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Synthesis of Ni/bentonite catalysts and its application for transesterification of sunflower oil into biodiesel

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ABSTRACT/RESUME

Abstract: *Biodiesel has been produced by the transesterification of sunflower oil with ethanol in the presence of a bentonite obtained from Maghnia (western Algeria) as heterogeneous catalyst, used as such and doped with nickel (III), at a mass ratio of metal/bentonite of 0.0625. The effect of reaction time (min) and catalyst type was studied. The conversion values in these catalytic systems were compared with the ones in the presence of NaOH. NaOH had the highest catalytic activity under the optimized reaction conditions. The maximum sunflower oil conversion of 92.94 % was obtained with homogeneous NaOH catalyst (1.5 %), at a reaction time 2 h and temperature of 70 °C. The conversion rates obtained on Ni/B and B were, respectively, of 91.01% and 18,37%, the same order concerning the initials reactions rates was found.*

I. Introduction

Energy demand and its resources are increasing day by day due to the rapid outgrowth of population and urbanization. Currently, the fuel crisis has globally affects the economy in every region, especially in the oil consuming countries due to its rapidly decrease of the available global stock[1,2] as a result of the grow in energy demand. The climate fast change and a rapid decline of accessible fossil fuel reserves involved the development of green, renewable energy sources, which continuously gains specialists' interest [3, 4]. In the recent years, biodiesel has been one of the most promising options to meet the energy challenges, especially in transportation sector [5].

Biodiesel contains mainly methyl esters of fatty acids produced by the alcoholysis of vegetable oils or animal fats in the presence of a catalyst, being an excellent substitute for conventional diesel fuels produced from crude oil. It is a nontoxic, biodegradable, renewable fuel, used as an alternative fuel [6]. Biodiesel is produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats, and seed plants oil. It has significantly lower emissions than petroleum-based diesel and has the major advantages of being almost sulfur-free, very low aromatic content and biodegradability [7].

Heterogeneous catalysts are the auspicious selection for biodiesel production from vegetable oils, being able to catalyze esterification and transesterification simultaneously. Catalytic activity for esterification and transesterification of vegetable oils has been reported widely [8].

The heterogeneous catalysts offer many advantages over homogeneous catalysts, such as simple catalyst recovery, catalyst reusability, simple product purification, less energy and water consumption, less added cost of purification and simple glycerol recovery. Moreover, the heterogeneous catalysts (especially alkaline ones) provide high reaction yields [9].

The original structure of the clay minerals derived from clays can be altered in a controlled way by various treatments to optimize their catalytic performance. The most commonly used means applied to clays are the treatments with mineral acids, the intercalation, pillaring and impregnation processes, which modify the local order of the clay sheets, the surface area, generates or modifies the active sites and facilitate the access of reagent molecules to active sites through the mesopores (average diameter of 20-500 Å) in the structure[12]. The clay minerals can be used as catalysts or as catalyst supports. The catalytic support helps obtaining superior catalysts, due to the increase of the surface area values and the improvement of the active phase dispersion, allowing obtaining of more active sites [13].

There are many types of clays naturally available such as kaolin and bentonite. The most abundant clay is bentonite, which has a good adsorption ability. It can be easily activated by thermal treatment and by alkali, to increase its basicity [8].

In this study we utilized bentonite from Maghnia (western Algeria) as a catalyst for the biodiesel production. In this study, nickel were used to modify the bentonite at a mass ratio of metal/bentonite of 0.0625(Meçabih, Z and Kacimi, S.and Bouchikhi, B)[14]. The metal/bentonite clays were characterized and used as catalysts for the transesterification of sunflower oil with ethanol. Sunflower oil was used as feedstock in biodiesel production, due to its large abundance and low price.

II. Materials and methods

II.1. Preliminary treatment

The clay used in this study is a bentonite from Hammam Boughrara, Maghnia, western Algeria. Commercial edible grade sunflower oil of Cevital variety was used as raw material for biodiesel production. Analytical grade ethanol, sodium hydroxide and sulfuric acid were obtained from Sigma Aldrich.

II.2. Catalyst preparation

The clay (bentonite from Maghnia, western Algeria) was purified in several stages: elimination of large solid particles (organic or mineral) by sieving, grinding, washing several times with water in order to eliminate compounds such as carbonates, organic materials, oxides and hydroxides of metanaturally included between the particles of clay and separation of clay particles (finer than 2 μm) from aggregates of larger sizes such as quartz.

The natural clays were washed several times with distilled water, then completely dispersed in water. After 17 hours at rest, the dispersion was centrifuged for one hour at 2400 rpm. The size of the clay particles obtained was < 2 μm[14].

For the activation of the clay, 20g of natural bentonite powder was added to 200 mL of sulfuric acid (1M) and the slurry was stirred continuously 24 hours at ambient temperature. The obtained suspension was then centrifuged, then the bentonite was washed several times with deionized water and dried overnight at 110°C[15]. The next step was the saturation of the bentonite by Na^+ ions, by mechanical stirring for 4 hours with NaOH solution (1M). The sodium bentonite was dried and ground to a fine powder [14].

The Ni/bentonite catalysts were synthesized using the wet impregnation method. A solution prepared by dissolving 3 g of $NiCl_2$ in 50 ml of water was added to 10 g of dried sodium bentonite and mixed with a -600 $r \cdot min^{-1}$ agitation at 70 °C for 24 h, to obtain a slurry. The slurry was dried at 120 °C for 12 h and then calcined at 400 °C for 4 h according to the work of(Karna, W and Muhammad ,A. K and Wahyu, D.S) [16] .

II.3.Characterization techniques

The X-ray diffraction patterns were registered using a Philips diffractometer (PW 1729), with a cobalt source (Kα = 1.79 Å) without rear monochromator, with an iron filter. The measurement interval 2θ varies between 2-14°, with an accumulation time of 3-20 seconds per step for the modified bentonite and 2-80 for the crude and purified bentonite. The acceleration voltage is 35 kV, the current of 30 mA. The diffractograms were indexed according to the JCPDS (Joint Committee on Powder Diffraction Standards) file. The samples are prepared using the oriented aggregate method of clay grains slammer then 2μm. The suspensions diluted to 1% in deionized water were deposited on glass tears (30-45 mm) and isolated. After 24 hours of drying at room temperature, a thin film of clay of uniform thickness glued to the wall of the blade was obtained.

The UV-Vis spectra of were recorded in the wavelength range of 370-850 nm using the Spekol 10 spectrophotometer and quartz cuvettes.

The X-ray fluorescence (XRF) is a simple technique that allows you to obtain the chemical composition of a solid, and of a clay in particular. The analysis of the purified and modified clay was carried out with a spectrometer type Lab-X 3500 - Oxford Instruments .

II.4. Transesterification reaction

II.4.1. Heterogeneous reaction

The natural bentonite (B) and nickel bentonite (Ni/B) were tested for transesterification of vegetable oil to biodiesel using ethanol. A slurry prepared from 40 ml ethanol, 60 ml refined sunflower oil 10 g solid catalyst were fed into a three-neck round bottom flask equipped with a temperature indicator and mechanical stirrer.

II.4.2. Homogeneous reaction

The ethanolysis of sunflower oil was carried out on a mixture of at 40 ml ethanol, 60 ml refined sunflower oil and 1.5%NaOH 1M .

II.5. Kinetic measurements

The reactants were stirred at 300 rpm under heating, to bring and keep the mixture at 70°C. After running the transesterification reaction for a desired duration, samples of 1mL were taken at intervals of 5 minutes from 0 to 60 minutes and filtered through filter paper to separate the solid catalyst from the mixture .

The amount of glycerol can be measured with a UV-Visible spectrophotometer using a two-step reaction process. This results in the formation of a yellow complex proportional to the amount of free glycerol in the sample. The sample is first treated with sodium periodate. Sodium periodate reacts with free glycerol in the sample to generate formaldehyde. Reaction between this formaldehyde and acetyl acetone produces the yellow complex, 3,5-diacetyl- 1,4-dihydrolutidine .This yellow compound exhibits a maximum absorbance peak at 410 nm, where its concentration in the sample is measured[17].

The calibration curve was obtained using solutions of glycerol in ethanol (Figure 1).

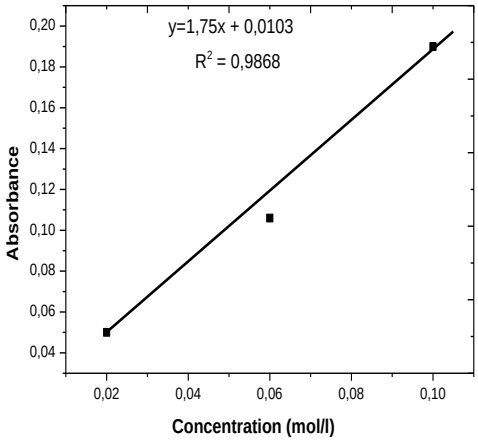

Figure 1. *Curve glycerol calibration at λ max =410nm.*

III. Results and discussion

III.1. Catalyst characterization

Figure. 2 shows the XRD patterns of bentonite and Ni/bentonite catalysts. The patterns showed obvious diffraction peaks at 2θ = 19.9° and 35.0°, which corresponded to the (101) and (107) planes of montmorillonite (JCPDS card NO. 29-1499). The diffraction peaks at 2θ = 20.9°, and 26.6° corresponded to the (101) and (107) planes of SiO2 (JCPDS card NO. 46-1045). These findings indicated that the support was a typical bentonite. The diffraction peaks at 2θ = 37.2°, and 62.7°corresponded to the (111) and (220) planes of cubic NiO (JCPDS card NO. 47-1049), respectively, and the metallic Ni was found at 2θ = 44.6° and 52.0° , which ascribed to the planes (111) and (200) of the metallic Ni (JCPDS card NO. 87-0712) [18, 19].

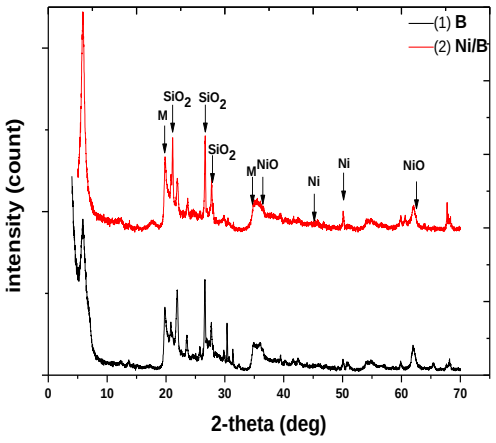

Figure 2. *The XRD patterns for natural /bentonite (B) and Ni/bentonite (Ni/B) catalyst*

III.2.Effect of reaction time

The reaction of the sunflower oil with ethanol in the presence of NaOH was carried out in order to compare the homogeneous with the heterogeneous catalysis. The ethanolysis under NaOH proved to be a very rapid and almost complete reaction in the first half-hour, with an apparent rate relative to glycerol formation of 9.14×10^{-4} mol $L^{-1}min^{-1}$. It can be seen from Figure 3 that the conversion of oil incrased from 76,48 after 15 min up to a maximum of about 92,94 % after one hours, subsequently changing very little.

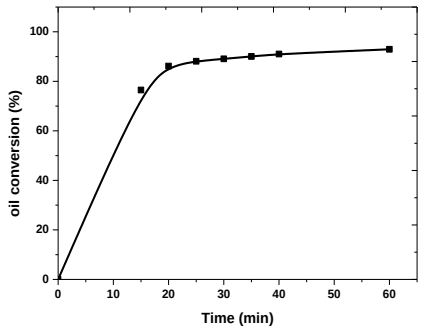

Figure 3. *Conversion rate of sunflower oil as a function of time. Reaction conditions were as follows: Catalyst amount: 1.5% of NaOH; temperature 70°C; reaction time: 120 min*

III.4. Effect of catalyst

The comparison of conversion of oil between heterogeneous (Ni/B and B) and homogeneous (NaOH) catalysts was studied. In figures 4 are displayed the kinetic results and oil conversion, compared with the ethanolysis in the presence of NaOH. This was found to be very rapid at 70°C with an oil conversion of 89,07 % in 30 min. In heterogeneous catalysis,the use of Ni/B and B gave conversion rates of 91.01% and 18,37%.The initials reactions rates varied in the following order: NaOH > Ni/B > B.

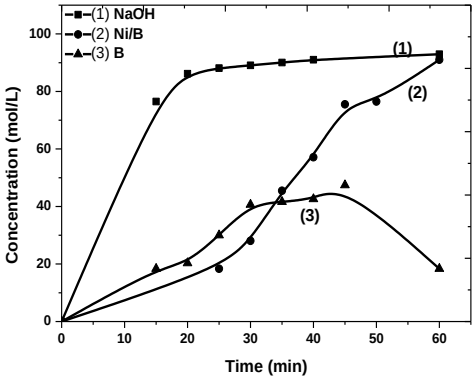

Figure 4. *Conversion rate of sunflower oil as a function of catalyst. Reaction condition: Catalyst amount 10%; temperature 70°C; reaction time: 120 min.*

As shown in Fig. 4, the maximum glycerol conversion was reached within 1 h both for the case of homogeneous and heterogeneous catalyst system. For the homogeneous catalyst system, the maximum glycerol conversion was higher than that of the heterogeneous catalyst system ,as usually happens, due mainly to the access of reactants to the active sites. However, the advantage of being a cleaner reaction in the presence of solid catalysts makes competitive the use of solids in this type of reactions.

III.3. Chemical composition of bentonite

The results (table1) show that the silica to alumina (SiO_2 / Al_2O_3) ratios of B/NA and B/Ni are 2.82 and 2.34 respectively, which confirms that the purified and modified clay is a montmorillonite. While that of raw bentonite is 3.19, this value indicates that this clay contains free particles of quartz. The relative percentage by mass of nickel is 6.5.

Table 1. *Maximum adsorption capacities for Cr(VI) ions removal by various biosorbents.*

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	NiO	Total
B	59,54	18,61	5,3	0,63	2,98	0,98	0,30	0,25	-	88 ,19
B /Na	45,81	16,23	4,69	1,36	3,28	3,73	1,89	0,03	-	77,02
B/Ni	44.51	19,0	4,1	1,3	3,2	1	1,8	0,3	6 .5	81,71

IV. Conclusion

In this study the transesterification of sunflower oil with ethanol was studied in a heterogeneous system using Ni/B and B as solid catalysts. Ni/bentonite catalyst was prepared by the impregnation method of nickel. Compared to natural bentonite catalysts, Ni/bentonite exhibited better catalytic properties in the transesterification process, producing 91,01 % conversion of sunflower oil. Both the small crystallite size of NiO and the high dispersion of NiO contributed to the conversion of sunflower oil. The conversion of sunflower oil was compared with the ethanolysis in the presence of NaOH. Our results showed that the activity of the heterogeneous catalyst (Ni/B and B) was inferior to that of the homogeneous NaOH catalyst at the reaction condition optimized to the homogeneous system. The maximum sunflower oil conversion of 92, 94 % was obtained with homogeneous NaOH catalyst (1.5 %), at a reaction time 2 h and temperature of 70 °C. The conversion rates obtained on Ni/B and B were, respectively, of 91,01% and 18,37%.

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