Biodiesel production from refined sunflower vegetable oil over KOH/ZSM5 catalysts

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A B S T R A C T

ZSM5 zeolite was impregnated with different KOH loadings (15 wt.%, 25 wt.% and 35 wt.%) to prepare a series of KOH/ZSM5 catalysts. The catalysts were calcined at 500 °C for 3 h and then characterized by N_2 adsorption−desorption and X-ray diffraction (XRD) techniques. The catalysts were tested in the transesterification reaction in a batch reactor at 60 °C and under atmospheric pressure. It was found that KOH/ZSM5 with 35 wt.% loading showed the best catalytic performance. The best reaction conditions in the presence of KOH/ZSM5 (35 wt.%) were determined while modifying the catalyst to oil ratio and the reaction time. The highest methyl ester yield (>95%) was obtained for a reaction time of 24 h, a catalyst to oil ratio of 18 wt.%, and a methanol to oil molar ratio of 12:1. The properties of produced biodiesel complied with the ASTM specifications. The catalytic stability test showed that 35KOH/ZSM5 was stable for 3 consecutive runs. Characterization of the spent catalyst indicated that a slight deactivation might be due to the leaching of potassium oxides active sites.

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1. Introduction

The worldwide economic growth and sustainable development are leading to an increase in energy demand. Fossil fuels (oil, gas and coal) are providing almost 80% of the world energy requirements [1]. However, fossil fuel reserves are shrinking rapidly due to increased growth in world population and industrialization [2]. Moreover, the global warming due to greenhouse gases emissions prompted the efforts to explore new sources of energy. Therefore, biodiesel production is receiving considerable attention nowadays because biodiesel is a promising alternative fuel to conventional diesel [3], is renewable, biodegradable, and produces less CO, hydrocarbons and particulates emissions than petroleum-based diesel [4,5]. Biodiesel and conventional diesel properties are very similar; however biodiesel has higher cetane number than conventional diesel, virtually no sulfur and no aromatics and high flash point [5–7].

Biodiesel, also known as Fatty Acid Methyl Esters (FAME), can be obtained by a transesterification reaction of triglycerides (in oil or fats) with methanol by using a catalyst [8]. This reaction gives glycerol as a by-product. In general, homogeneous base catalysts such as NaOH or KOH are the most suitable catalysts for transesterification reactions [6] since they are able to catalyze these reactions faster than acid catalysts [9,10]. However, homogeneous catalysts have some drawbacks, e.g. they produce large amount of waste water [11], low-quality glycerol and they cannot be reused [12]. Moreover, side reactions such as saponification can occur, imposing difficulties in the separation and purification of biodiesel [13]. On the other hand, heterogeneous catalysts are less corrosive, more environmentally friendly, safer, cheaper and they can be easily recovered, regenerated and reused [14,15].

Therefore, the use of heterogeneous catalysts for the production of biodiesel is gaining great interest. In general, heterogeneous basic catalysts are catalytically more active than acid catalysts, thus they require lower temperatures and shorter reaction times [16,17]. For instance, the alkali metals and their hydroxides supported on SBA-15 are highly active catalysts in the transesterification reaction [18]. In addition, CaO base catalysts give high yields of biodiesel, but they are highly sensitive to air [19]. It has been recently shown that lithium-based catalysts, in particular $LiAlO_2$ and Li_4SO_4, are highly active, air-insensitive and can be reused for many cycles [20–22].

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Moreover, KOH supported on Alumina, NaY zeolite [6], mordenite [23], bentonite [24], MgO [25] showed excellent catalytic activity in the production of biodiesel. However, it has been clearly documented in literature that the heterogeneous catalysts for biodiesel production deactivate or loose slightly their activity when used for several consecutive runs. This can be due to the leaching of the active phase in solution, or to the adsorption of hydrocarbons on the active sites [26–28].

To assess whether the KOH/ZSM5 catalysts perform well in the transesterification of sunflower oil with methanol, we tested a series of KOH/ZSM5 catalysts in the reaction and we evaluated the effect of active phase loading on the yield of biodiesel production.

This paper discusses the influence of active phase content in KOH/ZSM5 catalysts, the catalyst to oil ratio and the reaction time on the biodiesel production yield. The catalyst reusability is also investigated for several consecutive runs as it represents a key advantage for industrial biodiesel production.

2. Methods

2.1. Materials

Refined sunflower vegetable oil (Plein Soleil) was purchased from a local market and was analyzed based on density at 25 °C (ASTM D4052), kinematic viscosity (ASTM D445), free fatty acid content (AOCS Ca-5a-40), and water content (AOCS Aa 3–38). ZSM5 zeolite (CBV2314) was obtained from Zeolyst Company. Methanol (purity $\geq$ 99.8%), n-hexane, potassium hydroxide ($\geq$85%, pellets), and methyl heptadecanoate were supplied by Sigma–Aldrich.

2.2. Catalyst preparation

ZSM5 zeolite was used as support to prepare a series of KOH/ZSM5 catalysts with varying KOH loadings according to the wet impregnation method [6,25,35]. Appropriate amounts of KOH (1.76 g, 3.9 g and 6.33 g for 15 wt.%, 25 wt.% and 35 wt.% respectively) were dissolved in 50 mL of distilled water. Each aqueous solution of KOH was slowly added to 10 g of the ZSM5 support. The resulting slurry was then stirred (200 rpm) at 80 °C for 2 h. After impregnation, the catalysts were dried at 80 °C overnight and then calcined at 500 °C for 3 h at a heating rate of 0.5 °C/min. KOH/ZSM5 catalysts with different active phase loadings (15, 25 and 35 wt. %) were labeled 15KOH/ZSM5, 25KOH/ZSM5 and 35KOH/ZSM5, respectively.

2.3. Catalyst characterization

A Thermo-Electron QSurf M1 apparatus was used to determine the specific surface areas of the calcined catalysts, using the BET method. Prior to analysis, the samples were treated at 120 °C under helium flow for 30 min.

X-ray diffraction (XRD) experiments were performed on a Panalytical powder X-ray diffractometer. The diffraction patterns were recorded over an angular range of $5 < 2\Theta < 80°$ with a step-size of $(2\Theta) = 0.02°$. By comparing the XRD patterns to the ICDD files, the crystalline phases were identified.

X-ray Fluorescence (XRF) spectrometry was performed using a Thermo Scientific ARL 9900 Series. The potassium (K) content in the fresh and spent catalysts was measured by XRF.

FTIR Spectra of the samples were recorded on a Perkin Elmer spectrometer in the range of 500–4000 cm^{-1} with a resolution of 2 cm^{-1}. Before analysis, the samples were diluted with KBr powder and then pelletized.

The simultaneous differential scanning calorimetry/thermogravimetry (DSC/TG) analyses were carried out on a Setaram Labsys

EVO apparatus. The spent catalyst (~10 mg) was placed in an alumina crucible and introduced in the apparatus. The sample was heated from room temperature up to 600 °C (5 °C/min) under an air flow of 50 mL/min.

2.4. Transesterification reaction

All experiments were carried out in a round bottom flask batch reactor equipped with a magnetic stirrer, controlled temperature (60 °C), and a water-cooled condenser. The desired amounts of catalyst and methanol were added to the reactor and mixed together; the mixture was heated up to 60 °C. Subsequently, the sunflower oil preheated at 60 °C was added to the mixture under a stirring rate of 500 rpm. The transesterification reaction was carried out for all the catalysts with a methanol-to-oil molar ratio (MOMR) of 12:1, a temperature of 60 °C and a stirring rate of 500 rpm. The best reaction conditions were determined while varying: the amount of KOH impregnation, the catalyst-to-oil mass ratio (CTOR, wt.%) and the reaction time. At the end of the reaction, the catalyst was recovered from the mixture by means of vacuum filtration. A rotary evaporator was used to remove the excess of methanol from the filtrate. The residue was then centrifuged for 20 min at 3000 rpm to separate the biodiesel (FAME) from glycerol. The possibility to reuse the catalyst was also studied in order to check its ability to provide the same catalytic activity after many cycles.

A Gas Chromatography (Agilent 7890A series) equipped with a flame ionization detector (FID) and an HP-5 (30 m × 0.32 mm) column was used to determine the FAME content. According to the European regulated procedure EN14103, 250 mg of the ester layer were dissolved in 5 mL of the internal standard methyl heptadecanoate C$_{17}$ solution (10 g/L of C$_{17}$ in n-hexane). The FAME content was calculated using Eq. (1):

$$FAME\ (\%) = \frac{\sum A}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{W} \times 100 \tag{1}$$

where, ΣA is the total peak area of methyl esters, A_{IS} is the area of the internal standard (C$_{17}$), C_{IS} is the internal standard concentration (10 mg/mL), V_{IS} is the volume of the internal standard solution (in mL), and W is the sample weight (in mg) [29].

The physical properties, of the biodiesel produced in this work were determined according to the ASTM standard (Density at 15 °C: ASTM D.4052; kinematic viscosity: ASTM D.445; flash point: ASTM D.93).

3. Results and discussion

3.1. Characterization of vegetable oil

Table 1 shows the properties of the sunflower oil used in this study and its free fatty acid content. This oil showed the required properties for a basic transesterification reaction.

3.2. Catalyst characterization

The BET surface area of the support ZSM5 and the various

Table 1
Properties of the sunflower oil.

Properties	Sunflower oil
Density at 25 °C (Kg/m^3)	920.5
Kinematic Viscosity at 40 °C (cSt)	53.87
Water Content (wt.%)	0.09
FFA Content (wt.%)	0.22