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Synthesis of Mixed-phase Barium Titanium Oxide ($BaTiO_3/Ba_2TiO_4$) Perovskite Catalyst for Biofuel Production

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The mixed-phase barium titanium oxide perovskite nanoparticles were synthesized by calcining barium carbonate and titanium dioxide precursors at 900 °C. The nanoparticles were characterized using X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy and selective area diffraction analysis. The synthesized barium titanium oxide particles were found to have almost spherical shape with 6-15 nm size. The synthesized mixed-phase $BaTiO_3/Ba_2TiO_4$ perovskite nanoparticles are used for biofuel production. The formation of methyl ester after the transesterification reaction confirms the conversion of essential oil into biofuel, as analyzed by GC-MS.

Keywords: Perovskite, Barium titanium oxide, Biofuel production, Synthesis, Mixed phase.

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1. INTRODUCTION

Energy plays a vital role in the daily requirements across the globe. The demand for the fossil fuel is increasing day by day and its price is rising drastically. The widespread use of fossil fuel releases a huge amount of toxic gases such as CO, NO_x and SO_x. So, in order to overcome these calamities, a greener fuel has to be used [1]. Biofuels is a promising alternative fuel. Biodiesel, a monoalkyl ester can be synthesized by the process of transesterification from alcohol and various feedstocks such as animal fats, waste cooking oil, vegetable oil, etc. Biofuels is considered as a nonconventional or renewable fuel due to its non-toxic, carbon neutral and biodegradable natures [2].

The catalysts used for the synthesis of biofuel can be classified into three categories viz. homogeneous, heterogeneous and biocatalyst [3]. In biodiesel industry, homogenous catalysts are mostly used as they are cheap and highly active. Sodium and potassium hydroxide are the most commonly used homogenous catalysts. The homogenous catalysts have disadvantages as it uses large amount of water for the removal of impurities. Thus, the production cost becomes high, and the process becomes technically lengthy [4, 5]. The heterogeneous catalysts on the other hand are a good alternative to homogenous catalyst. It is easily separable from its product formed without water washing [6]. Further, heterogeneous catalyst can be reused and regenerated [7]. The heterogeneous catalyst possesses disadvantages like its mass transfer resistance, time consumption, fast deactivation, and inefficiency. These difficulties can be overcome by using heterogeneous nanocatalyst, as it has high specific surface area leading to a very high catalytic activity [8]. Among the heterogeneous catalyst, metal oxide-based perovskites are gaining more popularity because of its acid-base and redox properties [9].

Biofuel is synthesized by using different types of metal oxides. Dai and his research group studied the application of metal oxide i.e., Li_2TiO_3 catalyst for transesterification of soybean oil into biofuel. Li_2TiO_3 was synthesized by solid-state reaction which involves the mixing and grinding of TiO_2 and Li_2CO_3 with further calcination at 800 °C for 2 h. The prepared Li_2TiO_3 was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), BET, and the Hammett indicator is used to study the physical and chemical properties of synthesized metal oxide [10].

The aim of this work is to synthesize a heterogeneous perovskite-based catalyst consisting of mixed-phase of ABO_3 and A_2BO_4 type metal oxides, where A denotes alkaline-earth metal, alkaline metal, or rare earth metal whereas B is a transition metal in order to utilize it for biofuel synthesis.

2. MATERIALS AND METHODS

2.1 Materials and Instruments

Barium carbonate ($BaCO_3$) and titanium dioxide (TiO_2) were purchased from Aldrich chemicals and SRL chemicals, respectively. Methanol was purchased from ACS chemicals. The essential oil (i.e., virgin mustard oil) without having any anti foaming agent and antioxidants was purchased from the local market.

X-ray diffractometer (XRD), D8 Focus, Bruker AXS, Germany was used to determine the phase identification of the synthesized crystalline material. Morphology and particle size were determined by transmission electron microscope (TEM), JSM 6360, JEOL, JAPAN. Selective area diffraction (SAD) and energy-dispersive X-ray (EDX) were recorded using the module attachment with the JEOL make TEM. Chemical compositions of the biofuel were determined by gas chromatography-mass spectroscopy (GC-MS) Perkin Elmer Clarus 680 GC/600C MS, USA, and the functional group present in the samples was analyzed by Fourier transform infrared spectroscopy (FTIR), Impact 410, Nicolet, USA.

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2.2 Synthesis of Mixed-phase $BaTiO_3/Ba_2TiO_4$ Perovskite Nanomaterials

The mixed-phase barium titanium oxide perovskite was synthesized by using high purity barium carbonate and titanium dioxide. The precursors were mixed in stoichiometric proportions ($BaCO_3$:TiO_2:4:1) in distilled water. The aqueous mixture was stirred in room temperature at 500 rpm till it becomes homogeneously dispersed. The precursor mixture thus obtained was poured in a quartz crucible and kept in a furnace at 900 °C for 2 h. Finally, the mixed-phase barium titanium oxide perovskite was collected from the crucible and used in biofuel production as a catalyst.

2.3 Synthesis of Biofuel from Mixed-phase $BaTiO_3/Ba_2TiO_4$ Perovskite Catalyst

Biofuel was synthesized by transesterification of virgin mustard oil using the mixed-phase $BaTiO_3$/ Ba_2TiO_4 perovskite catalyst. Initially 0.2 mg of mixed-phase $BaTiO_3/Ba_2TiO_4$ perovskite catalyst was dispersed in 12.6 ml methanol using a stirrer for 20 min at 40 °C. Simultaneously, the mustard oil was heated at 60 °C in another beaker to remove the water/moisture present in the oil. The heated oil of 22.22 ml was poured into the beaker containing methanol and mixed-phase $BaTiO_3/Ba_2TiO_4$ perovskite catalyst. The molar ratio of methanol to oil was taken as 14:1. The reaction mixture was stirred at 600 rpm for 3 h at 60 °C and then transferred into a separating funnel to settle down. After 2 h, two distinct layers could be seen in the separating funnel, where the upper layer was the biofuel, and the lower layer was the mixture of glycerol and the catalyst. The biofuel and glycerol layers were separated.

3. RESULTS AND DISCUSSION

3.1 Characterization of Mixed-phase $BaTiO_3/Ba_2TiO_4$ Perovskite Nanomaterials

3.1.1 XRD Analysis

Fig. 1 shows the XRD pattern of mixed-phase barium titanium oxide. The peaks appearing at 23.87°, 27.68°, 31.53°, 34.11°, 34.54°,38.94°, 41.95°, 44.88°, 46.78°, 56.19° and 65.86° correspond to the respective crystal planes

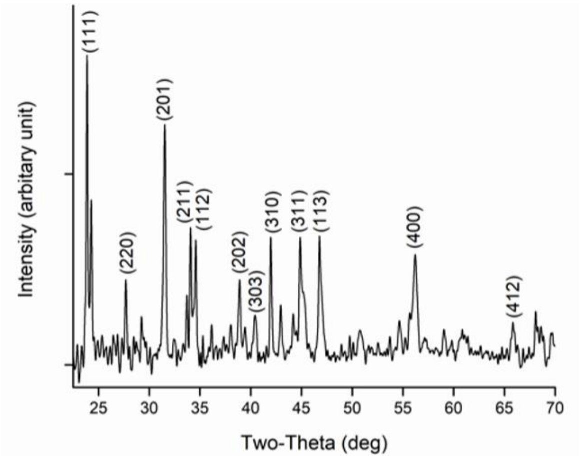


Fig 1 – XRD pattern of the mixed-phase barium titanium oxide

(111), (220), (201), (211), (112), (202), (303), (310), (311), (400) and (412) and their respective *d*-spacings 0.37, 0.32, 0.28, 0.26, 0.25, 0.23, 0.25, 0.20, 0.19, 0.16 and 0.14 nm. The 2 theta angle peaks at 23.87°, 31.53° and 38.94° correspond to the tetragonal phase of $BaTiO_3$ and the peaks at 27.68°, 34.54°, 44.88° and 46.78° correspond to the orthorhombic phase of Ba_2TiO_4 [11-13]. The synthesized perovskite nanoparticles are found to have mixed phases of tetragonal $BaTiO_3$ and orthorhombic Ba_2TiO_4 from the XRD data. The approximate crystallite size of the particles was determined to be 8.58 nm by using the Scherrer's equation.

3.1.2 FTIR Analysis

The FTIR spectrum of the mixed-phase barium titanium oxide perovskite nanoparticles is shown in Fig. 2. The peak at 3432 cm^{-1} corresponds to the stretching mode of O–H group and the peak at 1636 cm^{-1} corresponds to the bending mode of H–O–H group. H–O–H bond is formed due to water adsorbed by barium titanium oxide perovskite nanoparticles, whereas the peak at 1428 cm^{-1} is due to the stretching vibration of C–O in CO_3^{2-}, the band at 570 cm^{-1} corresponds to Ti–O stretching mode in barium titanium oxide perovskite and the band at 438 cm^{-1} is due to Ti–O bending vibration along the polar axis [14]. The band ranging from 500-580 cm^{-1} corresponds to Ba–O bond [15].

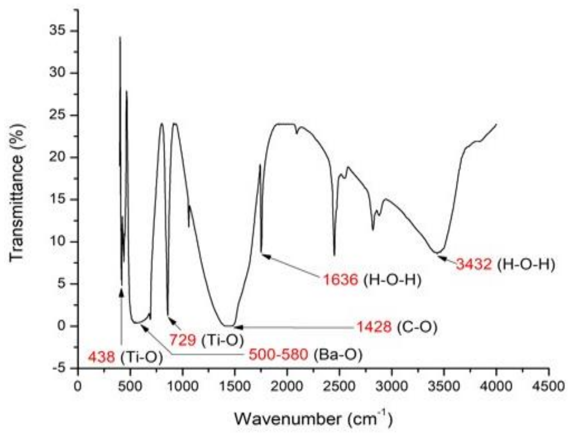
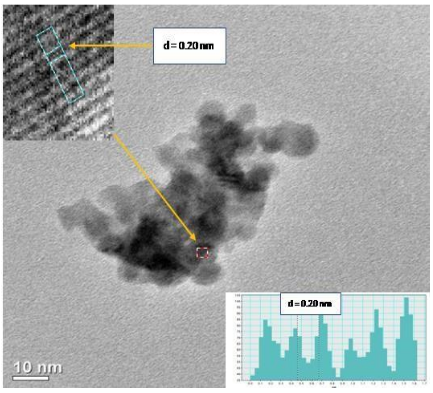


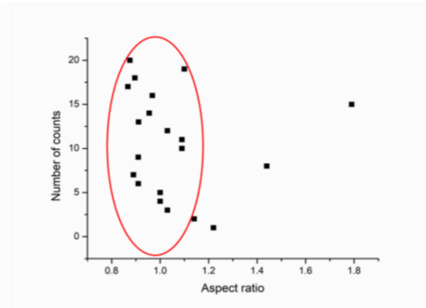
Fig. 2 – FTIR spectrum of the mixed-phase barium titanium oxide perovskite nanoparticles

3.1.3 TEM

Fig. 3a shows the TEM image of the synthesized mixed-phase barium titanium oxide perovskite nanoparticles. The particle size ranges from 06-15 nm. The high-resolution micrograph in Fig. 3a clearly shows the high crystallinity of the perovskite nanoparticles. A smaller size results in higher surface area and may result in higher catalytic activity leading to higher biofuel production [8]. The perovskite nanoparticles could be seen in clusters with almost uniform shape and size. The aspect ratio of the synthesized nanoparticles was calculated to study the shape of the particles. This was achieved by measuring the length to width ratio. The aspect ratio of the nanoparticles was found to be in the range of 0.9 to 1.5 as shown in Fig. 3b, confirming that the particles are almost spherical in shape.



a



b

Fig. 3 – (a) TEM image and (b) aspect ratio of the synthesized mixed-phase barium titanium oxide perovskite nanoparticles

The IFFT was taken from the TEM image for studying the *d*-spacing, as shown in Fig. 3a. The *d*-spacing of the synthesized mixed-phase barium titanium oxide perovskite nanoparticle was determined by using GATAN micrograph software. The *d*-spacing from the profile of IFFT was found to be 0.20 nm. The *d*-spacing value was found similar to the results from XRD at Miller indices (310). Fig. 4 shows the SAD of mixed-phase barium titanium oxide perovskite nanoparticles. The orientation at (211), (303), (310), (311) and (400) found by XRD measurement was found to be similar to the results obtained by SAD. The Miller indices at (310) found from SAD correspond to the 2-theta angle peak at 44.88° of XRD data attributed to the orthorhombic phase of Ba_2TiO_4, whereas the Miller indices at (400) found from SAD correspond to the 2-theta peak at 56.19° attributed to the tetragonal phase of $BaTiO_3$ [11]. Thus, from the SAD image it can be said that the synthesized nanomaterial possesses mixed-phase barium titanium oxide nanoparticles. The elemental dispersive X-ray (EDX) spectrum confirms the presence of barium (Ba), titanium (Ti) and oxygen (O) in the sample (Fig. 5).

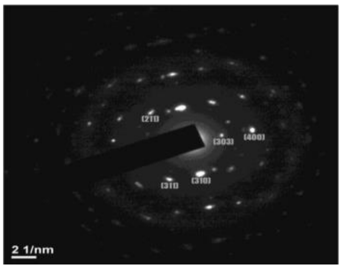


Fig. 4 – Selected area electron diffraction of mixed-phase barium titanium oxide perovskite nanoparticles

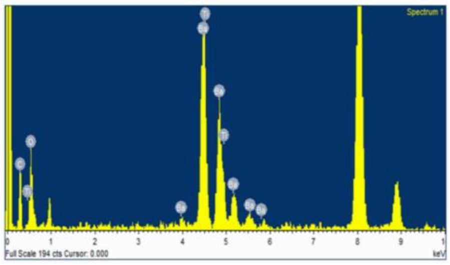


Fig. 5 – EDX spectrum of the mixed-phase barium titanium oxide perovskite nanoparticles

3.2 Characterization of Biofuel Synthesized Using Mixed-phase $BaTiO_3/Ba_2TiO_4$ Perovskite Catalyst

3.2.1 FTIR Analysis

The FTIR was evaluated to determine the functional group present in the biofuel synthesized from mustard oil using mixed-phase $BaTiO_3/Ba_2TiO_4$ perovskite as a heterogenous catalyst. Fig. 6 shows the FTIR spectra of the synthesized biofuel from mustard oil. Biofuel is comprised of monoalkyl esters of fatty acids. The bonds of C=O, O–CH_3, –CH_3 and –C–O– are very necessary for the formation of methyl ester. The region from 1700 to 1800 cm^{-1} is accredited for stretching of C=O characteristic of ester. The asymmetric stretching of –CH_3 appears at the peak 1446 cm^{-1} ascribed to O–CH_3 stretching thus may be attributed to the presence of biofuel in the sample [16].

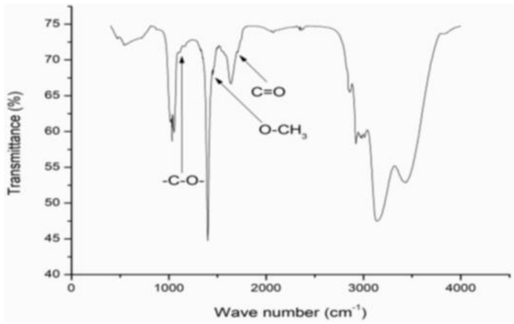


Fig. 6 – FTIR spectrum of biofuel from virgin mustard oil

3.2.2 GC-MS Analysis

The methyl esters percentages that were present in the synthesized biofuel were determined by GC-MS (Fig. 7). The methyl esters obtained from the analysis were 11-octadecenoic acid methyl ester/9-octadecenoic acid methyl ester (e)-, trans-13octadecenoic acid methyl ester, 13-docosenoic acid methyl ester/13-docosenoic acid methyl ester (z)-, cis11-eicosenoic acid, methyl ester 9, 12, 15-octa decatrienoic acid methyl ester, (z,z,z)-, cis-11-eicosenoic acid, methyl ester, 13-docosenoic acid, methyl ester and 13-docosenoic acid, methyl ester (z). Among the fatty acid methyl esters, docosenoic acid methyl ester and octadecenoic acid methyl ester possessed the highest percentage of about 25.9 % and 7.5 %. Fatty acid methyl ester composition is very necessary for biofuel as it determines the appropriateness for its use as a fuel. The docosenoic acid methyl ester and octadecanoic acid methyl ester are monounsaturated, so they have a propensity of maintaining constancy of the fuel. Higher degree of unsaturation in the methyl esters leads to the stability of the fuel.

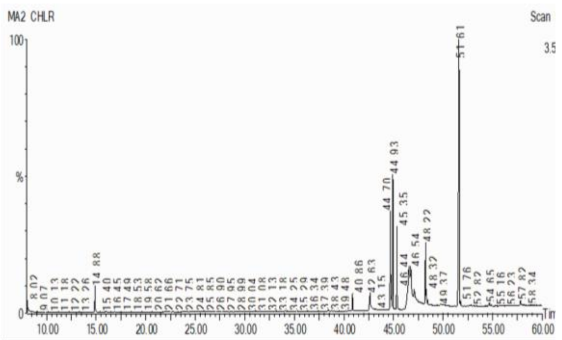


Fig. 7 – GC-MS of biofuel from mixed-phase barium titanium oxide nanoparticles

4. CONCLUSIONS

The present work reports successful synthesis of mixed-phase barium titanium oxide perovskite nanoparticles. The XRD shows the formation of mixed-phase $BaTiO_3$ and Ba_2TiO_4 perovskite. The perovskite particles were found to be highly crystalline and almost spherical as reveled from TEM, SAD and XRD analysis. The purity of the perovskite nanoparticles is confirmed by EDX analysis. The synthesized mixed-phase $BaTiO_3/Ba_2TiO_4$ perovskite catalyst was successfully used for the production of biofuel. The GC-MS and FTIR results confirm the formation of methyl ester, thus confirming the production of biofuel. Thus, the synthesized mixed-phase $BaTiO_3/Ba_2TiO_4$ perovskite catalyst nanomaterial is a good candidate to produce biofuel. The mixed-phase $BaTiO_3/Ba_2TiO_4$ perovskite catalyst may also be studied for the production of biofuel in detail in future for reusability of catalyst and engine performance testing.

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Синтез перовскітного каталізатора на основі титано-барієвого оксиду зі змішаними фазами ($BaTiO_3/Ba_2TiO_4$) для виробництва біопалива

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Наночастинки перовскіту на основі титано-барієвого оксиду зі змішаними фазами синтезували прожарюванням прекурсорів карбонату барію та діоксиду титану при температурі 900 °C. Отримані наночастинки характеризували за допомогою рентгенівської дифракції, інфрачервоної спектроскопії з перетворенням Фур'є, просвічуючої електронної мікроскопії, енергодисперсійної рентгенівської спектроскопії та селективного дифракційного аналізу. Встановлено, що синтезовані частинки титано-барієвого оксиду мають майже сферичну форму з розміром 6-15 нм. Синтезовані наночастинки перовскіту зі змішаними фазами $BaTiO_3/Ba_2TiO_4$ використовуються для виробництва біопалива. Утворення метилового ефіру після реакції міжмолекулярної переетерифікації підтверджує перетворення ефірної олії в біопаливо, яке проаналізовано за допомогою GC-MS.

Ключові слова: Перовскіт, Титано-барієвий оксид, Виробництво біопалива, Синтез, Змішана фаза.