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Manufacturing of zeolite based catalyst from zeolite tuft for biodiesel production from waste sunflower oil

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ABSTRACT

In the present work, zeolite based catalyst was prepared from zeolite tuft by impregnation methods. The zeolite tuft was initially treated with hydrochloric acid (16%) and then several KOH/zeolite catalysts were prepared by impregnation in KOH solutions. Various solutions of KOH with different molarities (1–6 M) were used. Further modification for the catalyst was performed by a 2nd step impregnation treatment by heating and stirring the KOH/zeolite to 80 °C for 4 h. The zeolite tuft and the prepared catalysts were characterized by several analytical techniques in order to explore their physicochemical properties. These tests include: X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), Zero point of Charge (PHzpc), Fourier Transform Infrared (FT-IR), Energy-dispersive X-Ray analysis (EDX) and X-Ray Diffraction (XRD). The catalysts were then used for transesterification of waste sunflower vegetable oil in order to produce biodiesel. Among the different catalysts prepared, the 1–4M KOH/TZT catalyst provided the maximum biodiesel yield of 96.7% at 50 °C reaction temperature, methanol to oil molar ratio of 11.5:1, agitation speed of 800 rpm, 335 μm catalyst particle size and 2 h reaction time. The physicochemical properties of the produced biodiesel comply with the EN and ASTM standard specifications.

1. Introduction

Due to the increasing demand for energy together with the expected depletion of fossil fuels resources and increasing the environmental concerns associated with fossil fuel consumption, many research have been carried out in order to find a new alternative renewable energy sources to substitute these dwindling energy reserves. Biodiesel is considered as a viable alternative fuel which can be used as petrodiesel substitutes. Biodiesel is synthesized by direct transesterification of the triglycerides that compose the vegetable oils or animal fats with a short-chain alcohol in the presence of a catalyst [1–5].

Compared with conventional diesel, it's a clean nontoxic burning fuel with approximately zero sulfur content. It has high degradability and produce low emission of carbon monoxide, particulate matter and unburned hydrocarbons [6–8]. Further, the combustion properties are similar to petroleum diesel, and hence it can replace it in diesel-fuelled combustion systems achieving nearly similar performance compounds [8–14]. The use of waste vegetable oils, which is relatively a cheap energy resource [15,16] for biodiesel production is considered an important step in reducing the biodiesel production cost and at the same time offers an environmentally acceptable way of disposing and recycling unwanted polluting waste.

For the production of biodiesel, a suitable catalyst is required to promote the transesterification reaction in order to obtain reasonable conversion to mono-alkyl esters (biodiesel) [17–20]. Homogeneous alkaline and acidic catalysts that are easily dissolved in the alcohol and are very active are usually used [6]. However, these catalysts have several problems, making the cost of biodiesel not economical as compared to petroleum diesel and affect the environmental impact of biodiesel manufacture. These problems include: formations of soap, reactor corrosion and catalysts loses (unrecyclable catalysts). The formation of soap in the product mixture leads to the loss of triglycerides molecules that can be used to form biodiesel and requires large amounts of water to wash the produced biodiesel. Thus, the waste water produced after washing requires suitable management and the separation of products from the catalyst becomes complex [21] leading to an increase in the overall biodiesel production cost [22]. Moreover, homogenous catalysts (acid or base) are corrosive in nature and their removal

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from the resulting biofuel is particularly problematic and energy intensive, requiring aqueous quench and neutralisation steps which result in the formation of stable emulsions and soaps [19].

The use of heterogeneous insoluble solid catalyst minimized problems associated with homogeneous catalysis in terms of soap formation, catalyst separation [23], recycling and regeneration [24–26]. Heterogeneous catalysts can be easily separated from the products by filtration, can be recycled and used several times. Thus, present fewer disposal problems and eliminate extensive product purification steps hence offer a more economical pathway for biodiesel production. Further, these catalysts are non-corrosive and environmentally friendly can be applied in either batch or continuous mode [27–29]. Zeolite based catalysts can represent a promising substitute for traditional catalyst in biodiesel production. Zeolites are micro-porous crystalline alumino-silicates with a three-dimensional porous structure composed of TO_4 tetrahedra (T = Si, Al) with O atoms connecting neighboring tetrahedral [30]. For a completely siliceous structure, combination of TO_4 (T = Si) units in this fashion leads to silica (SiO_2), which is an uncharged solid. Upon incorporation of Al into the silica framework, the +3 charge on the Al makes the framework negatively charged, and requires the presence of extra frame work cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral [31,32]. Zeolites have several properties that make them good catalyst for heterogeneous catalysis; (1) they exhibit high porosity and size selectivity (2) Zeolites exchanged with metal cations can be considered as solid Lewis acid–base materials. Lewis acidity is associated with the exchangeable cations and Lewis basicity with the lattice oxygen. Cation exchanged zeolites have recently received much attention as solid base catalysts. The basicity of given oxygen will be related to the density of the negative charge. Taking this into account, the basicity will be a function of framework composition (Si/Al) and the nature of extra framework cations [33,34]. Moreover, zeolites based catalysts have high thermal stability, large surface area, well defined pore structures with channels and cavities of molecular dimensions, and shape selectivity [35]. The use of zeolite in catalytic process for biodiesel production provides a number of advantages including the ease of separation from the liquid products, regenerability, and no toxicity, corrosion or environmental pollution.

The use of zeolite based catalyst for conversion of waste vegetable oils (WVO) into biodiesel has been investigated in several literature. Ramos et al. [36] used zeolites (mordenite, beta, and X) as a heterogeneous catalysts for transesterification of sunflower oil. The methyl ester yields ranged between 93.5 and 95.1 wt% at 60 °C reaction temperature. However, when the leaching studies were carried out, sodium was found to have leached in the mixture, giving the reaction a homogeneous pathway. Supes et al. [37] carried out the transesterification of soybean oil with methanol at different temperatures namely: 60 °C, 120 °C and 150 °C in the presence of NaX zeolite, ETS-10 zeolite and metal catalysts. At 60 °C and 24 h reaction time, the ETS-10 catalyst gave a conversion of 80.7 wt% whereas a conversion of 82.0 wt% was obtained by using NaX zeolite occluded with excess sodium species. Moreover, lower conversion was achieved in the work reported by Shu et al. [38] who performed the transesterification of soybean oil in the presence of zeolite beta modified with La^{3+}. For 14.5:1 methanol/oil ratio, reaction temperature of 60 °C, 14.5:1 methanol/oil ratio and 1.1 wt/wt catalyst concentration, the conversion to methyl ester was 48.9%. In almost all available work which used impregnation method for catalyst preparation, calcination was performed at high temperatures (500–900 °C) in order to transform potassium hydroxide molecules in zeolite surface and matrix into potassium oxide K_2O [36, 37, 39, 40). The K_2O represent the active site of the zeolite based catalyst.

The objective of this study was to develop a new heterogeneous catalytic system from Jordanian zeolitic tuff for biodiesel production from waste vegetable oil (WVO). The new proposed catalytic system needs to be more environmentally friendly, economically feasible and technically applicable with a minimum level of complexity in terms of preparation and use. The zeolite based catalyst was prepared from zeolite tuft by impregnation with KOH solution. The creation of the active site (K_2O) was achieved in impregnation step which combined with heating at temperatures ranges between 80 °C to 100 °C. The effects of KOH loading as well as the impregnation conditions were studied. Chemistry and the texture properties of the catalyst were studied to understanding the structures, reactivity, strengths, and amounts of the active sites on the surfaces in order to determine the most efficient preparation method of the catalyst and the desirable catalyst characteristics for transesterification of free fatty acids. The prepared catalysts were used for transesterification of waste sunflower vegetable oil in order to produce biodiesel.

2. Material and methods

2.1. Materials

Zeolitic tuff was obtained from the deposits of Tall Hassasn, Jabal-Arityan, south of Jordan the physical properties of the tuff are presented in Table A-1 (in Appendix A). Hydrochloric acid (HCl) analytical grade (37%) and potassium hydroxide (KOH, 90%) were obtained from Gulf Coast Company (GCC). For the transesterification reaction, waste vegetable oil (WVO), originally sunflower oil, was obtained from the main restaurant at the University of Jordan/Amman. The oil was used for frying beefsteak and French fries. Methanol of analytical grade (99.5%) and Potassium hydroxide (99%) were supplied by Gulf Coast Company (GCC).

2.2. Procedure

2.2.1. Treatment of zeolitic tuff

Raw zeolite tuff (RZT) was crushed, grinded and sieved. The particle size selected to carry acidic treatment was less than 150 μm. These particles were then washed several times with distilled water in order to remove all soluble salts covering the zeolite tuff surface, and dried in an oven at 105 °C for 4 h. Then, diluted hydrochloric acid (16%) was added to the dried RZT and the mixture was stirred with a magnetic stirrer at room temperature for about 24 h. The treated material was then filtered using 0.41-μm filter paper to remove the aqueous yellowish acidic solution, which was formed from the reaction of dilute hydrochloric acid and associated minerals. The treated zeolitic tuff (TZT) was then washed with distilled water until the filtrate solution become neutral, and then the sample of TZT was dried at a temperature 105 °C for four hours.

2.2.2. Catalyst preparation (KOH loaded TZT)

In the recent work, a series of zeolite-based catalysts were prepared by impregnation with KOH at different KOH concentrations.

2.2.2.1. Catalyst preparation without heating. The TZT was added to a KOH solution with various molarities (1–6 M), the solution was stirred at room temperature for 4 h, and then the solution was filtrated using 0.41 μm filter paper. The filtrate was dried at 105 °C for 4 h. After this base modification, the particles were agglomerated and grown. The resulting samples were denoted as 1M KOH/TZT, 2M KOH/TZT, 3M KOH/TZT, 4M KOH/TZT, 5M KOH/TZT and 6M