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Preparation and Characterization of Sulfonated Carbon Cryogel Doped Zinc as a Catalyst for Glucose Ethanolysis to Ethyl Levulinate

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Abstract. In this study, sulfonated carbon cryogel (CC) doped with zinc was prepared and used as a solid catalyst. Carbon cryogel was prepared by mixing urea and furfural, freeze-drying, and calcination. The CC was then sulfonated and impregnated with zinc (II) nitrate for ethyl levulinate production from ethanolysis of glucose. Experiment results showed that different types of catalyst prepared from CC precursor had different catalytic effects on the ethanolysis of glucose. Sulfonated carbon cryogel doped with zinc (SCC-Zn) which prepared at a calcination temperature of 300 °C showed better performance as a catalyst for the ethanolysis reaction of glucose. In addition, the 10 wt.% of Zn was recommended as optimum loading for the impregnation on the catalyst. The ethyl levulinate yield of 19.6 mol% was obtained at 180 °C for 6 h with 0.15 g catalyst loading and 0.4 g of glucose feed. The selected SCC-Zn catalyst was further characterized by using FTIR, TGA XRD, and SEM-EDX to evaluate its physical and chemical properties as a catalyst.

Keywords: Ethyl levulinate, Glucose, Ethanolysis, Sulfonated carbon, Zinc doping

INTRODUCTION

Biomass is a renewable and genuine source of carbon-based liquid fuels and biochemical. Bio-fuel from biomass sources has become an alternative approach due to the gradual consumption of fossil fuels and the increasing market price (Dai et al. 2018). Biomass hydrolysis is one of the thermal-conversion processes to produce many derivative products such as sugar, 5-hydroxymethylfurfural (5-HMF), furfural, and levulinic acid (LA). In addition, biomass can undergo an alcoholysis reaction, which produces useful biochemical products such as levulinate ester. Direct alcoholysis of biomass precursor or conversion biomass derivative product from biomass hydrolysis could be applied in the synthesis of levulinate ester. Ethyl levulinate (EL) is a potential levulinate ester for the application as a fuel additive, such as blending with up to 20% content in diesel formula. EL has a high-octane rating, good energy content, high lubricity, and high flashpoint which suitable as a gasoline blend-stock (Joshi et al., 2011).

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Several researchers have reported the conversion of biomass into EL using a homogenous catalyst such as sulfuric acid (Chang et al., 2012) and ionic liquid (Guan et al., 2018). A high reaction yield of EL was produced using a homogenous catalyst. However, the strong acid of homogenous catalyst has shown a drawback involving equipment corrosion and difficult separation and recycling (Zhang and Chen 2016). Heterogenous catalyst applied in the reaction system has attracted considerable interest in recent decades to overcome the above-mentioned homogenous catalyst drawback. This situation has directed developing new and environmentally benign heterogeneous catalysts with high activity to provide high yield and selectivity of levulinate esters.

The direct conversion of biomass to EL in the heterogeneous catalytic system required much improvement to obtain optimum EL yield. Thus, the prior study on the conversion of the biomass derivatives such as cellulose, glucose, furfuryl alcohol, and levulinic acid is required to understand the reaction behavior. To date, there are more studies on the conversion of levulinic acid or furfuryl alcohol to EL (Guo et al. 2020, Zainol et al. 2020), and the research progress has focused on other derivative feedstock. Glucose is a simple sugar, has been studied for the reaction to EL before applying a feedstock with a more complex structure such as cellulose and biomass.

Glucose has been utilized as a feedstock for conversion to EL using a catalyst such as $SO_4^{2-}/ZrO_2@Al_2O_3$ (Zhang and Yuan 2020), SO_4^{2-}/ZrO_2-PMO-SO_3H (Song et al. 2018), grafted SO_4^{2-}/ZrO_2/SBA-15 (Morales et al., 2014), and H-USY with SnO_2 (Heda et al. 2019). The utilization of glucose includes the development of a carbon-based acid catalyst for the ethanolysis reaction of glucose to EL, such as glucose-derived hydrothermal catalyst (HTC-400-S) (Bosilj et al. 2019), UCC-S-Fe-300 (Zainol et al., 2021), and cellulose-based modified catalyst (AC-Fe-SO_3H) (Zhang and Chen 2016). Carbon-based solid acid catalyst has shown its potential as a catalyst in producing high product yield and conversion.

Sulfonated (SO_3H-bearing) carbon materials are reported to act as sturdy solid acid catalysts. Besides, a various metal modified catalyst such as Zr, Fe, Sn, and Al has been developed to enhance the catalytic reaction. However, there is limited study on modified Zn catalyst for the derivation of alkyl levulinate. Recent work has applied zinc oxide nanorod-coated sulfonic carbon sphere catalyst, and their result shows a good performance on sucrose ethanolysis to EL (Karnjanakom et al. 2020). Another work was using zinc modified dendritic fibrous nano-silica to convert glucose into derived hexyl levulinate (Mohammadbagheri and Chermahini, 2020). However, the zinc-modified catalyst has not been conducted on glucose ethanolysis to EL. Thus, it shows the potential of Zn modified carbon catalyst for glucose derivation to EL.

The application of carbon gel is studied in this work due to its good surface structure characteristic and properties, which can potentially be catalysts or support. Further modification with Zn could be conducted on carbon cryogel in preparing an acid catalyst for the ethanolysis reaction. The recent work on Fe modified carbon cryogel has shown its potential as catalyst support for ethanolysis reaction (Zainol et al., 2021). In this study, various carbon cryogel based catalysts such as carbon cryogel (CC), sulfonated carbon cryogel (SCC), carbon cryogel doped zinc (CC-Zn), carbon cryogel doped zinc followed by sulfonation (CC-Zn-S), and sulfonated carbon cryogel with zinc (SCC-Zn) were prepared for reaction testing on ethanolysis of glucose to EL. The different percentage of zinc for doping on the selected catalyst was studied. The selected catalyst was characterized using a variety of techniques such as Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy- energy dispersive X-ray (SEM-EDX).

MATERIALS AND METHODS

Materials

Liquid chemicals used in this work were ethanol (C_2H_6O, 95%, Qrec), sulfuric acid (H_2SO_4, 95–97%, Qrec), and furfural (Merck), while solid chemicals were zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, Qrec), glucose (Qrec), and urea (Sigma–Aldrich). Sulfuric acid, urea, furfural, and zinc nitrate hexahydrate were utilized for catalyst preparation, while ethanol and glucose were used as feeds in the ethanolysis reaction. All chemicals were directly used as received.

Preparation of Modified Carbon Cryogel Catalyst

The synthesis of carbon cryogel (CC) from urea and furfural was followed a previous method (Zainol et al. 2020). First, urea and furfural were mixed with a molar ratio of 1:2 in a Schott bottle. Next, distilled water was added to the mixture as a diluent and stirred using a magnetic stirrer. 0.5 mL of H_2SO_4 was added into the solution and mixed for 15 min to produce a wet gel. Then, the gel was freeze-dried at -60 °C for 4 h to form a cryogel. The brownish cryogel was ground before calcined at 500°C at 2 h to prepare CC. The sulfonation was conducted by mixing 5 g of carbon cryogel with 50 mL of H_2SO_4 in a round bottom flask equipped with a condenser. It was then heated at 150 °C for 15 h. After the reaction, the mixture was repeatedly washed with distilled water and filtered until the pH value reduces to 7. The sample was dried and calcined at 400 °C for 2 h to yield sulfonated carbon cryogel (SCC). The preparation of sulfonated carbon cryogel doped with zinc (SCC-Zn) was conducted by impregnation of SCC with $Zn(NO_3)_2.6H_2O$ at different loading of zinc (5, 10, 15, 20 wt.%) in 50 mL of distilled water for 3 h. The mixture was filtered and dried in the oven for 1 h before further calcined for 3 h at 300 °C.

Characterization of Modified Carbon Cryogel Catalyst

FTIR spectroscopy (by Perkin-Elmer Spectrum with KBr pellet) was used to analyze the chemical bonding of the SCC-Zn sample. The spectrum was observed at Infra-Red (IR) spectrum range of 400 to 4000 cm^{-1}. Thermogravimetric analysis was conducted using Perkin Elmer TGA 7 instrument to study the thermal stability of the sample at a temperature ramp of 10 °C/min from 30 to 900 °C under N_2 flow. XRD was applied to analyze the phase structure of the samples using a Bruker D8 Advance diffractometer system (Cu K α radiation, 40 kV, 30 mA) for angle 2θ between 10-80°. SEM-EDX (Hitachi SU8020) was used to observe the morphology and measure the composition (C, O, S, N, and Zn) of the samples.

Ethanolysis of Glucose to Ethyl Levulinate

The stainless-steel reactor (Amar Equipments Pvt. Ltd.) was used to conduct the ethanolysis reaction of glucose to ethyl levulinate (EL) in the presence of SCC-Zn. The ethanolysis reaction of glucose was performed for all the samples to observe their catalytic performance. The reaction was conducted at the selected conditions: glucose feed of 0.4 g, catalyst loading of 0.15 g, reaction temperature of 180 °C, and 6 h. The ethyl levulinate concentration was analyzed using GC-FID 7820A gas chromatography system (Agilent Technology). The GC analysis with DB-Wax column (30 m, 0.25 mm, 0.25 µm) was conducted using condition of injector temperature (270 °C), column temperature (50 to 170 °C, 5 °C/min) and 170 to 240 °C, 15 °C/min), carrier gas of N_2 (1.0 mL/min). The percentage of EL yield was calculated by using Eq. (1) below.

$$\text{EL yield (mol\%)} = [(C_{EL} \times V_P) / 1000 / M_{EL}] / (W_i / M_G) \times 100 \quad (1)$$

where C_{EL} is the final product concentration of ethyl levulinate (mg/L), M_{EL} is the molecular weight of ethyl levulinate (g/mol), M_G is the molecular weight of glucose (g/mol), W_i is the weight of glucose, and V_P is the volume of the final product(L).

RESULTS AND DISCUSSION

Catalyst Screening for Ethanolysis of Glucose

Figure 1 shows the reaction performance of the different catalysts prepared for the glucose ethanolysis reaction. As shown in Figure 1(a), the SCC obtained 15.7 mol% EL yield, and the yield was increased to 19.6 mol% after the modification with Zn as the result of reaction using SCC-Zn calcinated at 300 °C (SCC-Zn(300)). The SCC-Zn calcined at 400 °C (SCC-Zn(400)) has obtained a low EL yield, which is less than 5 mol%. This result shows that sulfonation has played an essential role in providing a Bronsted acid for the reaction. This result indicates that a slight increase of EL was observed when the Zn is introduced. The SCC-Zn(400) was reduced its activity due to the decomposition of the sulfonated acid site that occurred above 300 °C. The decomposition of the sulfonated group was observed around 350-600 °C (Rocha et al. 2019). Thus, the reaction with SCC-Zn(400) has resulted in a low EL yield.

Similarly, CC-Zn is a catalyst prepared without sulfonation has shown low reaction due to lack of Bronsted acid site. In addition, further modification of CC-Zn via sulfonation to prepare CC-Zn-S was provided a low reaction yield. This is probably caused by the low interaction of the sulfonate group with Zn oxide on the surface of carbon cryogel. Incorporating Zn on CC followed by sulfonation may require an effective synthesis method to obtain a good active site catalyst. Besides, there are possibilities that sulfonation of CC-Zn has provided a high active site of catalyst, which caused the reaction to produce other products than EL. The effect of percentage Zn on the SCC was studied (Figure 1(b)) to determine the optimal loading of Zn for the preparation of the modified catalyst. The selected zinc loading for doping was chosen based on the EL yield obtained from the reaction. It can be observed that SCC-Zn with 10 wt.% of Zn shows the highest yield of EL. Further increased Zn loading has caused a significant decrease in EL yield.

The increasing of Zn loading has caused saturation on the surface of SCC and blocked the porous structure and active sites of the catalyst. This situation is similar as reported by Ramli and Amin (2015), which stated that a high percentage of Fe impregnated on HY zeolite has caused a reduction of surface area due to pore blockage. In addition, the presence of Fe_2O_3 has covered the acid site of HY zeolite which reduces the total acidity of the catalyst. Another previous work also showed that the increasing Zn content contributes to the decreasing specific surface area and pore volume of catalyst (Fatimah et al. 2016). Hence, the SCC-Zn with 10 wt.% of Zn loading is selected for characterization and reaction testing in the next study.

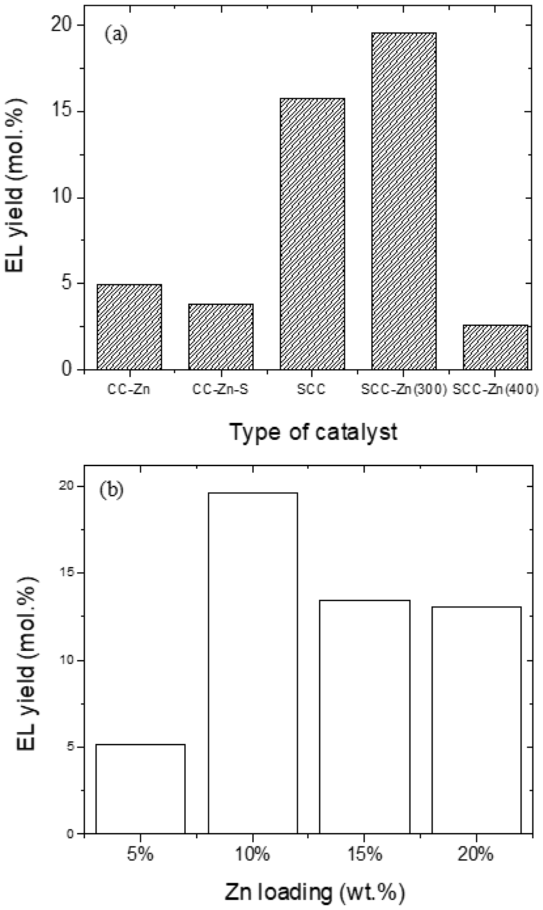

Fig. 1: Effect of different (a) type of catalyst and (b) percentage of Zn modified on SCC catalyst for glucose conversion to ethyl levulinate

The EL yield from glucose ethanolysis using SCC-Zn was compared with other reported sulfonated modified catalysts as shown in Table 1. Sulfonated-based catalysts have been conducted on catalyst support to improve the catalytic activity by providing strong Bronsted acid. The combination of Bronsted and Lewis acid sites could enhance the reaction conversion of glucose. The reaction using sulfonated zirconia oxide (SO_4^{2-}/ZrO_2) catalyst was conducted at 200 °C for 3 h to obtain 29.0 mol% of ethyl levulinate (Peng et al., 2011). The combination of sulfonate group and zirconia-based catalyst effectively enhance the reaction to perform at low catalyst loading and short reaction time. Similar to grafted SO_4^{2-}/ZrO_2/SBA-15 catalyst that provides good reaction yield with high EL of 31.0 mol% at a low reaction temperature of 140 °C (Morales et al., 2014). However, a long reaction time is required for the reaction to provide optimum yield.

Table 1. Glucose to ethyl levulinate using various sulfonated modified catalysts

Catalyst (Cat.)	Reaction condition	Yield (%)	Ref.
SO_4^{2-}/ZrO_2	2.5 g feed, 0.06 g cat., 200 °C, 3 h	29.0	(Peng et al., 2011)
Grafted SO_4^{2-}/ZrO_2/SBA-15	0.25 g feed, 0.5 g cat., 140 °C, 24 h	31.0	(Morales et al., 2014)
Sulfonated char	0.48 g feed, 0.1 g cat., 200 °C, 6 h	37.0	(Bosilj et al., 2019)
UCC-S-Fe-300	0.2 g feed, 1.0 g cat., 200 °C, 6.0 h	39.6	(Zainol et al., 2021)
AC-Fe-SO_3H	0.3 g feed, 0.15 g cat., 200 °C, 3.0 h	19.1	(Zhang and Chen, 2016)
SCC-Zn	0.4 g feed, 0.8 g cat., 180 °C, 6 h	19.6	This study

Besides, sulfonated carbon-based catalysts have also shown effective reaction performance on glucose ethanolysis. It can be observed via ethanolysis reaction by sulfonated char catalyst that yielded high EL of 37.0 mol% (Bosilj et al., 2019). The combination of sulfonation and metal oxide on carbon catalyst was prepared to enhance the catalytic performance. It includes the sulfonated carbon modified Fe (UCC-S-Fe-300) (Zainol et al., 2021) and metal salt-modified carbon catalysts (AC-Fe-SO_3H) (Zhang and Chen, 2016) as a solid acid catalyst for glucose ethanolysis. UCC-S-Fe-300 has obtained high EL yield, but the reaction has implemented high catalyst loading, while AC-Fe-SO_3H obtains 19.1 mol % of EL yield at low catalyst loading and short reaction time. Further improvement, including detailed parameters or optimization study, could be conducted to increase the yield. Similarly, this process could be conducted for the reaction with SCC-Zn catalyst in order to obtain optimum EL yield.

Catalyst Characterization

The FTIR spectrum of selected SCC-Zn (Figure 2(a)) shows the chemical bonding and surface chemistry of the catalyst structure. The existence of functional groups related to the sulfonation and doping of Zn could be observed through the IR peaks. N-H functional group was observed at the wavenumber between 3500 cm^{-1} to 3300 cm^{-1} related to the original structure urea in the carbon structure. C-H structure was recorded around 2900 cm^{-1} to 3000 cm^{-1}. The SO_3H bonding of the sulfonate group was confirmed based on the detection of S=O around 1150 cm^{-1} to 1250 cm^{-1} and S-O bonding around 1050 cm^{-1} (Zainol et al. 2017). The peak around 500 cm^{-1} was attributed to the Zn-O structure in the SCC-Zn catalyst. As reported by previous work, the Zn-O was represented by a strong band observed around 445 cm^{-1} to 556 cm^{-1} (Kaushik et al. 2019). The functional group related to the sulfonation and Zn doped on carbon cryogel was detected on SCC-Zn from the IR spectrum.

Thermal stability and decomposition studies of SCC-Zn are shown in Figure 2(b). Initial decomposition of SCC-Zn catalyst below 200 °C refers to the moisture content presented in catalyst structure. Meanwhile, the high thermal stability of the catalyst up to 400 °C is due to the parent material of CC. Further decomposition of SCC-Zn is related to the degradation of catalyst acid site and high molecular weight compound in the CC structure. About 30 wt.% of decomposition was observed from 400 to 800 °C, which suggested that the catalyst was thermally unstable above 400 °C.

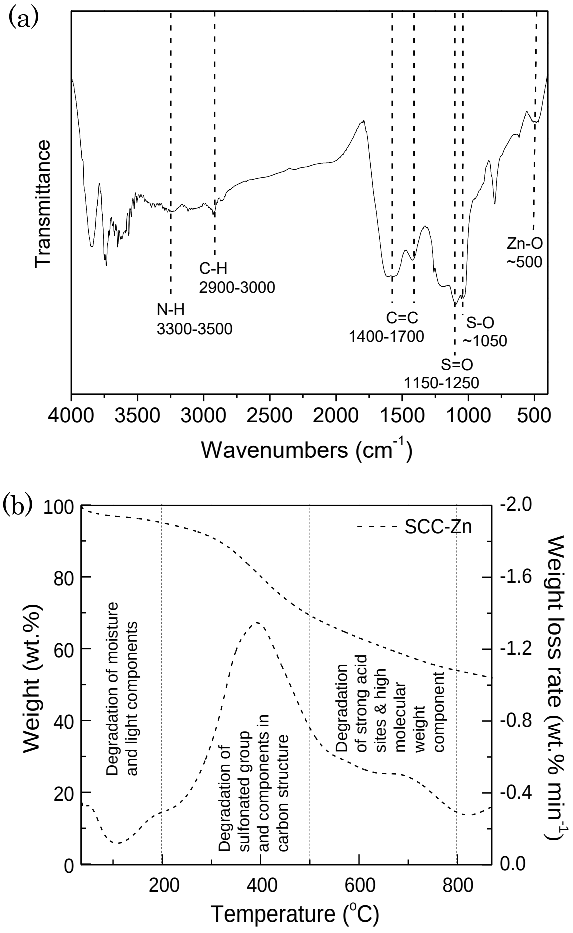

Fig. 2: (a) FTIR spectra of SCC-Zn and (b) TGA-DTG curve of SCC-Zn

High degradation of SCC-Zn could be

observed in the DTG graph (300-500 °C), which is related to the sulfonated group in the catalyst structure. The decomposition of the sample around 500-800 °C could be related to strong acid sites from the sulfonation and high molecular weight component in CC structure as the carbon precursor was stable up to 500 °C affected by calcination. The weight loss of sulfonated groups was observed between 350 °C and 600 °C (Rocha et al. 2019). The DTG graph shows a small degradation peak above 800 °C could be related to the decomposition of Zn compound in the catalyst structure.

The XRD patterns (Figure 3(a)) show the phase structure of CC, SCC, and SCC-Zn. Broad peaks around 10° to 30° were observed for all samples due to the amorphous structure of carbon cryogel precursor. The SCC and SCC-Zn catalysts prepared from the sulfonation followed by Zn doping did not show any effect or any crystals' peak formation, except for reducing the peak intensity. The peak intensity around 10° to 30° was reduced due to the sulfonation process involved by strong acid that affects the CC structure. In addition, the SCC and SCC-Zn peaks were shifted to the right which explains that crystallinity and structure of catalyst changed after modification. The absence of crystal peak of Zn is due to low Zn content distributed on SCC-Zn structure, or the zinc oxide formation possibly present as non-crystalline due to low calcination temperature.

Figure 3(b) shows the EDX graph of CC, SCC, and SCC-Zn, which presents the element composition on the catalyst's surface. CC consists of 78.5 wt% of C, 10.8 wt% of N, and 10.6 wt% of O. Meanwhile, SCC consists of 68.5 wt% of C, 21.4 wt% of O, 8.8 wt% of N, and 1.3 wt% of S. The S element is presented in the SCC sample due to the successful sulfonation process on CC. As for SCC-Zn, 67.5 wt% of C, 19.6 wt% of O, 11.2 wt% of N, 1.0 wt% of S, and 0.7 wt% of Zn were detected from the EDX analysis. Low Zn composition was detected probably due to low or inconsistent distribution of Zn on the sample's surface. That is also a possible reason why the crystal peak of Zn was not detected from the XRD spectra as discussed above.

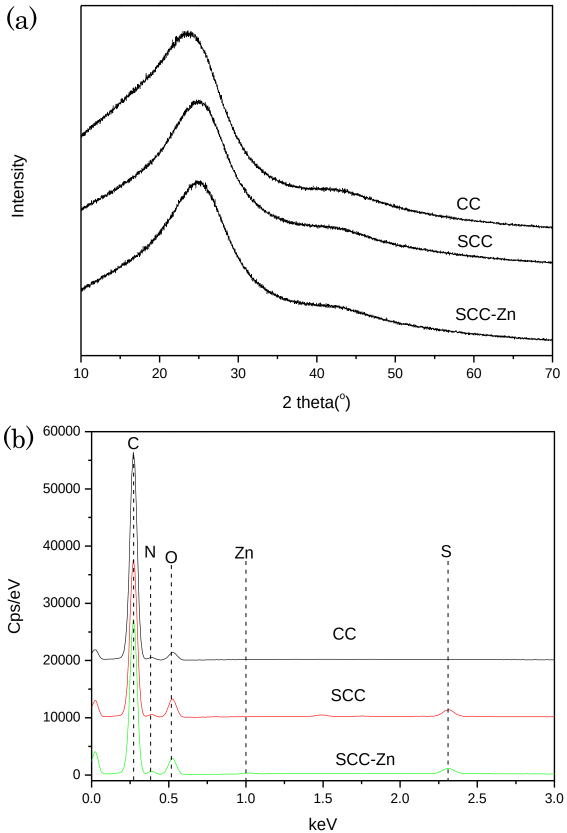

Fig. 3: (a) XRD patterns and (b) EDX graphs of CC, SCC, and SCC-Zn.

The surface morphology of CC, SCC, SCC-Zn are presented by SEM images in Figure 4. The SEM image shows the rough surface of carbon of CC sample, and it becomes more ruptured after the CC sample undergoes the sulfonation process. The ruptured and porous surface of SCC exposed more surface for the reaction. This condition theoretically would increase the surface area of the SCC sample. The image of SCC-Zn shows that the surface has been coated with small particles, and the ruptured surface is similar to the SCC image. Only slight differences can be observed from SCC and SCC-Zn samples related to zinc present on the catalyst.

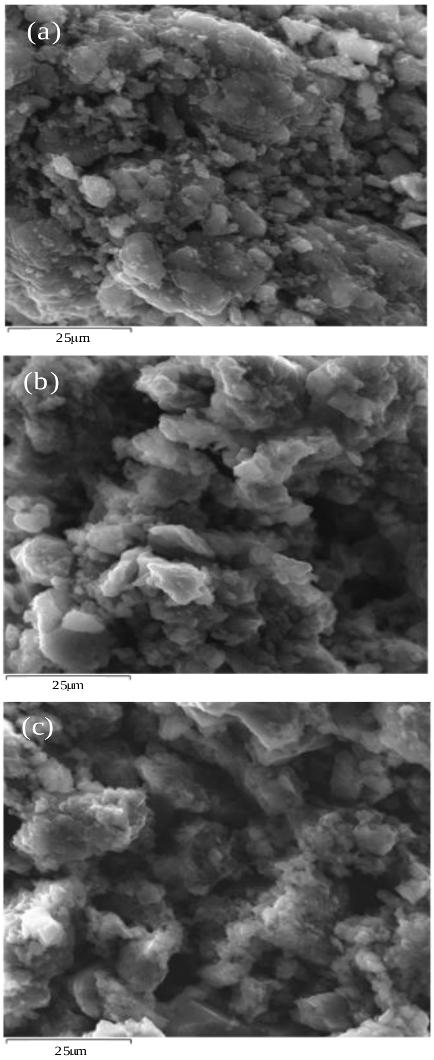

Fig. 4: SEM images of (a) CC, (b) SCC, and (c) SCC-Zn

CONCLUSIONS

The reaction was performed by the modification of carbon cryogel via sulfonation. It was then followed by Zn doping with calcination at 300 °C as a catalyst for glucose ethanolysis. 10 wt.% of Zn loading for doping of SCC provides high EL from the reaction. The characterization of the SCC-Zn shows that the CC was successfully modified via sulfonation and Zn impregnation. The important chemical bonding of SO_3H and Zn-O was presented in the IR spectra. The SCC-Zn's high thermal stability shows that the catalyst can be applied to the reaction without any degradation. Modification of CC has improved the surface morphology of SCC-Zn catalyst, and the element related to the sulfonation and Zn doping on CC has been detected via EDX analysis. Further reaction testing, including parameter studies on the ethanolysis of glucose using SCC-Zn could be conducted in future work.

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