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Application of Ceria Doped Titanium Nanomaterials for Biodiesel Production from Palm Oil

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Fast depletion of fossil fuel coupled with its environmental unfriendliness is at the top of the world's major issue, especially, in the energy industries. This study involves synthesis of catalyst for biodiesel production. Production of biodiesel was carried out with the synthesized ceria based nanomaterial. The CeO_2 - TiO_2 mixed metal oxides catalyst was synthesized by using impregnation method and characterized using FTIR, SAP, VPFESEM and Raman spectrometer. With palm oil feedstock of 0.11% free fatty acid (FFA), one-step transesterification was applied. The highest Biodiesel yield was 70.5%. This maximum yield was obtained at temperature, time, catalyst concentration and methanol oil ratio of 55°C, 150 min, 1% and 11.05:1 respectively. The reusability test showed that CeO_2 - TiO_2 can be reused up to five times at maximum yield decrease of 3%.

Keywords—Cerium Oxide; Titanium oxide; Biodiesel; transesterification

1 INTRODUCTION

Biodiesel is a renewable and biodegradable alternative fuel to diesel from petroleum. Transesterification is the most common method in biodiesel production. However, when the feedstock is treated with acid before base transesterification, FFA level in the produced biodiesel is reduced (Yusup & Khan, 2010). Fan *et al, 2013.* defined transesterification as chemical reaction involving triglycerides and alcohol, normally methanol or ethanol, in the presence of either homogeneous or heterogeneous catalyst to form esters and glycerol. In producing biodiesel, generally, homogeneous catalysts possess advantages including high activity and mild reaction. However, the use of homogeneous catalysts is associated with many drawbacks such as soap formation, catalyst consumption and expensive and difficult catalyst separation (Ramos et al, 2014). Therefore, the cost of biodiesel production using homogeneous catalysts is still not competitive compared to the cost of diesel produced from petroleum. Due to this scenario, the usage of heterogeneous catalysts gains the attention as they solve many drawbacks of traditional homogeneous catalysts. However, the efficiency of the heterogeneous process still depends on many variables such as; type of oil, molar ratio alcohol to oil, temperature and catalyst type (Romero et al, 2011).

Metal oxides are important class of materials used in many industrial processes including the conversion of fuel cells. One of them is mixed metal oxides generated by the doping of nanoparticles of an oxide on the surface of another oxide. This activity enhances the combination of structural and electronic properties to the oxide nanoparticles, also to the interfacial region between the oxide and the metal. In CeO_x/TiO_2 system, the two oxides are prototypical lanthanide (CeO_2) and transition metal (TiO_2) oxides. According to previous researches, a unique mixture of ceria morphologies on titania has a significant impact on the performance of the mixed-metal oxide in catalytic processes (Johnston-Peck et al., 2013). Titanium dioxide, the transition metal oxide has four commonly known polymorphs, which are anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic) (Gupta & Tripathi, 2011). The functional properties such as surface area, defects quantity, temperatures of phase transition, and the stability of the different phases are determined by the size and shape of the TiO_2 particles. Besides, the crystalline phase, the crystallite size and the porosity also affect the optical, textural, and catalytic properties of TiO_2. Therefore, the preparation of nanomaterials of TiO_2 nanomaterial with specific properties for several applications including biodiesel industry is of interest due to the new properties expected (Viana et al, 2010).

Cerium oxide is widely used with other metal catalysts in order to increase the catalytic activity in transesterification reactions. In 2011, Yu *et. al* used CaO-CeO_2 for transesterification of Pistacia chinensis oil. The results showed that the addition of cerium improved the stability of the solid base catalyst. That was as a result of Ce ion substitution for Ca ion on the surface of the heterogeneous catalyst. The best result was obtained with CaO-CeO_2 ratio of Ce/Ca 0.15 and calcination temperature of 700 °C (Yu et al, 2011). Manríquez et al, 2013 also used MgO-CeO_2 as solid base catalyst for converting waste cooking oil into biodiesel. At the conditions of 60 °C temperature, 4:1 methanol to oil ratio and 1 hour reaction time. Biodiesel yield was above 50%, which was better than MgO catalyst without CeO_2 deposition with only 44% yield. This shows that CeO_2 improved the catalytic ability of MgO (Manríquez-Ramírez et al., 2013). Soares et al, *2012b* used CeO_2 in the synthesis of Ce-Mg-Al catalyst for transesterification of soybean oil under reaction conditions of 9 : 1 methanol-oil ratio, 67°C temperature and 4 hours reaction time. The yield was above 90%, which is much higher than 67% biodiesel yield obtained by Wang et al, 2006 when Mg-Al hydrotalcite was used. These findings proved that CeO_2 improved the stability and catalytic ability of metal oxides catalysts used in the transesterification reactions.

Several edible and non-edible oils such as soybean, palm, rapeseed, sunflower seed, peanut, cottonseed, coconut, palm kernel, olive, jatropha, castor and rubber seed has been identified for the production of biodiesel (Fei & Teong, 2008; Shuit et al, 2010). Palm oil has been identified as the world's cheapest vegetable oil thus; it is widely used as feedstock for biodiesel production. Bo *et al, 2007* used palm oil as feedstock in producing biodiesel in the presence of KF/AL_2O_3 as base catalyst. The conditions of the reaction were temperature of 65°C, catalyst concentration of 4wt. %, methanol-oil ratio of 12:1 and reaction time of 3 hours. This reaction produced over 90% of Fatty Acid Methyl Ester (FAME)

In this study, the activity of synthesized CeO_2 doped TiO_2 was investigated by using the catalyst for production of biodiesel from palm oil. The effect of catalyst dosage and reaction time on produced biodiesel was examined. Also, the reusability of the catalyst was also investigated by carrying out several runs of biodiesel production at optimized conditions.

2 EXPERIMENTAL

The experimental procedure consists of catalyst preparation, catalyst characterization and biodiesel production

2.1 CATALYST PREPARATION

A solution of calculated amount of cerium nitrate hexahydrate, titanium dioxide and propanol was made and added into 100 ml of distilled water. The pH of the solution was adjusted to 2.5 using nitric acid (HNO_3). The mixture was stirred at 500 rpm for 3 hours, dried at 100°C for 3 hours and resultant product was calcined by heating at 300 °C for 4 hours.

2.3 BIODIESEL PRODUCTION

Fifty grams of oil was heated up to the desired temperature before calculated amount of methanol and catalyst was added. The mixture was stirred in the triple neck round bottom flask for the desired reaction time under constant speed and temperature. Water bath was used to promote the even heating. The sample was kept for 24 hours in separating funnel to allow separation.

2.4 CATALYST CHARACTERIZATION

The synthesized catalyst, CeO_2-TiO_2 was characterized using Raman Spectrometer (Model: Horiba JobinYvonHR800) to determine the phase, polymorph and molecular interaction within the catalyst. Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM, Zeiss Supra55 VP) was used to identify the surface topography, Surface Area and Pore Size Analyzer (Model: Micrometrics ASAP 2020) for determining the specific surface area and pore size while Fourier Transform Infrared Spectroscopy (Model: Perkin Almer) used to identify the functional groups of the catalyst.

3 RESULTS AND DISCUSSIONS

3.1 RAMAN SPECTROSCOPY

The Raman spectroscopy result in Fig. 1 shows results of (0.25, 0.4) wt. % loading of CeO_2-TiO_2 while the CeO_2-TiO_2(0.4)M is the modified catalyst that was prepared with propanol instead of distilled water like others. Some band resolution at 140.03 cm^{-1}, 197.87 cm^{-1}, 401.83 cm^{-1}, 465.75 cm^{-1}, 523.59 cm^{-1}, 651.45 cm^{-1} and 809.74 cm^{-1}. These characterize the anatase crystalline form of the TiO_2 and CeO_2(Liu, Guo et al. 2005).

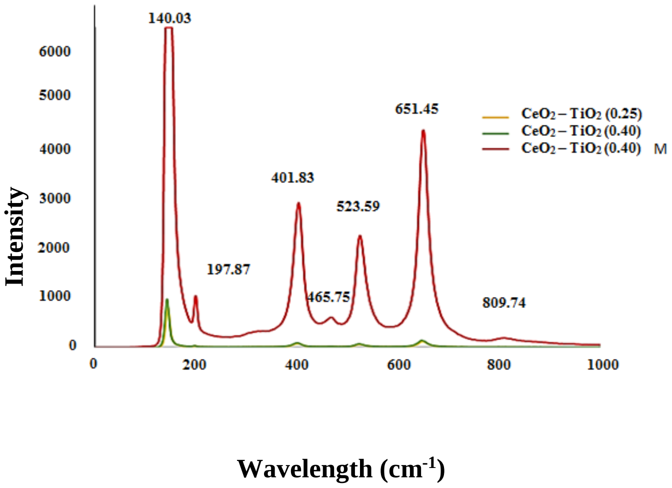

Figure 1 Raman Spectra for CeO_2-TiO_2

Titanium in anatase crystaline form has better catalytic activity than those other remaining forms. This is due to the presence of large numbers of active sites on its surface compared to others(de Almeida, Noda et al. 2008)

3.2 FTIR SPECTROSCOPY

The first part of the FTIR spectra as shown in Fig 2 indicates the bands for single bond, hydroxyl group, in this case H-O-H bond. There was no band resolution for second part of the spectra, which was supposed to indicate tripple bond moecule while the double bond part shows the band resolved for carboxylic group. The region of the spectra between 1500 cm^{-1} and 450 cm^{-1} is called fingerprint region.

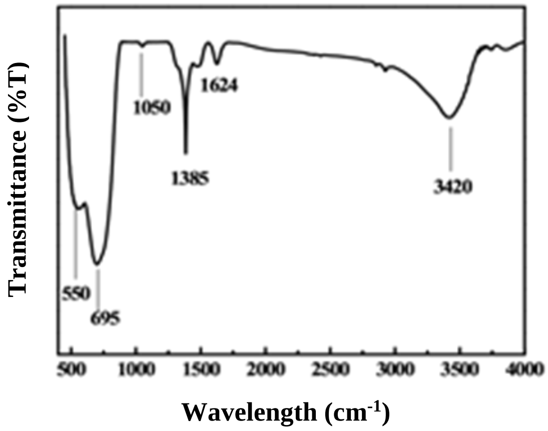

Figure 2 FTIR Spectra for CeO_2-TiO_2

3.3 SEM AND PORE DIAMETER DISTRIBUTION

The SEM image displayed in Fig 3 shows that the particle size of the catalyst are within the range of 81 and 142 nm. Though CeO_2 doped ZrO_2 was reported to have particles size of 30 nm (Yuan, Duan et al. 2009). Particle sizes of pure TiO_2 are usually smaller (10-15) nm and tend to agglomerate when dispersed in organic solvent Pan Hui et al,(2013)

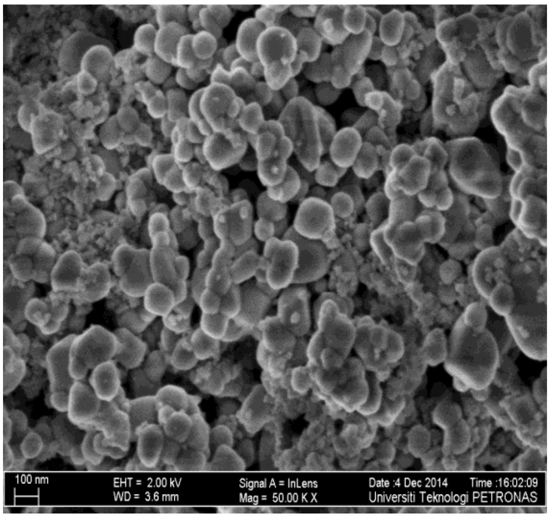

Figure 3 SEM image of CeO_2-TiO_2

Analysis of the pore diameter distribution in figure 4 indicates that the synthesized catalyst contains mesoporous sizes (2-50 nm). This contributed to the activity of the catalyst as reactions are faster when catalysts particle size are small compared to when they are big

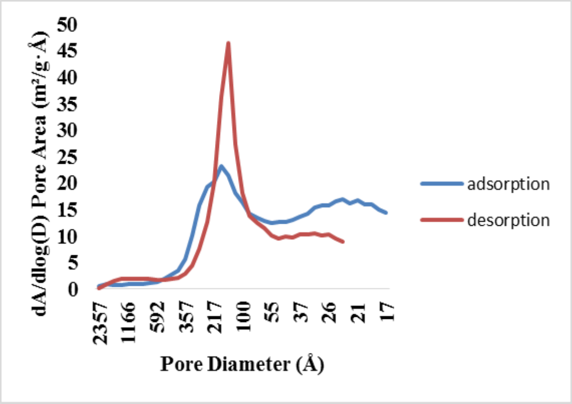

Figure **4** Pore mean diameter distribution of CeO_2-TiO_2

3.4 CATALYTIC PERFORMANCE AND REUSABILITY

In other to study catalyst dosage effect, transesterification reactions were carried out at varying catalyst weight percent, 55 °C, 11.5:1 methanol oil ratio and 1 hour reaction time. The results are shown in Fig. 5.

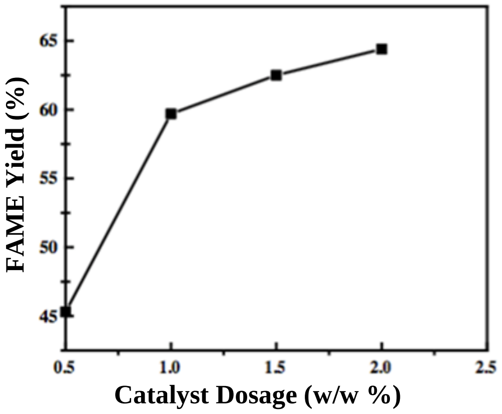

Figure 5 Effect of catalyst dosage

The yield increased rapidly from 45% to 65% when catalyst dosage was increase from 0.5% to 1%. Only 5% further increase in biodiesel yield was achieved when catalyst dosage was further increased to 2%. This was as a result of fast approach to catalyst maximum activity, thus further increase in dosage will not result in corresponding increase in yield.

Because of high activity of CeO_2-TiO_2 i.e. 60% at just 1 wt. % catalyst dosage, the reaction time effect was tested at 1 wt. %

catalyst dosage, 55 °C, and 11.05:1 methanol oil ratio. As shown in fig. 6 catalyst produced 60% yield in 1 hour. Additional increase in time up to one and half hour resulted in extra 10.5% yield.

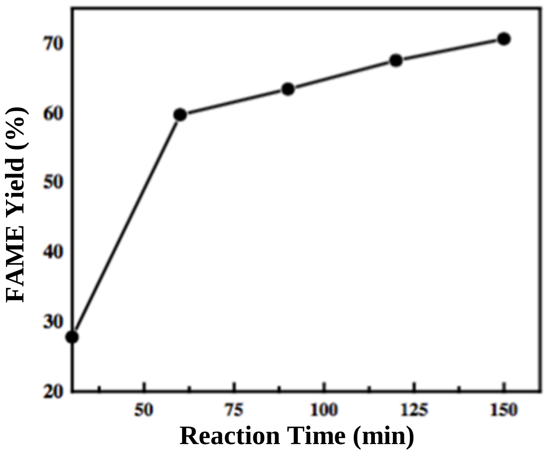

Figure 6 Effect of Reaction time

Catalyst reusability was tested at the same condition as that of the reaction time effect except that reaction time was fixed at 60 minutes. The result is summarized in Fig 7.

As shown in the chart, the achieved 56.3% yield after five experimental runs. This showed that the catalyst was both chemically and thermally stable and not easily deactivated.

Table 1 comparison of current work with other findings.

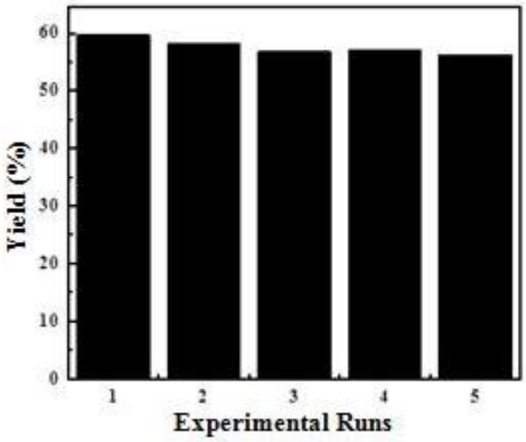

Figure 7 Catalyst Reusability

3.5 RESULT COMPARISON

The results of this research work was compared with previous works where ceria was used and presented in table 1

Author	Catalyst	Time (hour)	Temperature (°C)	Catalyst Concentration (Wt. %)	Methanol to oil ratio	Yield (%)
Current Study	CeO_2-TiO_2	2.5	55	1	11.5:1	70.5
(Manríquez-Ramírez et al., 2013)	MgO-CeO_2	1	60	4	4:1	56
(Soares Dias, Bernardo, Felizardo, & Neiva Correia, 2012a)	Ce-Mg-Al	4	67	5	9:1	95
(Yu et al., 2011)	CaO-CeO_2	6	100	9	3:1	91

4 CONCLUSION

Mixed oxide catalyst synthesized using impregnation method was successfully used for biodiesel production from palm oil. A maximum biodiesel yield of 70.5% was achieved. The addition 0.4% CeO_2 to TiO_2 leads to substitution of Ce ion for Ti ion in the lattice, hence creation of defects on the surface of the catalyst. The defects on the catalyst surface lead to improvement of the stability of the CeO_2-TiO_2 catalyst thereby resulting in improved catalytic activity. The reusability test of the catalyst showed that it can be recovered and reused for up to 5 times with only 3% decrease in yield. That is after 5 runs, the biodiesel yield decrease from 59.3% to 56.3%.

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