

Structural and Morphological Improvement of Silica-Alumina-Phosphate Nanostructure by Hard Template Addition Applied in Green Fuel Production

Hossein Zeinalzadeh, Mohammad Haghghi,* , Behzad Ebadinezhad

Chemical Engineering Faculty, Reactor and Catalysis Research Center (RCRC), Sahand University of Technology ,Tabriz, Iran.

*Corresponding author: Mohammad Haghghi, Chemical Engineering Faculty, Reactor and Catalysis Research Center (RCRC), Sahand University of Technology P.O.Box 51335-1996, Sahand New Town, Tabriz, Iran.

✉ rawazahmed@kissr.edu.krd

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Abstract

Free fatty acid molecules have difficulty penetrating SAPO-34 pores due to their large size. To solve this problem, synthesis of SAPO-34 by hydrothermal method, different weight percentages of activated Charcoal template were used with ultrasound waves to distribute the particles in a regular and uniform method. Also, to enhance the acidic strength and improve its performance, Ce was loaded into the SAPO-34 structure by solvothermal treatment. The synthesized samples were characterized by XRD and BET-BJH analysis. The X-ray diffraction results of the synthesized catalysts show the absence of impurities in the samples and the successful synthesis of the catalysts. Moreover, BET analysis showed that 4 wt. % of activated charcoal was the optimal amount of secondary template and Ce/SAPO-34 (4% CHA) nanocatalyst have the highest conversion rate of oleic acid to biodiesel which was 94%. Kinetic studies showed that the oil-to-biodiesel conversion reaction was first order and Ce/MSAPO-34 (CHA4-U) nanocatalyst had the highest reaction rate constant (0.0014 min⁻¹) among the synthesized samples.

Keywords: Biodiesel, Esterification, Oleic Acid, Ce/SAPO-34, Hard template

Introduction

Due to the high cost of biodiesel production, suitable catalyst design has a pivotal role in increasing efficiency and reduce biodiesel production time. The highest level of catalyst is the surface of the pores. Besides, because of large the feed molecules size (Oleic Acid, FFA), the catalyst which is selected should have not only the high surface area but also the pore in the range of macro and meso. Even though Ce/SAPO-34 catalyst has the appropriate surface and acidic strength feature for the reaction of FFA esterification with methanol

and then biodiesel production, it has a low average diameter of pores. For this reason, enhancement of pores diameter plays a key role in increasing the surface which is accessible to the molecules of FFA as a feed. One of the best methods for the porosity enhancement is using activated Charcoal template. In this study, a new mesoporous Ce/SAPO-34 catalyst is introduced toward biodiesel production and modification of its structure to increase the efficiency of the esterification reaction[1-5].

Materials and Methods

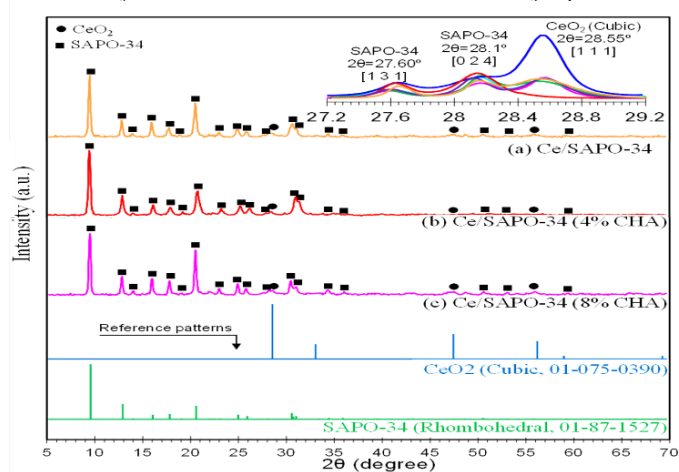
The table below provides general information about methods and the materials.

| Catalysts | CHA Wt. % | Ultrasound Time Power | Methods | |
|------------|-----------|-----------------------|--------------|--------------|
| | | | Support | Active Phase |
| Ce/SAPO-34 | 0 | 30 min 300 W | Hydrothermal | Solvothermal |
| Ce/SAPO-34 | 4 | 30 min 300 W | Hydrothermal | Solvothermal |
| Ce/SAPO-34 | 8 | 30 min 300 W | Hydrothermal | Solvothermal |

Results

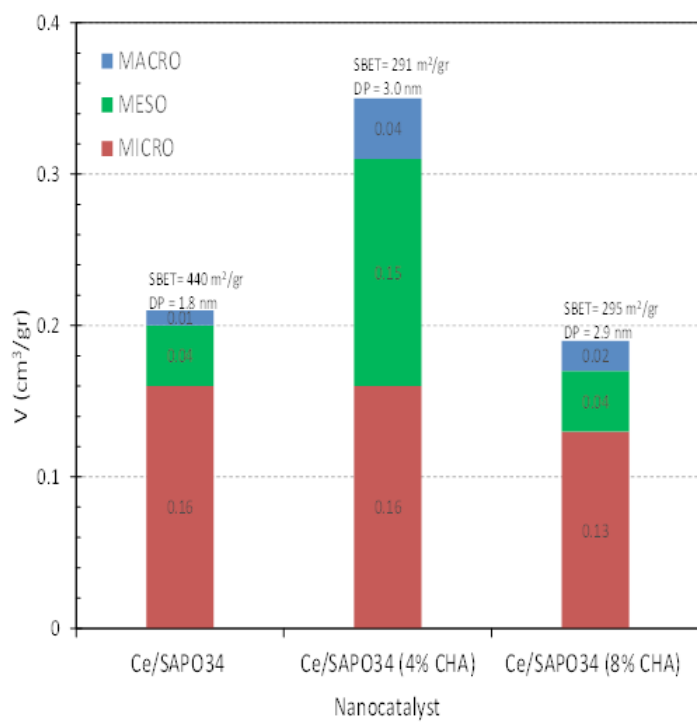
The X-ray diffraction patterns illustrate there are not any impurities in the synthesized catalysts. As can be seen, increasing Carbon loading from 4% to 8% as a secondary template causes to decreasing

intensity of the main peak which is related to the SAPO-34. According to the literature, addition of the hard template to initial solution made the decrement of catalytic crystallization. This section shows the successful synthesis of Ce/SAPO-34 because the major peak



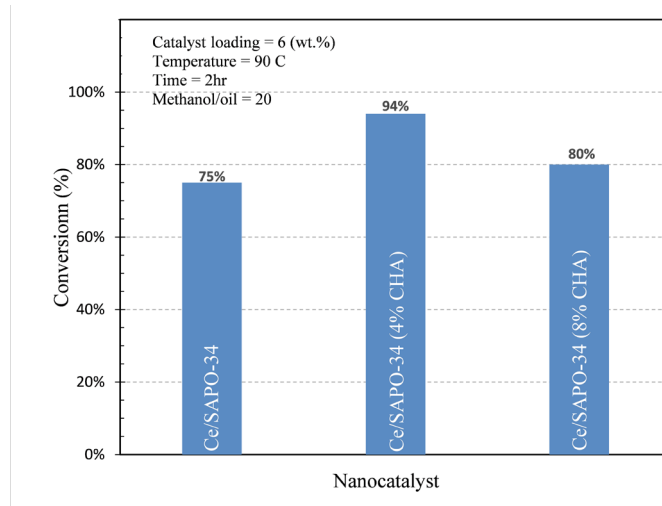
of cerium is seen in all of samples which was mentioned in the reference XRD pattern ($2\theta = 28.55$).

BET results show that increasing of activated charcoal causes to boosting the average pores diameter of and its volume. The amount of mesoporous volume in the sample of Ce/SAPO-34 is increased from 0.04 to 0.15 in the sample of Ce/SAPO-34 (4% CHA). Besides, the results show that the total pore volume was decreased by increment of the amount of hard template from 4 % to 8 %. In other words, the total pores diameter was reduced from 0.35 to 0.19 cm³/gr in Ce/SAPO-34 (8% CHA).



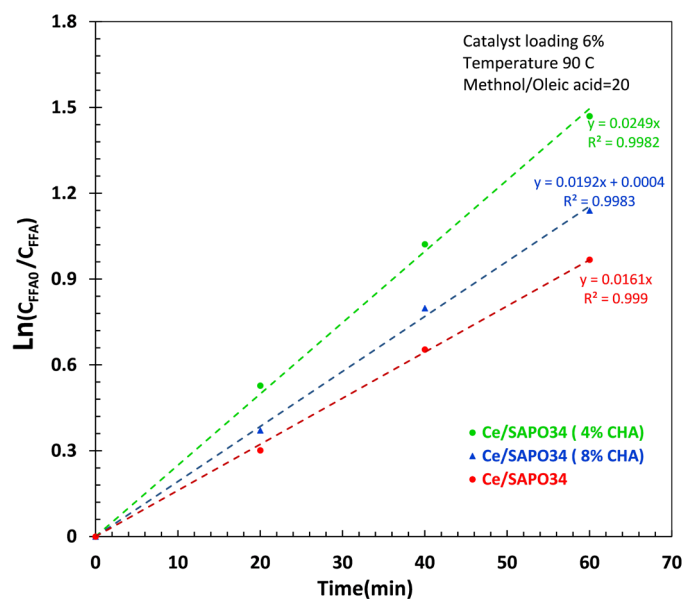
The performance of the synthesized nanocatalysts in biodiesel production and the effect of using 4% activated charcoal indicate that adding secondary template causes to enhancing conversion from

75% to 94%. This is because of boosting the amount of mesoporous and macro porous diameter catalysts and because of the increasing the active sites for the reactant. Additionally, more adding the hard template can be caused to decrease conversion which is in good agreement with BET analysis.



The linearization of the experimental data with Equation 1 and the velocity constants obtained by using the slope of lines shows that the Ce/SAPO-34 (4% CHA) nanocatalyst has the highest rate constant ($K = 0.0014 \text{ min}^{-1}$) than the other catalysts because methanol concentration is 20 times higher than FFA. Therefore, in the reaction kinetics study, with the methanol concentration constant, the rate of reaction of conversion of FFA to biodiesel is Equation 1:

$$-\ln \frac{C_{(FFA)}}{C_{(FFA)0}} = K't \quad , \quad K' = KC_{Meth}$$



Conclusion

Using activated charcoal secondary to modify the structure of the

SAPO-34 nanocatalyst increases specific surface area available and porosity. BET results showed that 4% of activated charcoal is the optimum amount. This means that the amounts less than 4% reduced the mean diameter of SAPO-34 and the greater amount of it disturbed at the calcination step and caused a slight drop in SAPO-34 structure. Furthermore, kinetic studies demonstrated that the modification of the SAPO-34 porosity by the secondary activated charcoal template increased the reaction rate due to the restriction of the penetration of large FFA molecules into the catalyst pores.

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