Middle-East Journal of Scientific Research 7 (1): 01-06, 2011
ISSN 1990-9233

Application of Synthesized γ-Al_2O_3/ZrO_2 Catalysts in Biodiesel Production

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Abstract: Biodiesel has been synthesized by esterification of oleic acid with ethanol in the presence of γ-Al_2O_3/ZrO_2 catalysts with $ZrCl_4$:$AlCl_3.6H_2O$ ratios of 1:1, 1:2 and 1:3. The catalysts were prepared by sol-gel method. The catalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) analysis and Brunauer-Emmett Teller (BET) surface area. The esterification reaction was carried out at 100°C with several mass ratios of FFA/ethanol from 1:5 to 5:5 and 10 g of catalyst in a batch reactor for 3 hours. The analysis showed that all nano alumina-zirconia particles with different ratios were mesoporous and were uniformly distributed in their crystalline phase but the catalyst with $ZrCl_4$: $AlCl_3.6H_2O$ ratio of 1:1 was finer than the other catalysts. The highest conversion of ethyl ester (97%) was obtained when using FFA/ethanol mass ratio of 5:5.

Key words: Biodiesel · Free fatty acid · Esterification · Sol-gel method · Alumina-zirconia catalysts

INTRODUCTION

Climate changes and constant rise in earth's average temperature, as a result of global warming caused by fossil fuel combustion which releases carbon dioxide, have been threatening environment and human health [1, 2]. Furthermore, experts have warned about depletion of the current sources of energy (fossil fuels) in near future and also the price of fossil fuels in international markets is increasing [3, 4]. These important reasons have simulated great interest in finding alternative sources for fossil fuels. One of the most promising alternative fuels is biodiesel. Biodiesel is attractive because it is non-toxic, biodegradable, renewable and eco-friendly [5-7]. Biodiesel is a fuel, composed of mono-alkyl esters of long chain fatty acids and is chiefly made by transesterification of vegetable oils or esterification of free fatty acids with lower alcohols [8-10]. In spite of several environmental advantages of biodiesel, it's production cost is quite high compared to common diesel fuel [11]. In order to reduce the cost, cheap raw materials such as non-refined oils, grease and recycled oils have been suggested [12]. These feed stocks have high content of free fatty acids (FFA) that may cause severe problems while base catalysts are used in esterification process. Base catalysts react with free fatty acids, forming soaps which accelerate deactivation of the catalyst and makes the separation of products troublesome [13-15]. In such cases, esterification with mineral acid catalysts such as sulfuric acid is recommended [16]. This process gives rise to problems related to corrosion, formation of high quantities of by products and long reaction times. Such problems may be overcome by the use of heterogeneous catalysts [17-19]. Ni and his coworkers have studied the esterification of palmitic acid dissolved in commercial sunflower oil with methanol using SAC-13 (Nafion/SiO_2) catalyst [20]. Ramu et al. used acid catalyst (WO_3/ZrO_2) in esterification of palmitic acid with methanol and they found a good correlation between acidity and catalyst activity [21]. Carmo et al. have obtained biodiesel by esterification of palmitic acid with methanol, ethanol and isopropanol in presence of Al-MCM-41 mesoporous molecular sieves with various Si/Al ratios. They have found that the Al-MCM-41 catalyst with the ratio of Si/Al : 8/1 had the maximum conversion values. The alcohol reactivity follows the order methanol > ethanol > isopropanol [22]. Park et al. have examined tungsten oxide zirconia, sulfated zirconia and amberlyst-15 as catalyst for conversion of

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used vegetable oils (UVOs) to fatty acid methyl esters (FAMEs). Among them, tungsten oxide zirconia was a promising heterogeneous catalyst for the production of biodiesel fuels [23]. Heydarzadeh *et al.* have optimized esterification reaction of oleic acid with ethanol by γ-Al_2O_3/ZrO_2 in a continuous packed bed reactor. They have found that at optimal conditions (mass ratio of 3:5 and reaction temperature 250°C), the FFA conversion to ethyl ester was 90% [24].

The present work aims to convert FFA to fatty acid ethyl ester using heterogeneous γ-Al_2O_3/ZrO_2 catalysts. Catalysts with several ratios of $ZrCl_4$: $AlCl_3.6H_2O$ from 1:1 to 1:3 were synthesized and characterized. The γ-Al_2O_3/ZrO_2 catalyst with $ZrCl_4$: $AlCl_3.6H_2O$ of 1:1 was used in the esterification reaction because of its finer agglomerates. Then the esterification reaction was carried out with several mass ratios of FFA/ethanol (1:5 to 5:5) to achieve the highest conversion.

Experimental

Chemicals: The oleic acid was supplied from Applichem company (Germany). The industrial grade ethanol with purity of 96% (Jahan Teb Company, Iran) was used in all experimental runs because of its nontoxicity and market availability. All chemical components of γ-Al_2O_3/ZrO_2 catalyst (alumina chloride, zirconium chloride, yttrium nitrate, citric acid and ethylene glycol) were purchased from Merck (Darmstadt, Germany).

Synthesis of γ-Al_2O_3/ZrO_2 Catalyst: The heterogeneous γ-Al_2O_3/ZrO_2 catalyst was prepared by sol-gel method. The catalyst is composed of alumina chloride ($AlCl_3.6H_2O$, Merck), zirconium chloride ($ZrCl_4$), yttrium nitrate ($Y(NO_3)_3.6H_2O$), citric acid ($C_6H_8O_7$) and ethylene glycol ($HOCH_2CH_2OH$). The preparation procedure of the catalyst include dissolving $AlCl_3.6H_2O$, $Y(NO_3)_3.6H_2O$ (1.5% mol) and $ZrCl_4$ each separately in water at 50°C. Then, all solutions with several ratios of $ZrCl_4$: $AlCl_3.6H_2O$ (1:1, 1:2 and 1:3 which are named as ZA1, ZA2 and ZA3, respectively) were thoroughly mixed and then citric acid at pH value of 4 and ethylene glycol were added to the mixture. Then the mixture was oven dried at 50°C for 18 h. The dried gel and coated clay plates were calcined at 700°C for 5.5 hours.

Powder X-ray diffraction (XRD) patterns were taken with Siemens diffractometer D500 model equipped with Cu-Kα radiation in the range of 10-70° with a step size of 0.02° and a normalized count time of 1 s/step. The morphology of calcined powders was examined using a Philips EM208S transmission electron microscope (TEM). Determination of BET surface area is an important parameter in catalytic studies. Crystalline size of the synthesized particle was calculated following Scherrer's equation as follows [25]:

$$D = \frac{0.9\lambda}{B\cos\theta}$$

Where D is the crystalline size (nm), λ is wavelength of X-ray radiation (1.54056 Å), θ is the Berg's angle, and B is the full width at half maximum. Fourier transform infrared spectroscopy (FTIR) analysis of the samples was carried out using a Nicollet Nexus 6700 spectrometer wave number, in the range of 400-4000 cm^{-1}, for studying the chemical groups. The BET surface area of the powders in air at 700°C for 5.5 h were determined by a surface analyzer model (Gemini 2375, USA) using N_2 as the adsorbate.

Esterification Reaction: Esterification reaction was conducted in a 500 ml three-necked rounded glass reaction vessel equipped with reflux condenser, thermometer and magnetic stirrer. The schematic diagram of the experimental setup is illustrated in Figure 1. All of the powders with three molar ratios of raw materials were suitable for nano particle applications as heterogeneous catalyst in chemical reactions. However, ZA1 catalysts were used in esterification reaction since they were in form of fine agglomerates. A fixed amount of catalyst (10 g) was primarily heated up to 100°C. The homogenized

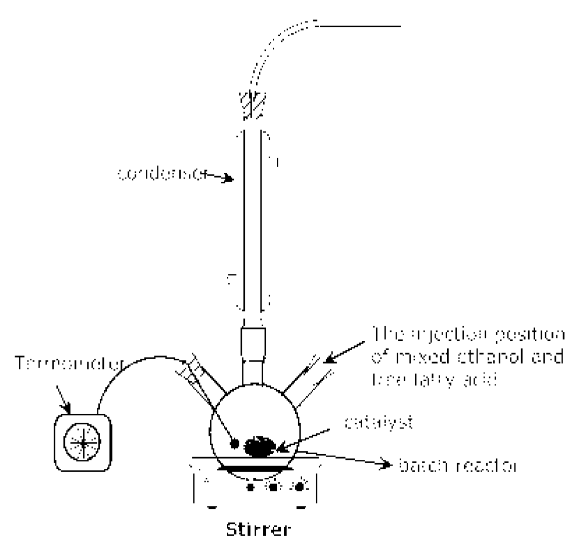

Fig. 1: Schematic diagram of experimental set up

mixture of ethanol and oleic acid were injected into the reaction vessel. Then the mixture was heated and agitated on magnetic stirrer hot plate (VELP company, model ARE, Europe) for reaction time of 3 hours. The operational variables were free fatty acid/ethanol mass ratio (1: 5, 1.5: 5, 2:5, 2.5:5 and 3:5). When the reaction was completed, the catalysts were filtered out and the remained product solution was characterized by GC-6890 gas chromatograph equipped with a capillary column (Agilent 19091J-133, 30 m × 0.25 mm × 0.2 μm) and a flame ionization detector (FID). The injector and detector temperatures were 40 and 250°C, respectively. Then the oven with initial temperature of 100°C was heated with rate of 5°C/min to 150°C and after that with the rate of 20°C/min reached to 280°C (holding for 3 min). Helium gas was used as carrier gas at a flow rate of 23.41 ml/min. The yield of ethyl ester formation was also determined by GC-MS spectrometer.

RESULTS AND DISCUSSION

The prepared catalysts were calcined and characterized. The catalysts particle size and porosity were investigated. The catalysts were mesoporous. The mesoporosity of the catalyst particles were evaluated by TEM image. The image showed that particles were all uniform and in spherical shape. Esterification reaction of ethanol with FFA mixture was carried out with aim of maximizing ethyl ester production. The experiments were conducted with several mass ratios of FFA/ethanol. In following sections characterization of the catalyst and effect of variable mass ratios of FFA/ethanol was studied.

Catalyst Characterization: Structural properties of catalysts were evaluated; (XRD) analysis of the variable catalyst loadings was performed. The XRD patterns indicated that the synthesized powders seem to be amorphous that was due to nature of organic compounds in the raw materials. The strong peak at 2θ=14.7°, was assigned to the lattice plan whereas the weak peak at 2θ=54.2°, and 55.3° were ascribed to lattice planes of γ-Al_2O_3. By increasing the molar ratio of aluminum/zirconium salts in catalyst, γ-Al_2O_3 peak became stronger. Also, the strong peak at 2θ=30.2° is assigned to the (111) lattice plan whereas the other weak peaks at 2θ=35.11°, 50.65°, 60.17°, and 63.10° may be associated with (200), (220), (131), and (222) lattice planes of tetragonal Zirconia (t-ZrO_2) phase, respectively. The yttrium in the solution has changed to yttrium oxide when

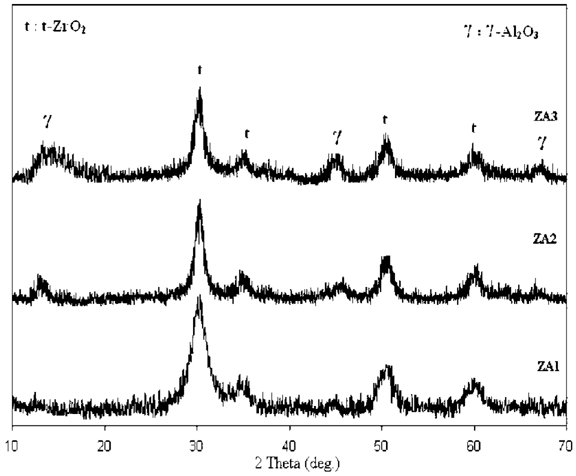

Fig. 2: XRD patterns of fabricated catalysts

it was heated to 700°C. The stabilization of t-ZrO_2 may be attributed to the structural similarity of the dopant Y_2O_3 to ZrO_2 and to larger dopant cation radius compared to Zr^{4+} radius [26]. It was concluded that the prepared nanopowders had distinct crystalline structure in which the alumina was diffused into the zirconia lattice and stabilized the crystal phase of zirconia in the prepared samples. The broadening of the peaks in XRD pattern confirmed that the average crystallite sizes were small. The XRD pattern is shown in Figure 2.

BET analysis was carried out to determine the surface area and pore volume of the catalyst. The surface area of ZA1, ZA2 and ZA3 powders were ~120, ~80, ~70 m^2/g, respectively. The provided surface of the particles was suitable for the catalytic activities. Increasing the amount of aluminum salt in the catalyst, caused specific areas of the nanopowders decreased and also the pore size narrowed. Hence, the surface area of the nano particle catalyst is directly dependent on the loading of aluminum salt in catalyst.

The size and morphology of the nano powder particles were examined by TEM. Figure 3 shows the micrographs of ZA1, ZA2 and ZA3 powders synthesized and calcined at 700°C for 5.5 h. Most of the particle sizes were in the range of 25-70 nm. The grain size and mesoporosity of ZA1 was smaller than ZA2 and ZA3. But there was no significant difference between ZA2 and ZA3 powders. According to TEM micrographs, the aspect ratio of particles was significantly increased by increasing molar ratio of aluminum salt. Also, TEM images show that ZA1 powders were agglomerated more than ZA2 and ZA3 powders.

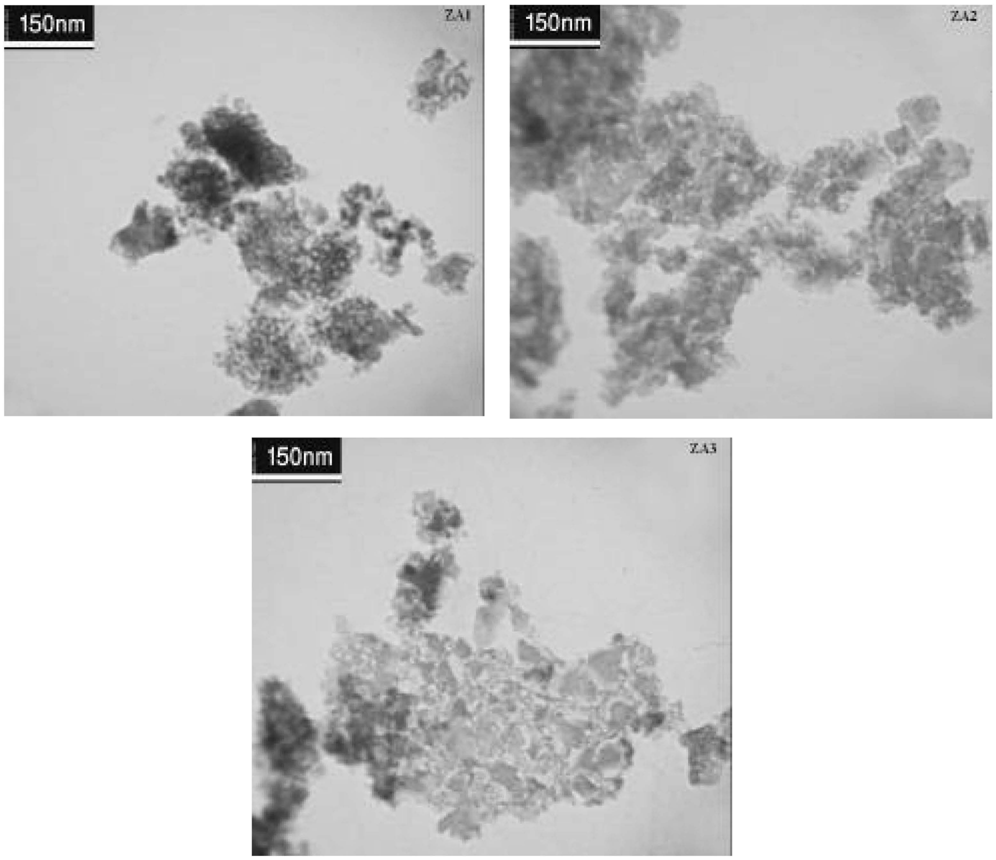

Fig. 3: Transmission electron micrographs of the ZA1, ZA2 and ZA3 powder particles

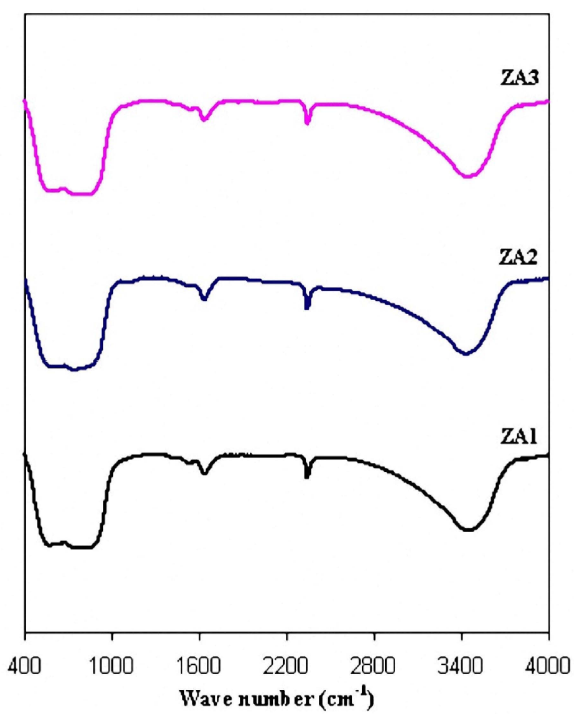

Fig. 4: FTIR spectrum of the synthesized catalysts

The FTIR spectrum of the samples (Figure 4) shows band centered at 470 cm^{-1} corresponds to the vibration absorption of Zr–O. The bands at ~600 and ~800 cm^{-1}, assigned to the Al–O bonding vibration, respectively. The structure of tetrahedral and octahedral environments, leads to γ-alumina [27, 28]. This can be explained by the relative contribution of Zr–O and Al–O bonds, and is consistent with the formation of ZrO_2–Al_2O_3 solid solution. The band located at ~3440 cm^{-1} is attributed to the O–H stretching vibration and the band at ~1620 cm^{-1} is assigned to H–O–H symmetric stretching vibration of adsorbed water molecules.

Effect of FFA/ethanol Mass Ratio on Ethyl Ester Formation: Since, the rate of esterification is strongly dependent on amount of raw materials, the mass ratio of fatty acid to ethanol was studied. Five sets of experiments were carried out with free fatty acid/ethanol mass ratio of 1:5, 2:5, 3:5, 4:5 and 5:5 to obtain a desired mass ratio. Figure 5 depicts the yield of ethyl ester formation as a function of mass ratio of free fatty acid/ethanol. For the stoichiometric esterification process the theoretical molar ratio of fatty acid to ethanol is expected to be 1:1.

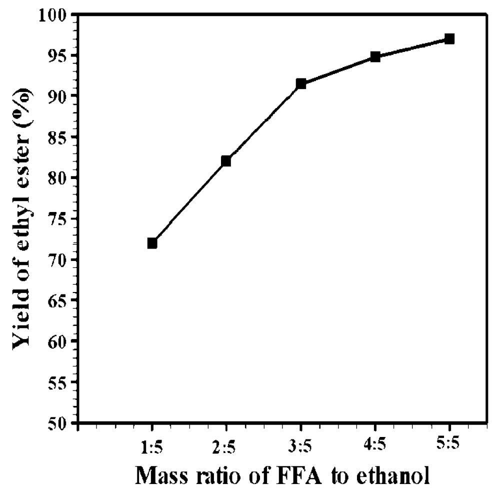

Fig. 5: Effect of mass ratio of FFA/ETOH on yield of ethyl ester

The obtained data showed that as the mass ratio of free fatty acid/ethanol increased, the ethyl ester production was also increased. For the mass ratio of 5:5 maximum ethyl ester yield was 97%. This finding confirmed that no excess amount of ethanol is needed for complete reaction. The obtained yield (97%) was much higher than the yield of similar experiment carried out in a continuous catalytic reactor (90%) by Heydarzadeh and his coworkers [24].

CONCLUSION

Sol-emulsion-gel method was used to synthesis Nano powder catalysts. Catalysts with three molar ratios of $ZrCl_4$:$AlCl_3.6H_2O$ were prepared. The synthesized γ-Al_2O_3 / t–ZrO_2 nanopowders were uniform and spherical shape with the particle size of 20–75 nm. The catalysts were heat treated and calcined at 700 and milled. As the molar ratio of $AlCl_3.6H_2O$:$ZrCl_4$ increased, the particle size increased while the surface area of the nanopowders decreased. The synthesized nano alumina-zirconia particles and were uniformly distributed in its crystalline phase and the structure was mesoporous. All of the prepared nanopowders with three different molar ratios of raw materials were suitable to be used as nano particle catalysts in heterogeneous chemical reactions. In the esterification reaction, as the mass ratio of free fatty acid/ethanol increased, the ethyl ester formation was also increased. With implementation of optimal mass ratio of FFA/ethanol (5:5), the maximum yield of approximately 97% was achieved.

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