Preparation and Characterization of Ce-Zr/Al-MCM-41 Bimetallic Catalyst for Transesterification of Jatropha Oil to Biodiesel

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Abstract. A series of bimetallic Ce-Zr heterogeneous catalysts supported on Al-MCM-41 aluminosilicate with cerium and zirconium loading ranging from 2.5 to 7.5 wt%, were prepared by co-impregnation method. The characterization of the catalysts obtained by various analytical methods; XRD, N\textsubscript{2} adsorption-desorption, FESEM, EDX and TPD NH\textsubscript{3}. The result shows that metals were well incorporated in the framework of the support, catalysts retained the mesoporous character and stability of structure after impregnation. The catalysts were active in one step transesterification of non-edible jatropha oil to produce fatty acid methyl esters (FAME) with methanol to oil ratio 6:1 at 90\textdegree}C, after 4 h reaction time. The FAME yield was found to have the maximum activity, higher than 80% with catalyst 5 wt% Ce and 5 wt% Zr loadings supported by Al-MCM-41 with catalyst loading 5 wt%. The catalyst was recovered by simple filtration.

1. Introduction
Recently, increasing attention has been paid to mesoporous molecular sieves having ordered hexagonal arrangements, high specific surface areas, and uniform pore diameters [1]. Modification of mesoporous aluminosilicates gives rise to a platform for wider application possibilities in industry and catalysis. The structurally stable mesoporous material, Al-MCM-41 has both hydrothermal stability and acidity properties unlike the parent material, MCM-41 [2].

According to Avhad and Marchetti [3], an ideal catalyst should have superior activity and selectivity, be abundant, less expensive, durable, reusable, and be easy to separate. Although Al-MCM-41 have the requirements necessary for solid catalysts, the activity in alkyl ester conversion was found to be low and this weak performance was related to the acidity of the catalyst [4]. Active metals are incorporated into the framework of Al-MCM-41 as a support, in order to regulate the acidity. Moreover, catalyst efficiency depends on factors such as surface area, pore size and activity sites [5].

Distribution of acid strength on the surface of molecular sieves is regulated to improve their activity, selectivity as well as the stability in biodiesel formation reaction processes. Ceria-zirconia-alumina samples synthesized by sol-gel process exhibited an increase in thermal instability at high temperature and high concentration of the ceria which was regulated with an increase in zirconia concentration [6]. According to the study conducted by Neto and Schmal [7] on iso-synthesis reaction with ceria and ceria-zirconia solid catalysts, strong basic sites and high selectivity was presented by ceria-zirconia as compared to ceria only.
2. Experimental

2.1. Materials and Methods
The chemicals used for the synthesis of bimetallic heterogeneous catalysts, Ce-Zr/Al-MCM-41 were aluminosilicate, Al-MCM-41 supplied by ACS Material, the metal precursors cerium nitrate hexahydrate, Ce(NO$_3$)$_3$.6H$_2$O and zirconium oxynitrate hydrate Zr(NO$_3$)$_2$.xH$_2$O were supplied by Sigma Aldrich. All chemicals were of analytical grade and used without further purification. The Jatropha oil used for the purpose of this study was purchased from BIONAS\textsuperscript{®}.

Al-MCM-41 support (Si/Al= 25) was activated in air at 500°C for 12 h. The bimetallic catalysts were prepared with 10 wt% of Ce and Zr metals by co-impregnation method. The catalysts were prepared by varying the weight percent of the active metals, 7.5 wt% Ce-2.5 wt% Zr (CZA7.5), 5.0 wt% Ce-5.0 wt% Zr (CZA5.0) and 2.5 wt% Ce-7.5 wt% Zr (CZA2.5) on the calcined support. Firstly, aqueous solutions containing Ce and Zr precursors were dissolved separately before they were added to the support and stirred for 10 h, then dried at 96°C for 24 h, followed by calcination in air at 500°C for 5 h.

2.2. Characterization Technique
Catalysts were characterized by X-ray diffraction (XRD) spectrometry using X’pert\textsuperscript{3} Powder and Empyrean, the scanning was performed in the $2\theta = 1 - 10^\circ$ scale with 0.01° step size. Surface area of the samples by N$_2$ adsorption-desorption isotherms at 77 K were recorded with Surface Area Analyser and Porosity System (Micromeritics ASAP 2020) N$_2$-adsorber, Field Emission Scanning Electron Microscopy (FESEM) was acquired on ZEISS 55 Supra VP microscope equipped with Energy Dispersive X-ray (EDX), as well as studies on acidity by TPD NH$_3$ (Thermo Fisher Scientific, TPDRO 1100).

The catalysts were directly applied in transesterification reaction of the Jatropha oil with high free fatty acid content (FFA %) for the initial study on the catalytic activity, without pre-treatment (esterification reaction). The feedstock was first analyzed to determine properties such as acid value, moisture content, density, viscosity, specific gravity, saponification value and flash point. Moisture content was removed from the oil at 65°C for 1 h, prior to the transesterification reaction. A lab-scale transesterification of jatropha oil was carried out in a three neck round bottom flask attached to a reflux system at temperature 90°C, reaction time 4 h, catalyst loading of 5 wt% (to the weight of oil) and methanol to oil molar ratio 6: 1.

3. Result And Discussion

3.1. Catalyst Characterization
Figure 1 shows the XRD diffractograms for the bimetallic catalysts and the calcined support. As shown in figure 1(a), the calcined support, Al-MCM-41 shows a broad peak at $2\theta = 2^\circ$ followed by two more peaks at $3$ and $4^\circ$ at lower intensities. However, the subsequent peaks disappear with impregnation of active metals, which shows that the metals are successfully incorporated in the framework of the support and possess disordered hexagonal structure. The prominent peak found in all the catalysts is characteristic peak of the MCM-41 [10]. Decrease in intensity with decrease in the surface area of the support which was found from 753 $\pm$ 2.01$m^2$/g (see Table 1), may be related to loss of crystalline structure. Moreover, owing to the decomposition of the nitrates during calcination
process, no peaks were found corresponding to the cerium and zirconium precursors, Ce(NO$_3$)$_3$.6H$_2$O and Zr(NO$_3$)$_2$.xH$_2$O.

![Figure 1. XRD patterns of 7.5Ce-2.5Zr/Al-MCM-41 (CZA7.5), 5.0Ce-5.0Zr/Al-MCM-41 (CZA5.0) and 2.5Ce-7.5Zr/Al-MCM-41 (CZA2.5) catalysts in comparison with the calcined support Al-MCM-41.](image)

The N$_2$ adsorption–desorption isotherms for the calcined support and the synthesized catalysts are shown in Figure 2(a). It can be seen that all the samples exhibited type IV adsorption isotherms, with hysteresis loops typical of uniform mesoporous silicate materials, more prominent with a sharp inflection for Al-MCM-41 [11]. Figure 2(b) shows the pore distribution of the prepared catalysts. The pore distribution is within the mesoporous range, but a forward shift is seen from the calcined support showing a decrease in both the pore volume and diameter as the active metals are deposited on the surface of the support.

![Figure 2. (a) N$_2$ adsorption-desorption isotherms and (b) pore distribution of Al-MCM-41, 7.5Ce-2.5Zr/Al-MCM-41 (CZA7.5), 5.0Ce-5.0Zr/Al-MCM-41 (CZA5.0) and 2.5Ce-7.5Zr/Al-MCM-41 (CZA2.5) catalysts.](image)

Table 1 shows the textural properties of the Al-MCM-41 based catalysts. It can be seen that the surface area of the calcined support decreases with incorporation of the active metals. The surface area significantly reduced when the amount of Ce incorporated is higher as compared to Zr. The same trend
is observed for the average pore volume, and pore diameter where Ce is higher than and equal to the amount of Zr loading on the support (Table 1).

**Table 1. Textural parameters of the calcined support, Al-MCM-41 before and after co-impregnation with Ce and Zr**

| Catalyst     | \(d_{(100)}\) (nm) | \(a_0\) (nm) | \(t\) (nm) | Surface area (m²/g) | Pore diameter (nm) | Pore volume (cm³/g) |
|--------------|---------------------|--------------|------------|---------------------|--------------------|---------------------|
| Al-MCM-41    | 4.17                | 4.82         | 0.65       | 753                 | 3.50               | 0.60                |
| CZA7.5       | 4.17                | 4.80         | 0.64       | 206                 | 4.40               | 0.30                |
| CZA5.0       | 4.19                | 4.84         | 0.65       | 261                 | 4.30               | 0.30                |
| CZA2.5       | 4.17                | 4.82         | 0.65       | 307                 | 4.10               | 0.40                |

*Unit cell parameter = \(2d_{(100)}/\sqrt{3}\)

# Wall thickness = \((2d_{(100)}/\sqrt{3} – d_{(100)})\)

An increase in cell parameter is attributed to the incorporation of larger metals in the mesoporous network [12]. The cell parameter increases in all the catalysts as compared with the support, except for CZA2.5 which is similar to the calcined support and CZA7.5, where the size was found to have decreased (Table 1). The wall thickness as shown in table 1, the prepared catalysts have the same thickness as the support except for CZA7.5, which is also very identical to the support. The thicker the cell wall the better the acidity and stability of the catalysts [12].

FESEM micrographs of the calcined support, Al-MCM-41 was studied and presented in Figure 3 (a), with a well-defined hexagonal arrangement and a fairly uniform pore structure similar to literature [13]. However, after impregnation, the levelled structure faced some changes. The presence of the observed agglomerated particles in all the synthesized catalyst was an indication of the incorporation of cerium and zirconium metals showing reconstructed morphologies, agglomerated with no definitive shape but more close to spheroidal (Figure 3 b - d).

From the micrographs, it is observed that increase in loading of ceria and zirconia particles on the support increases the agglomeration. However, ceria (up to 4 wt % on MCM-41) loading was uniform according to literature [14]. Nevertheless, when the ratio of ceria and zirconia incorporation is 1:1, the micrographs was found to be compacted and more uniformly spread (Figure 3 c). The active metals impregnation on the support was successful as confirmed from the EDX result attached to the micrographs of the catalysts in comparison with the support, Al-MCM-41 (Figure 3 a – d).

![Figure 3. FESEM micrographs and EDX of (a) Al-MCM-41, (b) 7.5Ce-2.5Zr/Al-MCM-41 (CZA7.5), (c)5.0Ce-5.0Zr/Al-MCM-41 (CZA5.0) and (d) 2.5Ce-7.5Zr/Al-MCM-41 (CZA2.5) catalysts.]
According to the TPD NH\textsubscript{3} profiles of the samples (Figure 4), sharp peaks at low temperatures (between 100- 200 °C) were detected corresponding to weak acids. Desorption peaks of the catalysts, decreases with increase in Ce-Zr incorporation, as such the highest peak was found to be that of the support. Studies on the acidity of the support reported that modified MCM-41 have two peaks, a sharp peak at low temperature and a weak peak at high temperature assigned to weak acids (NH\textsubscript{3} coordination with weak acid sites) and strong acids, respectively [15].

3.2. Catalytic Performance

The bimetallic catalysts were directly applied in one-step transesterification reaction process using jatropha oil and methanol to produce biodiesel. After the reaction catalyst was separated by filtration, biodiesel was washed with hot distilled water and dried with Na\textsubscript{2}SO\textsubscript{4}. The conversion rate of biodiesel was found to be highest for catalyst CZA5.0 at reaction temperature 90°C, reaction time 4 h, molar ratio 6: 1 and catalyst loading 5 wt% (Figure 4). The arrangement in terms of catalytic activity in decreasing order is 5.0Ce-5.0Zr/Al-MCM-41, 2.5Ce-7.5Zr/Al-MCM-41, 7.5Ce-2.5Zr/Al-MCM-41 and Al-MCM-41 with the least activity.

![Figure 4. TPD-NH\textsubscript{3} profiles of Al-MCM-41, 7.5Ce-2.5Zr/Al-MCM-41 (CZA7.5), 5.0Ce-5.0Zr/Al-MCM-41 (CZA5.0) and 2.5Ce-7.5Zr/Al-MCM-41 (CZA2.5) bimetallic catalysts.]

![Figure 5. Biodiesel conversion rate (%) using Al-MCM-41, 7.5Ce-2.5Zr/Al-MCM-41 (CZA7.5), 5.0Ce-5.0Zr/Al-MCM-41 (CZA5.0) and 2.5Ce-7.5Zr/Al-MCM-41 (CZA2.5) catalysts.]
4. Conclusion
In this study the bimetallic ceria-zirconia heterogeneous catalyst supported on mesoporous aluminosilicate, Al-MCM-41 support was successfully prepared by co-impregnation method. The active metals were successfully deposited on the surface of the support as confirmed by various characterization techniques. It was found out that the catalysts maintained the main characteristic peak of the parent hexagonal structured MCM-41 with a slight disorder as the amount of the ceria-zirconia increases. As compared with the calcined support, the catalysts showed decrease in surface area, in the same manner. The activity of the calcined support was enhanced by the impregnated active metals, 93% biodiesel yield was found for catalyst with the same amount of metals loaded 5.0Ce-5.0Zr/Al-MCM-41.

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