*Original Research Article*

Investigating the Feasibility of Using Alumina-Zirconia Catalysts in Energy Production

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Submitted: 2022-01-12

Revised: 2022-02-23

Accepted: 2022-03-20

Available online: 2022-04-30

Manuscript ID: PCBR-2203-1217

DOI: 10.22034/pcbr.2022.334130.1217

KEYWORDS

Biodiesel,

Microalgae,

Fatty acid,

Alumina zirconia catalyst,

Transesterification

ABSTRACT

The aim of this study was to investigate the feasibility of using alumina-zirconia catalysts in energy production. In recent years, the use of liquid biofuels in the transportation sector has grown significantly. Sustainability is a key principle in natural resource management, which includes considering operational efficiency to minimize destructive environmental impacts and socio-economic considerations. Given the depletion of global reserves of fossil fuels and the emission of greenhouse gases from their use, it does not seem wise to trust and rely on the continued use of fossil fuel energy sources. The first-generation biofuels, which have now reached the economic level of production, are often extracted from food and oil products such as rapeseed, sugarcane, sugar beet, and corn, as well as vegetable oils and animal fats using conventional technologies. The use of first-generation biofuels has caused much controversy, often because of their impact on the global food market and food security, especially in countries with vulnerable economies and consequently, there is much ambiguity about their potential to replace fossil fuels and sustain production they have been created.

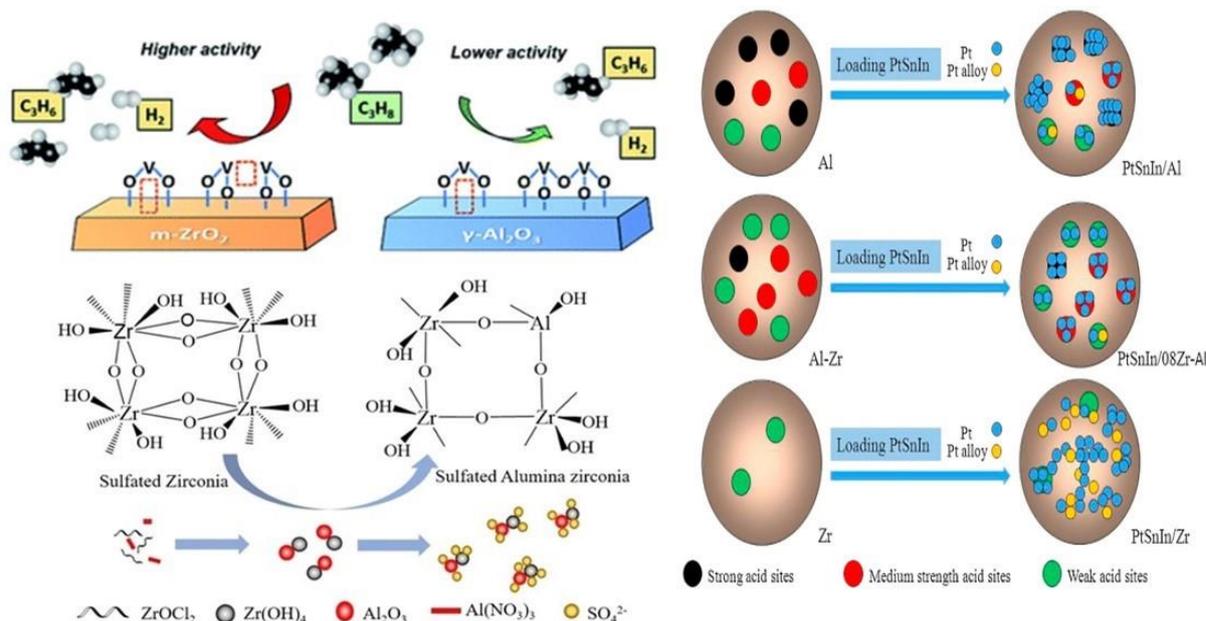
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GRAPHICAL ABSTRACT



Introduction

As a result, extensive research is being conducted around the world to develop and produce carbon-free renewable gas, liquid, and solid biofuels as the alternative energy sources [1-3]. Alternative energy sources related to first-generation biofuels derived from soil products such as sugarcane, sugar beet, corn, and canola have a special place in the global food market, and their improper cultivation and harvesting will lead to water shortages and deforestation around the world. Second-generation biofuels derived from forest tree residues and lignocellulosic materials of agricultural products and non-food products also have some disadvantages of first-generation biofuels [4-6]. Therefore, considering the current level of knowledge and technology, third generation biofuels, especially microalgae fuels, are a good option to replace fossil fuels. Third generation biofuels do not have the disadvantages of using first- and second-generation fuels [7-9]. Microalgae are photosynthetic microorganisms which require simple substances (light, sugars, carbon dioxide, nitrogen, phosphorus, and potassium) and can produce large amounts of fats, proteins, and carbohydrates in a short

period of growth [10-13]. These products can be converted into biofuels as well as valuable by-products. At the end of 2011, the world's annual energy consumption was estimated at 12274.6 million tons of oil. Fossil fuels provide 87% of the global energy consumption, including 33.1% oil, 30.3% coal, 23.6% natural gas, 4.4% nuclear energy, and 6.5% hydroelectricity. Given the vast technological advances, the existence of high-potential reserves, and the increasing extraction from new reserves such as natural gas, it is assumed that fossil fuels will be available for a considerably low price [14-16]. Unfortunately, the potential threats of global climate change have increased, and most of it is related to the emission of greenhouse gases from burning fossil fuels. Climate change can have far-reaching consequences for nature and mankind [17-19]. As a result, the sustainable use of fossil fuels does not make sense in terms of their limited resources and the negative effects of carbon dioxide emissions. Therefore, the need for increasing the global strategies to ensure energy security and reduce carbon dioxide emissions is necessary and inevitable. The most prominent strategy includes the need to increase energy efficiency, increase the use of clean fossil fuels

and of renewable energy [20]. Oils with high fatty acid levels can be esterified using acid catalysts. No soap is formed in this process; however, the reaction temperature and molar ratio of the substrate are higher than the base process. Acid catalysts are rarely used on an industrial scale. Because they are more corrosive than play catalysts, they reduce reaction speed and reduce efficiency. In any case, when the primary oil contains large amounts of free fatty acids, this fatty acid destroys the activity of the base catalyst. The acid catalyst can be used in combination with the base catalyst. An acid catalyst is utilized in the initial stage to convert free fatty acids to methyl esters. Acid catalysts can also be used in microalgae biomass in biodiesel production processes. For instance, Nagel et al. achieved a yield of 10 mg of FAME per 250 mg of lipid under the following conditions. Hydrochloric acid catalyst is 0.6 N, methanol, 0.1 h, temperature 70°C, and the microalgae *Ceratosaurus molar* if the test is repeated under the previous conditions, but use sodium hydroxide instead of hydrochloric acid. Only 3.3 mg of FAME is obtained [21-23].

Blarby et al. also proposed a simultaneous trans-esterification and extraction method for the production of biodiesel from microalgae fatty acids. Fatty acid was extracted from microalgal biomass that was dried under freezing or biomass pulp collected by centrifugation. The moisture content of biomass dough was 82% by weight. This biomass belonged to the diatom of *Adactylism trichornatum* or the green alga *Monodus subtranus* and the yield of 8.37 g of FAME was obtained from 10.8 lipids under the following conditions. Flavodactyl *Trichornatum* biomass paste (500g, 82% by weight moisture, and 12% by lipid), 1 liter of methanol and 50 ml of acetyl chloride [24]. Biodiesel production technology has evolved over the last century through the trans-esterification reaction using homogeneous catalysts; however there are many advantages to use heterogeneous catalysts

instead of homogeneous catalysts, which can be categorized as:

A) Ecological: Eliminating washing stage and thus, eliminating mass production of wastewater.

B) Economic: Using cheaper and recyclable catalysts.

C) Investment: Simplification of the process and consequently lower investment costs [25].

Although there is currently only one industrial unit which uses heterogeneous catalysts to carry out the trans-esterification reaction, extensive research is being done on biodiesel production and the discovery of suitable solid catalysts. The advantages that researchers are looking for are shorter contact times, less catalyst loading, lower reaction temperatures, and optimal alcohol/oil molar ratios. All of the above lead to increased efficiency and increased purity of the final product of the trans-esterification reaction. Numerous solid catalysts have been investigated to date, including metal oxides, metal complexes, active metals loaded on supports, zeolites, resins, and lipases. For example, the activities of oxides, methoxides, and hydroxides of alkaline earth metals have been identified, but the reaction conditions in this study depend on the reaction temperature and atmospheric pressure. Of the alkaline earth metal oxides, only MgO and CaO are valuable and noteworthy. Because BaO dissolves in methanol, SrO also reacts with water and carbon dioxide. Among Ca-based materials, only its oxide, neither hydroxide nor carbonate, indicated much activity in the trans-esterification reaction of soybean oil with methanol [26].

Saps et al. used the ETS-10 zeolite catalyst for the trans-esterification reaction of soybean oil and achieved efficiencies of more than 90% at 100°C. Kawashima et al. also prepared thirteen different metal oxides containing calcium, barium, magnesium, and lanthanum as catalysts. The activity of these catalysts was investigated for trans-esterification reaction at 60°C and the molar ratio of methanol to oil was 6:1 and the reaction time was 10 hours. Catalysts containing

CaTiO₃, CaMnO₃, Ca₂Fe₂O₅, CaZrO₃, and CaO-CeO₂ depicted high activity and their methyl ester yield reached more than 90% [27].

Synthesis of alumina catalysts

The calculations for the synthesis of alumina catalysts are similar to the calculations for the preparation of gamma alumina zirconia catalysts. In order to prepare 5 g of alumina catalyst, 23 g of 6-aqueous aluminum chloride was dissolved in 170 ml of distilled water. The solution was stirred at 90 °C for 2 hours. Distilled water containing 1.12 g of yttrium nitrate was slowly added to the solution (Figure 1). Pour 3 grams of polyvinyl chloride in 10 ml of hot distilled water

and dissolve completely on the heater [28-30]. Then, add about 50 ml (30% by volume) of it to the previous solution. The gelling process begins when the final solution is stirred vigorously at 80 °C for 2 hours and then at room temperature for 24 hours [31-33]. Place the container in the oven at a temperature of 50 cc to form a gel. This process takes about 7 days, after which the flask containing the gel is placed in an oven to dry, and finally placed in an oven with a temperature program similar to the synthesis of the gamma alumina zirconia catalyst synthesis to be calcined [34-36].

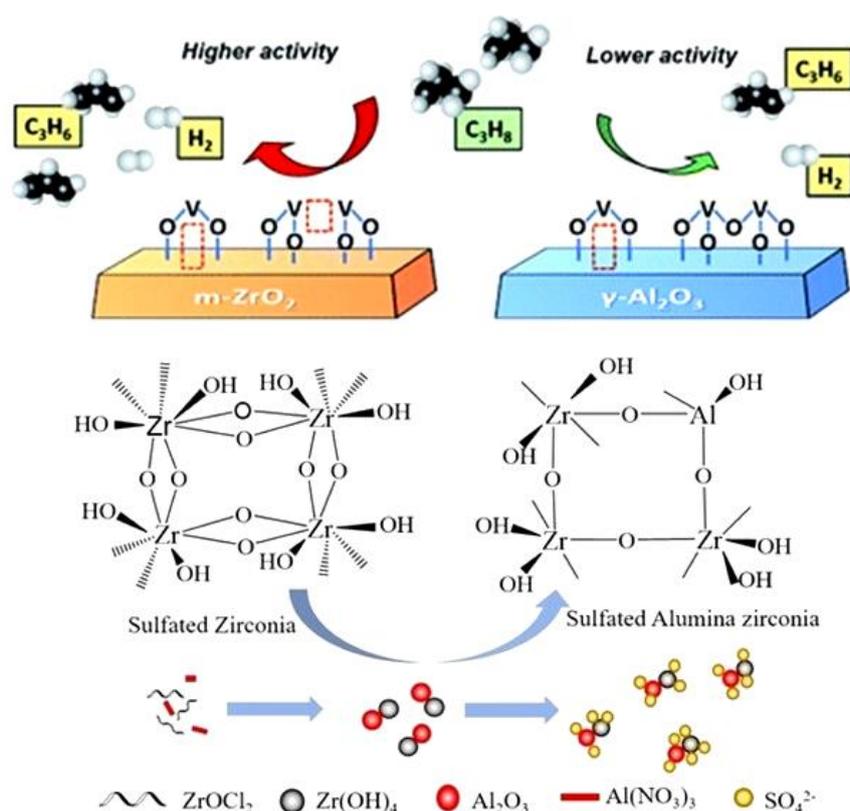


Figure 1. Synthesis of alumina catalysts

Catalyst specification analyzes

After preparing the catalysts, it is necessary to perform tests on them to determine their chemical and physical properties. For this, infrared spectroscopy (FTIR) analysis to

determine the structure and measurement of chemical species in the samples, X-ray diffraction spectroscopy analysis to determine the phases formed in the synthesized catalysts, scanning electron microscope to observe the surface

morphology of the catalysts, microscope transmission electrons were used to observe the internal structure, BET analysis was used to determine the specific surface area of the catalyst and the pore size, and BJH analysis was used to show the particle size distribution [37-39]. Fourier transform infrared (FTIR) spectroscopy analysis of gamma alumina zirconia catalyst FTIR analysis is used to determine the chemical groups and bonds in the structure of synthesized catalysts [40-42].

Alumina catalyst

The broad absorption peak, located at 3480 cm^{-1} wavelengths, indicates the tensile vibration of the O-H bond and actually justifies the presence of the water molecule. The vibration appearing in 1635 cm^{-1} is related to the symmetrical tensile vibration of the H-O-H molecule of the adsorbed water. Al-O and Al-O-Al vibrations are also located at 740 and 630 cm^{-1} wavelengths, respectively [43].

Zirconia Catalyst

The main peaks in the FTIR spectrum of zirconia catalysts are:

- ✓ The peak related to the tensile vibration of the O-H bond at the wavelength of 3420 cm^{-1}
- ✓ The peak related to the flexural vibration of the Zr-OH bond at 1627 cm^{-1} wavelength
- ✓ Zr-O bond flexural vibration peaks at wavelengths between $600\text{-}500\text{ cm}^{-1}$

Alumina catalyst

X-ray diffraction spectroscopy was performed on calcined alumina catalyst at 700°C . Alumina was expected to appear in the gamma phase at 700°C , and it can be concluded that the synthesized alumina catalyst is amorphous. A possible explanation for this phenomenon could be the presence of yttrium oxide in the composition [44]. The result is similar to that of Alkbero et al. They found that if yttrium oxide was in the alumina composition, the alumina would remain

amorphous at 800°C . Therefore, it seems that the presence of yttrium oxide causes the transition temperature to rise.

Zirconia Catalyst

X-ray diffraction analysis for zirconia catalyst was performed as in the prior two catalysts. In this model, three peaks appear. Comparing their Bragg angles with similar studies with other researchers and diffraction databases, it can be concluded that the synthesized catalyst is of the tetragonal type and the peaks appear at angles 2θ equal to 31 , 52 , and 60 degrees [45-47].

Catalyst value

The results show that increasing the amount of catalyst to more than 2% is actually a waste of catalyst and financial resources. It should be noted that so far, no amorphous alumina catalyst has been taken to perform the transesterification reaction. As a result, the return is not comparable to the other data; however the return is very significant [48].

Revitalization of synthesized catalysts

Rehabilitation and reuse of catalysts is very effective in their practical applications in industry. A good catalyst should be able to be used in reactions for several consecutive hours or several times with high efficiency. Another experiment was performed to demonstrate the capability of synthesized catalysts [49]. After the synthesized catalysts were used in the transesterification reaction, they were completely separated from the reaction medium and dried using precipitation and centrifugation. In the first experiment, in order to investigate the decrease in biodiesel production efficiency, a reaction was performed under optimal conditions in the presence of amorphous alumina catalyst. The results of this experiment indicated that the amount of biodiesel production without using the reduction process is reduced to 43.3% [50-52]. The probable cause of this event is that the catalyst particles are surrounded by oil and as a result its activity is reduced [53]. As a

consequence, the need to carry out the catalyst reduction process is quite obvious. In order to regenerate the catalysts, the calcination process

of sand was performed a 700 °C for 4 hours and the catalysts were re-entered into the reaction medium (Figure 2).

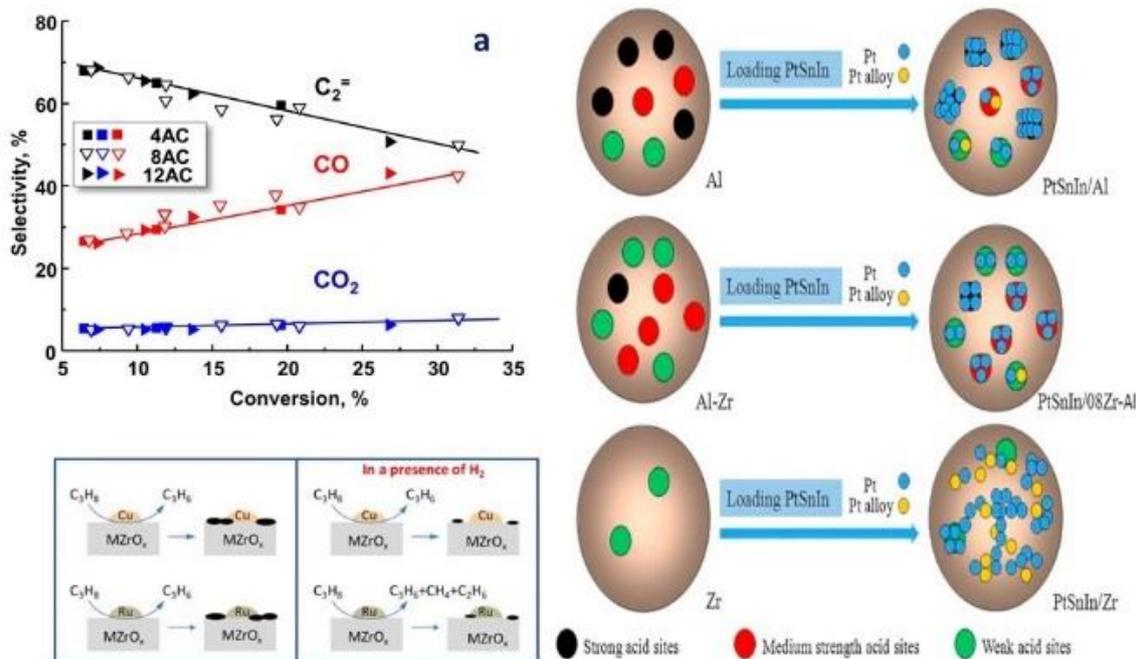


Figure 2. Revitalization of synthesized catalysts

Conclusion and Recommendations

The concerns about declining oil reserves, rising crude oil prices, rising greenhouse gas emissions and, of course, their environmental impact have made biodiesel one of the fastest growing industries in the world. Biodiesel is made up of fatty acid alkyl esters that are produced from triglycerides, diacyl glycerols, free fatty acids, and phospholipids found in oily plants or animal fats. Compared to conventional diesel, biodiesel has higher oxygen content and lower sulfur and nitrogen levels. Therefore, it produces less carbon monoxide, SO_x, NO_x, benzene, and toluene during combustion. The main problem which limits the development of the biodiesel industry is the provision and price of primary resources. It should be noted that these resources should be provided from non-food items that require less land for cultivation.

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HOW TO CITE THIS ARTICLE

Mina Jafari, Investigating the Feasibility of Using Alumina-Zirconia Catalysts in Energy Production, *Prog. Chem. Biochem. Res.* 5(2) (2022) 115-124.

DOI: 10.22034/pcbr.2022.334130.1217

URL: http://www.pcbiochemres.com/article_147385.html

