



Potassium Halides - Impregnated Eggshell as a Heterogeneous Nanocatalysts for Biodiesel Production

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Abstract

In this study, Potassium halides-doped Calcium Oxide (CaO) was synthesized as heterogeneous nanocatalysts for transesterification of waste cooking oil. The chicken eggshell wastes were used as raw materials to synthesize calcium oxide. The calcium carbonate (CaCO_3), principal constituent in the eggshell, was changed to calcium oxide by calcining at 873 K for 4 h. After that, the calcium oxide was impregnated with potassium iodide (KI) and potassium fluoride (KF) via wet impregnation method. The textural properties of the solid oxide catalyst were characterized by base strength, field emission scanning electron microscopy (FE-SEM), powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The basic strengths of the catalysts were determined applying Hammett indicator. The yield of nanocatalysts evaluated by using the prepared catalysts in waste cooking oil transesterification with methanol for at 338 K 2 h. the catalytic activity depends on several factors such as, base strength, Impregnation and calcination processes and impregnated Compound. The formed KCaF_3 was the major active element for the catalytic activity in KF/CaO nanocatalyst, however, this activity was not observed in KI/CaO nanocatalyst. For the reason of presenting of this component, the Ca^{2+} in KF/CaO acts as a stronger Lewis acid and exhibits high catalytic activity. Biodiesel yield for KF/CaO catalyst and KI/CaO was 91.18 % and 87.69%, respectively.

Keywords: Heterogeneous nanocatalyst, Eggshell wastes, Basic nanocatalyst, Biodiesel Production

1 Introduction

Renewable energy expansion has been focused universal, because of the limited reserve of fossil fuels and increase in oil prices and the increasing emissions of polluting [1]. Biodiesel is one of the most substituted energy resources and is environmental friendly. Biodiesel can be synthesized by different methods such as Trans-esterification. In this method the material is converted to a desired product at a reasonable rate, using a catalytic process [2, 3]. Biodiesel, identified as the fatty acid methyl esters, is made by Trans-esterification of renewable biological resources such as for example vegetable oils with an alcohol in the presence of the catalysts and in this technique glycerol is really a useful byproduct [4, 5]. A novel approach in this process is to use "green" method based on heterogeneous catalyst. Nature of catalyst is an

influential parameter in preparation of biodiesel. Catalysts can be either heterogeneous or homogeneous and basic or acidic. The reaction is carried out by homogeneous base catalysts faster than acidic catalysts. Homogeneous catalysts which are commonly used include sodium hydroxide and potassium hydroxide [3]. The homogeneous catalyst has many drawbacks such as instrument corrosiveness, difficulty in catalyst recovery, and health dangers to the operators because of the generation of enormous waste stream in washing steps [6].

In comparison, heterogeneous catalysts have the advantage that separation and regeneration of the catalyst is easy and inexpensive, making the production process more economical, causing less environmental problems and the product is pure [7-10]. Heterogeneous basic catalysts contain alkaline earth metal oxides, like hydrotalcites, magnesium oxide (MgO) and calcium oxide (CaO) [11, 12].

Recently the application of natural calcium resources from waste materials for biodiesel production has been considered as a novel trend [13]. By using eggshell wastes as raw material to synthesize the desired catalysts, the heterogeneous catalysts can be produced with low cost and

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eliminate the wastes [14]. The eggshells contain a network of protein fibers, in communication with crystals of magnesium carbonate (MgCO_3), calcium carbonate (CaCO_3), calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), organic materials and water. CaCO_3 , the key constituent of the eggshell (96%), can be an amorphous crystal that happens generally in the form of calcite [15, 16]. Using wastes draw great interest because of the eggshell waste as a renewable, low cost, Eco-material for synthesis of catalyst and eggs are part of daily meal the majority of the countries [17-19]. The catalytic activity of CaO can be enhanced with modification of CaO surface with potassium halides to create strong active basic sites [20-22].

Although the solid phase catalytic techniques have already been studied generally, the industrial applications are restricted [23, 24]. Heterogeneous catalytic techniques are often time consuming and mass transfer resistant [25]. New research indicates that nanocatalysts may solve above problems, because they have numerous active sites and high catalytic activities [26, 27].

The deposition of potassium halide nanoparticles increases the surface area of the catalyst and basic strength. Basic phases (like K_2O) are obtained from decomposition of potassium halides at high temperatures, associated with potassium halides which increase the activity of the catalyst [28].

herein, an eggshell has been utilized as a costless mean to introduce a heterogeneous catalyst for biodiesel synthesis of waste cooking oil. As mentioned earlier, potassium halides-doped CaO catalysts were well synthesized by wet impregnation method. The calcination and impregnation with particle sizes of (30–40 nm) improved the activity of catalyst surface. The high activity of KF/CaO revealed by the transesterification at 338 K, 400 rpm, 12:1 methanol ratio, owing to the formation of KCaF_3 as a novel crystalline phase, enhanced the activity and stability of catalyst. This paper is a sample of comprehensive report for management of municipal solid waste, which led to produce green fuel.

2. Material and Methods

2.1 Materials

Eggshells were obtained as wastes from university dormitory. To remove impurities and dust, the eggshell was washed with water. Finally, the eggshells were dried in oven. Waste cooking oil was purchased from Pastry factory in Tehran, Iran. Both potassium iodide and potassium fluoride were analytical grade (Merck, Germany). Methanol 99.5% and acetone 99.5% were purchased from Merck company, too. All solutions were prepared by using deionized water.

2.2 preparation of Catalyst

In the CaO catalyst production, calcination method was used. The dried eggshell waste (100 mesh) was calcined in the atmosphere pressure at 1273 K for 4 h (heating rate $2^\circ\text{C}/\text{min}$). Before usage, the resulting white powder was preserved in the fastened vessel to prevent reacting with moisture and carbon dioxide in air. Subsequently, the CaO catalyst was impregnated with potassium halides. All Catalysts were synthesized under the same conditions to be

comparable. The prepared CaO was powdered and immersed in 15–20 mL potassium halides solution by the mass ratio of 0.25 (mass proportion of potassium halides to CaO) for 1 h. Finally, the samples were heated at 373 K for 7 h followed by 4 h calcination in muffle furnace at 873 K [29].

2.3 Characterization

FT-IR spectra was recorded on a Shimadzu spectrometer 8400 spectrometer in the $4000\text{--}400\text{ cm}^{-1}$ scanning range (KBr pellet technique). PXRD patterns were attained by a JDX-8030 diffractometer using $\text{Cu-K}\alpha$ radiation operating at 30 kV and 20 mA over a wide angle (2θ range of $5\text{--}80^\circ$) with a step size of 0.015° at a scanning speed of $0.6^\circ\text{ min}^{-1}$. The morphology and surface features of the nanocatalysts and calcined eggshells were tested by a scanning electron microscope (SEM Camscan- Mira 3-XMU).

Hammett indicator were applied to determine the basic strengths of the catalysts. The sample (100 mg) was shaken with cyclohexane (5 mL), then three drops of a Hammett indicator (0.1% w/w in benzene) was added to a suspended sample during shaking vigorously. After equilibration, indicators undergo the following color changes in the presence of the basic samples: Benzidine ($H_- = 22$) colorless to purple, 4-nitroaniline ($H_- = 18.4$) yellow to orange, 2,4-dinitroaniline ($H_- = 15$) yellow to violet, and Phenophthalein ($H_- = 9.8$) colorless to red.

2.4 Transesterification reaction

The laboratory scale transesterification of waste cooking oil was carried out using a thermometer, magnetic stirrer and 250-mL 3-necked flask equipped with a water cooled condenser, in oil bath at a temperature of 338 K. At first 7.0 ml methanol was added to 0.2 g catalyst and stirred at 400 rpm. After a few minutes, 12.5 g heated refined oil was added to flask, this reaction lasted for 2 h. All experiments were performed under atmospheric pressure and repeated several times. Eventually, centrifuge is employed to separate the prepared catalyst.

2.5 Methyl ester analysis

A gas chromatograph equipped with a mass selective detector (Agilent 7890/5975C VLMSD) was used to analyze the biodiesel samples and HP-5 MS column was applied to separate the FAMES. FAMES samples were diluted (1:1000) in N-Heptan that contains an internal standard (GLC 90, SUPELCO). The chromatographic conditions included: detector: 523 K, injector: 513 K, column: 232-270 at 303 K min^{-1} , 200-232 at 275 K min^{-1} and 100-200 at 323 K min^{-1} . The methyl ester band area ratio to the internal standard band area was estimated for each run [30].

3 Results and Discussion

3.1 Characterization

The activities of catalysts were related to their basic strength, i.e. the higher base strength of the catalyst can lead to the higher biodiesel yields [28]. Impregnated catalysts showed intense increase (87.69% and 91.18%) in biodiesel yield. In contrast, oil percent conversion of CaO

catalyst is 20.62%. While the base strengths of catalysts are nearly average and identical about 9.8 to 15. KF/CaO revealed base strength less than 15.0 while it exhibited high catalytic activity. Therefore, higher base strength is needed for the catalytic transesterification reaction, but it's not enough. Thus, the catalytic activity depends on other factors [21].

Impregnation and calcination processes have allowed the creation of nanostructures with an average pore size that is recorded in Table 1. SEM analysis shows a layered structure of the calcined shells with a same irregular shapes Figure 1 (A), and two images of nanostructured impregnated catalysts Figure 1 (B,c) . As can be seen the crystal morphologies of KF/CaO Figure 1 (B) and KI/CaO Figure 1 (C) are totally different.

In addition, the enormous catalytic active site could enhance the contact between oil and alcohol, leading to improve catalytic efficiency. These results also indicated that Potassium halide doped-CaO catalyst can improve higher TONs compared to that of CaO catalyst, meaning

that there is no external mass transfer limitation for impregnated catalysts.

Figure 2 has shown the XRD pattern of CaO, KF/CaO and KI/CaO, in three catalysts which confirmed the existence of crystalline phase of CaO. Catalyst is composed of CaO (32.3°, 37.28°, 53.9°, 64.2°, 67.34°) Ca(OH)₂ (18°, 29°, 47.2°, 50.82°, 63°) [31]. As can be seen, diffraction peaks of KF and KI in KF/CaO and KI/CaO, are disappeared respectively, and a new diffraction peak is detected which is attributed to KCaF₃ (20°, 28.4°, 32.12°, 37.28°, 40.5°, 79.7°) and KF (34.1°, 71.8°). This phase was created during the impregnation of the Potassium fluoride in the supported lattice through capillary action and later activation process [21]. The existence of other forms, such as KO₂ and KO₃ in KF/CaO and KO₃ in KI/CaO is owing to the interaction between CaO and potassium halides. XRD patterns of nanocatalysts indicated the existence of calcium hydroxide, Ca(OH)₂, which is completely vanished at 873 K and converted to CaO.

Table 1: Basic strengths, particle size and catalytic performances of solid base catalysts

Catalyst	Tc (K)	Basic strength	Particle size (nm)	Conversion (%)
CaO	1000	H ₊ < 15.0	28.72	20.62
KF/CaO	600	9.8 < H ₊ < 15.0	29.96	91.18
KI/CaO	600	9.8 < H ₊ < 15.0	42.97	87.69

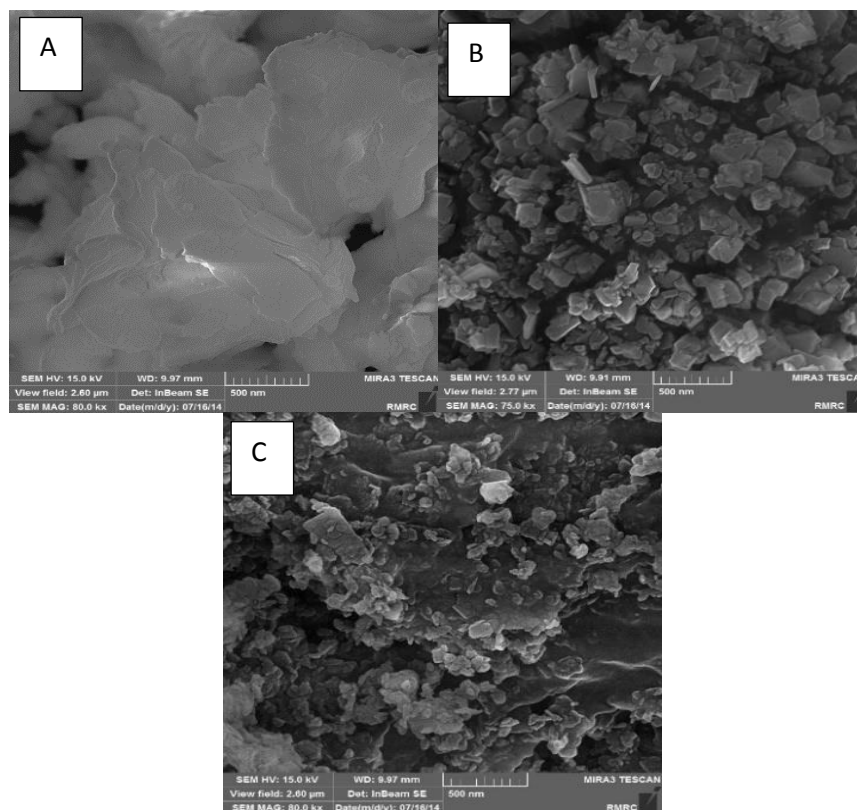


Figure 1: SEM images of catalysts; CaO (A), KF/CaO (B), KI/CaO (C).

However, this phase was generated by the reaction between water and calcined shells during wet impregnation. The crystallite sizes determined by XRD patterns of catalysts were all in the range of 30-40 nm [31, 32]. Figure 3 has depicted the FT-IR spectrums of prepared catalysts over the range of 4000-400 cm^{-1} . It can be seen that the sharp band at 3645 cm^{-1} is assigned to the OH^- groups of $\text{Ca}(\text{OH})_2$ of each sample, which was primarily identified by the XRD results. Although this phase has an ability to improve the catalytic activity but a high amount of $\text{Ca}(\text{OH})_2$ could simply cause saponification in biodiesel preparation [32, 33]. Also, Broad band in the range of 3100–3400 cm^{-1} and band at 1640 cm^{-1} are attributed to physically-sorbed water stretching vibrations [30].

Moreover, the occurrence of stretching vibrations of $\text{O}\backslash\text{C}\backslash\text{O}$ in carbonates was established by the broad band appeared at 1460 cm^{-1} and two stretching band at 712 cm^{-1} and 875 cm^{-1} [30].

3.2 Catalytic activity

The catalytic activity of CaO loaded with two potassium compounds in the waste cooking oil transesterification was done. For the suitable comparison, the same reaction conditions were applied for each prepared catalyst in all experiments (Table 1). Formation of $\text{Ca}(\text{OH})_2$, KO_2 and KO_3 enhanced Connecting locations for alcohol molecules, therefore increases catalytic activity.

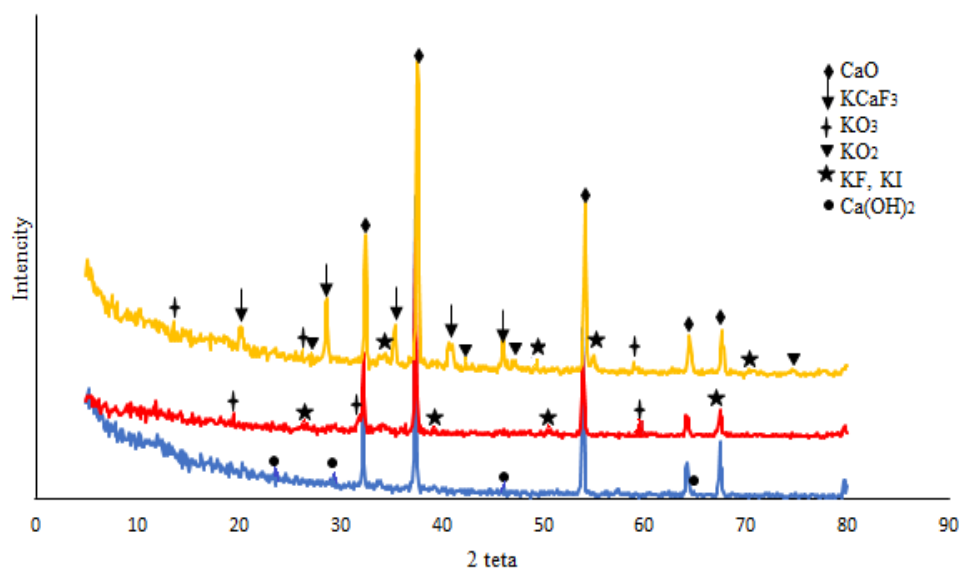


Figure 2: XRD patterns of catalysts, blue spectra for CaO, red spectra for KI/CaO and yellow spectra for KF/CaO

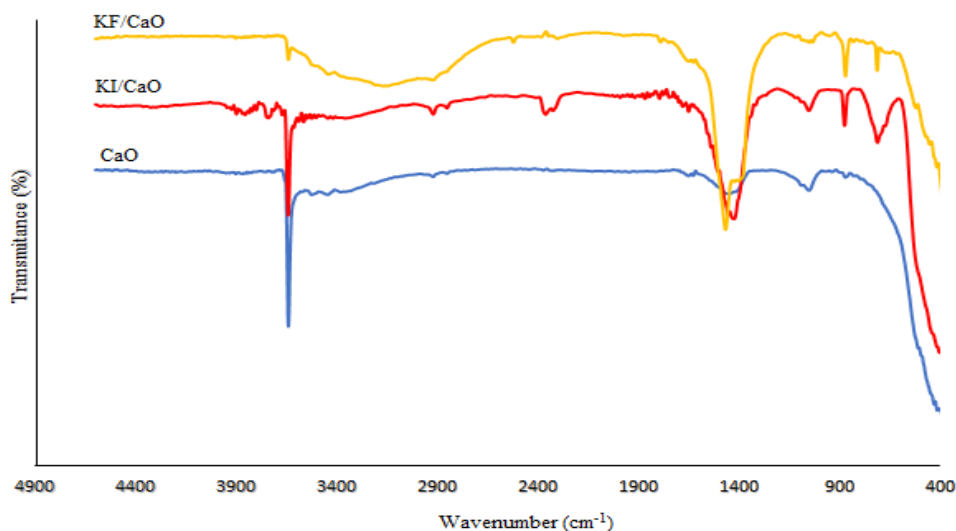


Figure 3: FT-IR spectra of catalysts.

It can be suggested that the obtained active sites are sufficient to react with triglyceride, leading to the completion of the reaction. "F" element has higher electronegativity than "I", for this reason "F" tends to form new structures with "Ca" and "K", and the new structure is KCaF₃ as active site. Based on eley-rideal mechanism, alcohol chemisorbed on to the single site of the catalyst surface, so presence of "F" causes the Ca²⁺ in KCaF₃ to be a stronger Lewis acid that has stronger attraction for CH₃O- [20]. The catalytic activity depends on ability to form methoxide ion. Also, F- is a stronger Lewis base with stronger attraction to H⁺, which makes it better to attack carbonyl group (C=O) and leads to further improve in rate and efficiency of transesterification. Accordingly, the KF/CaO with nanostructure and active KCaF₃ has higher catalytic activity than KI/CaO. Superior activity and stability are because of active component and its structure.

4 Conclusions

In this study, a solid waste i.e. eggshell has been used as a cheap resource to develop an inexpensive heterogeneous catalyst for biodiesel synthesis of waste cooking oil. In summary, potassium halides-doped CaO catalysts were successfully synthesized with wet impregnation method. Catalyst surface was consists of potassium halides and portlandite. The calcination and impregnation with particle sizes of 30–40 nm) improved active surface. The high activity of KF/CaO revealed for transesterification at 338 K, 400 rpm, 12:1 methanol ratio, because of formation of KCaF₃ as a new crystalline phase, which increased the catalytic activity and stability of catalyst. Catalyst activity is as follows: KF/CaO > KI/CaO. This paper is a comprehensive report for management of municipal solid waste used to produce green fuel.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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