



Novel heterogeneous basic catalysts for biodiesel production: Sodium titanate nanotubes doped with potassium



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ARTICLE INFO

Article history:

Received 15 November 2013
Received in revised form 25 February 2014
Accepted 16 March 2014
Available online 5 April 2014

Keywords:

Biodiesel
Transesterification
Heterogeneous catalyst
Sodium titanate nanotubes
Potassium incorporation

ABSTRACT

Sodium titanate nanotubes doped with potassium were synthesized by the Kasuga method and tested as catalysts for biodiesel production. Potassium was added to the nanotubes in order to increase their basicity and, consequently, improve their performance in the transesterification of soybean oil with methanol. The synthesis temperature and NaOH:KOH molar ratio used in the preparation were changed in order to define the best experimental conditions leading to solids with nanotubular morphology and improved potassium loading. Synthesized catalysts were characterized by N₂ physisorption, powder XRD, scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM), FT-IR, FT-Raman and CO₂ temperature-programmed desorption (CO₂-TPD). Obtained results showed that the optimal synthesis temperature was 140 °C. At this temperature, sodium trititanate nanotubes containing 1.5 wt.% of potassium were obtained when 10 M alkali solution with NaOH:KOH molar ratio of 9:1 was used. In this case, the proportion of sodium and potassium in the synthesized material was similar to that used in the synthesis. An increase in the proportion of KOH to 20 and 30 mol% in the NaOH–KOH solution used in the synthesis allowed obtaining sodium titanate nanotubes with larger potassium loadings (3.2 and 3.3 wt.%, respectively). Sodium titanate nanotubes doped with potassium showed a higher amount of medium and strong basic sites than the pure sodium counterpart (NaTNT) used as a reference. Their catalytic activity in the transesterification was also higher than that of the reference NaTNT sample. The best results were obtained with the samples containing 3.2–3.3 wt.% of potassium. Conversions of soybean oil to methyl esters obtained with these catalysts at 80 °C and 1 h reaction time were about 94–96%.

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1. Introduction

Nowadays, a clear increase in the requirements for high quality gasoline and diesel fuels is observed all over the world. The use of only petroleum-derived fuels cannot satisfy this demand, since fossil fuel resources are limited and petroleum price continually rises. For this reason the possibility of developing alternative energy sources able to replace traditionally used fossil fuels has attracted much attention in the last few decades. Biodiesel seems to be a promising substitute for conventional diesel fuel [1–4]. Biodiesel is defined as a fuel comprised of mono-alkyl esters of

long-chain fatty acids derived from vegetable oils or animal fats [5]. Biodiesel has a series of benefits in comparison with diesel fuel, namely, it is a renewable, non-toxic and biodegradable fuel with a low emission profile [6]. In addition, it is compatible with commercial diesel engines, which do not require any modifications. The most common way to produce biodiesel is by the transesterification of triglycerides with alcohols, principally methanol. In this reaction, triglycerides react with an alcohol to produce fatty acid mono-alkyl esters (FAME) and glycerol. Generally, basic catalysts are used in industry to increase the reaction rate and to produce biodiesel in moderate reaction conditions. Among them, dissolved alkaline catalysts (NaOH, KOH, etc.) are the most common [3]. However, the use of such homogeneous catalysts results in high biodiesel cost, which is mainly due to the difficulty of separation and purification of the obtained product and removal of the catalyst after the

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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 the simplification of the existing processes [7–15].

Many different solid basic catalysts have been tested recently for biodiesel production showing promising results with good-to-high biodiesel yields [4,8–10,13–15]. Most of these catalysts contain alkali or alkaline earth metals providing them basic character: Na/NaOH/ γ -Al₂O₃ [2], KNO₃/Al₂O₃ [7], K₂CO₃, KOH and NaOH supported on MgO [11,12,16], KNO₃/NaX [17], CaO supported on NaY, KL and NaZSM-5 zeolites [18], KF/CaO–MgO catalyst [19], Zn doped heteropoly acid Zn_{1.2}H_{0.6}PW₁₂O₄₀ [20], etc. Some of these catalysts were prepared in the form of nanostructured materials (nanocrystals or nanotubes) in order to increase surface area and the amount of catalytically active sites [19,20]. However, the majority of the above mentioned catalysts have some disadvantages: high cost, high reaction temperature and long reaction time, need for high temperature activation before use, low stability during storage in the presence of water and CO₂, leaching of the catalytically active species in the reaction medium, etc. The above explains a growing interest in the development of new catalytic systems for biodiesel synthesis, easier to manage and reuse.

Recently, in our group, sodium trititanate nanotubes were synthesized and tested in the transesterification of soybean oil with methanol [21]. This material was synthesized by the method proposed by Kasuga et al. [22,23], which consists in the hydrothermal treatment of the titania precursor with concentrated (10 M) NaOH aqueous solution. The nanotubular material synthesized by us had attractive textural properties (200 m²/g surface area and 0.61 cm³/g pore volume) and contained 10.3 wt.% of Na. Temperature programmed desorption of CO₂ showed that it had a high proportion of weak and medium strength basic sites, and only a small amount of strong ones. Nevertheless, the synthesized solid was able to catalyze the transesterification reaction. High biodiesel yields (97–100%) were obtained at 8 h reaction time at methanol reflux temperature with 2 wt.% of the catalyst and 40:1 methanol:oil molar ratio, or at higher reaction temperature (100–120 °C) but with lower catalyst loading (1 wt.%) and methanol to oil molar ratio (20:1). In addition, it was found that the synthesized nanotubular catalyst does not require high temperature thermal pre-treatment (activation) before the transesterification reaction, and it can be reused for several times without a significant decrease in the catalytic activity.

As a continuation of this work, we inquired here into the possibility of increasing the strength of basic sites of such sodium trititanate nanotubes by the incorporation of potassium in order to improve their performance in transesterification. Previously, it was shown that nanotubular titanate structures were not formed when the NaOH solution was completely replaced by KOH in the Kasuga synthesis [24]. It was concluded that sodium plays an important role in the formation and stability of titanate nanotubes [24,25]. We took this information into account and decided to substitute only a small fraction of NaOH used in the synthesis of nanotubes by KOH (10–30 mol%). In the present work, we report results on the synthesis, characterization and catalytic activity of sodium trititanate nanotubes doped with potassium in the transesterification of soybean oil with methanol. Two series of nanostructured solids were synthesized. In the first one, the molar ratio of NaOH to KOH used in the synthesis was maintained constant (9:1), and the temperature of the hydrothermal treatment of the titania precursor was varied between 100 and 160 °C in order to determine the optimal synthesis temperature. When the optimal synthesis conditions were defined, the second series of materials was prepared keeping constant the reaction temperature and varying NaOH:KOH molar ratio from 9:1 to 7:3, with the aim of increasing potassium loading in the nanotubular structures. Synthesized materials loaded with

potassium were compared with pure sodium titanate nanotubes reported in our previous work [21].

2. Experimental

2.1. Catalyst preparation

Sodium titanate nanotubes doped with potassium were synthesized by an alkali hydrothermal treatment following a procedure reported by Kasuga et al. [22,23]. Low surface area (8 m²/g) commercial titanium dioxide (anatase, Aldrich) was used as the TiO₂ source. In each synthesis, 10 g of TiO₂ were mixed with 150 ml of a 10 M alkali solution, followed by hydrothermal treatment in a Teflon-lined autoclave for 20 h upon constant magnetic stirring. After the hydrothermal reaction, the white powder of 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. Two series of materials were prepared following the above procedure. In the first one, a 10 M alkali solution was prepared using both NaOH and KOH in molar ratio 9:1. In this case, the temperature of the hydrothermal treatment of the titania precursor was varied between 100 and 160 °C to determine the optimal reaction temperature. The second series of samples was prepared at 140 °C reaction temperature varying NaOH:KOH molar ratio in 10 M alkali solution from 9:1 to 8:2 and 7:3. For convenience, hereafter we denote titanate nanotubes from the first series of experiments as NaKTNT(*T*), where *T* represents the synthesis temperature (*T* = 100, 120, 140 or 160 °C). Regarding the second series of samples, the nomenclature is NaK(%TNT), where % corresponds to molar percentage of KOH present in 10 M alkali solution used in the synthesis.

2.2. Catalyst characterization

Synthesized sodium titanate nanotubes doped with potassium were characterized by N₂ physisorption, X-ray powder diffraction (XRD), scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), FT-IR, FT-Raman and CO₂ temperature-programmed desorption (CO₂-TPD). Nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP 2020 automatic analyzer at liquid N₂ 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, pore diameters (D_p) and pore size distributions were obtained from the adsorption isotherms by the BJH method. The X-ray powder diffraction patterns of the synthesized samples were recorded at room temperature with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) on a Bruker D8 Advance diffractometer having θ – θ configuration. Diffraction intensity was measured in the 2θ range between 4° and 110°, with a 2θ step of 0.039° for 52.8 s per point. Chemical composition of the synthesized materials was determined by SEM-EDX using JEOL 5900 LV microscope with OXFORD ISIS equipment. Transmission electron microscopy (TEM) images were recorded with a JEOL 2010 microscope operating at 200 kV (resolving power 1.9 Å). The solids were ultrasonically dispersed in heptane and the suspension was collected on carbon-coated grids. TEM pictures were taken from different parts of the same sample dispersed on the microscope grid. TGA analysis was used to determine the amount of chemisorbed water in the synthesized materials [26]. TGA experiments were performed on a Mettler-Toledo TGA/SDTA 851° in dry air flow (50 ml/min) in a temperature range 25–1000 °C with a heating-up rate of 10 °C/min. FT-IR spectra were recorded on a Varian 640-IR spectrometer equipped with a PIKE accessory. Micro-Raman

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