Journal of Nano- and Electronic Physics
Vol. **14** No 3, 03005(4pp) (2022)

Журнал нано- та електронної фізики
Том **14** № 3, 03005(4cc) (2022)

Transition Metal Oxide Nanoparticles for Biofuel Production

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(Received 24 May 2022; revised manuscript received 24 June 2022; published online 30 June 2022)

The depletion of fossil fuels and population growth led to the search for alternative resources. Biodiesel is an alternative to fossil fuel. It can be obtained from plant oils, animal fats and waste cooking oil. Transesterification is a process used to synthesize biodiesel. Two types of catalysts are mainly responsible for the synthesis of biodiesel. These are homogenous and heterogeneous catalysts. Commercially homogenous catalysts are mostly used in industry for the synthesis of biodiesel. The homogenous catalyst needs water washing to remove impurities, and thus the production cost is high. The most important disadvantage is that the catalyst once used cannot be recovered. The heterogeneous catalyst has many advantages over homogenous catalyst such as reusability and needs no water wash. Among heterogeneous catalysts, transition metals can be used for biodiesel production. They come under the d-block in the periodic table. Many researchers reported the synthesis of biodiesel by transition metal oxide nanocatalysts. The transition metal oxide catalyst is a good substitute for the synthesis of biodiesel. They possess heterogeneous properties and have an advantage of reusability. Further, the transition metal oxide catalysts enhance the reaction rate and thus possess higher biodiesel yield.

Keywords: Synthesis, Biodiesel, Heterogeneous, Transition metal oxide, Catalyst, Reusability.

DOI: 10.21272/jnep.14(3).03005 PACS numbers: 77.84.Bw, 74.62.Bf

1. INTRODUCTION

Continuous use of fossil fuels and excessive emission of toxic gases (i.e., carbon dioxide, carbon monoxide, particulate matter, sulfur oxides, volatile organic compounds, and unburned hydrocarbons) has led to the search for an alternative to fossil fuels. Biodiesel is a good alternative to petroleum fuels. The oxygen content of biodiesel is higher than petroleum fuels. Biodiesel is produced from vegetable oil, animal fat, and waste cooking oil. It can reduce the carbon footprint. There are several advantages of biodiesel over fossil fuels. The advantages are: (1) it is biodegradable, (2) it exhausts low emission of toxic gases, (3) no engine modification is required for the use of biodiesel, (4) the cetane number of biodiesels is high so it gives better engine performance [1, 2].

Vegetable oils, waste cooking oil, and animal fats have higher viscosities which accumulate the knocking problem in the engine or even face difficulties during the combustion process. In order to use in the engines, the viscosity should be decreased to a certain limit [3]. Transesterification is the process used for the synthesis of biodiesel. The reaction takes place by the chemical reaction of oil, catalyst, and alcohol. Fig. 1 shows the stoichiometric reaction of the synthesis of biodiesel.

The catalyst used may be homogenous or heterogeneous and the alcohol used may be methanol or ethanol. Methanol is most commonly used because of its physical and chemical properties [4]. There are three types of catalysts that are mostly used for the production of biodiesel. The catalysts are classified as shown in Fig. 2 along with their sub-classification [5].

Commercially homogenous catalysts are mostly used because they are cheaper in price. There are several drawbacks of using the homogeneous catalyst i.e., water washing is required for removal of impurities, catalyst once used cannot be recovered and hence economically not viable. On the other hand, heterogeneous catalysts do not require any water washing to separate the impurities. The catalysts used for the synthesis can be easily recoverable by using centrifugation and reused till their catalytic activity. Despite having advantages over the homogeneous catalyst, the heterogeneous catalyst possesses some demerits such as fast

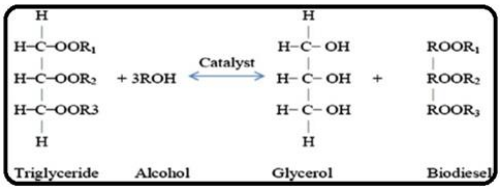

Fig. 1– Transesterification reaction

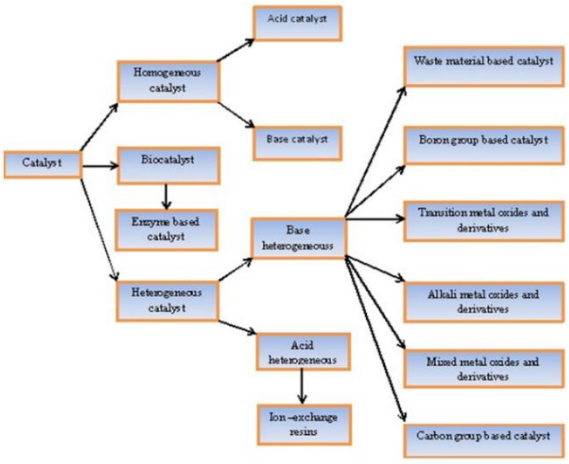

Fig. 2 – Catalyst and its types

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The results were presented at the 2nd International Conference on Innovative Research in Renewable Energy Technologies (IRRET-2022)

deactivation, mass transfer, and inefficiency. These drawbacks can be overcome by heterogeneous nanocatalyst because of its high surface area [6].

The transesterification process depends upon the effect of parameters such as reaction temperature, reaction time, alcohol to oil molar ratio, type of alcohol, type, and number of catalysts used. The viscosities of the oil decreased with the high reaction temperature which enhances the trans-esterification reaction. The present study focuses on the transition metal oxide nanocatalyst for the synthesis of biodiesel because of its amid advantages [7].

2. CATALYST

2.1 Transition Metal-Oxide Based Catalyst

Transition metal oxides are the most attractive group of solids. The structure and properties of these metal oxides are multifarious. The metal-oxygen bonding alters between ionic to highly covalent or metallic. The exceptional properties of transition metal oxides are due to the unique nature of the outer d-electrons. The general formulae of the transition metal oxides are MO, MO_2, MO_3, M_2O_3, M_2O_5, M_nO_{2n-1}, M_nO_{2n+1}. The crystal structure varies from cubic to triclinic symmetry. The MO possesses the rock-salt structure while the MO_2 possesses fluorite, rutile, distorted rutile or even more complex structures and M_2O_3 possesses the corundum structure. Perovskites, spinels, bronzes, and garnets are the ternary oxides. Most of the oxides are reported to that it transforms from one crystal structure to show interesting phase transitions from one crystal structure to a new structure possessing variation in electrical, magnetic, and various other [8].

The transition metal oxides are classified based upon the oxides of 3*d*, 4*d*, and 5*d* transition element.

3. SYNTHESIS OF TRANSITION METAL-OXIDE NANOPARTICLES

The synthesis of nanoparticles is classified according to their categories as (a) top-down technologies and (b) bottom-up technologies. The various routes for the synthesis of nanoparticles are shown in Fig. 3 [9].

Zinc oxide a transition metal oxide catalyst was synthesized by a modified sol gel method. The gel obtained was calcined at different temperatures such as 470, 700 and 1000 °C for 90 min. The white color obtained signifies the ZnO nanoparticles. The XRD results exhibit that pure hexagonal phase ZnO powders were formed. The particle sizes of nanoparticles were between 30 and 40 nm. The ZnO nanoparticles were also analyzed by TG-DTA, SEM, XRD, FTIR, and UV-Vis [10].

Zirconium oxide nanoparticle was synthesized by sol-gel method. First, when zirconium oxide was synthesized without the addition of ammonia and nitric acid, the zirconium oxide particles agglomerate into each other. Second, the zirconium oxide was synthesized by adding ammonia solution, and resulted in a less agglomeration. Last, Zirconium oxide was synthesized by adding nitric acid, and resulted in fine nanoparticles [11].

Kumar et al. synthesized MnO_2 nanoparticles by co-precipitation method. The crystallinity of the catalyst was determined by XRD. The average particle size of the nanocrystals was 25-30 nm. The catalyst was further characterized by UV-Visible and FTIR techniques. The MnO_2 has wide applications such as biosensor, molecular adsorption, etc. [12].

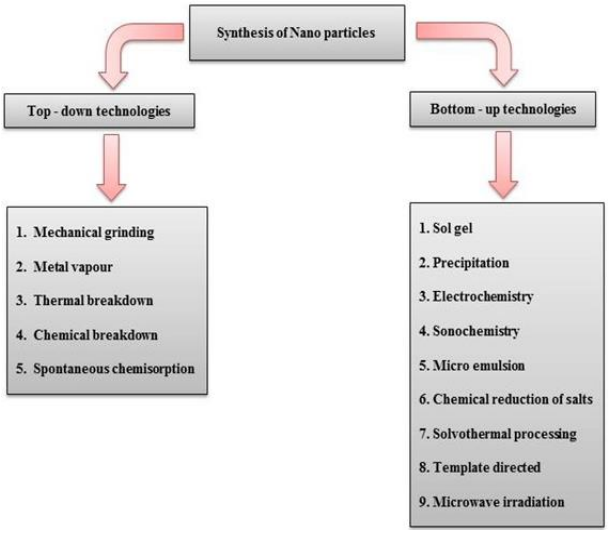

Fig. 3– Different types of routes to synthesize nanoparticles

He et al. reported the synthesis of biodiesel from sulfated ZrO_2 and TiO_2. The catalyst loaded was 2 w. % for the individual catalyst. The catalysts were synthesized by the precipitation method. The results from the experiment showed that the BET surface area of catalyst ZrO_2 and TiO_2 increased by the sulfation process. With the increase in the surface area, the catalytic activity also increases. ZrO_2 and TiO_2 had weak Lewis acid sides and showed poor catalytic activity, whereas ZrO_2/SO_4^{2-} and TiO_2/SO_4^{2-} possessed strong Bronsted acid sites on their surface and showed good catalytic activity [13].

4. TRANSESTERIFICATION BY TRANSITION METAL-OXIDE CATALYST

Madhuvillaku reported the synthesis of biodiesel by a mixed transition metal oxide catalyst. The reaction was carried out by a mixture of oil and methanol with the appropriate weight percentage of catalyst in a 3-necked round-bottom flask immersed in the constant-temperature water bath placed on the plate of the magnetic stirrer fitted with a condenser in the middle neck and thermometer in the side neck. The mixture was stirred for 5 h at 50-80 °C. The products obtained were allowed to settle overnight producing three distinct phases (i.e., methyl ester on top, glycerol in the middle layer, and catalyst phase at the bottom). [14].

Zirconium oxide, titanium oxide, and zinc oxide gain attention towards the synthesis of biodiesel. Zirconia-supported isopoly and heteropoly tungstates (HPAs) were used to synthesize sunflower oil with methanol [15].

Alhassan et al. reported that the ferric manganese doped tungstated/molybdena nanoparticle catalyst was used for the synthesis of biodiesel from waste cooking oil. The high FFAs of the waste cooking oil was reduced

to 0.620 %. The biodiesel yield was approximately 92.3 %. The doped catalyst was advantageous to both esterification and transesterification. Further, the catalyst was recycled for six times [16].

The author reported that kesambi oil was used for the synthesis of biodiesel using alumina-supported zinc oxide solid catalysts. The catalyst was synthesized by the precipitation and gel method. The effect of parameters showed a considerable effect on the yield of biodiesel. A maximum of 92.29 % biodiesel yield was achieved at a 1:12 molar ratio [17].

The non-edible seed oil of Silybum eburneum was used for the production of biodiesel. Heterogeneous nanocomposite catalysts MgO, Al_2O_3-CaO and TiO_2 were used for the synthesis. The catalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM) techniques. The highest yield was acquired by MgO nanocomposite accompanied by Al_2O_3-CaO and TiO_2 [18].

5. EFFECT OF PARAMETERS FOR SYNTHESIS OF BIODIESEL

5.1 Effect of Catalyst Loading

The effect of catalyst loading plays a tremendous role in the conversion of biodiesel. Semwal et al. reported the production of biodiesel from natural waste. The catalyst concentration was significantly increased in between 3-12 w. % of vegetable oils. Catalyst at 10 w. % showed 95 % biodiesel yield, whereas at higher catalyst loading i.e., more than 10 % results did not show any upliftment of yield [19].

Asri and his group investigated the synthesis of biodiesel with alumina supported zinc oxide catalyst. The methanol to oil ratio was taken as 12:1. The catalyst loading was used with an increasing concentration from 1-6 wt. % of the kesambi oil. When the catalyst loading was 1 wt. %, this led to a biodiesel yield of 70.12 %. Second, the catalyst loading was increased from 1 to 2 wt. %, which resulted in an increasing yield from 70.12 % to 81.40 %. Again, the catalyst loading increases to 3wt% and it leads to yield of 90.12 %. The maximum biodiesel yield was achieved at catalyst loading of 4 % i.e., 92.29 %. Further increasing in catalyst amount results into decreased in yield [18].

5.2 Effect of Reaction Temperature

The biodiesel was synthesized at 60 °C. The biodiesel conversion was tested at various temperatures. Initially, the synthesis was done at 40 °C and 50 °C, and the results showed an incomplete reaction, then the temperature was maintained at 60 °C, the biodiesel yield was 92.2 %. Further, the temperature was increased, and the yield was lesser. Again at 70 °C and 80 °C, it tends to decrease slightly. Hence an optimum temperature is required for the synthesis of biodiesel [14].

5.3 Effect of Reaction Time

A proper reaction time is necessary for an optimum biodiesel yield. The author reported that the biodiesel was synthesized using Ni doped transition metal oxide Zn catalyst by taking a 1:8 molar ratio of oil to methanol. A conversion of 95 % was attained at 60 min. Further reaction time was increased with the increase in temperature and hence results in a better yield [20].

Alumina-supported zinc oxide catalyst was used for the synthesis of biodiesel from kesambi oil. The reaction was conducted at 1 h intervals starting from 1 to 7 h. With the increase of time, there is a significant increase in the biodiesel yield. The optimum temperature for this investigation was found to be at 60 °C. The maximum yield achieved was 92.31 % at 7 h [17].

5.4 Effect of Molar Ratio

For a good transesterification process, proper methanol to oil molar ratio is of utmost importance. So, a better ratio ends up in an increase in the percentage of biodiesel yield. An appropriate ratio increases the reaction rate. Semwal and his group reported the effect of molar ratio (Jatropha oil: Methanol). The molar ratio was tested from 1:5 to 1:30. Initially, the molar ratio was taken as 1:5. This ratio resulted into a complete conversion to methyl ester in 10 h. The ratio was further increased to 1:20 which resulted into a complete conversion of methyl ester in 3 h. Further, the ratio was increased from 1:20 till 1:30; the reaction time remains the same [19].

To study the influences in the biodiesel yield, Feyzi et al. reported that oil:methanol molar ratio was varied from 1:3 to 1:18. The reaction time was 4 h and the catalyst loading was 3 wt. % at 338 K. The biodiesel yield was 31.7 %. The molar ratio was gradually increased, and it was found that the maximum biodiesel yield of 96.9 % was achieved at 18:1 (methanol to oil molar ratio). Further increase in the molar ratio did not show any changes in the biodiesel yield [4].

6. CONCLUSIONS

Several transition metal oxide nanocatalysts have been discussed for biodiesel synthesis. Transition metal oxides are a better replacement for the homogenous catalyst. For the synthesis of biodiesel parameters such as the effect of temperature, time, and molar ratio plays an important role in the maximum biodiesel yield. The reactions at optimum parameters give maximum yield. A slight increase or decrease of the said parameters does not have any effect on the biodiesel yield. Thus, transition metal oxides are a good substitute for homogeneous catalysts and have a potential for reusability.

ACKNOWLEDGEMENTS

The authors are also thankful to the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), India for the financial support (EMR/2016/002430) to carry out this research work.

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Наночастинки оксидів перехідних металів для виробництва біопалива

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Виснаження запасів викопного палива та зростання населення призвели до пошуку альтернативних ресурсів. Біодизель є альтернативою викопному паливу. Його можна отримати з рослинних олій, тваринних жирів та відходів кулінарної олії. Переетерифікація – це процес, який використовується для синтезу біодизеля. За синтез біодизеля переважно відповідають два типи каталізаторів. Це гомогенні та гетерогенні каталізатори. Комерційно гомогенні каталізатори в основному використовуються в промисловості для синтезу біодизеля. Гомогенний каталізатор потребує промивання водою для видалення домішок, тому вартість виробництва висока. Найважливішим недоліком є те, що одного разу використаний каталізатор не може бути використаний повторно. Гетерогенний каталізатор має багато переваг у порівнянні з гомогенним каталізатором, наприклад, можливість повторного використання та відсутність необхідності промивання водою. Серед гетерогенних каталізаторів перехідні метали можуть бути використані для виробництва біодизеля. Вони відносяться до d-блоку періодичної таблиці. Багато дослідників повідомляли про синтез біодизеля за допомогою нанокаталізаторів з оксидів перехідних металів. Каталізатори на основі оксидів перехідних металів є гарною заміною для синтезу біодизеля. Вони мають гетерогенні властивості та перевагу повторного використання. Крім того, каталізатори на основі оксидів перехідних металів підвищують швидкість реакції і, таким чином, забезпечують вищий вихід біодизеля.

Ключові слова: Синтез, Біодизель, Гетерогенний, Оксид перехідного металу, Каталізатор, Повторне використання.