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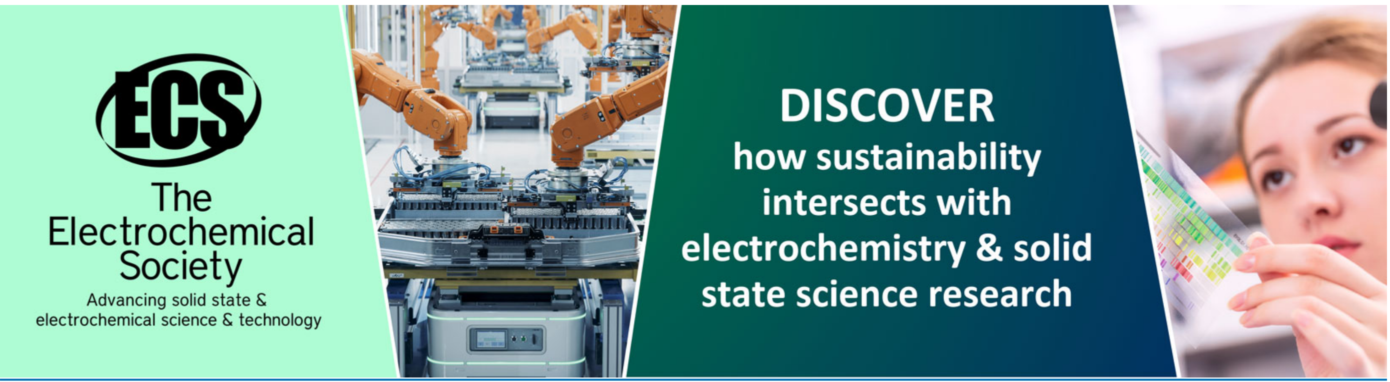

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ZrO_2/bamboo leaves ash (BLA) Catalyst in Biodiesel Conversion of Rice Bran Oil

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Abstract. Preparation, characterization and catalytic activity of ZrO_2/bamboo leaves ash (BLA) catalyst for conversion of rice bran oil to biodiesel have been investigated. The catalyst was prepared by impregnation method of $ZrOCl_2$ as ZrO_2 precursor with BLA at a theoretical content of 20% wt. followed by calcination. The physicochemical properties of the catalyst material were characterized by x-ray diffraction (XRD), FTIR and surface acidity measurement. Activity test of materials in biodiesel conversion of rice bran oil was used by reflux method and microwave (MW) assisted method. Reaction variables studied in the investigation were the effect of catalyst weight and time of MW irradiation compared with the use reflux method. The results showed that ZrO2/BLA catalyst exhibited competitively effective and efficient processes for the production of biodiesel. The reflux method demonstrated an higher conversion (%) compared to MW method, however MW method showed the better reusable properties.

1. Introduction

Alternative energy is still the focus of human need due to the limitation of fossil fuel availability. In this scheme, biodiesel is one important fuel alternative having a potency to be developed in Asian region since it is synthesized by transesterification of vegetable/animal oils which are abundantly present. The conversion reaction of vegetable/animal oil via transesterification reaction can be carried out using both acidic and basic (homogeneous or heterogeneous) catalysts and usually the NaOH or KOH homogeneous base catalyst were employed. The use of both kinds of basic solution has drawback in non-reusability as well as consumable material for production. Referring to some principles of green chemistry, the use of a heterogeneous catalyst is an important consideration. Beside the catalyst election as a concern, the use of rapid procedure including the use of microwave irradiation procedure is also widely reported. Many previous works reported the use of active metal oxide catalyst to replace homogeneous catalyst[1–3]. They consist of silica-alumina, clay, zeolite-based materials instead of a well-known metal oxide of ZrO_2. In another scheme, seeking low-cost catalyst is an interesting concern[4]. For this purpose, many investigations reported the catalytic activity of natural materials containing silica as a composite builder with a metal oxide active catalyst. The use of rice husk ash as the material of catalyst composite with ZrO_2, $KHCO_3$, and other metal demonstrated activity in biodiesel production has been reported (references??). As other alternative for low-cost catalyst in biodiesel production, in this research the use of Bamboo leaves ash for the composite builder with ZrO_2 was attempted. Bamboos plant is grown well in south-east Asia including Indonesia. It's approximately 1,000 kinds of bamboo in 80 countries, about 200 species of 20 countries found in Southeast Asia. In Indonesia, bamboo plants grow well in the lowlands to the mountains with a height of about 3,000 m above sea level and generally found in open places and their regions are free from flooding. Bamboo leave is a part of bamboo plant which is not utilized well, and from the previous report it was known that silica content in bamboo leaves was high. By this reason, this work took advantage by utilizing bamboo leave ash as a silica source for supporting zirconia catalyst for biodiesel production in the form of ZrO_2-SiO_2. Research aimed to evaluate the physicochemical character of the composite and its activity in biodiesel production. Another consideration of MW irradiation utilization was to evaluate the economical aspect of the conversion which also intensively studied[5,6].

2. Materials and Methods

2.1. Materials

The materials used in this study were bamboo leaves obtained from village plantation in Sleman, Yogyakarta Province, Indonesia. Zirconium (IV) oxide chloride ($ZrOCl_2$), tetra ethyl ortho silicate, NaOH, methanol (CH_3OH), HCl, n-hexane, (H_3PO_4) the Phenol phthalin ($C_{20}H_{14}O_4$) were purchased from Merck. For biodiesel production, the rice bran oil produced by PT. Indofood was utilized.

The equipment used for physicochemical characterization in this study consisted of a furnace, the analytic balance, mortar pestle, a porcelain, glass clock, stone melting, stat and the clamps, the mouthpiece of divorce, the erlenmeyer mouthpiece, beaker glasses, a peck, a spray bottle, magnetic stirrer. The physicochemical character of the samples was performed using FTIR (Shimadzu Type IRPrestige21), SEM-EDX (JEOL JED-2300), XRD (Shimadzu X6000).

2.2. Preparation of ZrO_2/bamboo leaves ash (ZrO_2/BLA) Catalyst.

The catalyst of ZrO_2/BLA was prepared by two main steps: Bamboo leaves ashing and ZrO_2 immobilization. First, the leaves of bamboo were washed with clean water to remove the polluter, followed by sun drying before calcined in the furnace at 500 °C for 4 hours. The ash was milled using a mortar. The aim of calcination in this step was to remove the organic content of bamboo leaves and the ash was rich in silica. The bamboo leaves ash was then mixed with the precursor of ZrO_2 by zirconium (IV) Oxide chloride. The solution was added dropwise into an ash suspension followed by stirring for 24 hours before drying in the oven. The dry solid was then calcined to obtain the catalyst. For comparison purpose, the synthesis of ZrO_2-SiO_2 was also conducted. A similar procedure with the synthesis of ZrO_2/BLA was applied however the Bamboo ash suspension was replaced by tetra ethyl ortho silicate (TEOS). The schematic procedure of the synthesis is described in Fig. 1.

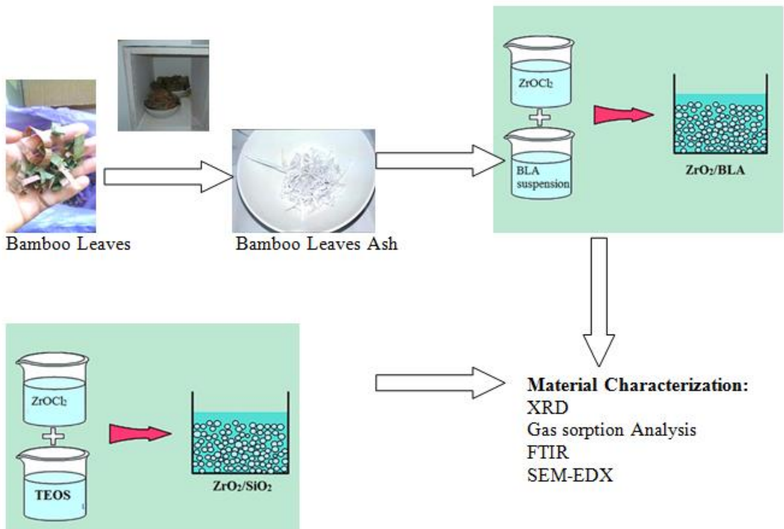

Fig. 1. Schematic representation of ZrO_2/BLA synthesis

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The material was characterized using XRD, gas sorption analyzer and SEM-EDX. A Ni-filtered Cu-Kα radiation was utilized for x-ray analysis in the 2θ of 5-40° with the ramp rate of 2°/min.

2.3 Catalytic activity testing

The catalytic activity of ZrO_2/BLA in the biodiesel conversion was tested using rice bran oil as a vegetable oil source. The biodiesel conversion was conducted by methanol to oil ratio of 1:5 under a varied time of reflux; 2, 3 and 5 hours. The conversion was also conducted using microwave irradiation method for 30 minutes. The results of each reaction were separated into the separating funnel and the biodiesel fraction was examined using GCMS analysis (using GCMS (Shimadzu Type GCMS QP2010 Plus).

3. Results & Discussion

Initial evaluation of BLA content was performed by SEM-EDX analysis and the result is presented in Fig.2. From the EDX analysis results (Table 1) it can be seen that Si presented at more than 78% and was the major component of BLA with some impurities consist of Ca, C, P, Na and Mg. Based on the result it can be concluded that BLA had potential as a support for metal oxide. This assumption was referred to the silica content of rice husk ash and bagasse ash reported by previous reports [7,8].

Table 1. Result of EDX analysis of BLA

Component	Percentage (% wt.)
SiO_2	78.98
C	5.09
MgO	4.99
Na_2O	2.80
K_2O	1.58
P_2O_5	2.77
CaO	3.08

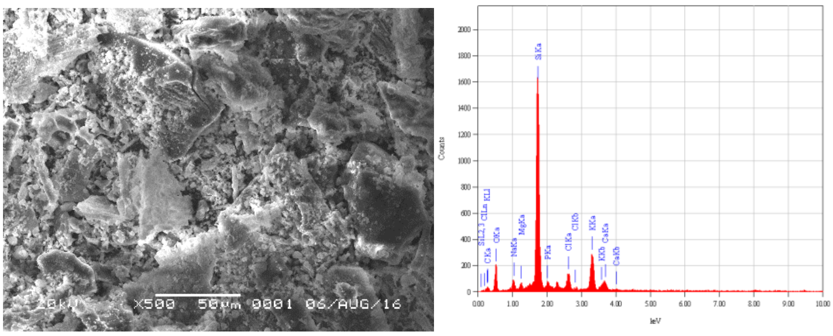

Fig.2. SEM profile and EDX analysis result of BLA

XRD pattern of the ZrO_2/BLA compared with the pattern of bamboo leaves ash (BLA) and ZrO_2/BLA in comparison with ZrO_2-SiO_2 is presented by Fig. 3. XRD pattern of ZrO_2/SiO_2 as standard showed the reflections of ZrO_2 in mixture phase of monoclinic and tetragonal phases. BLA did not reflect any crystalline phase as an indication of amorphous silica content. The BLA pattern showed the amorphous structure of silica as presented by a broad peak at around 20°. After composite formation with ZrO_2, the amorphous structure appeared as a broad peak corresponding to silica content which there was a reflection match with the peak of ZrO_2 in tetragonal phase as represented by the reflection at around 30°

[9–11]. The surface profile of ZrO_2/BLA in comparison with ZrO_2-SiO_2 is presented in Fig. 4. A rougher surface is appeared by ZrO_2/BLA representing the distribution of ZrO_2 on the surface. The profile is in line with the surface analysis of presented by adsorption-desorption profile and calculated parameters (Table 2).

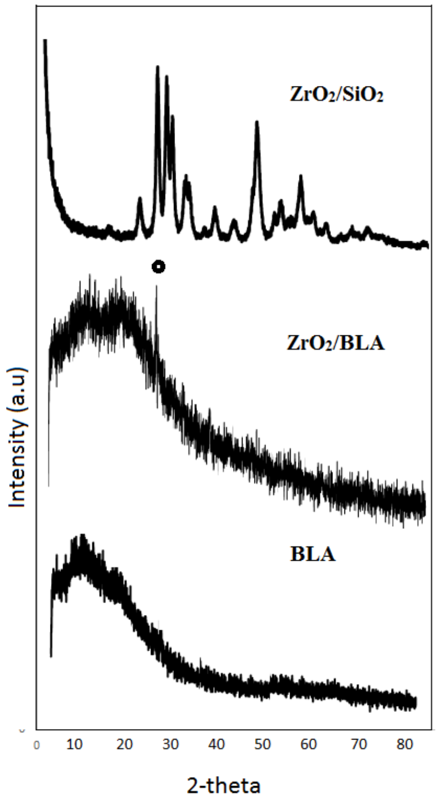

Fig. 3. XRD pattern of materials (• = *t*-ZrO_2)

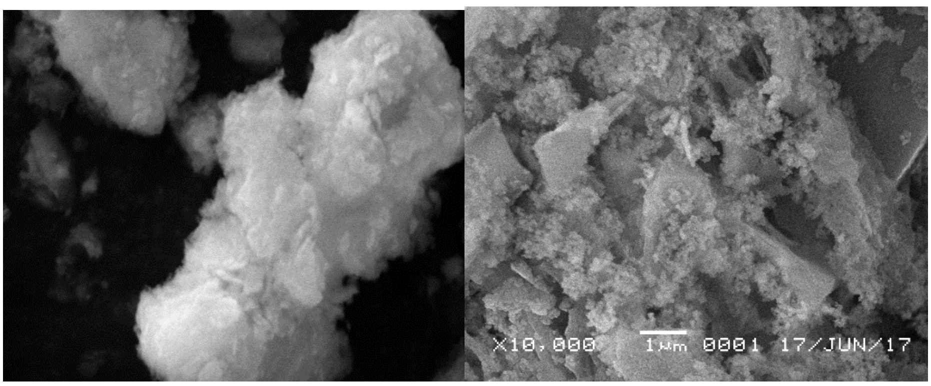

Fig. 4. SEM profile of (a) ZrO_2/SiO_2 (b) ZrO_2/BLA

Table 2. Composition of ZrO_2/SiO_2 and ZrO_2/BLA

Component	ZrO_2/SiO_2 **(% wt.)**	ZrO_2/BLA **(% wt.)**
SiO_2	58.98	38.88
ZrO_2	11.03	6.58
MgO	-	1.24
Al_2O_3	-	0.3

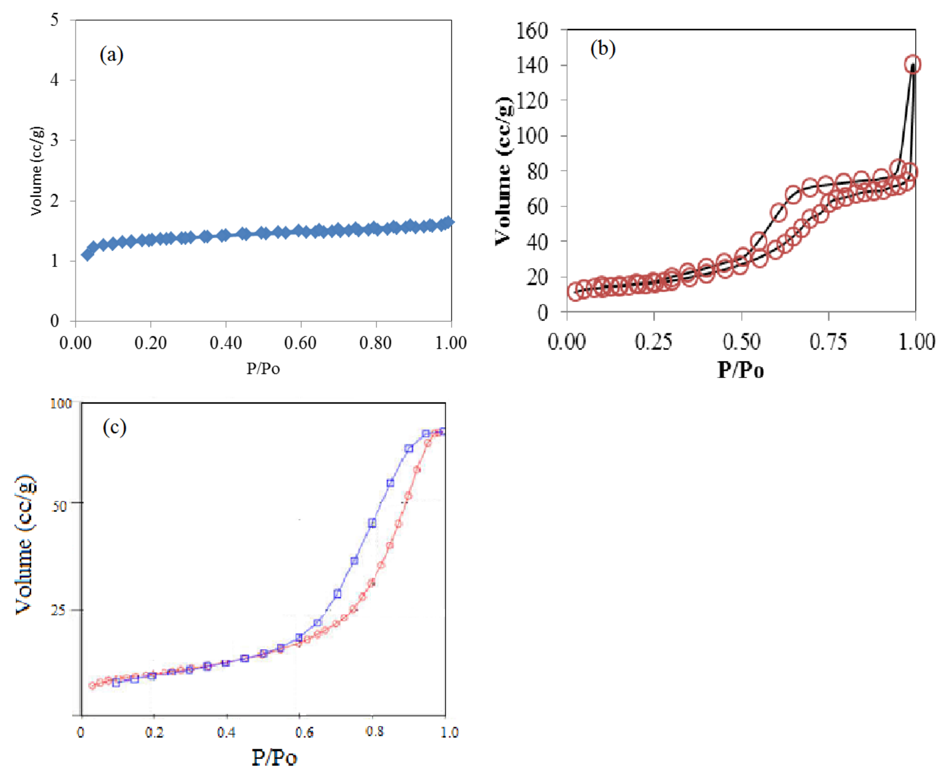

Fig. 5. Adsorption-desorption pattern of (a) BLA (b) ZrO_2/BLA (c) ZrO_2/SiO_2

The adsorption-desorption pattern of ZrO_2/BLA represented the micropore structure of material which is referred to the IUPAC type III – adsorption-desorption curve classification with hysteresis loop indicating the mesoporous formation in the structure (Fig. 5). The pattern was commonly found in the amorphous structure and silica-based materials. Different with the pattern, BLA expressed the micropore structure while ZrO_2/SiO_2 profile suggested the hysteresis loop meant the mesoporous content in the structure. The specific surface area, pore volume, and pore radius data measured based on the adsorption-desorption pattern are listed in Table 3.

Table 3. Specific surface area, pore volume and pore radius data of materials

Parameter	ZrO_2**/BLA**	**BLA**	ZrO_2/SiO_2
BET Specific surface area (m^2/g)	103.09	14.45	58.02
Pore Radius (Å)	18.45	14.05	14.34
Pore Volume (cc/g)	0.568	0.036	0.126

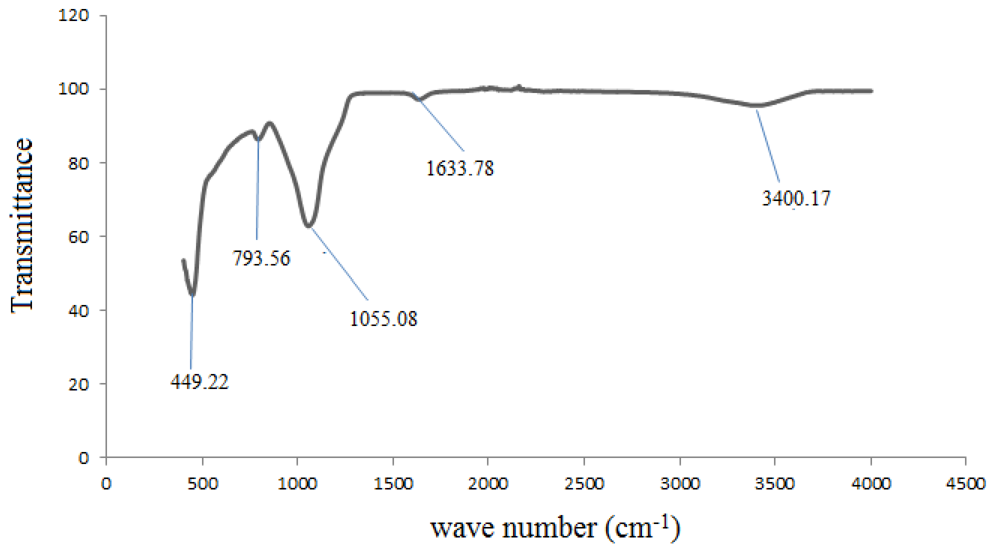

Fig. 6. FT-IR spectra of ZrO2/BLA

From spectra of FTIR analysis (Fig.6), it can be seen that Si-O-Si asymmetric stretching at 1055.08 cm^{-1} corresponding to SiO_2 is observed. The characteristic peaks of Si–OH at 793.50 cm^{-1} may be attributed to the silanol groups on the SiO_2 particles. In both spectra, the peaks which appear at about 3400,17 cm^{-1} are due to the bending vibration of OH from the water. The presence of Si-O-Zr interaction can be assigned from the spectra at 1055 cm^{-1} which are attributed to the silica network forming the Si-O-Zr band[10,12]. These reports are consistent with our findings and verified the oxygen bridge between Si and Zr. This means that there is a composite formation of ZrO_2 with SiO_2.

Catalytic activity

The catalytic activity of material was tested by biodiesel conversion. Yield and percentage of fatty acid methyl ester (FAME) content is listed in Table 4. The yield of biodiesel fraction is calculated by the following equation:

$$\%\text{Yield} = \frac{Vol.Biodiesel\ fraction}{Vol.of\ Oil}.100\% \quad (1)$$

and the percentage of fatty acid methyl ester (FAME) was measured based on GCMS data interpretation.

Table 4. Yield of biodiesel conversion

Reaction condition	Catalyst	Yield (%)	FAME(%)
Reflux-2h	ZrO_2/BLA	50.15	100
Reflux-3h	ZrO_2/BLA	100	100
Reflux-5h	ZrO_2/BLA	100	100
MW- 30 mins	ZrO_2/BLA	80.5	100
Reflux-3h	BLA	43.22	89.03
Reflux-3h	ZrO_2/SiO_2	100	100

From the data in Table 3 it is concluded that both reflux and microwave irradiation method of biodiesel conversion give 100% of FAME composition in the biodiesel fraction. Based on the variation of reaction condition it can be concluded that ZrO_2/BLA exhibits the same activity with ZrO_2/SiO_2 in 3 h reflux method. This data suggests that the activity of prepared material is comparative. By the use of MW irradiation it is also seen that shorter time of reaction may be applied to give comparative results.

4. Conclusion

The results showed that physicochemical characterization of BLA could be applied for preparing the heterogeneous catalyst of ZrO_2/BLA in biodiesel conversion application. The material exhibited the microporous in mixture with mesoporous structure and accommodating ZrO_2 in tetrahedral phase in form. The catalytic activity of material was comparable respect to the use of ZrO_2/SiO_2 in which the composite give the maximum yield over reflux for 2h and 3h as well as over MW irradiation for 30 mins.

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