



Potassium titanate for the production of biodiesel



D. Salinas^{a,*}, S. Guerrero^b, A. Cross^c, P. Araya^d, E.E. Wolf^c

^a Department of Physical Chemistry, Faculty of Sciences, University of Concepcion, Post Office 160-C, Concepción, Chile

^b Faculty of Engineering and Applied Sciences, Universidad de los Andes, Monseñor Álvaro del Portillo 12455, Las Condes, Santiago, Chile

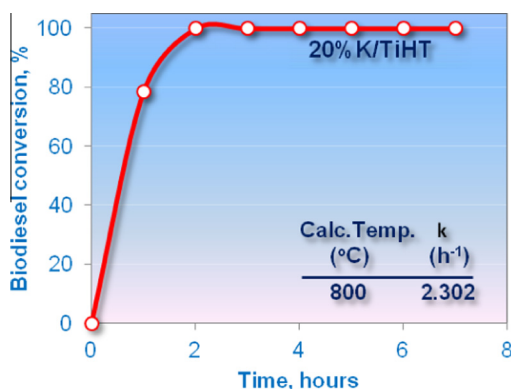
^c Department of Chemical and Biomolecular Engineering, University of Notre Dame, IN 46556, USA

^d Department of Chemical Engineering and Biotechnology, Universidad de Chile, Post Office 2777, Santiago, Chile

HIGHLIGHTS

- High calcination temperature resulted in of highly active titanates.
- Potassium oxide changed to potassium titanate when calcining at high temperature.
- Calcining at 700–800 °C led to total conversion to methyl esters after 2 h.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 August 2015

Received in revised form 30 October 2015

Accepted 31 October 2015

Available online 6 November 2015

Keywords:

TiO₂

Potassium oxide

Potassium titanate

Transesterification

Canola oil

ABSTRACT

The temperature effect and basic structural features of a potassium catalyst supported on hydrothermal TiO₂ were studied. The calcination of a 20%K/TiHT catalyst at temperatures higher than 600 °C, led to a change of the crystalline phase of potassium oxide into a potassium titanate. Despite the low surface area of the catalyst calcined at high temperature total conversion to methyl esters was achieved at 2 h of reaction. These results are explained by the presence of highly strong basic sites associated with the potassium titanate structure formed on these catalysts.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The production of biodiesel from vegetable oil has attracted increasing attention in recent years. Traditionally, the transesterification reaction is one of the best known mechanism for producing liquid fuels from biomass. Currently, the majority of biodiesel production is based on homogenous catalytic systems using corro-

sive bases like: NaOH, KOH, NaOCH₃ or KOCH₃ [1–3]. Although these catalysts are highly active, it is not possible to recover the used alkali and the product needs to be purified, which leads to large amounts of wastewater. In contrast, heterogeneous catalysts can be recovered after reaction and reused several times, which in turn produces less wastewater. These benefits have increased the interest in the development of a heterogeneous catalyst for biodiesel production.

The current literature reports about various new solid basic catalysts for the heterogeneous transesterification to biodiesel [4,5].

* Corresponding author.

Different bulk metal oxides have demonstrated to be active in this reaction such as MgO [6], CaO [7–9], and basic zeolites [10]. Many reports exist on supported metal oxides such as KNO₃/Al₂O₃ [11,12], KI/Al₂O₃ [13], K₂CO₃/Al₂O₃ [14], CaO/MCM-41, CaO/SBA-15 [7], Mg/ZrO₂ [15].

From the above literature it follows that, the most common alkaline metal found on these catalysts are potassium and sodium. Guan et al. reported on the use of K₃PO₄ as a solid catalysts being active on the transesterification of used oils [16]. Bazi et al. [17] studied different salts, and among others, they reported a KF catalyst supported on a natural phosphate. The results were not very promising, however, due to the poor interaction between the KF phase and the phosphate support. Similarly, Fan et al. [18], using a KF-modified CaO–MgO catalyst achieved 97.9% conversion, which decreased down to 86.7% after four successive reactions. They ascribed the activity of the catalyst to the formation of KCaF₃ and K₂MgF₄ as active centers. On the other hand, Kumar and Ali [19] found that it was possible to use a K/CaO catalyst and to achieve total conversion in each cycle. Nevertheless, three successive cycles showed that each reaction cycle required 2.5 h, 4.3 h, and 5.8 h to obtain full conversion. Using a SBA-15 zeolite as support, Galvao et al. [20], found that a KI/SBA-15 catalyst achieved a conversion to methyl esters of 85% and Xie et al. [21], found that SBA15-pr-NH₃OH system achieved conversion over 80% at 30 min of reaction. Xien et al. [9] report new solid system where silica supported tin oxide is used like acid solid allowing to do esterification and transesterification in the same reaction system where the solid was able to yield over 80% biodiesel conversion. Intarapong et al. [22] studied the use of potassium hydroxide supported on ZrO₂. They found that the highly basic KOH/ZrO₂ catalyst was able to yield a 99% conversion to methyl esters. MacLeod et al. [23] studied the stability of metal oxides doped with alkaline earth metals. One of these oxides was KNO₃/CaO, which was a highly basic and very active regardless of having a surface area lower than 2 m² g⁻¹. In spite of the large reported literature, factors such as the specific kind of basic strength of surface sites, their relation with catalytic activity, and the effect of calcination temperature of the catalysts are not well known. In the present work, we further study the role of the calcination temperature on the formation of the titanate phase, and how this new phase contributes to the formation of acid and basic sites with different roles in the catalytic activity.

2. Experimental

Commercial grade edible canola oil (Mazzola oil) was used. Methanol (EMSURE grade, Merck) was GC grade (99.9%) with less than 0.05% water. The TiO₂ support was prepared by a hydrothermal treatment [24]. In brief, 2 g of TiO₂ (99.9% Anatase, Aldrich) were mixed with a 10M solution of NaOH and heated in a closed Teflon vessel up to 110 °C for 24 h. Then, this mixture was put in contact with a 0.1M solution of HNO₃ overnight at room temperature. The filtered solid was then washed and dried. The obtained support, denoted TiHT, had a surface area of 286 m²/g. Using the TiHT as support, a set of potassium catalysts were prepared using KNO₃ (Merck) as a metallic precursor. The dry support was impregnated with 20 wt% of potassium. The fresh 20%K/TiHT catalysts were calcined in air at 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C for 3 h.

The transesterification reaction of canola oil (20 g) was carried out in a glass batch reactor under reflux of methanol (23.1 g) at 65 °C and under stirring. No inert atmosphere was used and all reaction occurred in contact with air and at ambient pressure. The potassium catalyst loaded in the reactor (1.2 g) corresponded to 6 wt% of the loaded canola oil. A molar ratio of methanol to oil of 36:1 was used. The profile of fatty acid in the commercial canola

oil used in this study was determined by gas–liquid chromatography and, as indicated in Table 1, the composition was similar to the one reported in literature [25]. The transesterification reaction was repeated several times, which allowed determining an error of 7.6% for conversions below full conversion possibly due to the steep reaction rate at the beginning of the reaction

To monitor the evolution of the transesterification reaction, a small aliquot was analyzed by gas/liquid chromatography using the following sampling procedure: in order to stop the reaction 0.5 mL of sample was injected into a vial containing 0.5 mL of a 0.1 M HCl solution. Then, 0.5 mL of an extracting solution was added into the same vial. The extracting solution consisted of hexane: diethyl ether (1:1 M ratio), which contained a reference standard (eicosane, 5000 ppm). The vial was then stirred and centrifuged to separate the phases. A small aliquot from the organic layer, which contained the methyl esters, were injected into the chromatograph. The chromatograph (Perkin Elmer, Autosystem) was equipped with a FID detector and an Omegawax 250 capillary column (30 m × 0.25 mm × 0.25 μm) (Supelco).

The crystal structure of the different catalyst was determined by X-ray diffraction, which was carried out on a Siemens D-5000 diffractometer using Cu K_α radiation at a scan rate of 0.02°/min. The morphology of samples was determined by scanning electron microscopy using a Magellan 400 (FEI-USA).

The TGA and DSC analysis were done in Mettler Toledo TGA/DSC 1 Start^E System. 20 mg of 20%K/TiHT was heated in air flow of 80 cc/min and the range of temperature was from 25 °C to 800 °C with a ramp of 50 °C/min. The same equipment was used for DSC analysis.

The XPS measurements were performed by a PHI 5000 Versa Probe II Scanning XPS Microprobe UHV using Mg K_α radiation and anode operated at 250 W. In order to avoid any contamination, ultra high vacuum (10⁻⁷–10⁻⁸ Pa) was used in all measurements. The C1s line (284.5 eV) was employed as a binding energy standard using Casa XPS software for data analysis.

The acid sites were determined using pyridine as a probe molecule by monitoring the infrared spectrum range of 1400–1600 cm⁻¹, which corresponds to the ring vibration modes of pyridine. The catalyst samples (previously over nightdries at 100 °C) and KBr reference for IR analysis were ground in agate mortar. Compression powder was done until wafer was formed and put into the vacuum pumping where pyridine vapors going the line and wafer. Pyridine adsorption was carried out at 200 °C, 400 °C and 500 °C, and at room temperature. The IR spectrums were taken after pyridine desorption. The in situ cell was carried for analysis spectrum which was taken between 2000 cm⁻¹ and 500 cm⁻¹. The IR measurements were determined using FTIR Nicolet Nexus and the spectra were recorded with 4 cm⁻¹ resolution and 250 scans.

The IR spectrum of pyridine shows two bands: 1450 cm⁻¹ (Lewis acid site) and 1330 cm⁻¹ (Brønsted acid site) [1,26]. The number of Lewis and Brønsted acid sites (LAS and BAS) was calculated by the equation:

$$\text{LAS or BAS} = \frac{A_i \times \pi \times R^2}{w \times \epsilon_i} [\mu\text{mol/g}] \quad (1)$$

Table 1

Fatty acid composition of canola oil Ref. [25] and commercial canola oil used in transesterification reaction.

Fatty acid composition (wt%)	Canola oil Ref. [25]	Commercial canola oil
Palmitic (C16:0)	5.5	4.4
Oleic (C18:1)	55	55
Linoleic (C18:2)	24	31
Linolenic (C18:3)	8.8	7.8

Download English Version:

<https://daneshyari.com/en/article/6634251>

Download Persian Version:

<https://daneshyari.com/article/6634251>

[Daneshyari.com](https://daneshyari.com)