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Biodiesel Production via Functionalized LECA-Tungsten Oxide (W_3O_{10} -LECA@OH) catalyst

Ensie Bekhradinassab *[1]

[1] Chemical Engineering Department, Faculty of Engineering, Behbahan Khatam Alanbia University of Technology, Behbahan, Iran.

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1. ABSTRACT

This study explores W_3O_{10}-LECA@OH as a catalyst for biodiesel production. Characterization (XRD, FESEM, FTIR, TEM, and BET-BJH) confirmed increased active surface area and effective W_3O_{10} loading. The catalyst had a 0.0256 cm³/g pore volume, 9.6 nm pore diameter, and well-dispersed W_3O_{10}. Under optimal conditions (3 wt% catalyst, 95 °C, 2 h, 20:1 methanol-to-oil ratio), it achieved 91.28% conversion.

Keywords: Biodiesel, Functionalization, LECA, W_3O_{10}-LECA@OH catalyst.

2. INTRODUCTION

One method for biodiesel production is the esterification of feedstocks based on free fatty acids, which require acid catalysts [1]. Various acid catalysts, such as Mn(0.4)-doped TiO_2 [2], ZSM-5 [3], and CaO-ZrO_2/kaolin [4], have been used in this field.

This research focuses on biodiesel production using the W_3O_{10}-LECA@OH catalyst (functionalized LECA-tungsten oxide). The developed catalyst in this study combines the porous mineral material "LECA," functionalized with OH groups, and effectively loaded with tungsten oxide. The main innovation of this research is the creation of an active and accessible surface for the proper loading of W_3O_{10} through the functionalization of LECA with OH groups, enhancing the catalyst's efficiency in the biodiesel production process. The combination of porous mineral materials and tungsten oxide as a catalyst provides advantages such as good dispersion of the active phase and an improved active surface for catalytic reactions, especially in biodiesel production. Advanced techniques such as XRD, FESEM, FTIR, TEM, and BET-BJH were utilized to evaluate the structure and characteristics of this catalyst precisely. The results of this study indicate that the W_3O_{10}-LECA@OH catalyst demonstrates excellent performance, achieving a high conversion rate of 91% under relatively low temperatures and optimal conditions in biodiesel production.

3. MATERIALS AND METHODS

3.1. Materials Used for Catalyst Synthesis and Process Tests

For catalyst synthesis, LECA obtained from the Iran LECA company was used. The LECA was first milled and then passed through a 200-mesh sieve, with the sieved material used as the support. Additionally, sodium hydroxide (Merck), ethanol (Merck), and $H_3PW_{12}O_{40}$ (Sigma-Aldrich) were used. For process tests, oleic acid (Sigma-Aldrich), methanol (Merck), ethanol (Merck), and n-hexane (Merck) were utilized.

3.2. Catalyst Synthesis Method

For the functionalization of LECA, first a 2 M sodium hydroxide solution was prepared by dissolving 8 g of sodium hydroxide in 100 ml of double-distilled water, and then LECA was added to it, and the mixture was refluxed at 80 ºC for

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* en.bekhradinassab@bkatu.ac.ir

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8 hours. Then the solution was washed using filter paper and deionized water, and the washing was continued until the solution passed through the filter paper and reached neutral pH. Then the solid was dried in a conventional oven at 110 ºC for 24 hours. This material was named LECA@OH. In the next step, $H_3PW_{12}O_{40}$ was poured into ethanol and stirred by magnetic stirring for one hour. Then LECA@OH was added as a base and the mixture was stirred again by magnetic stirring for one hour. In order to evaporate the solvent, the mixture was exposed to ambient air for 24 hours. Then the remaining solids were dried in a conventional oven at 110 ºC for 24 hours. This material was named W_3O_{10}-LECA@OH.

3.3. Method for Conducting Biodiesel Production Experiments

A catalyst loading of 3 wt% was used, with a molar ratio of methanol to oil of 20:1. The reaction was carried out at 95 °C. After 1 h, the process was stopped and the reactor was cooled. The resulting mixture was then separated into catalyst and liquid fractions. The liquid fraction was also heated to 60 °C for 0.5 h to evaporate the methanol. After this, 3 ml of double distilled water was added to the mixture and then stirred for 10 min. The mixture was centrifuged for 10 min at 4000 rpm and the whole process was repeated once more. This resulted in the formation of two separate phases: the upper phase contained biodiesel and unreacted oleic acid along with some residual methanol, while the lower phase contained water and residual methanol. The upper phase was heated again at 60 ºC to evaporate the methanol. The biodiesel yield was determined via titration method using 1M KOH to assess the conversion of free fatty acids (FFAs). The acid values of the feedstock and the produced biodiesel were evaluated according to EN 14104 standards, as detailed in equations 1 and 2. Ac_2 refers to the final acid number of the oil, while Ac_1 indicates its initial acid number.

$$\text{Acid value,}\quad mg_{KOH}/g_{oil}=\frac{(56.1056\,gKOH/mole)\times 0.1(moleKOH/L)\times V_{KOH}}{g_{oil}} \tag{1}$$

$$\text{Conversion,}\quad x\%=\frac{Ac_2\text{-}Ac_1}{Ac_1}\times 100 \tag{2}$$

3.4. Devices and methods used to determine the characteristics of the catalyst

XRD analysis, using Cu Kα X-ray radiation, was used to examine the degree of crystallinity and phase configuration in the range of 10-80 º. XRF analysis was used by an X-ray fluorescence spectrometer made by Philips, Netherlands. The pore system dimensions, such as specific surface area, pore size distribution, and pore volume of the nanomaterials, were evaluated using N_2 adsorption and desorption isotherms with Chrome Chem BET 3000 and BET-BJH approaches. Micrometrics 2910 TPD-NH_3 analysis was used to determine the amount, concentration, and strength of acidic sites.

4. RESULTS AND DISCUSSION

4.1. Analyses and characterizations of LECA and LECA@OH

4.1.1. XRF Analysis

XRF analysis was used to examine the elements present in the lichen, which is presented in Table 1. According to the results of this analysis, this material is mainly composed of the elements silica and aluminum. The amount of iron, magnesium, and calcium is also noteworthy. The results of this analysis help to correctly analyze the results of XRD analysis.

Table 1. XRF analysis of LECA

Elements	L.O.I	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu	Ni	Zn	Sr	Zr	As	Ba	Cr
Percantag	1.31	1.507	3.503	16.003	61.048	0.194	0.468	0.075	3.6	4.961	0.602	0.121	6.394	0.006	0.01	0.008	0.091	0.013	0.005	0.072	0.012

4.1.2 XRD Analysis

The XRD patterns for the two materials LECA and LECA@OH are shown in Figure 1, which depicts their phases. By comparing these patterns with JCPDS, it was found that the two samples exhibit the following phases: silicon oxide (SiO_2:00-033-1161), hexagonal aluminum phosphate ($AlPO_4$:01-076-0228), monoclinic calcium aluminosilicate ($CaAl_2Si_2O_8.4H_2O$:00-020-0452) and cubic magnetite (Fe_2O_3:96-101-1033). A close comparison between Figure 1 (a) and (b) shows that the modification process has resulted in a significant increase in the peak intensity.

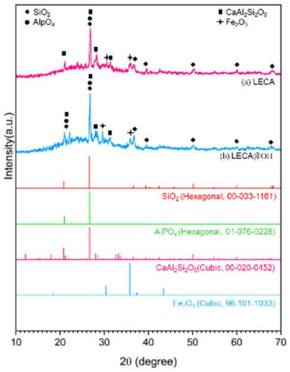

Figure 1. XRD analysis of (a) LECA and (b) LECA@OH

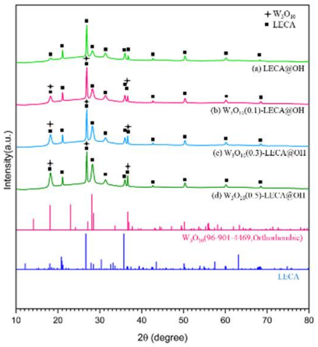

Figure 2. XRD analysis of W_3O_{10}-LECA@OH catalysts

This increase can be attributed to the effective removal of amorphous phases as well as the enhanced crystal growth resulting from the modification of LECA by KOH. XRD analysis provides convincing evidence of the structural changes that occurred during the modification of these materials, underscoring the effectiveness of the KOH modification method in optimizing the phase composition and crystallinity.

4.2. Analysis and Characterization of W_3O_{10}-LECA@OH

4.2.1. XRD Analysis

The XRD patterns for the two catalysts LECA@OH, W_3O_{10} (0.1)-LECA@OH, W_3O_{10} (0.3)-LECA@OH and W_3O_{10}(0.5)-LECA@OH are shown in Figure 2, which depicts their phases. By comparing these patterns with JCPDS, it was found that all four samples contain LECA. In Figure 2 (b) to (d), the phase related to W_3O_{10} with reference code 4469-901-96 is observed. With increasing W_3O_{10} content, the intensity of the peaks related to LECA has decreased, which means that the contribution of W_3O_{10} in the catalyst has increased. The presence of W_3O_{10} increases the acid strength of the catalyst, and increasing the acid strength of the catalyst increases biodiesel production. Of course, it should be noted that the excessive presence of W_3O_{10} causes the accumulation and loss of acidic sites.

4.2.2. BET-BJH Analysis

A BET-BJH analysis was performed on the (0.3)W_3O_{10}-LECA@OH catalyst, the results of which are presented in Table 2. The results of this analysis show that the specific surface area is 4.71 cm^2/g and the total pore volume is 0.0256 cm^3/g, of which about 79.1% are mesopores and 19.2% are macropores. These results indicate that this catalyst is mainly composed of meso- and macropores. The presence of meso- and macropores allows molecules to enter and exit the pores more easily, resulting in increased diffusion and mass transfer rates.

Table 2. Surface area, volume, and pore diameter of W_3O_{10} (0.3)-LECA@OH catalyst

Mean pore diameter (nm)	Total pore volume (cm^3/g)	BET surface area (m^2/g)
9.6	0.0256	4.71

4.2.3. Catalyst Evaluation in Biodiesel Production Process

Catalytic performance of all synthesized catalysts under the conditions of 3% catalyst weight percentage, methanol to oil mole ratio of 20, reaction temperature of 95 ºC, and time of 2 h were evaluated. The observed conversion rates for the catalysts are as follows: 68.23% for W_3O_{10} (0.1)-LECA@OH, 91.28% for W_3O_{10} (0.3)-LECA@OH and 88.59% for W_3O_{10} (0.5)-LECA@OH. These results are in good agreement with the findings and results of BET-BJH, FESEM and TEM analyses. Because the best result is related to (0.3)W_3O_{10}-LECA@OH, where W_3O_{10} is uniformly dispersed and also the amount of W_3O_{10} in it is higher than W_3O_{10} (0.1)-LECA@OH, as a result, the available acid sites are more. With increasing amount of tungsten oxide, the conversion rate decreased because agglomeration occurred.

5. CONCLUSION

The results of this study show that the W_3O_{10}-LECA@OH catalyst has excellent performance in the biodiesel production process due to its favorable structural and surface properties. Functionalization of LECA with OH groups and loading of the W3O10 active phase increased the active surface area and improved the dispersion of the active phase. Under optimal process conditions, this catalyst was able to achieve a conversion efficiency of 91.28%, indicating its high potential for use in the biodiesel production industry. According to the results obtained, the W_3O_{10} (0.3)-LECA@OH catalyst can be used as a promising option for the production of biodiesel with high efficiency and lower costs.

6. REFERENCES

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