Journal of Molecular Catalysis A: Chemical xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

K_2MgSiO_4: A novel K^+-trapped biodiesel heterogeneous catalyst produced from serpentinite $Mg_3Si_2O_5(OH)_4$

Fabiane Carvalho Ballotin[a], Thérèse Ebambi Cibaka[a], Tatiana A. Ribeiro-Santos[a], Eleonice Moreira Santos[b], Ana Paula de Carvalho Teixeira[a], Rochel Montero Lago[a],*

[a] *Universidade Federal de Minas Gerais, Instituto de Ciências Exatas, Departamento de Química, Belo Horizonte, MG 31270-901, Brazil*
[b] *Universidade Federal de Ouro Preto, Escola de Nutrição – ENUT, Departamento de Alimentos, Ouro Preto, MG 35400-000, Brazil*

ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form 1 February 2016
Accepted 2 February 2016
Available online xxx

Keywords:
K_2MgSiO_4
Serpentinite
Biodiesel

ABSTRACT

In this study, a new catalyst for biodiesel synthesis, based on K_2MgSiO_4, was produced from the mineral serpentinite. TG, SEM, XRD, AA, BET analyses showed that serpentinite $Mg_3Si_2O_5(OH)_4$ impregnated with KOH (5,10 and 20 wt%), and thermally treated at 500 °C, 700 and 900 °C, can be converted to the main crystalline phase K_2MgSiO_4. Analyses by TPD-MS (CO_2) and titration suggested the presence of weak/medium basic sites in relatively high concentrations. Biodiesel production using soybean oil (methanol:soybean oil ratio of 1:12, 1:9; 1:6, 60 °C) showed yields higher than 95% with catalyst at 10 wt%, which can be reused for three consecutive times without significant decrease on the reaction yield. The obtained results are discussed in terms of a new catalytic phase based on K^+ ions trapped in the cavities of the $MgSiO_4^{2-}$ structure containing negatively charged oxygen basic sites.

1. Introduction

Basic catalysts, such as alkaline metal hydroxides and methoxides are widely employed as homogeneous catalysts in the biodiesel industrial process [1,2]. However, the use of homogeneous catalysts, leads to some problems such as: the need of a washing step, the formation of emulsions, large volumes of wastewater, the need of a drying step and loss of the catalyst [2–4]. On the other hand, heterogeneous catalysts can offer several advantages such as the possibility of reuse [5], elimination of some steps in the process and simple separation from the final product [6], resulting in significant decrease on production costs [7].

Different basic heterogeneous catalysts have been investigated, such as mixed oxides CaO–CeO_2 [8], alumina supported metals [9], and especially earth alkaline metals oxides, e.g., CaO [10] and MgO [11], which are the most used for biodiesel synthesis. Several studies have shown that the basicity and activity of biodiesel catalysts can be increased by the addition of different elements, especially potassium. Some examples are K^+ doped titanate nanotubes [12] K^+ supported on TiO_2 [13], KOH/bentonite [14] and K^+/chrysotile [15].

In this work, serpentinite $Mg_3Si_2O_5(OH)_4$ was used as precursor to produce a K^+ basic catalyst for biodiesel synthesis. Serpentinite, an inexpensive mineral and in some cases a waste, is formed by a Si oxide tetrahedral sheet bound to $Mg(OH)_2$ based octahedral layer [16]. Serpentinite has been used in simple applications such as construction, steel mills, magnesium production [17], fertilizer [18] and for CO_2 storage [17,19]. Serpentinite can be a very versatile precursor to produce Mg based materials since under controlled thermal treatment, the $Mg_3Si_2O_5(OH)_4$ phase dehydrates to produce different Mg containing phases such as dispersed MgO, Mg_2SiO_4 besides other SiO_2 based phases. A simplified equation can be used to represent the serpentinite decomposition:

$$Mg_3Si_2O_5(OH)_4 \rightarrow MgO + Mg_2SiO_4 + SiO_2 + 2H_2O \quad (1)$$

Here on, it is described the reaction of serpentinite with KOH to produce the phase K_2MgSiO_4 with basic properties, where K^+ ions are trapped in the cavities formed by the SiO_4 and MgO_4 structural tetrahedra (Fig. 1).

---

* Corresponding author. Fax: +55 31 3409 5777.
E-mail addresses: fballotin@ufmg.br (F.C. Ballotin), tcibaka@gmail.com (T.E. Cibaka), tatianaaribeiros@yahoo.com.br (T.A. Ribeiro-Santos), emsquimica@hotmail.com (E.M. Santos), anapct@ufmg.br (A.P.d.C. Teixeira), rochel@ufmg.br (R.M. Lago).

http://dx.doi.org/10.1016/j.molcata.2016.02.006
1381-1169/

Please cite this article in press as: F.C. Ballotin, et al., J. Mol. Catal. A: Chem. (2016), http://dx.doi.org/10.1016/j.molcata.2016.02.006

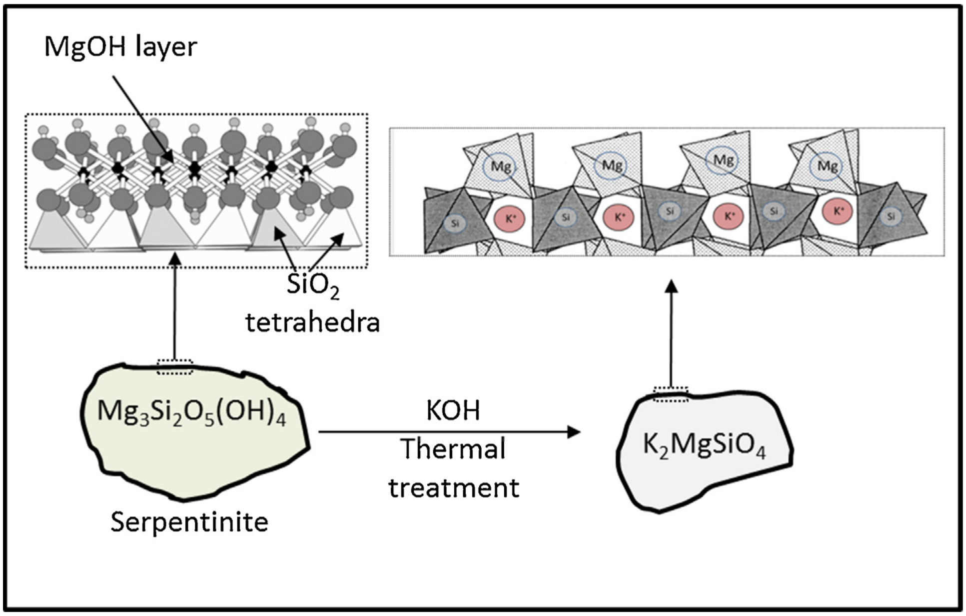

Fig. 1. Schematic representation of the thermal decomposition of serpentinite KOH/$Mg_3Si_2O_5(OH)_4$ to form the phase K_2MgSiO_4.

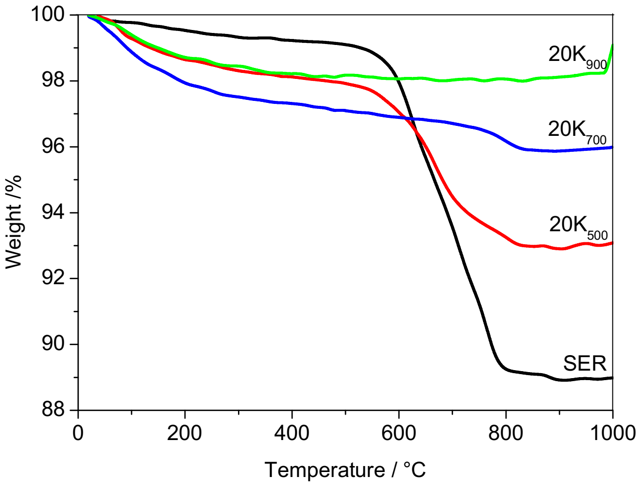

Fig. 2. TG/DTG curves for serpentinite (SER) and serpentinite samples impregnated with K^+ after thermal treatment at 500, 700 and 900 °C ($20K_{500}$, $20K_{700}$ and $20K_{900}$).

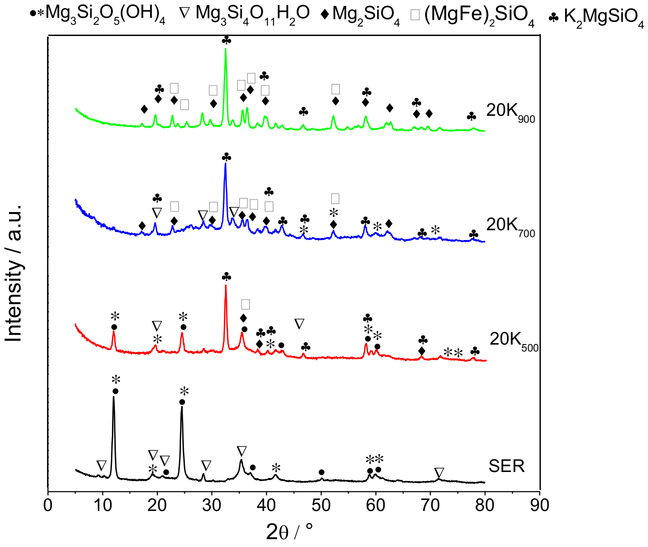

Fig. 3. XRD patterns of serpentinite samples SER, and $20K_{500}$, $20K_{700}$ and $20K_{900}$.

2. Experimental

2.1. Catalysts synthesis

Pulverized serpentinite samples (Pedras Congonhas Ltda) were sieved (#200) and impregnated with aqueous KOH in proportions of 0, 5, 10 and 20 wt% of potassium. The materials were dried for 24 h and thermally treated at 500, 700 or 900 °C for 3 h in air atmosphere. These catalysts are named here on as $20K_{700}$, where 20K indicates 20 wt% of K and thermal treatment at 700 °C.

2.2. Catalysts characterization

The metals (magnesium and iron) were analyzed by atomic absorption spectrometry (Hitachi-Z8200). The SEM images were obtained in a FEI Quanta 200-FEG equipment. The XRD studies were done on a Shimadzu diffractometer, model XRD-7000 with CuKα with a scan speed of $4° min^{-1}$.

Thermogravimetric analyses (TGA) were performed in a Shimadzu DTG 60H with air flow ($50 mL min^{-1}$) with heating rate of $10 °C min^{-1}$ up to 1000 °C. In order to determine the basic properties of the material $20K_{700}$, a simultaneous TGA-MS (mass spectrometry) analysis was applied. The base peak ($m/z = 44$) was selected to be monitored in a NETZSCH TG/STA equipment coupled with Aelos spectrometer, model 7.0. The catalysts were previously treated in N_2 atmosphere ($50 mL min^{-1}$) at 500 °C for 1 h, followed by treatment at 50 °C under CO_2 flow ($50 mL min^{-1}$) for 1 h. Then, the material was heated to 900 °C in argon at a rate of $10 °C min^{-1}$.

In order to determine the total basic sites, 0.5 g of the samples were dispersed in 50 mL of HCl 0.1 $mol L^{-1}$ and 20 mL of distilled water. After 24 h of stirring, 25 mL of the solution was titrated with NaOH 0.1 $mol L^{-1}$ and phenolphthalein as indicator.

The specific surface areas of the samples were analyzed by adsorption of N_2 at 77K using an Autosorb1-MP Quantachrome. The samples were degassed at 200 °C for 24 h before the analyses.