration of moisture and compounds such as –NO₃ and –Cl that was loosely attached to the support during the wet-etching pre-treatment. The second stage weight loss was at 260°C for SCDCAl, 245 °C for SCDCSi and 195°C for SCDCCl. These are associated with the decomposition of -OH and -COOH compounds. The results showed that the temperature range was suitable to dehydrate most of the
hydroxides, leaving only carbon char. The samples weight remained constant from 360 °C to 400 °C. The total weight loss was less than 10% from room temperature to 400 °C.

Figure 6. Derivative thermal analysis of SCDCAl, SCDCCl and SCDCSi

Figure 7. Thermo-gravimetric analysis of SCDCAl, SCDCSi, SCDCCl

4. Conclusions
Sugar catalyst was deposited on three different supports namely aluminum, silica and clay using dip coating method. The results showed that sugar catalyst could be deposited on these supports, but the amount of sugar catalyst is very low which influenced the total acidity. The total acidity of supported sugar catalyst at SCDCAl, SCDCSi, and SCDCCl were 0.9 mmol/g, 0.4 mmol/g and 0.2 mmol/g, respectively. Aluminum support was coated the highest ratio of char with 4.97 g/g, and has the highest total acidity. The higher amount of char deposited, the higher the total acidity could be achieved. The FT-IR spectra coupled with EDX data indicated that SCDCAl and SCDCSi contained high amount of oxygen, that the carbon sheets deposited consist of polycyclic aromatic carbon sheets containing –SO$_3$H, –COOH, and –OH moieties except SCDCCl, which showed the presence of similar groups in FTIR, but EDX data showed the absence of sulphur element. The pore size of SCDCAl, SCDCSi and SCDCCl are classified as macropores. The sugar catalyst deposited was amorphous as shown by diffraction pattern in XRD analysis. The supported sugar catalysts underwent two stages of weight loss from room temperature to 400 °C, the total loss was less than 10%.
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