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Biodiesel production with nanotubular sodium titanate as a catalyst

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A B S T R A C T

Sodium titanate nanotubes (STNT) with a chemical formula $Na_2Ti_3O_7 \cdot nH_2O$ were synthesized and tested as a heterogeneous catalyst in the transesterification of soybean oil with methanol. The catalyst was characterized by N_2 physisorption, powder XRD, scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM) and CO_2 temperature-programmed desorption (CO_2-TPD). It was found that the prepared catalyst had nanotubular structure, high sodium content (10.3 wt.%) and attractive textural characteristics (surface area around 200 m^2/g and total pore volume of 0.61 cm^3/g). The influence of the catalyst's loading, methanol to oil molar ratio, reaction time and temperature on the biodiesel yield was investigated. High biodiesel yields (97–100%) were obtained with the STNT catalyst at 8 h reaction time at methanol reflux temperature with 1–2 wt.% of the catalyst and 40:1 methanol:oil molar ratio. Increase in the reaction temperature to 100–120 °C had a positive effect on the biodiesel yield. In this case, 99–100% yields were obtained with a lower catalyst loading (~1 wt.%) and methanol to oil molar ratio (20:1). In addition, it was found that the STNT catalyst does not require high temperature thermal pre-treatment (activation) before the transesterification reaction. The reuse of the same catalyst in the transesterification reaction three times showed a decrease of about 10% in the catalytic activity.

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1. Introduction

Nowadays, most of the existing motor vehicles operate with petroleum-derived fuels such as gasoline and diesel. However, the continuous use of these fuels has resulted in serious environmental problems all over the world. In addition, fossil fuel resources are limited. In order to reduce the use of petroleum-based fuels it is necessary to develop alternative clean fuels derived from renewable sources, which can be used without significant modifications to existing engines. Among the many possible options, biodiesel fuel derived from vegetable oil and usually composed of fatty acid methyl esters (FAME) attracts attention as a promising substitute for conventional diesel fuels [1–4]. Most biodiesel is produced today by the transesterification of triglycerides with mono-alkyl alcohols, principally methanol, using a dissolved alkaline catalyst (NaOH, KOH, etc.) [3]. Current biodiesel production costs are still rather high compared with petroleum-derived diesel. This is mainly due to the high cost of processing, which includes different steps of separation and purification, and to the difficulty of removal of the homogeneous catalyst after the reaction for its possible reutilization. This problem can be solved in the near future by replacing conventional homogeneous catalysts with highly active, environmentally friendly heterogeneous ones, allowing simplification of the existing processes [5–13].

A large variety of solid basic catalysts have been developed for the transesterification of vegetable oils over the past decade: $Na/NaOH/\gamma\text{-}Al_2O_3$ [2], KNO_3/Al_2O_3 [5], MgO [7], CaO [14], K_2CO_3, KOH and NaOH supported on MgO [9,10,15], $MgO\text{-}CeO_2$ mixed oxides [15], KNO_3/NaX [16], CaO supported on NaY, KL and NaZSM-5 zeolites [17], tetramethylguanidine supported on SBA-15 silica [18], etc. Most of these catalysts are based on the use of alkali and alkaline earth metals or various other compounds showing active basic sites. Some reviews about heterogeneous catalysts for biodiesel production have been published recently [4,6–8,11–13]. Among different basic solids studied, nanostructured catalysts have attracted special attention, because it is well known that heterogeneous catalyst activity is surface dependent. Catalytically active materials reduced to nano-scale (1–100 nm) can show a much larger surface/volume ratio compared to their properties on the macro-scale [4]. With the aim of increasing surface area

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and concentration of active sites, several metal oxides (CaO [19], MgO [20,21], Al_2O_3 [22], La and Mg mixed oxides [23], etc.) and compounds (mesoporous nanosized KF/CaO-MgO catalyst [24], Zn doped heteropoly acid $Zn_{1.2}H_{0.6}PW_{12}O_{40}$ [25], etc.) were prepared in the form of nanocrystals and nanotubes. However, despite the fact that most of the above catalysts have shown promising results with good-to-high biodiesel yields, the majority of them have some disadvantages. These include high cost, high reaction temperature and long reaction time, need for high temperature pre-treatment (activation) before use, sensitivity to the presence of water and CO_2 during storage, leaching of the catalytically active species in the reaction medium, etc. The above explains why the interest in the development of new catalytic systems for biodiesel synthesis, easier to manage and reuse, continues growing.

In the present work, we report results obtained from the transesterification of soybean oil with methanol in the presence of sodium titanate nanotubes (STNT) as a catalyst. Nanotubular titanate was synthesized for the first time by Kasuga et al. [26,27] by a hydrothermal alkali treatment of a TiO_2 precursor at relatively low temperatures. This material, nanostructured in one dimension (1D), can be synthesized from a variety of TiO_2 precursors, on a relatively large scale with uniform morphology and high efficiency. Regarding the chemical composition of the as-synthesized nanotubes, it is generally accepted that as a result of hydrothermal treatment with concentrated NaOH aqueous solution, the titania precursor is transformed into a hydrous sodium trititanate with a chemical formula $Na_2Ti_3O_7 \cdot nH_2O$, which forms multi-walled scroll-type nanotubes [28]. Sodium plays an important role in the formation of the nanotubular structure. Sodium atoms are located on the surface of sodium titanate nanotubes, as well as in the interlayer space of the nanotube's wall, which contributes to stabilize the nanotubular structure [29,30]. Since the as-synthesized nanotubes have high sodium content and attractive textural properties, it is interesting to inquire into the possibility of their use for biodiesel production. To the best of our knowledge, nanostructured sodium trititanate has not been tested previously in the transesterification reaction. Results from the catalyst's characterization are also presented.

2. Experimental

2.1. Catalyst preparation

Sodium titanate nanotubes were synthesized by an alkali hydrothermal treatment following a procedure reported by Kasuga et al. [26,27]. Low surface area ($7.6 \, m^2/g$) commercial titanium dioxide (anatase, Aldrich) was used as the TiO_2 source. For the sodium titanate nanotube synthesis, 10 g of TiO_2 were mixed with 150 ml of a 10 M NaOH solution, followed by hydrothermal treatment in a Teflon-lined autoclave at 140 °C for 20 h upon constant magnetic stirring. After the hydrothermal reaction, the white powder of sodium titanate nanotubes was filtered in vacuum, washed several times with deionized water to eliminate the excess of non-reacted caustic soda and dried at 120 °C for 12 h. For convenience, we hereafter denote synthesized sodium titanate nanotubes as STNT.

2.2. Catalyst characterization

Synthesized sodium titanate nanotubes were characterized by N_2 physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM) and CO_2 temperature-programmed desorption (CO_2-TPD). Nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP 2020 automatic analyzer at liquid N_2

temperature. Prior to the experiments, the samples were degassed ($p < 10^{-1}$ Pa) at 250 °C for 6 h. Specific surface areas (S_{BET}) were calculated by the BET method, the total pore volume (V_p) was determined by nitrogen adsorption at a relative pressure of 0.98, average pore diameter (D_P) and pore size distributions were obtained from the adsorption isotherms by the BJH method. XRD patterns were recorded from 3° to 80° (2Θ) on a Bruker D8 Advance diffractometer, using CuK_{α} radiation ($\lambda = 1.5406 \, Å$) and a goniometer speed of $1°(2\Theta) \, min^{-1}$. Morphology and chemical composition of the STNT support was determined by SEM-EDX using JEOL 5900 LV microscope with OXFORD ISIS equipment. High-resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) patterns were recorded with a Jeol 2010 microscope (resolving power 1.9 Å at 200 kV). The solid was ultrasonically dispersed in heptane and the suspension was collected on carbon-coated grids. HRTEM pictures were taken from different parts of the same sample dispersed on the microscope grid. Temperature-programmed desorption of adsorbed CO_2 (CO_2-TPD) was used to obtain information on the basic sites of the STNT catalyst. The TPD analysis was performed using 0.1 g of catalyst placed in a fixed-bed U-shaped quartz reactor. The sample was first pre-treated in He flow (30 mL min^{-1}) at 350 °C for 2 h, then the sample was cooled at room temperature and flushed with a CO_2/He gas mixture (50%, 30 mL min^{-1}) for 30 min followed by purging of the remaining CO_2 with He flow. Finally, the TPD was run from room temperature to 600 °C at a constant heating rate of 10 °C min^{-1} in He stream gas. The effluent gas was analyzed by mass spectrometry (MS HPR20, Hiden Analytical). The MS intensity for CO_2 ($m/e = 44$) was recorded as a function of temperature. Basicity was estimated as being the total amount of CO_2 released through thermal programmed desorption per gram of the STNT sample, inasmuch as the number of desorbed molecules is supposed to be equal to that of the adsorption sites present on the catalyst surface. The temperature required to release adsorbed CO_2 molecules characterized the base strength.

2.3. Transesterification of soybean oil with methanol

Commercial edible-grade soybean oil was obtained from the market. Transesterification reactions of this oil with methanol were performed using two different reaction systems: a glass flask reactor operating at atmospheric pressure at methanol boiling temperature, and a batch reactor able to operate at different reaction temperatures and pressures. In the first case, a 250 cm^3 three-necked glass flask with a water-cooled condenser was charged with 27 g of soybean oil, different volumes of anhydrous methanol (99.8%, Aldrich), and varied amounts of catalyst. The mixture was refluxed for 2 or 8 h of reaction time under vigorous stirring. This reaction system was used to study the effects of reaction time, oil to methanol molar ratio and the amount of the catalyst on biodiesel yield. In the second case, reactions were carried out in a 300 ml stainless steel batch reactor (Parr) equipped with a stirrer and a cooling jacket surrounded by a heating mantle controlled by a temperature controller. Soybean oil (54 g) and methanol (40 g, methanol to soybean oil molar ratio = 20:1) were added together with 1 g of catalyst into the reactor, and then the temperature was raised to 60, 80, 100 or 120 °C under stirring at 600 rpm. In this case, the transesterification was carried out for 8 h. This reaction system was used to study the effect of the reaction temperature on biodiesel yield. After the reactions, the solid catalyst was separated from the reaction mixture by centrifugation, and the residual methanol was separated from the liquid phase via rotary evaporation. Then, the liquid was put into a separation funnel and kept at ambient temperature for 24 h, after which two liquid phases appeared. The upper layer was biodiesel with some traces of unreacted oil and methanol, and the lower layer was glycerol.