Low Metal Loading Palladium Mixed-Oxides Catalyst for the Synthesis of Glycerol Carbonate

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ABSTRACT— *Glycerol carbonate can be readily synthesized from glycerol and urea catalyzed by PdZnO, PdSnO$_2$, SnO$_2$, and ZnO. The superior catalytic activity of ZnO over SnO$_2$ is mainly due to basicity property. The incorporation of low metal loading of Pd on both SnO$_2$ and ZnO produced higher yield of glycerol carbonate to bulk material counterpart. In addition, the sol-gel technique was shown to have higher turn-over frequency (TOF) due to highly disperse Pd with small crystallite size.*

Keywords - Glycerol, Glycerol Carbonate, Palladium, Metal Oxide Catalyst

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1. INTRODUCTION

The continuous production expansion of biodiesel has resulted in a significant increase in the worldwide production of glycerol, which may adversely affect the industry. The production of glycerol as coproduct, produced at a rate of 10% production of biodiesel has rapidly increased the market supply of glycerol thus contributed to a sharp decrease in its price. Therefore, it is important to find new synthesis to valorize glycerol by utilizing its as sole carbon and energy sources. [1] Glycerol can be utilized as platforms in the synthesis of various fine chemicals such as docosahexaenoic acid, acrolein, polyglycerols, 1,3-propanediol, and glycerol carbonate. Glycerol carbonate for example finds applications as surfactants, elastomers, and adhesives. It is also widely used as a useful solvent in lithium-ion batteries and in the paint industry as well as polymers, such as polycarbonates, polyamides, lubricating oils, polyesters, polyurethanes, and surfactants. [2]

Until now, glycerol carbonate can be produced through various methods such as phosgenation of methanol, trans-esterification of ethylene carbonate or propene carbonate and direct carbonylation using CO_2 [3]. However, the aforementioned techniques suffered from several setbacks such as thermodynamic limitation, utilization of corrosive and hazardous substances and in the presence of expensive catalyst with higher metal loading. Thus, one of the alternative and promising routes has been introduced through glycerolysis of urea. [4] The catalytic reaction required the presence of catalyst that having a well-balanced acid–base characteristic. It was reported that Lewis acid will activates the carbonyl group of urea whereas the other conjugated basic sites will activate the hydroxyl group of the glycerol. [5, 6] Of that reason, most of the reported literature utilized metal oxide as catalyst due to availability of metal-oxygen ion pairs. Among the tested metal oxide catalysts, Zinc Oxide (ZnO) has been reported as one of the catalyst with an optimum acid–base pair. For instance, as the basicity of the conjugated base of ZnO is increased by preparing Zinc Aluminium (Zn–Al) mixed oxide, the selectivity and yield of glycerol carbonate significantly higher than ZnO alone. Other than ZnO, SnO$_2$ has been shown to have the capability to activate the glycerol into glycerol carbonate. [7]

Additional approach to increase the yield of glycerol carbonate is by carry out the reaction in the presence of mixed oxide composite or noble metal supported on metal oxide catalyst. For example, gold and palladium supported catalyst has shown to be effective catalysts for the transformation of glycerol into glycerol carbonate. [8] Different catalyst preparation techniques were shown to produce different catalytic performance toward production of glycerol carbonate as target product. Therefore, in this study, we explore the possibility of Palladium Zinc Oxide and Palladium Tin Oxide catalyst synthesized using sol-gel and impregnation techniques for the glycerolysis of urea to glycerol carbonate.

2.   EXPERIMENTAL

2.1 Materials

The chemicals used throughout the experiment are Nitrogen Gas (99.9%), Glycerol (Friendemann Schmidt Chemical) and Urea (QReC). Whereas, the chemicals required in order to synthesis catalysts are Tin Chloride Pentahydrate with 98% purity, Palladium Chloride (59% Pd content), and Zinc Nitrate Hexahydrate (98% extra pure) which are purchased from Acros Organics. The other chemicals involved are Acetone, Methanol and aqueous Ammonia solution (Systerm ChemPur).

2.2 Catalyst Synthesis

2.2.1   Synthesis of Tin Oxide and Zinc Oxide

Tin Oxide (SnO_2) and Zinc Oxide (ZnO) catalyst were prepared in accordance to the method used by Virender and his co-researchers [9]; whereby Tin Chloride Pentahydrate ($SnCl_4·5H_2O$) acts as raw material for the preparation of SnO_2 catalyst and Zinc Nitrate Hexahydrate ($Zn(NO_3)_3·6H_2O$) used for the preparation of ZnO. The preparation process conducted in several steps as follows: Firstly, 7.00 g of main reactant were dissolved in 200 mL of ethanol under continuous stirring in order to prepare the transparent sol solution. Then, 8 mL of aqueous ammonia solution were added drop wise under constant stirring. The resulting gel is then filtered and washed with ethanol for purification and dried for 3 hours at 100 ^{o}C in the oven. Next, the obtained powder is calcined at 400 ^{o}C for 2 hours in tube furnace.

2.2.2.   Synthesis of Palladium Tin Oxide and Palladium Zinc Oxide using Sol-Gel Technique

The preparation method for Palladium Tin Oxide ($PdSnO_2$) catalysts is the same as the preparation of SnO_2 catalyst mentioned above. However, the different is at the initial step, in which catalyst is formed by simultaneous mixing of Palladium Chloride ($PdCl_2$) and Tin Chloride Pentahydrate ($SnCl_4·5H_2O$) before adding ethanol. Other than that, for the preparation of Palladium Zinc Oxide (denoted as PdZnO), $Zn(NO_3)_3·6H_2O$ is used instead of $SnCl_4·5H_2O$. The amount of Pd is around 1.0 wt%.

2.2.3.   Synthesis of Palladium Zinc Oxide using Impregnation Technique

In order to study the effect of catalyst preparation technique, Palladium Zinc Oxide was also synthesized by wet-impregnation technique. This method is described as follow: Firstly, a stock solution of $PdCl_2$ prepared by dissolving 0.02 g of $PdCl_2$ in 100 mL of ultra-pure water. Then, 1.99 g of sol-gel synthesized ZnO was dissolved in 83.5 mL of stock solution. The solution was stirred until slurry form being observed. Next, the solution was filtered and dried for 16 hours at 110 ^{o}C. The obtained powder is then calcined at 400 ^{o}C for 2 hours in tube furnace. The catalyst obtained then denoted as Pd/ZnO

2.3 Characterization of Catalyst

The crystallographic phase presence in catalyst has been analyzed by using X-Ray Diffractometer (X'Pert Pro model of PANalytical). The data were collected over a CuKα radiation within 3 degree to 80 degree at 2 Theta.

The analysis of BET surface area was measured by performing nitrogen adsorption–desorption isotherm at 77 K using ASAP 200 of Micromeretic brand.

SEM analysis (JSM-7600F; JEOL, USA) was used to determine the surface morphology. The catalyst powder was directly sprinkled over the carbon tape, and images were taken under optimum operating conditions.

The characterization of catalyst by FTIR (Spectrum 100, Perkin Elmer) is done via solid powder analysis by preparing Potassium Bromide (KBr) disc with the ratio of sample to KBr powder at 1:10 ratio.

2.4   Catalytic Testing

The procedure of conducting catalyst testing is based on the method applied by Ab. Rahim et. al [8]. All the reactant of glycerol, urea and catalyst are weighed at respective amount of 13.8 g, 13.5 g and 0.25 g. Before the reaction start, Nitrogen (N_2) gas are allowed to flow around 20 minutes before urea and catalyst are added at temperature of 150 ^{o}C under atmospheric pressure. Typically, the reaction is conducted for 4 hours and sampling is taken at interval reaction time.

2.5 Analysis of Product

Analysis of reaction solution was carried out using Gas Chromatography equipped with FID detector (GC-FID) (Agilent Technologies 7890A, Varian CP Porabond Q). Standard glycerol and glycerol carbonate with different range of concentration were used for calibration purpose. Tetraethylene glycol (TEG) was used as an external standard. **Table 1** shows the method used in GC-FID analysis.

Table 1: GC-FID method description

Inlet Parameters	Oven Parameters	FID Detector
Inject- 1μL	Initial Temperature-80^{0}C	Detector Temp- 250^{0}C
Injection Temp- 225^{0}C	Hold Time- 2 minutes	Hydrogen Flow-35mL/min
Mode-Split	Rate1-0	Air Flow-350mL/min
Split Flow-14mL/min	Temperature 2-300^{0}C	Make-Up Gas-26mL/min
Constant Flow	Hold Time-5 minutes	
Pressure-6.0784psi		
Column Flow-3mL/min		

To corroborate the GC-FID data, the sample taken at 4th hours of reaction time was analyzed using Attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer, USA) with resolution of 4 cm^{-1} per second. In this case, 50 μL of sample was immediately sampled and one drop was placed onto the sample holder. The sample was then immediately analyzed.

3. RESULTS AND DISCUSSION

3.1 Catalytic Evaluation
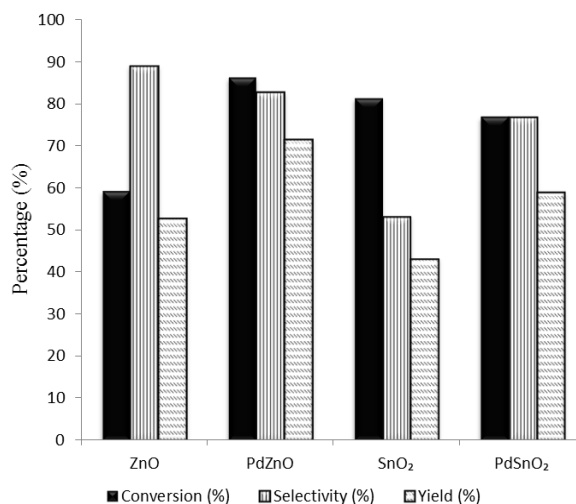
3.1.1 Reaction with Mono-Metal Oxide Catalysts

There are two mono-metal oxides catalyst being tested in the synthesis of glycerol carbonate which consists of ZnO and SnO$_2$ prepared using so-gel technique. The effectiveness of the catalytic reactions by adopting these catalysts is demonstrated in **Figure 1.** It can be seen that the blank reaction without presence of any catalyst produced high conversion of glycerol. The observation is in-line with previous reported literature in which catalyst mainly plays a crucial role in controlling the selectivity of glycerol carbonate by controlling selective transformation of glycerol carbamate intermediate. This was clearly true since both ZnO and SnO$_2$ formed higher percentages of glycerol carbonate selectivity compare to uncatalysed reaction counterpart. The ability of ZnO in selectively produced glycerol carbonate is well studied [10, 11] Nevertheless, the catalytic activity of ZnO synthesized herein via sol-gel technique is higher (53% yield of glycerol carbonate) compared to the commercial ZnO reported by Fujita et al in which the yield of glycerol carbonate produced by ZnO is only 42%. [10] Fujita and co-workers also revealed that the catalytic activity of Zn based catalyst was due to the homogeneous reaction involving leached Zn species. Thus reduce the possibility of catalyst to be recycled. In case of SnO$_2$, the sol gel technique successfully produced SnO$_2$ with superior characteristic compared to similar material synthesized via co-precipitation technique [7] which later on contributed to higher yield of glycerol carbonate. Lower yield of glycerol carbonate obtained from the reaction with SnO$_2$ is believed due to the acido-basic property, it was reported in literature that SnO$_2$ possessed the weaker basic sites and gave low selectivity of glycerol carbonate [12], while ZnO owned the basic strength (H−) in the range of $15.0 > H− > 9.8$ and thereby, exhibiting higher catalytic activities. [5] It is important to note that the synthesis of glycerol carbonate from glycerol and urea typically required basic catalyst. [6, 8] The dominance effect of catalyst acidity is further supported by catalyst surface area data since SnO$_2$ with significantly higher BET surface area than ZnO did not produced higher yield of glycerol carbonate.
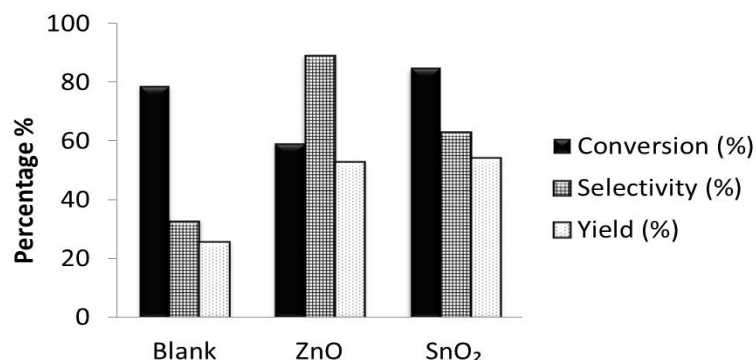
Figure 1: Catalytic activity with ZnO and SnO$_2$ catalyst synthesized via sol-gel technique.

3.1.2   Reaction with Palladium Mixed Oxide

Based on **Figure 2**, the incorporation of highly dispersed of Pd metal onto the surface of ZnO catalyst successfully increased the catalytic performance, whereby the yield percentage obtained is increased from 52.7% to 71.5%. Whilst for SnO_2 catalyst, the presence of Pd on its surface causes positive impact as in ZnO. This can be proven by observing an increasing pattern of selectivity and yield compared to bulk SnO_2. The obtained catalytic data is in-line with the previous study on the effect of Pd metal in increasing the catalytic activity of metal oxide catalysts towards glycerol carbonate production. [8, 13]

Figure 2: Effect of supported palladium metal oxides catalysts. Typical reaction condition applied.

3.1.3   Effect of Different Preparation Method of Palladium Zinc Oxide Catalyst

Figure 3 shows that the selectivity and yield produced by Palladium Zinc Oxide catalyst prepared by sol-gel is superior compare to the catalyst prepared via impregnation method. There are two possible factors contributing to the higher yield of target product obtained for sol-gel synthesized catalyst. Firstly, the amount of Pd available in each catalyst and secondly, the characteristic of ZnO itself, either being altered during impregnation of Pd precursor or virtually unchanged throughout the process. Thus, the catalytic activity comparison is made by comparing the turn over frequency (TOF) based on mol of Pd metal. Clearly, the PdZnO synthesized via sol gel technique showed higher TOF value, *i.e.* 893 h^{-1} compare to 670 h^{-1} for impregnated catalyst. The TOF value for PdZnO is comparable to the Pd supported MgO catalyst reported by Ab. Rahim et al. [8] Higher catalytic performance of sol-gel catalyst might due to the highly disperse with small particle size of Pd as suggested by close observation on XRD data. In addition, XRD analysis might also suggest that the slight different in crystalline structure of PdZnO synthesized via sol gel technique might contributed to the catalytic activity. The XRD data is in-line with FT-IR data in which PdZnO shows slightly different spectrum compare to Pd/ZnO catalyst. Thus, indirectly explains the important role of Pd and ZnO characteristic toward the difference in catalytic activity between both catalysts.
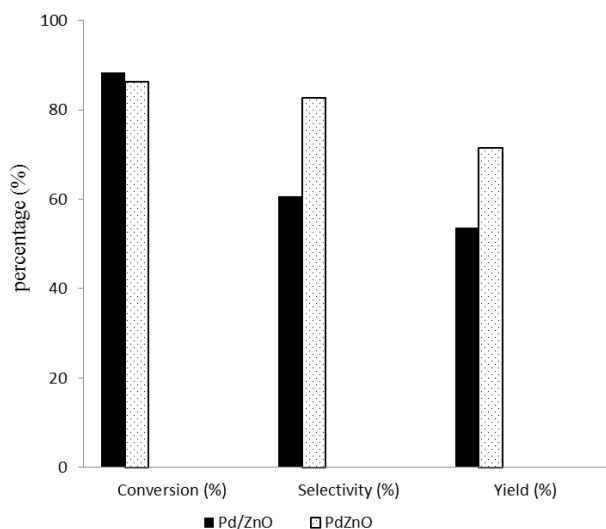
Figure 3: Effect of different preparation method of Pd/ZnO (wet-impregnation method), PdZnO (sol-gel method) catalyst.

The FTIR spectrum of both liquid reaction catalyzed by PdZnO and Pd/ZnO is illustrated in **Figure 4**. The existence of glycerol carbonate in the final product is verified by the presence of glycerol carbonate stretching in the FTIR spectrum as functional group can be seen at 1786 cm^{-1} and for urea at 1670 cm^{-1} and 1620 cm^{-1}. [14] Whilst, the stretching for glycerol carbamate and isocyanic acid can be observed at 1712 cm^{-1} and 2250 cm^{-1} respectively. Both of glycerol carbamate and isocyanic acid compound has been previously reported as the intermediate product in the production of glycerol carbonate by using glycerol and urea as the raw materials. [5, 14]
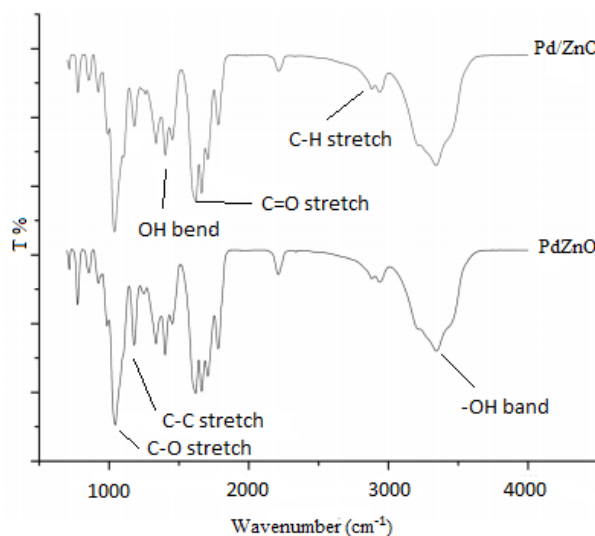
Figure 4: FTIR spectra of product of reaction catalyzed by Pd/ZnO and PdZnO at 4 h reaction time.

3.2 Catalyst Characterization

3.2.1 BET Surface area (S_{BET})

There are four catalysts which have been analyzed with BET in order to determine its total surface area. These catalysts are consisting of ZnO, SnO$_2$, PdZnO, and PdSnO$_2$. All essential data are tabulated in **Table 2.**

Table 2: BET surface area, pore volume and pore size of catalysts.

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
ZnO	0.13	0.0049	166.66
PdZnO	11.24	0.0373	12.92
SnO$_2$	66.56	0.1535	8.93
PdSnO$_2$	69.29	0.2296	12.87

According to table 2, catalyst that has the highest surface area is PdSnO$_2$ followed by SnO$_2$ with 69.29 m^2/g and 66.56 m^2/g respectively. It was important to note here that the SnO$_2$ catalyst synthesized in this study has 4 times higher surface area compared to similar compound reported by previous study reported by Yuan and Xu.[15] In their study, the surface area of SnO$_2$ reported around 16.57 m^2/g. Therefore, this confirms that the catalyst preparation method plays an important role in tuning the physico-chemical properties of catalytic material. In this case, the SnO$_2$ catalyst was prepared using sol-gel technique whereas Yuan and Xu synthesized their analogue catalyst using constant temperature hydrolysis method. The results also showed that when the metal oxides of ZnO and SnO$_2$ dispersed with Pd, the catalyst surface area increases. This scenario indicate that the addition of Pd is proven to show a significant difference in the metal oxide catalyst properties, since in previous study, Hou and co-researchers reported that by promoting the dispersion of the Pd nanoparticles on SnO$_2$ will provide smaller particle size and thus increasing the surface area which beneficial for catalytic activity. [16]

3.2.2 X-Ray Diffraction (XRD)

Palladium Zinc Oxide catalyst in this study was prepared by wet-impregnation and sol-gel method, respectively. The impregnated catalyst showed highly crystalline material and there is no diffraction peaks correspond to any Pd or PdO being observed (**Figure 5**). In theory, the observed Pd intense peaks should be appeared at 40, 46, 68, 82, and 87°, whereas for PdO, the diffraction peaks can be observed at 33.6, 41.7 and 54.4^o. [17, 18] The observation might due to highly disperse Pd and also due to detection limit of XRD instrument used since the Pd loading is considerably low., *i.e.* 1.0 wt%.
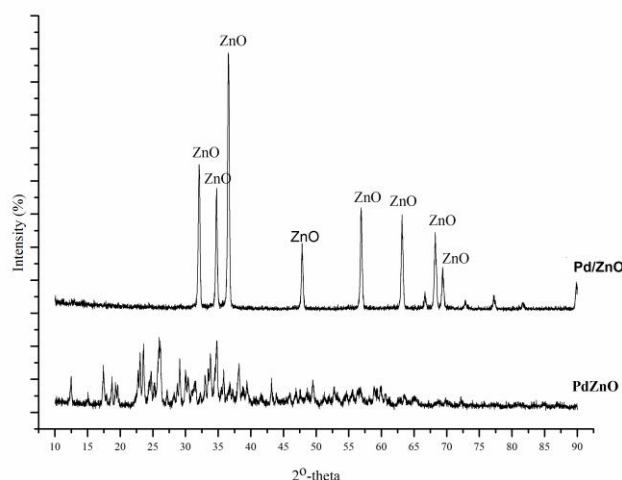
Figure 5: XRD diffractogram of Pd/ZnO (wet-impregnation) and PdZnO (sol-gel)

SnO$_2$ catalyst and PdSnO$_2$ catalysts prepared in this study are having smaller crystallite size compared to SnO$_2$ prepared by Virender et al. [9] since their catalyst has crystallite size of 18.45 nm (as calculated using Debye-Scherrer equation, [19] which is 5.61 nm larger than studied catalyst. Unavailability of Pd related diffraction peaks (**Figure 6**) were due to the similar reason stated above.
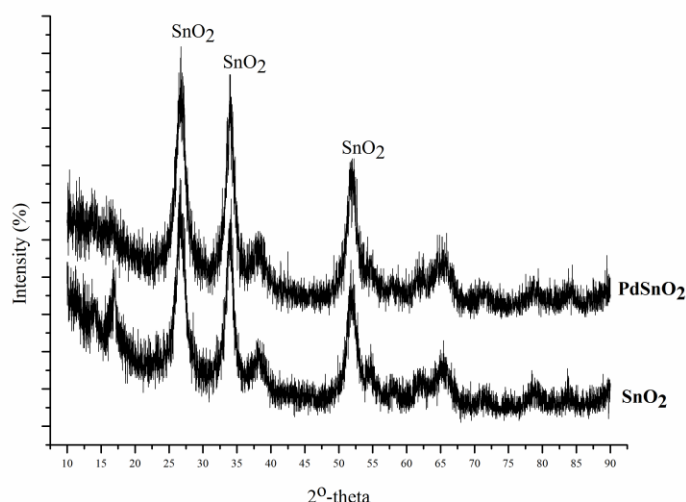
Figure 6: XRD diffractogram of SnO_2 and $PdSnO_2$

3.2.3 Scanning Electron Microscope (SEM)

There are four catalysts being characterized by using this instrument which consist of PdZnO catalyst which are prepared via wet-impregnation and sol-gel, followed by $PdSnO_2$ and SnO_2 which are prepared by sol-gel method. **Figure 7** shows SEM image of palladium zinc oxide catalyst prepared by two different methods. According to the SEM micrograph, palladium zinc oxide shows almost similar visual morphology, and suggested the surface area of both catalysts is large with Pd dispersed on ZnO. Whereas, for **Figure 8**, SnO_2 and $PdSnO_2$ have a slightly different in terms of their visual morphology since the dispersion of Palladium metal on SnO_2 catalyst contributed to larger total surface area.
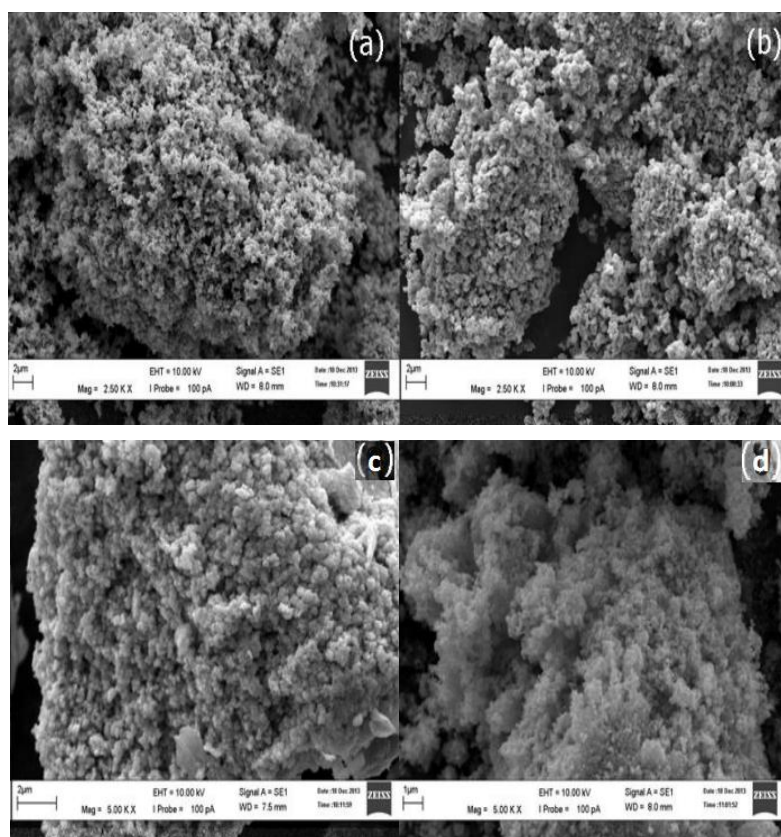

Figure 7: SEM micrograph for (a) Pd/ZnO (wet-impregnation), (b) PdZnO (sol-gel), (c) SnO_2 and (d) $PdSnO_2$

3.2.4 Fourier Transform-Infra Red (FT-IR)

The catalysts in **Figure 8** are synthesized via sol-gel method. It can be observed that the effect of addition Pd noble metal as mixed oxide composite does not affect much towards the FTIR pattern. However, different preparation technique of Palladium Zinc Oxide showed slightly difference in FT-IR spectra (**Figure 9**). According to Nasrin and Farzaneh study, the synthesis condition is found to be highly affecting the morphology of the catalyst, and thus will affect the amount of infrared radiation being absorbed and as the consequences the spectrum produce by the FT-IR analysis will bring about slightly different pattern. [20]
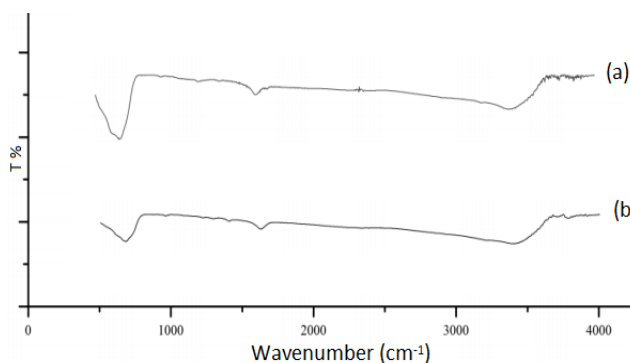
Figure 8: FTIR spectrum of (a) $PdSnO_2$ and (b)SnO_2
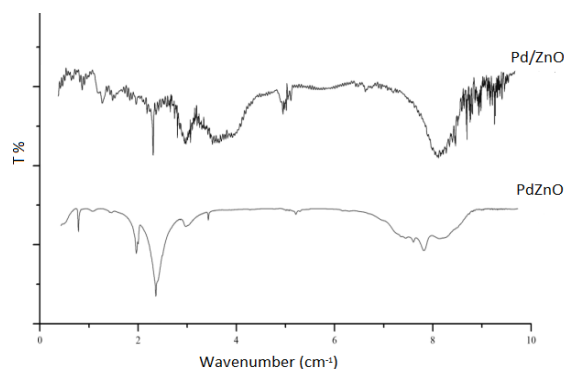
Figure 9: FTIR spectra of PdZnO (wet-impregnation) and Pd/ZnO (sol-gel)

4.   CONCLUSION

By comparing the effectiveness of catalyst prepared in this study, ZnO has showed higher yield of glycerol carbonate than SnO_2 due to the basicity property and the catalyst surface area is found to play insignificant role. It is also proven that by allowing the dispersion of low metal loading of Pd onto ZnO and SnO_2 surface, catalytic activity for both mono-metal oxides is increased. Besides, the selectivity and yield of the product catalyzed by Palladium Zinc Oxide prepared catalyst via sol-gel method is higher than the yield obtained from analogue catalyst which being prepared by wet-impregnation method.

5.   ACKNOWLEDGEMENT

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