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ARTICLE



Biodiesel production via esterification of oleic acid catalyzed by MnO₂@Mn(btc) as a novel and heterogeneous catalyst

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Funding information Islamic Azad University, Shahreza Branch The main objective of this study is to develop efficient and environmentally benign heterogeneous catalysts for biodiesel production. For this purpose, a heterogeneous MnO₂@Mn(btc) catalyst was prepared by the solvothermal method, and the prepared catalyst was tested for the esterification of oleic acid. Various techniques such as X-ray diffraction, scanning and transmission electron microscopy, Brunauer–Emmett–Teller (BET) method, infrared spectroscopy, thermogravimetry, and NH₃-TPD (temperature programmed desorption) analysis were employed for the characterization of the solid catalyst. The solid catalyst with MnO₂@Mn(btc) loading of 15% showed high catalytic activity and long durability in the esterification of oleic acid, in which the fatty acid methyl ester yield reached 98% consecutively for at least five cycles under mild conditions.

KEYWORDS

biodiesel, esterification, heterogeneous catalyst, metal-organic frameworks (MOFs), oleic acid

1 | INTRODUCTION

Methyl and ethyl esters derived from vegetable oils or animal fat, known as biodiesel, have acceptable ability as an alternative to diesel fuel. Biodiesel consisting of long-chain fatty acid methyl esters (FAMEs) has appeared as a usable alternative fuel with the benefits of non-toxicity, renewability, biodegradability, and low emission profiles.^[1,2] The conventional method of producing biodiesel from vegetable oils involves the use of alkali catalysts, which, in the presence of free fatty acids (FFAs), form soap, which is undesirable, as it consumes the catalyst, makes separation of products more complicated, and decreases the biodiesel yield. Instead of using an alkali catalyst, an acid catalyst can be employed to convert the FFAs into biodiesel through the esterification reaction.^[3–5] In recent years, many surveys on catalysts for the esterification or transesterification step have indicated the use of sulfated alumina,^[6] carbon-based solid acid,^[7] supported heteropolyacids,^[8] cation-exchange resins with strong acidity,^[9] waste silicone solid base,^[10] fe304@gly,^[11] LiFe $_5O_8$ -LiFe O_2 ,^[12] Li $_2$ Ti O_3 ,^[13] or Li $_4$ Si O_4 .^[14]

These catalysts can replace sulfuric acid and thereby solve process problems such as environmental pollution and tool corrosion. However, the synthesis of these catalysts is quite complicated, they are hard to recycle, and their production cost is high. Therefore, it is vital to develop efficient, environmentally friendly, and novel catalysts for the synthesis of biodiesel by esterification.^[15]

Metal-organic frameworks (MOFs) are a novel class of inorganic–organic hybrid materials constructed from inorganic metal nodes and organic linkers. Their structurally sequenced and molecularly tunable aspects make them a perfect framework to assimilate distinct functional moieties. The integration between various individual doped species will provide such composite materials with excellent potential applications, notably in the catalytic field. High surface areas, controllable pore sizes, and tunable pore environments of MOFs would promote the MOF supports to trap different nanoparticles (NPs).^[16–20] Moreover, the crystalline porous

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structure, together with heteroatom donors on MOFs, would effectively limit the accumulation and migration of small, active catalytic NPs in the solid state, thereby making the NPs involved in NPs@MOFs catalysts to be highly active and reusable.^[21]

 MnO_2 with the benefits of environmental friendliness, ideal cycle stability, natural abundance, low cost, and efficient charge–discharge characteristics has turned out to be a promising material for catalysts. Wang et al. expanded the synthesis of mesoporous MnO_x for catalytic oxidation removal of low-concentration HCHO.^[22] The $MnO_x/HZSM$ -5 system served as catalyst for the oxidation of toluene,^[23] and decontamination of sulfur mustard was reported by MnO_2 -ZnO.^[24] The aim of this work was to examine solid $MnO_2@Mn(btc)$ catalysts' use in biodiesel production and evaluate the optimum values of the ethanol/oil ratio, catalyst amounts, reaction time, and reaction temperature. Furthermore, the $MnO_2@Mn(btc)$ catalyst was highly active and air-insensitive and could be reused for at least 10 cycles without loss of activity.

2 | RESULTS AND DISCUSSION

2.1 | Physicochemical characterization

The Fourier transform infrared (FT-IR) spectra of the Mn(btc) and MnO₂@Mn(btc) are shown in Figure 1. The Mn–O stretching vibration appears at 690 cm⁻¹.^[25] The broad band due to the symmetric stretching vibration of water is at 3,406 cm⁻¹.^[26] The asymmetric and symmetric stretching vibrations of the bound carboxylic groups (CO₂M) appear at 1,631–1,500 and 1,441–1,372 cm⁻¹, respectively.^[27] The bands occurring at 853 and 759 cm⁻¹ are clearly related to the stretching and out-of-plane deformation vibrations of the of benzene C–C and C–H groups, respectively. Complete deprotonation of the btc ligand is



FIGURE 1 FTIR spectra of (a) Mn(btc) and (b) MnO₂@Mn(btc)

proved by the absence of the absorption bands in the region $1,680-1,800 \text{ cm}^{-1}$.^[28]

The X-ray diffraction (XRD) patterns of hollow MnO_2 , Mn(btc), and $MnO_2@Mn(btc)$ are displayed in Figure 2. The similarity of the diffraction peaks of Mn(btc) and MnO_2@Mn(btc) suggests that the loading of the MnO₂ species has hardly changed the framework of Mn(btc). Because of relatively low concentration and the good dispersion of the MnO₂ species on Mn(btc), the characteristic diffraction peaks attributed to MnO₂ on the catalysts are not observed.

The scanning and transmission electron microscopy (SEM and TEM) images of the MOF-derived MnO₂@Mn (btc) particles, shown in Figure 3, suggest they are well-



FIGURE 2 XRD patterns of (a) hollow MnO₂, (b) Mn(btc), and (c) MnO₂@Mn(btc)



FIGURE 3 (a-e) SEM image with different magnifications. (f) TEM image of MnO₂@Mn(btc)

shaped rectangular bars with smaller broken particles in the range $3-16 \,\mu\text{m}$ in length, $0.2-2 \,\mu\text{m}$ in width, and $150-200 \,\text{nm}$ in thickness, with a comparatively smooth surface.

Figure 4 shows the thermal decomposition of the $MnO_2@Mn(btc)$ catalyst precursor. As can be seen from the thermogravimetry (TG) curves, the TG profile shows two mass loss events. The initial mass loss of 22.85% accompanied by an endothermic event occurs in the temperature range 25–240°C and is due to the loss of physically absorbed water and dimethylformamide (DMF). The second mass loss of 71.41%, overlapping a broad endothermic DTA peak over a wide temperature range of 240–665°C, refers mainly to the thermal decomposition of $MnO_2@Mn(btc)$ into their corresponding metal oxides. Beyond 665°C, there is almost no mass loss detected in the TG curve. These thermal analysis results suggest that the thermal decomposition of metal oxide precursors is completed at a temperature of 665°C.

The Brunauer–Emmett–Teller (BET)-Barrett Joyner Halenda (BJH) adsorption isotherms are depicted in Figure 5. The N₂ adsorption curves (Figure 5) of MnO₂@Mn(btc) obviously represent type IV isotherms, which prove that the samples would include both microporous (diameter < 20 Å) and mesoporous materials, based on the IUPAC categorization ^[29]. MnO₂@Mn(btc) gives a BET surface area of 10.867 m²/g and a pore volume of 0.039 cm³/g.

The NH₃ temperature programmed desorption (TPD) curve of $MnO_2@Mn(btc)$ (Figure 6) shows three peaks. The two peaks at around 414 and 456°C imply the weak acidic sites and the third peak at around 540°C displays the strong acidic sites. These strong acidic sites are due to the Lewis acidity of MnO_2 NPs. It should be noted that Mn(btc) decomposed at about 300°C, so there exists the possibility that the NH₃ adsorption could destroy the structural integrity of Mn(btc).^[30]



FIGURE 4 N₂ adsorption-desorption isotherms and (insert) pore size distributions calculated by the BJH method of Pd@Mn(btc)



FIGURE 5 (a) TG (b) DTG, and (c) DTA analysis of MnO₂@Mn(btc)

$\label{eq:2.2} \begin{array}{c} | & \mbox{Effects of esterification reaction conditions on the} \\ \mbox{catalytic activity of } MnO_2@Mn(btc) \end{array}$

2.2.1 | Effect of molar ratio between ethanol and oleic acid The molar ratio of ethanol to oleic acid is one of the significant parameters that influence the ester yield. As displayed in Figure 7, with the other experimental conditions maintained constant, the molar ratio of ethanol to oleic acid was



FIGURE 6 NH₃-TPD spectra of $MnO_2@Mn(btc)$ measured between 100 and 900°C



JOURNAL OF THE CHINESE

FIGURE 7 Molar ratio experiments run at 100°C and catalyst amount of 3% with the final conversion shown for each separate experiment with ratios between moles of ethanol and moles of fatty acid of 4:1, to 20:1

varied from 4:1 to 20:1. The conversion of oleic acid is enhanced because the excess ethanol moved the equilibrium to the product side when the molar ratio is increased from 4:1 to 12:1. However, when the molar ratio is further increased to 12:1, the conversion of oleic acid reduced. It continues to decrease when the ratio is further increased to 20:1. It is considered that further increase in ethanol molecules may overfill the active sites of the catalyst, thus obstructing the protonation of oleic acid at the active sites.^[25] Therefore, besides the excess of the reactant shifting the equilibrium, the higher conversion could be ascribed to the accessibility of the active sites. In addition, further excess of ethanol may also insert more water, which may react with the FAME to transform it back to oleic acid. Thus, the ratio 12:1 was found to be the optimal ethanol/oleic acid molar ratio.



FIGURE 8 Catalyst amount experiments run at 100° C and the ratio between moles of ethanol and moles of fatty acid of 12:1 with catalyst amount at 1, 3, and 5%



Catalyst dosage is another essential parameter that determines the ester yield. As illustrated in Figure 8, the $MnO_2@Mn(btc)$ amount is varied from 1% to 5% w/w of oleic acid. The results demonstrate that when the catalyst dosage is increased from 1 to 3 wt%, the FAME yield increases from 82% to 100%. It may be that there are not sufficient active sites for the reaction at low catalyst dosages and extra catalyst is required. However, upon further increase of the catalyst dosage from 3 to 5 wt%, no enhancement in the FAME yield is detected. This means 3 wt% of the catalyst is optimal for this reaction.

2.2.3 | Effect of reaction temperature

The effect of reaction temperature on the FAME yield in MnO₂@Mn(btc)-catalyzed esterification of oleic acid was examined, and the results are shown in Figure 9. The reaction temperatures considered were 80, 100, and 120°C. It can be seen that the activity of MnO₂@Mn(btc) is nearly the same at 100 and 120°C. One possible cause for the reduction in activity at 80°C may be the accumulation of the water molecules generated on the surface that block the active sites. It is seen that a temperature higher than the boiling point of water may help decrease the chance of the asformed water molecules remaining on the surface of the catalyst, which finally becomes strongly bounded to the active sites and is hard to remove even when the catalyst is washed and regenerated. As a low reaction temperature has considerable economic advantage, 100°C is chosen as the optimal reaction temperature. In short, in the MnO₂@Mn(btc)catalyzed esterification of oleic acid, the FAME yield could reach 98% consecutively for at least five cycles under the following optimal conditions: the molar ratio of ethanol to oleic acid 12:1, 3 wt% catalyst, reaction temperature 100°C, and reaction time 12 hr.



FIGURE 9 Effect of reaction temperature on MnO₂@Mn(btc)-catalyzed esterification of oleic acid with ethanol. Reaction conditions: 3% MnO₂@Mn(btc), molar ratio of ethanol to oleic acid 12:1

3 | EXPERIMENTAL

A Perkin Elmer Spectrum 65 spectrophotometer was used to record the infrared spectra in the range 400-4,000 cm⁻¹ using KBr pellets. Cu Ka (1.54056 Å) radiation with automatic control was employed to obtain the powder XRD diffraction patterns on Bruker D8 ADVANCE and PW1830 instruments. Adsorption/desorption of nitrogen at liquid nitrogen temperature was carried out to determine the BET specific surface areas and pore volumes of the catalysts, using a Micromeritics BELSORT mini II instrument. The samples were outgassed at 623 K for 12 hr under a vacuum of 10^{-4} Pa prior to the adsorption measurements. The catalyst's pore sizes were arrived at from the peak positions of the distribution curves detected by the adsorption branches of the isotherms. In NH₃-TPD (Nano sort-NS91), 0.1 g of the catalyst was taken in a U-shaped, flow-through quartz sample tube. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a BAHR-STA-504 apparatus. Thermal analyses were carried out in the range of 25-800°C, at the heating rate of 10 K/min.

3.1 | Preparation of Mn(btc)

Synthesis of mesoporous Mn(btc) was done according to the literature procedure ^[31]. Initially, a mixture of MnCl₂cdH₂O (3.0 mmol, 0.5937 g), H₃BTC (1.0 mmol, 0.210 g), DMF (5.0 mL), and distilled water (5.0 mL) was placed in a 25-mL Teflon-lined stainless autoclave and heated to 120°C at a rate of a 10°C/hr under autogenous pressure for 5 days. Then, the autoclave was cooled to room temperature at a rate of 5°C/hr. Finally, the obtained colorless crystals were filtered, washed with DMF and distilled water, and then dried in air.

3.2 | Preparation of hollow MnO₂

At the beginning, in 70-mL portions of distilled water, MnSO₄·H₂O (0.169 g) and NaHCO₃ (0.84 g) were separately dissolved.^[32] Then, 7 mL of ethanol was added to the MnSO₄ solution under stirring, and the NaHCO₃ solution was then directly added. The obtained mixture was then kept at room temperature for 3 hr, followed by washing many times with distilled water and ethanol. For MnO₂ hollow microspheres, 0.1 g of the as-prepared MnCO₃ solid microspheres were distributed in 20 mL of H₂O. Next, 5 mL of 0.032 mol/L KMnO₄ solution was added under stirring. After 6 min, 5 mL of 0.01 mol/L HCl was added and the mixture stirred for 1 min. Finally, MnO₂ hollow microspheres were obtained after centrifugation, which were washed several times with water.

3.3 | Preparation MnO₂@Mn(btc)

Mn(btc) (1 g), hollow MnO₂ (0.15 g), and 20 mL of ethanol were mixed together and the mixture was transferred to a

Teflon-lined stainless autoclave for 6 hr at 80°C. The resulting black precipitate was filtered under vacuum, washed several times with deionized water, and finally dried at 120°C for 12 hr.

4 | CONCLUSIONS

In summary, novel and efficient catalyst MnO₂@Mn(btc) was prepared under hydrothermal conditions and characterized by XRD, SEM, BET, IR, TGA, and NH₃-TPD analyses. The catalytic activity of MnO₂@Mn(btc) was investigated for biodiesel production from the esterification of the FFA oleic acid. The significant advantages of this procedure are short reaction times, high yields, mild reaction conditions, and reusability of catalyst for several times.

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JOURNAL OF THE CHINESE CHEMICAL SOCIETY

6

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