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Catalytic influence of Mo/SBA-15 towards the transesterification reaction using waste cooking palm oil

M. Shanmugam, A. Abilarasu and T. Somanathan*

Department of Chemistry & Nanoscience, School of Basic Sciences, Vels University, Chennai, Tamilnadu, India-600117

Abstract: Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl or propyl) esters. It is typically made by chemically reacting lipids with an alcohol producing fatty acid esters. Used cooking oil is one of the economical sources for biodiesel production. In this work, we have prepared mesoporous Mo/SBA-15 by varying different weight percentage of Molybdenum via the wet impregnation method. Synthesised catalysts were characterized by using X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and N_2 physisorption studies. The catalytic activities of the catalyst were tested towards the production of biodiesel. The effect of reaction time, temperature, catalyst weight percentage and molar ratio were investigated. Finally biodiesel product was confirmed by using Gas chromatography and fourier transform infra red (FT-IR) spectroscopy. By using this catalyst, an eco-friendly more benign process for the transesterification of waste cooking palm oil in a heterogeneous manner is developed.
Key words: Waste cooking oil, Biodiesel, methyl esters, Mo/SBA-15, Glycerol

Introduction

Biodiesel is a natural and renewable domestic fuel alternative for diesel engine made from animal fat, edible and non edible oil. Biodiesel is a pollution free, cleaner-burning fuel than petroleum diesel as it doesn't contain sulfur or aromatic[1,2]. Numerous methods were develop to synthesis of biodiesel, such as acid-catalyzed process[3,4], supercritical process[5,6], enzymatic process and heterogeneous catalytic process[7]. Habitually, the transesterification reaction for biodiesel synthesis has been catalyzed by homogeneous catalysts[8]. This catalyst is corrosive for equipment and also reacts with free fatty acids to form unwanted soap by-products [9]. Use of heterogeneous catalysts offers a potential solution to this problem, as the catalyst can be easily separated from reaction mixture by filtration[10]. Acid catalyzed processes could produce biodiesel from the low-cost feedstock thus lowering the production cost[11]. Heterogeneous acid-catalyzed processes have met with promising success, as they have the highest rate-of-return, lowest capital investment, and need technically simple apparatus[12].

In recent years, metal nanocomposites based on ordered mesoporous silicas with tunable structure and tailored composition have been extensively investigated in broad applications ranging from adsorbent, gas separation, catalysis, to biological uses. One of the attractive features of these materials is that they combine in a single solid, the chemical functionalities arising mainly from an anchored metal with high surface area, ordered narrow pore size distribution and highly mechanical stable structure. In this content the use of waste cooking oil for biodiesel production is the most extensively used meat all-around the world. It can be used as a very low cost renewable source to produce biodiesel of comparable price to conventional petroleum diesel. Recently reported that V/SBA-15 is a promising and ecofriendly acid catalyst for transesterification of various fatty acids and vegetable oil[13].

In this present work, we have synthesised metal impregnated SBA-15 mesoporous molecular sieves as a catalyst and their activity towards the transesterification process of waste cooking oil with methanol. The effect of various parameters such as temperature and reaction time were evaluated.

Experimental

Chemicals & Materials

Chemicals such as P-123 poly (ethylene glycol)-block- poly (propylene glycol)-block-poly (ethylene glycol) triblock copolymer hydrochloric acid; TEOS (tetra ethyl ortho silicate), ammonium molybdate and methanol were purchased from E-Merck for the synthesis of metal oxide nanoparticles. The glassware's used in all the experiments were made up of Schott Duran.

Catalyst Preparation

Mesoporous siliceous SBA-15 was prepared employing the optimized procedure as described elsewhere[14]. In a typical synthesis, 4 g amphilic triblock copolymer (Pluronic P123) in 30 ml water was stirred for 4 h. Thereafter, 120 g hydrochloric acid solution (2 M) was added to it and the gel was stirred for another 2 h. Then, 9 g TEOS was added to it and continued the stirring for 24 h at 40 ºC. The mixture was finally heated in an autoclave at 100 ºC for 48 h. The solid product thus obtained was filtered, dried at 100 ºC and then calcined at 550 ºC in air to expel the template. About 1g of calcined SBA-15 was treated with required amount of 1M ammonium molybdate solution with different percentage loading 5, 10, 15, 20 and 25 wt%. The mixture is stirred at room temperature for 3hr in ethanol which followed by filtration and drying at 80 ºC. Then the obtained solid products were calcined at 550 ºC for 3hr.

Transesterification of Waste Cooking Oil

All catalytic tests were carried out using 250 mL round bottom glass reactor equipped with a condenser and a magnetic stirrer. Typically 0.2 g of Mo/SBA-15 as a catalyst and keeping constant the molar ratio of oil: methanol (1:6). The reaction temperature was varied between 60 – 120 °C. At this point, a mixture of methanol and catalyst was added to the oil and the transesterification reaction took place for 6 h. After reaction the mixture were cool to room temperature and transferred into separation funnel to separate the product. The samples were subjected to GC analysis to confirm the products.

Result and Discussion

XRD pattern of SBA-15

Low angle XRD pattern (Fig. 1) show that the mesoporous silica templates have highly ordered mesostructures, with at least three well-resolved diffraction peaks indexed as 100, 110 and 200 of hexagonal structure for the mesoporous silica SBA-15[15,16].

SEM and TEM image of SBA-15

The SEM image which is shown in Fig. 2 (a) clearly indicates the formation of uniform rod like particles. Fig. 2 (b) show the High resolution TEM image of Mo/SBA-15 sample which clearly provides a direct observation of the highly ordered hexagonal mesoporous structure and the distribution of molybdenum oxide nanoparticles in the SBA-15 matrix [15,16.]

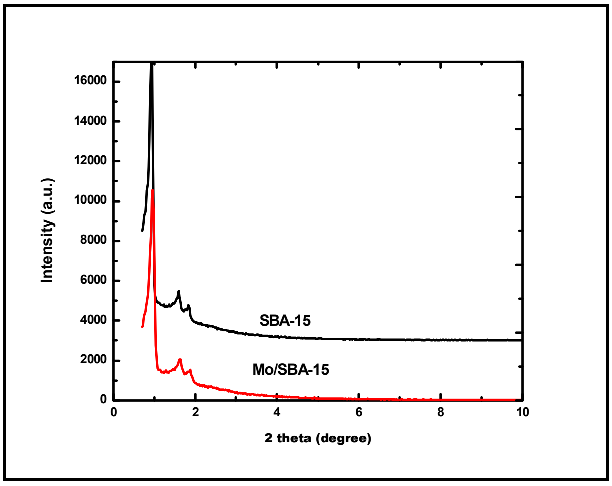

Fig. 1 XRD pattern of SBA-15 and Mo/SBA-15

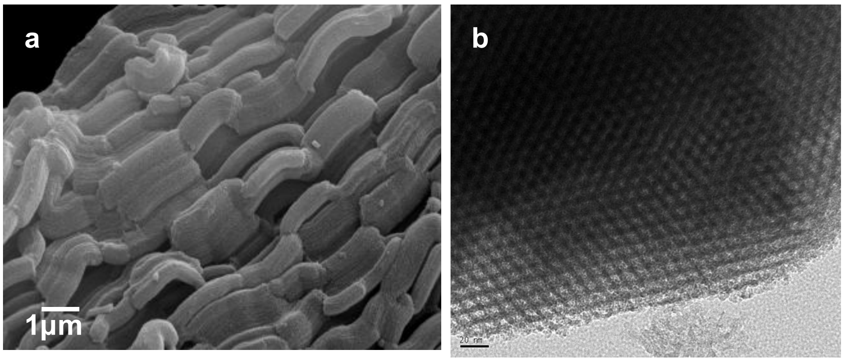

Fig. 2 (a) SEM image of SBA-15 and (b) TEM image of Mo/SBA-15 Catalytic Activity Study of Mo/SBA-15 for the Biodiesel Synthesis

Effect of Time

Catalytic reaction was carried out with different time interval using waste (cooking oil): and methanol in the mole ratio (1:6) with Mo/SBA-15 as a catalyst (0.2g) at 80 °C. Fig. 3 shows the effect of time in transesterification reaction. The yield of the product is gradually increased with increase in time.

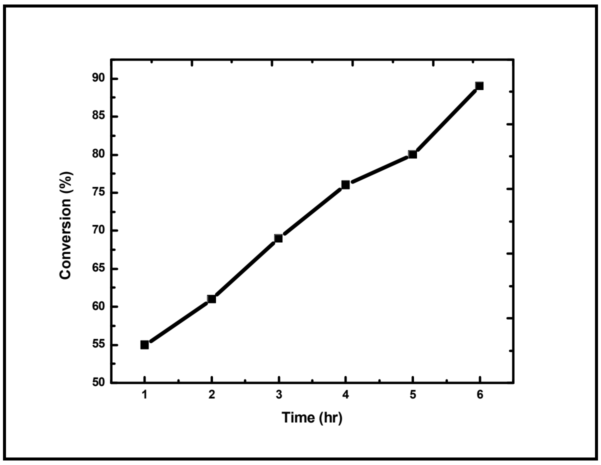

Fig. 3 Effect of time vs conversion

Effect of Temperature

Fig. 4 illustrates the effect of different temperatures for the conversion of biodiesel through transesterification reaction. The conversion of the product were increased when increase in the temperature such as 60 °C, 80°C, 100 °C, 120 °C and conversion is 67%, 75%, 83% and 95%, respectively. A common trend in conversion over catalyst is increase of oil conversion with increase with temperature. Since transesterification involves establishment of equilibrium, it is evident from these results that the shift in equilibrium towards ester side occurs with increase in temperature due to increase in activation energy.

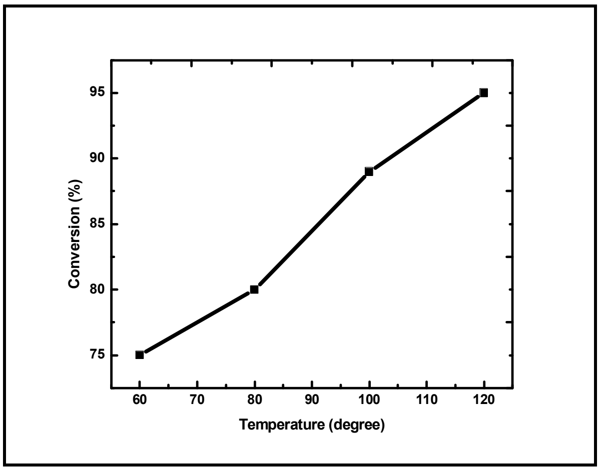

Fig. 4. Effect of temperature vs conversion of the product

Conclusions

Mo/SBA-15 mesoporous materials were synthesized by wet impregnation method. The synthesized materials were well characterized by using various physicochemical techniques like XRD, SEM and TEM. We observed that XRD showed well ordered hexagonal mesoporous structure. The SEM image clearly shows the uniform rod like morphology and TEM image shows the hexagonal arrangement of porous materials. The catalytic activity of the mesoporous materials were tested towards the transesterification of waste cooking palm oil and methanol. We have obtained 95% conversion of the product at 120 °C using Mo/SBA-15 for a period of 6hr. Despite of simplicity of a wet chemistry procedure, low reaction temperature and lack of post growth annealing at high temperature we obtained high quality metal oxide nanoparticles by simplest method.

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