Article

Biodiesel Production Using a Banana Peel Extract-Mediated Highly Basic Heterogeneous Nanocatalyst

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Abstract: Greener methods for the production of nanoparticles (NPs) are highly investigated to minimize the harmfulness of chemical synthetic processes. In this study, CaO (calcium oxide) NPs were synthesized using extracts of banana (Musa acuminata) leaves. The precipitate of Ca(OH)₂ (calcium hydroxide) obtained from the precursor Ca(NO₃)₂ (calcium nitrate) was calcined at 900 °C in a muffle furnace to form CaO. The catalytic activity of the prepared CaO was studied in transesterification of soybean oil. From the ¹H-NMR analysis, a high soybean oil conversion of 98.0% was obtained under the optimum reaction conditions of 8 wt% of catalyst loading, 2 h reaction time, and a 15:1 methanol to oil molar ratio at 65 °C temperature. ¹H-NMR, ¹³C-NMR, and FT-IR spectroscopic studies of the product proved the formation of biodiesel. The CaO nanocatalyst was characterized using XRD, SEM-EDS, TEM, FT-IR, XPS, and BET analyses. The average diameter of the catalyst was determined as 46.2 nm from TEM analyses. The catalyst can be used successfully even after five active reaction cycles without substantial loss in the activity of the catalyst.

Keywords: transesterification; biodiesel; heterogeneous catalyst; CaO; biosynthesis; Musa acuminata

1. Introduction

The escalating energy consumption and the subsequent environmental concerns are imposing a shift from conventional fossil fuels to renewable biofuels [1]. To meet the rising need for energy and simultaneously minimize CO₂ (carbon dioxide) emissions to hold back the agitating rate of global warming in a sustainable and harmonious way, the use of renewable resources is crucial. From this perspective, biodiesel has been employed as a sustainable alternative to conventional non-renewable fossil fuels [2]. Biodiesel can be extracted from renewable benign sources like vegetable oils, animal fats, etc., by carrying out esterification or transesterification [3]. Traditional diesel engines can run with biodiesel without any changes in the engine [4]. In the last few decades, the biodiesel industry has been growing; emphasizing the need for more research on this field.

In the present scenario, commercial biodiesel is prepared using homogenous catalysts by transesterification of C₁₇–C₂₆ triglyceride components of lipids with C₁–C₄ alcohols into fatty acid methyl esters (FAMEs). Various alcohols like methanol, ethanol, amyl alcohol, etc., are used for this transformation but methanol is considered to be the most suitable alcohol in terms of reactivity, green chemistry metrics, and cost-effectiveness [5–7]. In transesterification with homogenous catalysts, side reactions such as hydrolysis of the ester [8,9] and saponification [10] can occur. Even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced esters [8,9], which may lead to an undesirable saponification reaction. The soap molecules generated will act as a surfactant between the two final immiscible products (biodiesel and glycerol) making their separation difficult [10].
It also may damage the equipment. Poor isolation from reaction mixture, single time use, and sensitivity to water are some other disadvantages of homogenous catalysts, which confine their practical use in biodiesel production [11]. In recent years, heterogeneous catalysts have been broadly investigated because of environmental concerns and the need for sustainable development. They have advantages such as easy separation, recyclability, and non-toxicity [12]. Frequently used heterogeneous catalysts for biodiesel production are Al2O3 (aluminum oxide) [13], CaO (calcium oxide) [14], TiO2 (titanium dioxide) [15], ZrO2 (zirconium dioxide) [16], ZnO (zinc oxide) [13], SrO (strontium oxide) [17], Mg-Al hydroxylate [18], MgO (magnesium oxide) [13], zeolites [19], etc.

The large-scale biodiesel production necessary to satisfy global energy requirements has directed researchers’ interest towards the synthesis of eco-friendly green and sustainable heterogeneous catalysts from renewable sources [13]. Bio-derived catalysts are highly appreciated for biodiesel production over various of synthetic heterogeneous catalysts produced by various chemical industries because of their sustainability and green nature [13]. For biosynthesis of NPs, plant extracts from various parts of the plant body such as fruits, fruit peels, trunks, leaves, tannin, etc., and also from living or inactive parts of the plant can be utilized. Many living microorganisms contain biomaterials such as flavonoids and phenolic acids that can reduce the metal ions to NPs; additionally, they contribute to stabilizing the NPs. Furthermore, these bio-components are capable of controlling the particle size distribution [20]. Many reports are found on the synthesis of NPs with organic biomass extracts such as ZnO NPs with aqueous oat extract [21] and Halimeda opuntia extract [22]. Also, synthesis of Ag (silver) NPs with coffee waste extract [23], cell-free Trichoderma reesei extract [24], and neem extract [25], etc., are investigated. But large numbers of investigations are still needed so that nanocatalysts can be prepared with benefits such as lower synthetic cost, effortless synthetic processes, environmental amiability, easy obtainability, secure handling, effective control of size and shape of the NPs, safer by-products, substantial efficient synthetic abilities, no use of hazardous chemicals, etc. [20].

Recently, many nanocatalysts have been utilized to produce biodiesel as shown in Table 1. Kattimani et al. [26] produced 93.1% of biodiesel using a magnetic NiFe3O4 catalyst and conducted a kinetic and thermodynamic investigation which revealed that the enthalpy and entropy of the system were ~27.5 kJ mol⁻¹ and ~0.18 kJ mol K⁻¹, respectively. In this study Acacia farnesiana was used both for catalyst preparation and also as the feedstock for biodiesel production [26]. The importance of using waste cooking oil for cost-effective biodiesel production was investigated in many studies [27,28]. Maleki et al. [27] reported the synthesis of a magnetic Fe3O4/SiO2@ZnO catalyst for biodiesel production from waste cooking oil (WCO). It was found that incorporation of SiO2 and ZnO NPs on the Fe3O4 surface led to a decrease in magnetic properties compared to the state of pure Fe3O4. An optimized biodiesel yield of 97.2% was obtained using response surface methodology (RSM) and Box–Behnken design (BBD) [27]. In another report, a new non-edible oil of Diospyros malabarica (Malabar ebony) was analyzed for the synthesis of eco-friendly biodiesel using newly synthesized green NPs of CdO (cadmium oxide) prepared from a leaf extract of Buxus papillosa via a biological method followed by an in situ wet impregnation approach [29]. In another study, a novel microbial strain, the Rhodotorula mucilaginosa strain SML (RM-SML), was used as a source of oil for biodiesel production using a CaO catalyst. A maximum of 38.8% CaO was obtained by calcination of eggshells at 850 °C muffle temperature for 3 h [30]. Xie et al. [31] investigated used frying oil (UFO) as a biodiesel feedstock to reduce environmental pollution and compared the activity of the novel nanocatalyst CaO-MgFeO3@K2CO3 with that of CaO. The biodiesel yield obtained with CaO-MgFeO3@K2CO3 was higher (96.5%) than that given by CaO (93.5%). Additionally, thermodynamic and kinetic studies of transesterification showed that the biodiesel generation process using CaO-MgFeO3@K2CO3 was endothermic (ΔH° = 61.9 kJ/mol) and nonspontaneous (ΔG° > 0). Also, the catalyst had fewer
negative impacts on the environment than common catalysts such as KOH and NaOH, as found from life cycle assessments [31].

Hanif et al. [32] synthesized a novel Li-TiO$_2$/feldspar catalyst (a Li-impregnated TiO$_2$ catalyst loaded on feldspar mineral) and investigated five waste plant oils—*Citrullus colocynthis* (bitter apple), *Pongamia pinnata* (karanja), *Sinapis arvensis* (wild mustard), *Ricinus communis* (castor), and *Carthamus oxyacantha* (wild safflower)—for biodiesel production with the aim to look for a universal transesterification catalyst. All the feedstocks gave satisfactory biodiesel yields (>80–90%) with karanja giving the maximum yield indicating that it is a universal catalyst with good efficiency [32]. Munir et al. [33] studied biodiesel production from a novel, non-edible, waste feedstock *Carthamus lanatus* L. seed oil (SSO) using a novel nanocatalyst, cobalt–tungstate-loaded reduced graphene oxide (CoWO$_3$@rGO). The catalyst showed excellent reusability, giving 93.5% yield after the ninth reaction cycle. In another report, a Bi$_2$O$_3$ (bismuth oxide) nanocatalyst was synthesized using *Euphorbia royealeana* (Falc.) Boiss. leaves extract [34]. Thermodynamic and kinetic studies conducted by them showed the activation energy to be $0.241 \times 10^4$ cal/mol (0.574 kJ mol$^{-1}$), the enthalpy as 11.3 kJ mol$^{-1}$, and the entropy as $-0.043$ kJ mol$^{-1}$K$^{-1}$ [34]. Maleki et al. [35] synthesized a novel UiO-66-NH$_2$/ZnO/TiO$_2$ nanocatalyst to produce biodiesel from dairy waste scum oil (DWSO). The catalyst exhibited a high specific surface area of 568 m$^2$g$^{-1}$. In 30 min, 98.7% of biodiesel conversion was obtained, which was the highest methyl ester achieved from DWSO to date. The process was found to be nonspontaneous and endothermic as the Gibbs free energy and the enthalpy value were 88.9 and 46.0 kJ mol$^{-1}$, respectively. In a recent study, Abu-Ghazala et al. [36] reported a CaO/Al$_2$O$_3$ catalyst prepared using industrial aluminum waste for biodiesel production from waste cooking oil. Kinetic and thermodynamic investigations displayed that the activation energy and entropy of this transesterification were 39 kJ mol$^{-1}$ and $-161$ J mol$^{-1}$K$^{-1}$, respectively. This catalyst showed excellent catalytic activity due to its high basicity as a result of the electronic effect of the supporting Al$_2$O$_3$ on CaO, facilitating hydrogen abstracting to form methoxide [36]. Furthermore, biofuel production processes could be intensified which can boost the economic and environmental features of the whole process [37]. Wang et al. [37] used a novel bionic flow-induced peristaltic reactor reporting a conversion rate of soybean oil of 528% min$^{-1}$, which was 17–60 times higher compared to other intensified reactors.
Table 1. Latest research works for biodiesel production using nanocatalysts.

<table>
<thead>
<tr>
<th>Nanocatalyst</th>
<th>Size (nm)</th>
<th>Biodiesel Feedstocks</th>
<th>BD Yield (%)</th>
<th>Reaction Conditions</th>
<th>Reusability Cycles</th>
<th>BD Yield with Reused Catalyst (%)</th>
<th>Activation Energy (kJ mol⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe₂O₄ (magnetic)</td>
<td>~ 15.5 a</td>
<td><em>Acacia furnesiana</em></td>
<td>93.1</td>
<td>14:1, 4.61, 65, 53</td>
<td>4</td>
<td>80</td>
<td>~ 44.5</td>
<td>[26]</td>
</tr>
<tr>
<td>Fe₃O₄/SiO₂@ZnO (magnetic)</td>
<td>10.4 b</td>
<td>WCO</td>
<td>97.2</td>
<td>9.90:1, 2.67, ~30.1</td>
<td>7</td>
<td>88.4</td>
<td>39</td>
<td>[27]</td>
</tr>
<tr>
<td>CaO/Al₂O₃</td>
<td>-</td>
<td>WCO</td>
<td>95 d</td>
<td>7:1, 3, 45, 180</td>
<td>5</td>
<td>62.9 d</td>
<td>39</td>
<td>[36]</td>
</tr>
<tr>
<td>CdO₂</td>
<td>45 c</td>
<td><em>Diospyros malabarica</em></td>
<td>94</td>
<td>9:1, 0.5, 90, 180</td>
<td>6</td>
<td>&lt;60</td>
<td>-</td>
<td>[29]</td>
</tr>
<tr>
<td>CaO</td>
<td>10 d</td>
<td>RM-SML</td>
<td>98.3 d</td>
<td>8:1 g, 3.5, 200W i 90</td>
<td>7</td>
<td>66.3 d</td>
<td>-</td>
<td>[30]</td>
</tr>
<tr>
<td>CaO-MgFe₂O₄@K₂CO₃</td>
<td>&lt;100 e</td>
<td>UFO</td>
<td>96.5</td>
<td>18:1, 4, 70, 300</td>
<td>4</td>
<td>&gt;90</td>
<td>64.6</td>
<td>[31]</td>
</tr>
<tr>
<td>Li-TiO₂/feldspar</td>
<td>41.8 a</td>
<td>Karanja oil</td>
<td>98.4</td>
<td>10:1, 2, 50, 120</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[32]</td>
</tr>
<tr>
<td>CoWO@rGO</td>
<td>23.4 a</td>
<td>CSO</td>
<td>99.7</td>
<td>12:1, 0.8, 65, 120</td>
<td>9</td>
<td>93.5</td>
<td>178</td>
<td>[33]</td>
</tr>
<tr>
<td>B₡O₃</td>
<td>43 c</td>
<td>Cannabis sativa</td>
<td>92</td>
<td>12:1, 1.5, 92, 210</td>
<td>9</td>
<td>33.78</td>
<td>0.574</td>
<td>[34]</td>
</tr>
<tr>
<td>UiO-66-NH₂/ZnO/TiO₂</td>
<td>28.3 e</td>
<td>DWSO</td>
<td>98.7 d</td>
<td>9.8:1, 2, 61, 30</td>
<td>7</td>
<td>90.14 d</td>
<td>48.7</td>
<td>[35]</td>
</tr>
</tbody>
</table>

a = crystallite size; b = pore size; c = particle size; d = conversion of feedstock; f = methanol to oil molar ratio, catalyst wt%, temperature, time in min; g = v/v; i = ultrasonic power.
CaO is a widely used solid (heterogeneous) catalyst that helps in transesterification of various precursors to biodiesel. It is abundant and inexpensive in comparison to many other catalysts. It is eco-friendly and does not cause any corrosion of equipment. CaO comes with safer handling; it is highly basic and does not dissolve in the reaction mixture making its reuse and regeneration very efficient. All these qualities make CaO a very proficient catalyst in the field of biodiesel. Owing to the aforementioned benefits, a lot of academics are investigating CaO so that its general potential and efficiency can be upgraded. It has been found that preparing CaO in nano form increases its surface area and results in enhanced activity in catalyzing transesterification of the feedstocks [14]. Materials with dimensions of 1–100 nm are termed as nano materials. A lot of recent studies are investigating nanocatalysts for the production of biodiesel. CaO prepared in nano form has been investigated in transesterification in some studies [14,38]. In the present work, we have prepared CaO NPs using extract of banana (Musa acuminata) leaves using Ca(NO₃)₂ as a precursor. From our extensive literature survey it has been observed that banana peel was never utilized to synthesize a CaO catalyst to the best of our knowledge. Plants contain a wide range of bioactive compounds which include alkaloids, flavonoids, terpenoids, steroids, etc., which act as reducing agents in the synthesis of NPs [39]. The organic compounds in banana peel extract help to stabilize the CaO NPs. The catalyst has been extensively analyzed using many analytical techniques and finally it was used to produce biodiesel from soybean oil.

2. Materials and Method

The synthetic procedure for the banana peel extract-mediated CaO catalyst and the different analytical techniques for the characterization of the catalyst and the biodiesel product are discussed in this section.

2.1. Chemicals Used

Ca(NO₃)₂ (>99%) and NaOH (sodium hydroxide) (>97%) were purchased from Sigma Aldrich, Bangalore, Karnataka, India. Banana leaf extract was prepared by collecting banana leaves from NIT Silchar campus.

2.2. Preparation of Catalyst

Fresh banana leaves were collected from NIT Silchar campus. They were washed using tap water and were kept inside an oven for 6 to 7 days. The dried leaves were cut into tiny pieces, followed by fine grinding. The ground leaf powder was kept in a soxhlet apparatus with a mixture of ethanol and water (40:60 v/v) for 12 h, after which the extract was collected. It was stored in a glass bottle inside the refrigerator for catalyst preparation. To prepare Ca(OH)₂, equal amounts of plant extract and 1M Ca(NO₃)₂ were put in a beaker. A concentration of 0.1M NaOH was added to the above mixture dropwise until a significant amount of Ca(OH)₂ precipitate had formed. The contents of the beaker were then filtered and washed to obtain the neutral Ca(OH)₂. It was then dried and finally calcined at 900 °C for 3 h in a muffle furnace to get CaO. The CaO catalyst was stored safely for further reactions and characterizations.

2.3. Characterization of Catalyst

In order to find the crystallite size of the CaO nanocatalyst, Cu-Kα radiation with 2θ = 10–90° was used to perform X-ray powder diffraction (XRD) on a PANalytical X’Pert Pro diffractometer. The working current and voltage were 100 mA and 40 kV, respectively. To determine the various functional groups present, Fourier transform infrared spectroscopy (FTIR-Spectrum 100, Perkin Elmer, USA) was performed within a range of 550–4000 cm⁻¹. To study the rate of weight loss of the sample with respect to temperature, a Metter Toledo TGA/DSC was used which gave the required TGA data in the range 50–850 °C with a heating rate of 10 °C min⁻¹ at a constant flow of N₂. To determine the sur-
face area and porosity of the catalyst using the Brunauer–Emmett–Teller (BET) technique, a QuantaChrome Nova 2200e was used. To study the morphology of the catalyst, scanning electron microscopy (SEM) using a JEOL JSM-7600F microscope was employed and energy dispersive X-ray spectroscopy (EDS) was performed at a beam current of 100 mA, a voltage of 30 kV, and a magnification power of 2000x. TEM photographs were taken using a JEOL JEM2100 microscope. The elemental composition of the catalyst was found using X-ray photoelectron spectroscopy using a K-alpha XPS spectrometer (Thermo) with a monochromatic Al kα X-ray source.

2.4. Transesterification of Methanol and Soybean Oil

The catalytic activity of the prepared CaO catalyst was investigated in transesterification of soybean oil. Soybean oil, methanol, and the catalyst were placed in a sealed pressure tube which was again kept on a hot metal plate equipped with magnetic stirrer. The reaction was carried out with a varying catalyst content, methanol to oil molar ratio (MTOR), reaction temperature, and time. The catalyst content was varied from 2 to 12 wt%, the MTOR from 6:1 to 18:1, the reaction temperature from 45 to 85 °C, and the time from 0.5 to 2.5 h. The progress of the reaction was continuously monitored using thin layer chromatography. After the attainment of maximum yield, the product was separated from the reaction mixture using centrifugation. Excess methanol present was evaporated using a rotary evaporator. The yield of biodiesel was calculated using (Equation (1)) [40], given by

$$\text{Biodiesel yield (\%)} = \frac{\text{Weight of biodiesel}}{\text{Weight of soybean oil}} \times 100$$ (1)

2.5. Characterization of Product

The product obtained in the transesterification reaction of soybean oil was investigated using various analyses. A Bruker Advance spectrometer (500 MHz) was utilized for 1H and 13C NMR studies. A GC-MS QP 2010 Ultra mass spectrometer configured with a GC-FID was used to study gas chromatography (GC). Finally, to determine the various functional groups present, Fourier transform infrared spectroscopy (FTIR-Spectrum 100, Perkin Elmer, USA) was performed.

2.6. Catalyst Reusability

The reusability of the catalyst is one of key indicators to evaluate the performance of the catalyst. The reaction was first conducted using the optimized reaction parameters. After completion of the reaction, the reaction mixture was centrifuged to isolate the catalyst. The catalyst was then washed with methanol and hexane for removal of impurities and unwanted substances. After that, the catalyst was dried in an oven for 5 h at 100 °C followed by calcination at 900 °C. Then it was utilized in the next reaction cycle and the catalyst washing, drying, and calcining steps were repeated. This way the catalyst was reused for four cycles under optimal reaction conditions.

3. Results and Discussion

The CaO catalyst and the biodiesel product were analyzed using different analytical techniques as explained below.

3.1. Catalyst Characterization

The CaO catalyst was characterized using XRD, FT-IR, TGA, BET, SEM-EDX, XPS, and TEM analyses to study its properties. Its activity and stability were examined in transesterification of soybean oil. The reused catalyst was again analyzed using SEM-EDX analysis.
3.1.1. X-ray Diffraction Analysis

The XRD pattern for the CaO nanocatalyst was recorded between $2\theta = 10^\circ$ and $70^\circ$ as shown in Figure 1. The XRD peaks were detected at $2\theta = 32^\circ$, $34^\circ$, $37^\circ$, $54^\circ$, and $64^\circ$, and they met the criteria set in the international center for diffraction data file for nanocatalyst CaO (JCPDS 37-1497) [41]. The data collected from the XRD analysis showed high clarity and crystallinity of the sample. The Debye–Scherrer equation (Equation (2)) was used for calculation of crystallite size of the nanocatalyst and it was found to be 36.8 nm.

$$D = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

Here, $k$ stands for the crystalline shape factor whose value is 0.9; $\lambda$ stands for wavelength of the X-ray; $\beta$ (FWHM) stands for full width at half maximum; $\theta$ stands for Bragg's angle.

![Figure 1. XRD patterns of the synthesized CaO nanocatalyst with Miller indices.](image)

3.1.2. Fourier Transform Infrared Spectroscopy Analysis

FT-IR analysis was carried out to find out the functional groups present in the catalyst and the results are presented in Figure 2. The band at 536 cm$^{-1}$ was due to vibration of Ca-O bonds [42,43]. The band obtained at 3642 cm$^{-1}$ indicated the presence of O-H bonds. The weak bands around 871 and 1466 cm$^{-1}$ were due to asymmetric C=O stretching of the carbonyl groups present in the catalyst species [43,44]. Thus, conversion of Ca(OH)$_2$ to CaO was pointed out by the FT-IR results, though a small amount of Ca(OH)$_2$ and CaCO$_3$ (calcium carbonate) was still there due to moisture and CO$_2$ absorption. Similar findings were reported by Habte et al. [42] and Roy et al. [43].
3.1.3. Thermogravimetric Analysis

The CaO nanocatalyst was investigated using TGA and the results are presented in Figure 3. It shows the rate of weight loss of the sample as a function of temperature. A weight loss of 1% is observed up to a temperature of 99 °C due to moisture evaporation from the sample. From 99 to 389 °C, the catalyst had undergone decomposition in N₂ environment leading to about 10% weight loss. Beyond 389 °C, further depletion of catalyst mass was observed, which was attributed to the oxidation of carbonaceous materials of the catalyst to CO₂ and CO (carbon monoxide) [13].

3.1.4. Brunauer–Emmett-Teller Analysis

BET analysis was performed to study the total surface area, pore size distribution, and total pore volume of the CaO catalyst. Figure 4 depicts the N₂ adsorption–desorption isotherm of the catalyst, which resembles a type IV hysteresis loop that specifically corresponds to mesoporous materials [45]. The estimated surface area, pore volume, and pore size of the catalyst were 10.9 m² g⁻¹, 0.022 cc g⁻¹, and 2.66 nm, respectively. Figure 4 shows that the evaluated size of the pores using the BET method match the range assigned for mesoporous materials. The available surface area, size, and structure of the
pores are highly influential in determining the rate of catalytic activity of a nanocatalyst. Pores are highly essential for easy and unhindered transfer of reactant and product molecules. Mesoporous materials speed up the reaction by facilitating the diffusion of reactants and products into the pores. Microporous materials on the other hand, let the reaction occur only at the entry of pores and lead to a noticeably lower rate of reaction than the mesoporous materials [46]. Thus, our mesoporous nanocatalyst CaO can boost the rate of the reaction significantly during biodiesel production.

![Graph](image)

**Figure 4.** N2 adsorption–desorption curve (main image) with BJH pore size distribution curve (inset) for the CaO catalyst.

3.1.5. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

SEM analysis was performed to study the morphology of the catalyst. The SEM images in dimensions of 10, 4, and 3 µm are depicted in Figure 5. According to the SEM images, the structure is determined to be very porous, containing a significant number of active sites. The shape and size of the particles are also uniform. Also, several aggregates with mesoporous and sheet-like structure were observed. Calcination may cause sintering and partial agglomeration of mineral particles resulting in the formation of aggregated particles with asymmetrical shapes and diverse sizes [40,47]. The elemental weight % as shown in Figure 5f, the SEM-EDX mapping, include Ca (43 wt%), O (46.4 wt%), C (9.1 wt%), and Si (0.7 wt%).
Figure 5. Representative scanning electron microscopy images (a–c) of the prepared CaO catalyst. Respective scale bars and magnifications: (a) 30 µm, 300 x; (b) 4 µm, 2.00 kx; (c) 3 µm, 3.00 kx; elemental mapping of prepared catalyst showing presence of (d) calcium and (e) oxygen; (f) the EDX spectrum with elemental composition (inset).

3.1.6. X-ray Photoelectron Spectroscopy

XPS analysis of a sample was performed to find out the constituents present on the surface. Figure 6a, below, illustrates the full scan XPS spectra of the CaO nanocatalyst. The predominant constituents present on the catalyst surface are oxygen (54.4%), calcium (22.4%), carbon (18.5%), silicon (2.17%), magnesium (1.59%), and phosphorus (0.82%). From Figure 6b, two peaks at 350.2 and 346.8 eV corresponding to Ca2p3/2 and Ca2p1/2 are observed for the Ca spectrum [48]. The binding energy separation of 3.4 eV is due to the result of spin-orbit splitting of Ca2p, which is in accordance with the results reported by Dhankar et al. [49]. One peak at 531.1 eV corresponding to metal oxide was found for oxygen O1s as shown in Figure 6c [50]. As depicted in XPS spectra of carbon in Figure 6d, the pattern obtained at 284.8 eV is due to C-C and the peak obtained at 289.7 eV is due to C=O bonds [51,52]. Traces of Mg and Si were also found on the catalyst’s surface, which could possibly be from the leaf extract.
Figure 6. (a) XPS survey spectrum of the CaO catalyst; experimental spectra of deconvolution for (b) Ca2p; (c) O1s; and (d) C1s.

3.1.7. Transmission Electron Microscopy

TEM was performed to study the quantitative measures of particles, the size distribution, and, basically, for morphology, as shown in Figure 7. TEM images defined the catalyst to be granular and powdered with a spherical shape. The granules were formed from a large number of smaller granules with an average diameter of 46.2 nm. The pictures show that there existed no agglomeration of the granules. Because of the porous nature of the CaO nanocatalyst, there was easy contact between the catalyst surface and the substrate, which was the reason for enhancement in the catalytic activity [53]. HRTEM images in Figure 7e reveal that the lattice fringes with an interplanar distance of 0.27 nm are consistent with the (202) plane of CaO.
Figure 7. HR-TEM images of the CaO catalyst: scale bars (a) 50 nm, (b) 50 nm, (c) 20 nm, (d) 20 nm, and (e) 2 nm; (f) particle size distribution curve.

3.2. Product Characterization

The product was characterized with FT-IR, NMR, and GC studies to confirm its production and stability.

3.2.1. Fourier Transform Infrared Spectroscopy Analysis

The product was analyzed with FT-IR as shown in Figure S1 (see Supplementary Material. Corresponding to stretching vibrations of the C-H bond of alkane, two peaks were observed at 2850 and 2922 cm\(^{-1}\). Peaks observed at 1355, 1465 and 700–720 cm\(^{-1}\) were results of C-H bending vibrations of the alkane groups present in biodiesel [54]. A sharp peak obtained at 1739 cm\(^{-1}\) was due to the presence of ester groups present in the product. Again, the stretching vibrations of the methyl ester functional group were observed between 1100 and 1350 cm\(^{-1}\) [54].

3.2.2. Nuclear Magnetic Resonance Analysis

NMR spectroscopy of the product was performed as shown in Figure S2. In the \(^1\)H-NMR spectra of biodiesel, a characteristic methoxy proton peak was obtained at 3.64 ppm as a singlet, and a characteristic \(\alpha\)-CH\(_2\) proton peak was observed at 2.28 ppm as a clear triplet. Formation of the desired product was proven by these two distinct peaks. Characteristic olefinic hydrogen peaks were seen at 5.31 ppm [55,56]. A quantitative estimation of soybean oil conversion was performed by using the integration areas of methoxy protons and \(\alpha\)-CH\(_2\) protons in Equation (3).

\[
\text{Conversion (\%)} = \left( \frac{2A_{OMe}}{3A_{\alpha-CH_2}} \right) \times 100
\]  

In the above equation, \(A_{OMe}\) represents the integration area of methoxy protons; \(A_{CH2}\) represents the integration area of \(\alpha\)-CH\(_2\) protons. On taking \(A_{OMe} = 1\) and \(A_{CH2} = 0.68\) from \(^1\)H-NMR spectroscopic data, the soybean oil conversion from Equation (3) is found to be 98.03\%. Biodiesel formation was also confirmed from \(^{13}\)C-NMR spectra studies as shown in Figure S2b (see Supplementary Material). Signals observed at 174.52 and 51.60 ppm were due to (-COO-) and (-CO-) which are characteristic peaks confirming the formation.
of biodiesel [55]. The peaks obtained at 130.27 and 128.14 ppm were due to the presence of unsaturated methyl esters in the biodiesel. Peaks were also observed at 22.82 and 24.21 ppm and were attributed to long chain carbon of biodiesel. Finally, the peak at 14.21 ppm indicated the presence of terminal carbon atoms of the methyl group [55].

3.2.3. Gas Chromatography

A gas chromatography study was conducted to find out the various types of fatty acid methyl esters present in biodiesel as shown in Figure S3 (see Supplementary Material). The biodiesel composition was further calculated quantitatively by analyzing the fatty acid methyl ester peak areas and the results are summed up in Table 2. The GC study revealed the extensive constituents present in the product to be 9-octadecenoic acid, methyl ester, (E) (37.7%), 6,9-octadecadienoic acid, methyl ester (36.2%), hexadecanoic acid, methyl ester (13.6%), and stearic acid, methyl ester (7.18%).
Table 2. GC-MS studies of biodiesel.

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Retention Time (min)</th>
<th>Free Fatty Acid Composition</th>
<th>Composition (%)</th>
<th>Corresponding Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.605</td>
<td>Hexadecanoic acid, methyl ester</td>
<td>13.6</td>
<td>C16:0</td>
</tr>
<tr>
<td>2</td>
<td>13.745</td>
<td>6,9-octadecadienoic acid, methyl ester</td>
<td>36.2</td>
<td>C18:2</td>
</tr>
<tr>
<td>3</td>
<td>13.775</td>
<td>9-octadecenoic acid, methyl ester, (E)</td>
<td>37.7</td>
<td>C18:1</td>
</tr>
<tr>
<td>4</td>
<td>13.860</td>
<td>9,12,15-octadecatrienoic acid, methyl ester, (Z,Z,Z)-</td>
<td>1.01</td>
<td>C18:3</td>
</tr>
<tr>
<td>5</td>
<td>13.905</td>
<td>Stearic acid, methyl ester</td>
<td>7.18</td>
<td>C20:0</td>
</tr>
<tr>
<td>6</td>
<td>14.965</td>
<td>Cis-11-eicosenoic acid, methyl ester</td>
<td>1.26</td>
<td>C20:1</td>
</tr>
<tr>
<td>7</td>
<td>15.090</td>
<td>18-methylnonadecanoic acid, methyl ester</td>
<td>1.60</td>
<td>C20:0</td>
</tr>
<tr>
<td>8</td>
<td>16.190</td>
<td>Docosanoic acid, methyl ester</td>
<td>1.37</td>
<td>C22:0</td>
</tr>
</tbody>
</table>
3.2.4. Physicochemical and Fuel Properties

The physicochemical properties of the biodiesel were tested as per ASTM standard as displayed in Table 3.

Table 3. Physicochemical and fuel properties of biodiesel produced under optimum reaction conditions.

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Limits</th>
<th>Present Biodiesel</th>
<th>Testing Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>&lt;0.79</td>
<td>0.32</td>
<td>D 664</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>0.86–0.90</td>
<td>0.885</td>
<td>D 1448–1972</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>≥130</td>
<td>147</td>
<td>D 93</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>−15 to +6</td>
<td>3.9</td>
<td>D 97</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>−3 to +12</td>
<td>3</td>
<td>D 2500</td>
</tr>
<tr>
<td>Water content (wt%)</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Heat value (MJ L$^{-1}$)</td>
<td>30–40</td>
<td>34</td>
<td>D 6571</td>
</tr>
<tr>
<td>Cetane number</td>
<td>≥47</td>
<td>77</td>
<td>D 6890</td>
</tr>
<tr>
<td>Kinematic viscosity (mm$^2$ s$^{-1}$)@ 40 °C</td>
<td>1.9–6.0</td>
<td>2.87</td>
<td>D 445</td>
</tr>
<tr>
<td>Sulphur content (wt%)</td>
<td>0.005</td>
<td>0.001</td>
<td>D 6751</td>
</tr>
</tbody>
</table>

3.3. Optimization of the Transesterification Process

In order to ensure an optimized biodiesel yield, various reaction conditions such as MTOR, catalyst loading, reaction time, and temperature were rigorously experimentally tested and are shown in Table 4 and Figure S4.

3.3.1. Catalyst Loading

The effect of catalyst loading on biodiesel yield by changing the amount of catalyst from 4 to 12 wt% is shown in Figure S4a. The three other reaction parameters were kept constant at an MTOR of 18:1, a temperature of 75 °C, and a time of 2 h. At a catalyst loading of 4 wt%, the yield was 59.4%, which increased up to 92.1% with increasing catalyst loading to 8 wt%. However, beyond that the yield reduced to 90.2%. With increasing catalyst loading, the viscosity of the reaction medium also increases. It lowers the mass transfer rate from the reactants to catalyst surface causing a reduction in the reaction rate [57]. From these observations, the optimum catalyst loading was found to be 8 wt%.

3.3.2. Reaction Temperature

With the intention to find out the optimum reaction temperature, transesterification was conducted using temperatures of 45–85 °C. In this investigation, the optimum catalyst loading of 8 wt% was used. For the other two parameters, an MTOR of 18:1 and a time of 2 h were chosen. The yield increased continuously until 65 °C, after that it diminished because of vaporization of methanol molecules which resulted in a reduced interaction between methanol and soybean oil [58] as shown in Figure S4b. Hence, 65 °C was considered the optimum temperature.

3.3.3. Methanol to Oil Molar Ratio

The MTOR is the most essential parameter that not only affects the biodiesel yield but affects the production cost of biodiesel as well. As found from the above studies, the optimum catalyst loading and reaction temperature, 8 wt% and 65 °C, respectively, were used for the next optimization studies. Transesterification of soybean oil, which is nothing but the conversion of a triglyceride into biodiesel, takes place in three consecutive steps. First, triglyceride is converted to diglyceride, which is again converted to mono-
glyceride, and finally to glycerol, producing a mole of biodiesel in each successive step as the reaction proceeds [59]. From stoichiometric calculations, three moles of methanol are required for production of one mole of product. Since the transesterification reaction is a reversible reaction, the reaction can move backward so an excess amount of methanol is required to stop the reverse reaction [7,60]. Reactions were carried out using many MTORs such as 6:1, 9:1, 12:1, 15:1, and 18:1 as shown in Figure S4c. The yield increased as the MTOR was increased from 6:1 to 15:1. The reason for this could be the excess amount of methanol available on the surface of the catalyst, for which the equilibrium shifts forward giving a push to the reaction rate. Another impeccable advantage of methanol is that it separates molecules of the product from the catalyst’s surface, thereby keeping the active sites free for further reactions to take place [61]. A larger MTOR is unadvisable as it interferes in the removal of the by-product glycerol but methanol, as it has a polar hydroxyl group, acts as an emulsifier during glycerol separation [62] and also glycerol gets dissolved in excess methanol, due to which the rate gets diminished [63]. From the above data, a 15:1 MTOR is used as the optimized condition for a greater biodiesel yield.

3.3.4. Reaction Time

Using optimum values for the catalyst loading, temperature, and MTOR, the effect of the reaction time on the biodiesel yield was studied as shown in Table 3 as well as Figure S4d. The yield increased from 51.6 to 96.1% with an increase in the reaction time from 0.5 to 2 h. However, after that a decline in the yield was observed which could be because of soap formation which took place due to the hydrolysis of esters with increased reaction time [64]. Also, due to the reversibility of the reaction, it may move backward once the equilibrium has been achieved [65]. Hence, the optimized reaction conditions for the conversion of soybean oil to biodiesel in the presence of the CaO nanocatalyst were 8 wt% of catalyst content, 65 °C reaction temperature, a 15:1 MTOR, and a 2 h reaction time.

**Table 4.** Single factor optimization of biodiesel production using the CaO catalyst.
3.4. Kinetics of Soybean Oil Esterification

In order to study the kinetics of the reaction, the transesterification reaction was performed at various requisite temperature intervals (35, 45, 55, and 65 °C). Methanol was used in an excess amount; hence, the reaction is expected to follow pseudo first-order kinetics. The data obtained from the experiments accurately fit to a straight line so it seems to follow a pseudo first-order reaction (Figure 8a). As per various literature data and reports, researchers claim that the transesterification reaction of soybean oil with methanol to produce biodiesel follows pseudo first-order kinetics [66]. The equation for first-order reaction kinetics is given below in Equation (4) in which \( k \) is the rate constant and can be derived from the slope of the graph of \(-\ln(1 - X_t)\) vs. time.

\[
-\ln(1 - X_t) = kt
\]

where \( (1 - X_t) \) represents the amount of reactant remaining after time \( t \).

After the rate constants at the specific reaction temperatures were found, a ln\( k \) vs. \( 1/T \) plot was drawn as shown in Figure 8b. It is a linear plot which again shows that the reaction follows first-order kinetics. From the slope of this plot, the activation energy can be found with the help of the Arrhenius equation, Equation (5),

\[
k = A \times e^{\left(-\frac{E_a}{RT}\right)}
\]

\[
\ln k = \frac{-E_a}{RT} + \ln A
\]

where ‘\( E_a \)’ represents the activation energy, ‘\( R \)’ stands for the universal gas constant whose value is 8.314 J K\(^{-1}\) mol\(^{-1}\), ‘\( T \)’ represents the temperature of the reaction and ‘\( A \)’ is a constant called pre-exponential factor. The value of the activation energy and the pre-exponential factor were found to be 38.2 kJ mol\(^{-1}\) and \( 10^7 \), respectively. The activation energy values for biodiesel production via transesterification of oil usually lie between 21 and 84 kJ mol\(^{-1}\) [67]. The activation energy of the CaO nanocatalyst lies perfectly in the range; hence, it is preferred to be used in the process of production of biodiesel.

![Figure 8. Kinetic study of transesterification of soybean oil to biodiesel: (a) \(-\ln(1 - X)\) vs. time (\( X = \) soybean oil conversion) and (b) the relevant Arrhenius plot of ln\( k \) vs. \( 1/T \).]
3.5. Catalyst Heterogeneity Test

To study the heterogeneity of the CaO nanocatalyst, a ‘hot filtration method (Sheldon’s test)’ was performed [68]. After an interval of 1.5 h, when the yield was estimated to be 79.9%, the catalyst was taken out of the reaction through filtration in hot conditions. When the reaction was carried out in the absence of the catalyst for more than 3 h, a yield of around 80.9% was found. It was nearly an increase of 1% compared to the previous conversion as shown in Figure S5 (see Supplementary Materials). The above comparison data reveal that our catalyst is heterogeneous since the filtrate lacked an appreciable quantity of soluble catalytically active substances (catalytic agents).

3.6. Catalyst Reusability Test

To avoid scarcity of resources, recycling is an indispensable part of production. Catalysts with a healthy lifespan and unchallenging retrieval are attractive both for the researcher and user and are greatly employed at an industrial scale. Along with environmental concerns, economic deliberations also demand technologies which work on catalyst durability, easy recovery, and reuse [69,70]. To investigate catalyst reusability, the catalyst was first isolated using filtration of the reaction mixture after completion of the reaction. It was then revived by rinsing thoroughly with methanol and hexane to remove the physisorbed compounds from the catalyst surface after which it was kept for drying in oven for 5 h at 100 °C followed by calcination at 900 °C. Then, this catalyst was used for the next reaction cycle with a repeat of the washing, drying, and calcination steps. With each following cycle, a small decrease in the conversion of soybean oil was observed as shown in Figure 9. The yield was around 80.3 ± 0.5% during the fifth cycle of the reaction. The remnants of the reaction could get accumulated on the catalyst sites, which might have been the cause for the gradual and steady deactivation of the nanocatalyst [71]. The CaO nanocatalyst has outstanding performance results and can reportedly be reused five times probably with minimal loss in performance. SEM was also performed for recovered catalyst as shown in Figure S6 (see SI) at 2 µm and 3 µm and the morphology was quite similar to the fresh catalyst. FT-IR of the recovered catalyst is shown in Figure S7 (see SI); this was also comparable with the fresh catalyst. These results indicate the stability of the CaO catalyst even after repeated reuse for five cycles. Thus, the catalyst had undergone five active reaction cycles without appreciable loss in its properties.

![Figure 9](image_url)

**Figure 9.** Reusability test performed for the CaO nanocatalyst. Reaction conditions: MTOR 15:1, catalyst loading 8 wt%, temperature 65 °C, and time 2 h.
3.7. Comparison of CaO Nanocatalyst with Other Reported Heterogeneous Catalysts

Various reported catalysts have been employed for biodiesel production as per the literature. Table 5 summarizes the useful details (i.e., catalyst employed, precursor, reaction conditions, yield (%)) for comparison with our catalyst. Several catalysts defined in the literature studies, such as waste snail shell [7], quintite [72], and a Li-doped MgO catalyst [73] required considerable time and temperature for production of biodiesel. Many other catalysts such as NaKTNT [12], ZIF-90-Gua [74], silica-impregnated CaO [75], and AIL-HPMo-MIL-100(Fe) [76] gave lower yields. Waste snail shell [7], K2O/NaX and Na2O/NaX [7], Na modified fluorapatite (Na/FAP) [77], and AIL-HPMo-MIL-100(Fe) [76] took prolonged time for reaction. Biodiesel production involving Na-modified fluorapatite (Na/FAP) [77] and AIL-HPMo-MIL-100(Fe) [76] were performed in higher temperatures. In accordance with the reaction parameters, the performance of the present CaO was better than several compared catalysts mentioned in Table 5.
**Table 5.** Comparison of various heterogeneous catalysts with the present CaO nanocatalyst for biodiesel production.

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Catalyst</th>
<th>Precursor</th>
<th>Conditions *</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NaKTNT</td>
<td>Soybean</td>
<td>20:1, 1, 80, 1</td>
<td>96.2</td>
<td>[12]</td>
</tr>
<tr>
<td>2.</td>
<td>Waste snail shell</td>
<td>Soybean</td>
<td>6:1, 3, 900, 7</td>
<td>98.0</td>
<td>[7]</td>
</tr>
<tr>
<td>3.</td>
<td>K2O/NaX and Na2O/NaX</td>
<td>Safflower</td>
<td>18:1, 12.5, 61, 7</td>
<td>98.0</td>
<td>[7]</td>
</tr>
<tr>
<td>4.</td>
<td>Quintite</td>
<td>Waste vegetable</td>
<td>12:1, 10, 75, 2</td>
<td>96.0</td>
<td>[72]</td>
</tr>
<tr>
<td>5.</td>
<td>Li-doped MgO catalyst</td>
<td>Vegetable oil</td>
<td>12:1, 9, 65, 2</td>
<td>93.9</td>
<td>[73]</td>
</tr>
<tr>
<td>6.</td>
<td>Metal-oxide catalysts (CaTiO3, CaMnO3, Ca3Fe2O9, CaZrO3)</td>
<td>Rapeseed</td>
<td>6:1, - , 60, 10</td>
<td>90.0</td>
<td>[19]</td>
</tr>
<tr>
<td>7.</td>
<td>ZIF-90-Gua</td>
<td>Soybean</td>
<td>15:1, 1, 65, 6</td>
<td>95.4</td>
<td>[74]</td>
</tr>
<tr>
<td>8.</td>
<td>Silica-impregnated CaO</td>
<td>Palm</td>
<td>20:1, 3, 60, 2</td>
<td>90.0</td>
<td>[75]</td>
</tr>
<tr>
<td>9.</td>
<td>Na-modified fluorapatite (Na/FAP)</td>
<td>Rapeseed</td>
<td>10:1, 6, 120, 8</td>
<td>98.0</td>
<td>[77]</td>
</tr>
<tr>
<td>10.</td>
<td>AIL-HPMo-MIL-100(Fe)</td>
<td>Soybean</td>
<td>30:1, 9, 120, 8</td>
<td>92.3</td>
<td>[76]</td>
</tr>
<tr>
<td>11.</td>
<td>CaO</td>
<td>Soybean</td>
<td>15:1, 8, 65, 2.0</td>
<td>96.1</td>
<td>Present work</td>
</tr>
</tbody>
</table>

* Methanol to oil molar ratio, catalyst loading (wt%), reaction temperature in °C, reaction time in h. NaKTNT: sodium titanate nanotubes doped with potassium. AIL-HPMo-MIL-100(Fe): acidic ionic liquid (AIL)–phosphomolybdic acid (HPMo)–metal organic framework MIL–100(Fe).
4. Conclusions and Prospects

A CaO nanocatalyst was prepared with the help of waste Musa acuminata peel extract. From XRD and TEM analyses the successful synthesis of CaO was confirmed. In TEM, spherical particles without any agglomeration were observed. In BET studies, the material was found to be mesoporous, which is very useful in catalysis. The surface area and pore size of the CaO were found to be 10.9 m²g⁻¹ and 2.66 nm, respectively. A kinetic study of this transesterification reaction of soybean yielded the activation energy to be 38.2 kJ mol⁻¹. The present catalyst was found to strongly outperform other reported heterogeneous solid catalyst employed in the transesterification process of oil to biodiesel, be it in terms of reaction conditions or yield. Reusability studies conducted for up to five reaction cycles showed that the catalyst could be successfully re-used to give 80.3% biodiesel yield. Because of the catalyst’s strong reusability and ability to be reused over numerous reaction cycles, the cost of biodiesel production can be reduced. The catalyst can be used to industrially manufacture biodiesel from oils. The extract’s organic components reduce the calcium ion with the least amount of chemical intervention while also stabilizing the nanoparticles. The catalyst has the advantage of being green, bio-degradable, easily prepared, abundantly available, and cost-effective, making it a competent source for the economic production of biodiesel at an industrial scale.

Despite the advantages of this work, it has limitations such as use of edible soybean oil. Non-edible oil should be used for low-cost biodiesel production. Non edible oils such as waste cooking oil contain higher amounts of free fatty acids, so CaO, being a basic catalyst, will not be an effective catalyst. After reusing the present CaO catalyst, the calcium amount decreased from 43% to 38.7%. Also, the nanoparticles may agglomerate. This CaO catalyst can be modified to a bifunctional catalyst containing both acidic and basic components, which will enhance its efficacy in biodiesel production as well as minimize Ca leaching. Also, use of effective stabilizers will increase the stability of the catalyst and lower the nanoparticle agglomeration. Again, life cycle assessment of this work could be done by future researchers to investigate the environmental impact of the process. Further extending the research to exergy studies, uncertainty analysis, energy balance, and mass balance studies could also be interesting for future research. The cumulative results of these tools would be very helpful for policy makers with respect to sustainable development of biofuels.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su15141332/s1, Figure S1: FT-IR spectra of the biodiesel product showing different peak positions; Figure S2: 1H-NMR and 13C-NMR analysis of the biodiesel product; Figure S3: Gas chromatography analysis of the biodiesel product; Figure S4: Optimization of reaction parameters; Figure S5: Heterogeneity test of the CaO catalyst in transesterification of soybean; Figure S6: SEM and EDX images of reused catalyst; Figure S7: FT-IR spectrum of reused CaO catalyst after 5 reaction cycles; Figure S8: XPS deconvolution spectra of magnesium (Mg1s), silicon (Si2p), phosphorus (P2p)

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Conflicts of Interest: We declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript

1. NP  Nanoparticle
2. NPs  Nanoparticles
3. CaO  Calcium oxide
4. Ca(OH)₂  Calcium hydroxide
5. Ca(NO₃)₂  Calcium nitrate
6. ¹H-NMR  Nuclear magnetic resonance
7. FT-IR  Fourier transform infrared spectroscopy
8. XRD  X-Ray diffraction
9. SEM  Scanning electron microscope
10. EDS  Energy-dispersive X-ray spectroscopy
11. TEM  Transmission electron microscope
12. XPS  X-ray photoelectron spectroscopy
13. BET  Brunauer–Emmett–Teller
14. NaKTN  Sodium titanate nanotubes doped with potassium
15. AIL-HPMo-MIL-100(Fe)  Acidic ionic liquid–phosphomolybdic acid–metal organic framework MIL-100(Fe)
16. TGA  Thermogravimetric analysis

References

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