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Influence of preparation methods on physicochemical properties of zirconia for transesterification of *Nannochloropsis oculata* microalga’s oil

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Abstract. In this study, zirconia was successfully synthesized using precipitation, sol-gel and hydrothermal methods. The effect of different preparation methods on the physicochemical properties of zirconia were studied using FTIR, surface area and pore analyzer, XRD, FESEM, NH₃-TPD and CO₂-TPD. The performance of synthesized zirconia as heterogeneous catalyst to convert *Nannochloropsis oculata* (*N. oculata*) oil to biodiesel was also investigated. FTIR results confirmed that the selected calcination temperature is suitable for complete decomposition of organic components and the formation of zirconia phase. It was found that zirconia synthesized using precipitation method shows the highest surface area. However, zirconia synthesized by sol-gel method shows the highest composition of tetragonal crystallite structure. All the samples possess both the acid and basic sites with different strength. The highest lipid conversion (67.86 %) is obtained using zirconia synthesized using sol-gel method.

1. Introduction

Biodiesel from microalgae present an exciting opportunity and offer many advantages as feedstock over edible oil such as high growth rates, non-food resource and can use salt and waste water streams for the cultivation. Furthermore, microalgae production is not seasonal and does not compete with arable land. Many microalgae are exceedingly rich in oil which can be converted to biodiesel. In particular, species like *Chorella*, *Nannochloropsis*, *Dunaliella* and *Botryococcus* have been reported in the literature as they can accumulate important lipid amounts [1].

The common procedures of biodiesel preparation from microalgae usually used homogeneous catalysts such as KOH, NaOH, H₂SO₄ or HCl to enhance the reaction conversion. However, the application of homogeneous catalysts resulted in complexity of products purification and environmental issues. Therefore, heterogeneous catalysts are gaining interest for conversion of oils to biodiesel due to ease in separation of the biodiesel from reaction mixture and reusability of the catalyst.

Among various heterogeneous catalysts, zirconia is very interesting candidate due to its high thermal stability, resistance to thermal shock, good chemical stability and biocompatibility which has diverse applications in fuel-cell technology, catalysis and nanocomposite materials [2]. Furthermore,
Zirconia exhibits amphoteric nature by having acid and basic properties on the surface of the catalyst [2]. A major advantage of the base properties is the mild reaction conditions with fast conversion, while acid properties is necessary to reduce the high free fatty acids content of feedstock such that found in microalgae oil. Moreover, it allows the biodiesel process to be carried out using one-step process [3].

Preparation of zirconia for heterogeneous catalysis can be carried out through numerous routes, for example by microwave plasma, sol-gel, precipitation, hydrothermal synthesis and polyol synthesis [4]. Different synthesis methods and treatment of zirconia may give different physical and chemical properties of the catalysts. The objective of this paper is to determine incisive relationships between the physicochemical properties of the synthesized zirconia and their performance in transesterification of N. oculata oil to biodiesel. In this work, three preparation methods were used for synthesis of zirconia; precipitation ZrO$_2$ (P), sol-gel ZrO$_2$ (S) and hydrothermal ZrO$_2$ (H).

2. Materials and methods

2.1. Catalyst synthesis

In precipitation method, 8.1 g of zirconyl nitrate pentahydrate (ZrO(NO$_3$)$_2$.5H$_2$O, Sigma Aldrich) was dissolved in 30 mL distilled water. While the solution was stirred, ammonium solution 25% was added dropwise until pH 8 is attained with a white precipitate was produced. This precipitate was washed several times with distilled water, dried at 120 °C and calcined at 500 °C for 4 h [5].

In sol-gel method, 8.1 g ZrO(NO$_3$)$_2$.5H$_2$O was dissolved in 30 mL distilled water and 120 mL absolute ethanol was added. While the solution was stirred, ammonium solution 25% was added dropwise until pH 8 is attained. The new solution was stirred continuously in water bath at 80 °C for 2 h until gelling. The sample was washed several times with distilled water, dried at 120 °C and calcined at 500 °C for 4 h [5].

In hydrothermal method, 8.1 g ZrO(NO$_3$)$_2$.5H$_2$O was dissolved in 30 mL distilled water and 120 mL absolute ethanol was added. While the solution was stirred, ammonium solution 25% was added dropwise until pH 8 is attained. The new solution was stirred continuously until gelling. After that, the sample was transferred into hydrothermal vessel. The vessel was sealed and heated at 120 °C for 24 h. The resulting gel was washed several times with distilled water, dried at 120 °C and calcined at 500 °C for 4 h.

2.2. Catalyst characterization

2.2.1 Functional group

The functional groups of zirconia were determined using Fourier Transform Infrared spectrophotometer (Thermo Scientific, iS50 FT-IR).

2.2.2 Surface area and porosity

The surface area and porosity of zirconia were determined using surface area analyzer and porosimetry system model ASAP 2020 (Micromeritics).

2.2.3 Crystallite structure

Crystallite structures of zirconia were investigated by using X-ray diffractions (XRD) on Bruker AXS D8 Advance Diffractometer with Mn filtered Cu-Kα radiations. Most patterns covered the 2θ angle range of 10-80°. The XRD patterns were compared with the diffraction files (ICDD-FDP database) for identification.

2.2.4 Morphology
The morphology of zirconia were investigated by Field Emission Scanning Electron Microscope (FESEM) with ultra-high-resolution imaging (Carl Zeiss AG, SUPRA 55VP).

2.2.5 Acid-base properties
The acid and basic strength of zirconia was measured by using ammonia (NH\textsubscript{3}-TPD) and carbon dioxide (CO\textsubscript{2}-TPD) temperature-programmed desorption (Thermo Scientific TPDRO 1100).

2.3. Catalyst testing
The synthesized zirconia was used for conversion of N. oculata lipids to biodiesel. The transesterification process was performed in a water bath shaker using 3:1 methanol to lipid mass ratio, 10 wt % catalysts loading and 4 h reaction time at 65 °C. After the transesterification process, the mixture was filtered to remove catalyst and any solid particles. Biodiesel was obtained by evaporation to remove the excess solvent. The fatty acid (FAME) compositions were determined by a Shimadzu GC-2010 gas chromatography with flame ionization detector (GC-FID) fitted with BPX-20 column. Helium was used as carrier gas at a flow rate of 1.73 mL/min and pressure of 83.9 kPa. The initial column temperature was set at 150 °C and later increased to 240 °C at the rate of 5 °C/min while both the injector and FID temperatures were set at 250 °C. The injection volume was 1 µL with a split ratio of 10:1. Methyl heptadecanoate (C17:0) was used as an internal standard to quantify the individual FAME content. The conversion to biodiesel is defined as:

\[
\text{Conversion (wt. %)} = \frac{\text{[amount of biodiesel (g) produced]}}{\text{[initial amount of microalga lipid (g)]}} \times 100\%
\]

3. Results and discussions

3.1 Functional group
Figure 1 shows the functional groups of the prepared zirconia catalysts after drying and calcined. After drying, all the three samples show multiple peaks between 1200 and 1600 cm\textsuperscript{-1} due to the water vapour and nitrate contents. However, after calcined all the samples show peaks only between 400 and 800 cm\textsuperscript{-1} due to the formation of metal oxide network (Zr-O-Zr) and indicated the complete decomposition of the volatile components upon calcination at 500 °C.

![Figure 1](image)

**Figure 1.** Infrared spectra of synthesized zirconia after drying and calcined.

3.2 Surface area
The effect of preparation methods on the surface area of zirconia is shown in Table 1. From the results, ZrO\textsubscript{2} (P) give the highest BET surface area (47 m\textsuperscript{2}/g) followed by ZrO\textsubscript{2} (H) (37 m\textsuperscript{2}/g); while ZrO\textsubscript{2} (S) has the lowest BET surface area (13 m\textsuperscript{2}/g). Tyagi et al. [5] also reported that precipitation
method resulted in materials with higher surface area than sol-gel. In order to explain this condition, we propose that the hydrous condition of precipitation sample increases the separation of zirconium-zirconium particles compare to jelly-like structure of sol-gel sample. The bigger the distance between zirconium-zirconium particles is believed to increase the surface area as well as the pore size. Under hydrothermal conditions, a hydrostatic pressure is generated in which subsequently increase the surface area of resulting zirconia than by sol-gel. Average pore size of $\text{ZrO}_2$ (P), $\text{ZrO}_2$ (S) and $\text{ZrO}_2$ (H) samples are 9.8, 6.4 and 5.6 nm respectively in which can be categorized as mesoporous zirconia structure.

| Preparation Method | BET Surface Area $(\text{m}^2/\text{g})$ | Pore Volume $(\text{cm}^3/\text{g})$ | Pore Size $(\text{nm})$ |
|--------------------|-----------------------------------------|-------------------------------------|------------------------|
| $\text{ZrO}_2$ (P) | 47                                      | 0.125                               | 9.8                    |
| $\text{ZrO}_2$ (S) | 13                                      | 0.022                               | 6.4                    |
| $\text{ZrO}_2$ (H) | 37                                      | 0.055                               | 5.6                    |

### 3.3 Crystalline structure

The XRD patterns of prepared zirconia are comparatively shown in Figure 2. The sharp peaks obtained indicate that the crystallinity of the synthesized zirconia. All the prepared samples show the presence of monoclinic and tetragonal phases. The peaks attributed to monoclinic phase of nano-crystalline zirconia are observed at peaks $2\theta = 28^\circ$, $31^\circ$ and $41^\circ$ while the tetragonal phase are observed at $2\theta = 30^\circ$, $35^\circ$, $50^\circ$, $60^\circ$ and $63^\circ$ [6]. From the XRD patterns, $\text{ZrO}_2$ (S) resulted in the highest tetragonal peak at $2\theta = 30^\circ$ followed by $\text{ZrO}_2$ (H) and $\text{ZrO}_2$ (P). Zirconia with high tetragonal surface structure is reported to be catalytically active for many reactions compared to monoclinic phase [7-9]. In addition, Chuah et al. [10] have reported that aging process at 80 °C or higher temperature greatly influence the structure of the resulting zirconia. In aging process, more dehydrated oxo-hydroxide precursor was formed and this substance gives rise to the tetragonal phase upon calcination; while more hydrated precursor leads to monoclinic phase as in the precipitation technique [10].

![XRD patterns of synthesized zirconia](image)

**Figure 2.** XRD patterns of synthesized zirconia.

### 3.4 Morphology

From the FESEM micrographs (Figure 3), it can be clearly seen that $\text{ZrO}_2$ (P) consists of more highly aggregated particles than $\text{ZrO}_2$ (S) and $\text{ZrO}_2$ (H). The large aggregation of the particles is due to the inhomogeneous phases in which associated with the presence of more water molecules during precipitation procedure [5]. In $\text{ZrO}_2$ (S) and $\text{ZrO}_2$ (H) samples, hydroxyl ions from water and ethanol are homogeneously distributed in the whole sample resulted in the uniform distribution of zirconia.
particles. The formation of spherical-like pores is clearly observed in ZrO$_2$ (S), while close packed grain arrangement with the smallest pore diameter is observed in ZrO$_2$ (H).

**Figure 3.** FESEM micrographs (at 50 kx magnification) of synthesized zirconia a) ZrO$_2$ (P), b) ZrO$_2$ (S) and c) ZrO$_2$ (H).

### 3.5 Acidity and basicity

NH$_3$-TPD and CO$_2$-TPD were performed to study the distribution of acid sites and basic sites on the surface of prepared catalysts. The patterns and the density of acid and basic sites for synthesized zirconia are illustrated in Figure 4 and Table 2. The strength of the acid and basic sites are represented by the desorption temperature, where desorption peak at 100–250 °C can be attributed as weak, 250–500 °C as moderate and over than 500 °C as strong acid and basic sites. The NH$_3$-TPD results indicate the existence of only medium strength of acid sites for all synthesized zirconia. The total density of acid sites can be arranged in decreasing order as ZrO$_2$ (P) > ZrO$_2$ (H) > ZrO$_2$ (S). From CO$_2$-TPD results, ZrO$_2$ (P) and ZrO$_2$ (S) show basic sites with weak and medium strength, whereas only a medium strength of basic site appeared in ZrO$_2$ (H) sample. The total density of basic sites can be arranged in decreasing order as ZrO$_2$ (S) > ZrO$_2$ (P) > ZrO$_2$ (H). Overall, all the synthesized zirconia shows both acid and basic sites with variable strength which indicates that they have a remarkable potential to carry out simultaneous esterification and transesterification, especially in a high free fatty acids (FFA) content feedstock [11].

**Figure 4.** NH$_3$-TPD and CO$_2$-TPD patterns of synthesized zirconia.
Table 2. Density of acid and basic sites of synthesized zirconia.

| Catalyst  | Type of acid (µmol/g) | Total acidity (µmol/g) |
|-----------|-----------------------|------------------------|
|           | Weak                  | Medium                 | Strong                 |
| ZrO₂ (P)  | Not detected          | 129.68                 | Not detected           | 129.68                  |
| ZrO₂ (S)  | Not detected          | 43.31                  | Not detected           | 43.31                   |
| ZrO₂ (H)  | Not detected          | 80.55                  | Not detected           | 80.55                   |

| Catalyst  | Type of basic (µmol/g) | Total basicity (µmol/g) |
|-----------|------------------------|-------------------------|
|           | Weak                   | Medium                  | Strong                 |
| ZrO₂ (P)  | 168.23                 | 235.72                  | Not detected           | 403.95                  |
| ZrO₂ (S)  | 320.65                 | 407.04                  | Not detected           | 727.69                  |
| ZrO₂ (H)  | Not detected           | 167.28                 | Not detected           | 167.28                  |

3.6 Transesterification of N. oculata lipid

Table 3 shows the lipid conversion and FAME compositions of biodiesel from N. oculata lipids using ZrO₂ (P), ZrO₂ (S) and ZrO₂ (H) at the pre-determined reaction parameters. ZrO₂ (S) shows the highest lipid conversion of 67.86% followed by ZrO₂ (H) with 55.74% and ZrO₂ (P) with 49.57%. The trend in N. oculata lipid conversion is in-line with the trend in the intensity of tetragonal peak from XRD analysis. The results show that the presence of tetragonal phase in zirconia catalyst is important for the conversion of N. oculata lipid to biodiesel. This finding sharply supports the work reported by Nayebzadeh et al. [7] which suggested that tetragonal phase of zirconia is more active than that of monoclinc phase.

The carbon chain length and the degree of saturation of FAME have great influence on the biodiesel properties. All the synthesized zirconia showed high percentage of saturated fatty acid indicating that the biodiesel synthesis has suitable oxidative stability and desirable cetane number [12]. According to ASTM D6751 and EN 14214 standards, FAME should contain more than 60% saturated FAME and less than 20% polyunsaturated FAME. Therefore, in this study only FAME produced in the presence of ZrO₂ (S) meets the ASTM D6751 and EN 14214 standards.

Table 3. Lipid conversion and FAME compositions of N. oculata lipids to biodiesel in the presence of synthesized zirconia.

| Percentage   | Catalysts | ZrO₂ (P) | ZrO₂ (S) | ZrO₂ (H) |
|--------------|-----------|----------|----------|----------|
| Conversion   |           | 49.57    | 67.86    | 55.74    |
| Saturated FAME |         | 59.92    | 79.65    | 72.36    |
| Monounsaturated FAME | | 8.41    | 2.30     | 6.74     |
| Polyunsaturated FAME | | 31.50 | 18.05    | 20.90    |

4. Conclusion

Different preparation methods greatly influence the physicochemical properties of the synthesized zirconia. Based on these findings, crystallite structure of zirconia shows the most significant effect on the catalytic activity of the catalyst. The highest N. oculata lipid conversion of 67.86% is observed using ZrO₂ (S) with adequate amount of FAME compositions.
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