This study is focused on the catalytic activity of monometallic and bimetallic Al-MCM-41 supported Ce and Zr heterogeneous catalysts prepared by impregnation and co-impregnation methods, respectively. Physicochemical properties of the catalysts determined, such as N₂ adsorption isotherms and X-ray diffraction (XRD) studies show that the catalysts were mesoporous aluminosilicates with disordered hexagonal structure. The prepared catalysts were applied in simultaneous esterification and transesterification reactions of Jatropha oil for biodiesel production. The bimetallic catalyst was found to be more active than both the monometallic catalysts and the support. The bifunctional activity of the synthesized catalysts was observed at varied reaction conditions. Influence of the reaction conditions shows the highest conversion of biodiesel was obtained at methanol to oil ratio 6:1, reaction temperature 90 °C, reaction time 4 h and catalyst loading 5 wt%. The high performance of the bimetallic catalyst in the reaction process is attributed to optimum regulation of active sites by both Ce and Zr metals on the surface of the catalyst. Results from the GC-FID chromatograph shows the successful conversion of triglyceride to methyl esters.

Key Words
Bimetallic catalyst, Mesoporous Aluminosilicate, Monometallic catalyst

1. Introduction

The use of a heterogeneous catalyst in the transesterification processes limits the problems caused by using conventional catalysts, such as wastewater during purification and corrosion in engines as found in literature 1). The limited catalytic activity of mesoporous silica, MCM-41 due to lack of acidity, hydrothermal stability and mechanical strength was found to be improved with incorporation of metals, for instance, bimetallic Cu-Mn/MCM-41 catalyst used for oxidation of toluene 2) and tungsten oxide supported on Zr-MCM-41 used as a catalyst for biodiesel production 3).

Mesoporous aluminosilicate, Al-MCM-41 has been well studied and applied in various catalytic activities due to improvement in the acidity and stability of the MCM-41 4). The acidic characteristic of Al-MCM-41 may be affected by the synthesis method, the source of Al or the Si/Al ratio. Metal incorporation in the mesoporous framework as reported in previous studies 5) 6) improves catalytic activity in reaction processes. Al-MCM-41 can be used in biodiesel production as a solid catalyst or a support. The concentration of acidic sites of Al-MCM-41, as reported in studies 7) 8), provided a platform for esterification of free fatty acids (FFA) in low quality oils.

In literature 9), Pd-Al-MCM-41 acted as a bifunctional catalyst for the dimerization-hydrogenation reaction. Thus, active metals incorporation in the framework of mesoporous aluminosilicates regulates the acidity and improves the catalytic activity. In this study, research was conducted on cerium and zirconium supported on Al-MCM-41 catalysts for conversion of triglycerides to methyl esters. Monometallic and bimetallic catalysts synthesized were used in one step esterification transesterification of Jatropha oil to biodiesel.

2. Experimental

Al-MCM-41 support supplied by ACS material was activated at 500 °C for 12 h. A slurry of the support was prepared with deionized water then impregnated with
aqueous metals solutions prepared by dissolving cerium (III) nitrate hexahydrate and zirconium (IV) oxyxnitrate hydrate precursors supplied by Sigma Aldrich with deionized water. 10 wt% each of Ce and Zr metals (0.01 and 0.02 M, respectively) were separately impregnated on the support for the synthesis of monometallic catalysts, Ce/Al-MCM-41 and Zr/Al-MCM-41. For the bimetallic catalyst Ce-Zr/ Al-MCM-41, 5 wt% each of Ce and Zr metals (0.005 and 0.01 M, respectively) were co-impregnated on the support. The catalysts were stirred for 10 h on a hot plate using a magnetic stirrer at room temperature, dried at 96°C for 24 h and calcined in air at 500°C for 5 h.

Characterization of the catalysts was carried out by N₂ adsorption-desorption isotherms recorded with Surface Area Analyzer and Porosity System (Micromeritics ASAP 2020) for determination of specific surface area using Brunauer-Emmett-Teller method (BET), pore volume and pore size distribution using Barrett-Joyner-Halenda method (BJH). X-ray diffraction (XRD) spectrometry performed on X’pert Powder and Empyrean at a 2θ angle range of 1-80° using Bruker D8 Advanced Diffractometer (ICDD database interpretation). The non-edible jatropha oil was pretreated using a fine cloth and filter paper on a vacuum filter to remove solid impurities, dried and finally stored in a tightly-capped plastic bottle. The physicochemical properties of the jatropha oil were then determined by titration methods to evaluate the quality of the oil as a feedstock for transesterification reaction. Properties such as acid value, moisture content, density, viscosity, specific gravity, saponification value and flash point, were found according to the American Society for Testing and Materials (ASTM) standards.

Transesterification reaction process was conducted in a three-necked round bottom flask (250 mL) attached to a reflux system. The reaction was kept under constant stirring speed with a magnetic stirrer and a thermometer was used to monitor the temperature. The jatropha oil was dried in an oven at 65°C for 1 h. The reaction conditions were studied by varying the amount of catalysts used, the reaction temperature and the reaction time to get the possible highest biodiesel yield. The biodiesel was prepared in small batches in the presence of excess alcohol to shift the reaction forward, methanol to oil molar ratio 6:1 (in this study 8 mL of methanol to 30 mL oil was used), catalyst concentration 2.5, 3, 5, 6 and 7 wt% based on the weight of the oil, reaction temperature 65, 70, 80, 90 and 100°C and reaction time 1 to 4 h. The conversion of jatropha oil to biodiesel was calculated as according to the literature [30]. The fatty acid methyl esters (FAME) composition of the biodiesel were identified using Gas Chromatography equipped with Flame Ionization Detector (GC-FID) analysis using methyl heptadecanoate as the internal standard.

### Table 1 Textural properties of the calcined support before and after impregnation with Ce and Zr metals

| Catalyst          | Al-MCM-41 | Ce/Al-MCM-41 | Zr/Al-MCM-41 | Ce-Zr/Al-MCM-41 |
|-------------------|-----------|--------------|--------------|-----------------|
| BET surface area (m²/g) | 738       | 158          | 433          | 261             |
| Pore Diameter (nm)  | 3.5       | 4.9          | 3.8          | 4.3             |
| Pore volume (cm³/g) | 0.6       | 0.2          | 0.3          | 0.2             |

### 3. Results and Discussion

The surface area of the support decreases with impregnation of metals as shown in Table 1. The decrease in the surface area observed in all the catalysts is attributed to the incorporation of metals in the mesoporous framework. After incorporation of both cerium and zirconium, the surface area of the bimetallic catalyst was found to be higher than the monometallic catalyst with cerium, but lower than the catalyst with zirconium (Table 1). As such, Ce/Al-MCM-41 catalyst has the lowest surface area, closely followed by Ce-Zr/Al-MCM-41, Zr/ Al-MCM-41 in an increasing order. According to [11], Al-MCM-41 has three stages of isotherms, characteristics of typical mesopores; monolayer adsorption on the mesoporous wall, capillary condensation in the mesopore and multilayer adsorption on the mesoporous surface, corresponding to type IV isotherms. In comparison with the support, all the catalysts show a decrease in pore volume and an increase in pore diameter. Thus, incorporation of the active metals changes the uniform mesoporous characteristic of the catalysts (Table 1).

Fig. 1 (a) and (b) show the XRD diffractograms of the calcined support, Al-MCM-41, the monometallic catalysts, Ce/Al-MCM-41, Zr/Al-MCM-41 and the bimetallic catalyst, Ce-Zr/Al-MCM-41. In Fig. 1a both the monometallic and bimetallic catalysts prepared showed one sharp peak at 2θ = 2° the same as that of the support, indicating that the hexagonal structure of mesoporous silica although disordered, was not lost after impregnation of the metals in the framework. In contrast, significant changes in the XRD peaks were observed at 2θ angle 20-80° (Fig. 1 (b)), which may be a result of dispersion of the active metals in the amorphous. These findings are similar to the result found
in literature\textsuperscript{12}. The peaks shown in the XRD patterns of both Ce/Al-MCM-41 and Ce-Zr/Al-MCM-41 catalysts were sharp, but for Zr/Al-MCM-41 catalyst only a broad peak was observed (Fig 1 (b)). The broadness of the peak in the Zr based catalyst may be attributed to several factors such as; incorporation the larger Zr metal in the mesoporous framework, loss of crystalline character, defect sites and possible bond strain (Fig. 1 (b)).

Table 2 shows the physicochemical properties of the Jatropha oil used for transesterification reaction. These include moisture content, acid value, viscosity, density, specific gravity, saponification value and flash point determined using the American Standard Methods of Testing (ASTM).

| Property                      | Value | Unit   | Method          |
|-------------------------------|-------|--------|-----------------|
| Acid value                    | 14.3  | mg KOH/g | ASTM D974      |
| Moisture content              | 0.06  | %      | ASTM D6304     |
| Density (20°C)                | 0.91  | g/cc   | ASTM D7042     |
| Kinematic viscosity           | 0.06  | cSt    | ASTM D445      |
| Specific gravity (20°C)       | 0.92  | g/cc   | ASTM D7042     |
| Saponification value          | 131.84| mg KOH/g | ASTM D5558     |
| Flash point                   | 242   | °C     | ASTM D93       |

Transesterification reaction of jatropha oil with methanol was conducted in the presence of Al-MCM-41 as a catalyst, Ce/Al-MCM-41 and Zr/Al-MCM-41 monometallic catalysts, and Ce-Zr/Al-MCM-41 bimetallic catalyst to determine the catalytic activity in biodiesel production. Biodiesel yield is affected by reaction parameters, such as the amount of FFA present in the feedstock, water content, reaction temperature, duration of the reaction, methanol to oil molar ratio, type and catalyst concentration\textsuperscript{12}. In order to select the best catalyst to study the influence of reaction conditions, the performance of all the catalysts in the conversion of jatropha oil to biodiesel at reaction temperature of 65 °C, reaction time of 1 h, catalyst loading, 2.5 wt% and methanol to oil ratio, 6:1 were considered. Under these conditions, the highest biodiesel yield was found with the bimetallic catalyst Ce-Zr/Al-MCM-41, which was higher than the yields found using both of the monometallic catalysts and the support (See Fig. 3). Thus, the bimetallic catalyst was selected to study the effect of the reaction conditions on the biodiesel yield by varying the initial reaction temperature, reaction time and catalyst loading (Fig. 2 (a)-(c)).

In order to study the optimum reaction condition...
for biodiesel yield, two of the three reaction conditions (i.e. reaction temperature, reaction time and catalyst loading) were kept constant when the third was studied as shown in Fig. 2 (a)-(c). For the reaction temperature, the initial duration of the reaction time and catalyst loading were fixed at 1 h and 2.5 wt%, respectively. Then, the temperature was raised by 5 °C, but it was observed that the difference in biodiesel yield was not much. Subsequently, the temperature was increased by 10 °C and the yield was recorded up to 100 °C, as shown in Fig. 2 (a). An increase in the biodiesel yield was found with an increase in temperature. The highest conversion rate of the biodiesel was achieved at 90 °C. However, at 100 °C there is a decrease in the biodiesel yield (Fig. 2 (a)). Thus, the reaction temperature is an important parameter in the biodiesel conversion process.

Increase in reaction time was found to have a significant effect on the biodiesel yield. The performance of Ce-Zr/Al-MCM-41 catalyst was observed at reaction temperature 90 °C, reaction time from 1 to 4 h and catalyst loading 2.5 wt%. A gradual increase of biodiesel yield was observed and the maximum activity of the catalyst was found after 4 h reaction duration as shown in Fig. 2 (b). Thus, the use of the catalyst in the transesterification of jatropha oil to biodiesel requires longer reaction time for better methyl ester yield. In Fig. 2 (c), the activity of the bimetallic catalyst in the transesterification reaction with jatropha oil shows that with an increase in catalyst loading from 2.5 to 5 wt%, higher conversion of biodiesel yield (93%) was obtained at reaction temperature 90 °C and reaction time 4 h. Although, when the catalyst loading was above 5 wt%, a gradual decrease in the yield was observed. The optimum reaction conditions for biodiesel yield in this study was observed at 90 °C, 4 h and 5 wt% catalyst loading.

Fig. 3 shows a comparison of the results for biodiesel yield at initial (reaction temperature 65 °C, reaction time 1 h and catalyst loading 2.5 wt%) and optimum reaction conditions (reaction temperature 90 °C, reaction time 4 h and catalyst loading 5 wt%) as observed from the highest yield achieved using the bimetallic catalyst. Although, there was an increase in the performance of Al-MCM-41 and both Ce/Al-MCM-41 and Zr/Al-MCM-41 monometallic catalysts, the biodiesel yield obtained with the bimetallic catalyst, Ce-Zr/Al-MCM-41 was higher. Thus, the highest biodiesel yield was found at methanol to oil ratio 6:1, catalyst loading 5 wt%, reaction time 4 h and reaction temperature 90 °C to be 73, 80, 82 and 93% for Al-MCM-41, Ce/Al-MCM-41, Zr/Al-MCM-41, and Ce-Zr/Al-MCM-41, respectively (Fig 3). The composition of the ester content as determined by GC shows that, the biodiesel produced from jatropha oil by transesterification reaction, is composed of four main methyl esters; methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), and methyl linoleate (C18:2) as compared to other methyl esters.

4. Conclusion

In this paper, monometallic catalysts (Ce/Al-MCM-41 and Zr/Al-MCM-41) and bimetallic catalyst (Ce-Zr/Al-MCM-41) were successfully synthesized for the transesterification of jatropha oil to biodiesel. The effect of cerium and zirconium metals on the support with respect to catalytic activity shows better performance in the conversion of jatropha oil to biodiesel using the bimetallic catalyst than both the monometallic catalysts and Al-MCM-41. The experimental result shows that the Ce-Zr/Al-MCM-41 bimetallic catalyst has high performance of in the transesterification reaction and 93% biodiesel yield was obtained. Thus, incorporation of both cerium and zirconium in the framework of Al-MCM-41 has effectively improved

Fig. 3 Comparison of biodiesel yield at initial (65 °C, 1 h, 2.5 wt%) and optimum (90 °C, 4 h, 5 wt%) reaction conditions using Al-MCM-41, Ce/Al-MCM-41, Zr/AlMCM-41 and Ce-Zr/Al-MCM-41 catalysts
the catalytic activity in biodiesel production.

Acknowledgment

The authors acknowledge financial support from Yayasan Universiti Teknologi PETRONAS (YUTP).

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