K₂MgSiO₄: A novel K⁺-trapped biodiesel heterogeneous catalyst produced from serpentinite Mg₃Si₂O₅(OH)₄

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ABSTRACT

In this study, a new catalyst for biodiesel synthesis, based on K₂MgSiO₄, was produced from the mineral serpentinite. TG, SEM, XRD, AA, BET analyses showed that serpentinite Mg₃Si₂O₅(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 K₂MgSiO₄. Analyses by TPD-MS (CO₂) 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 MgSiO₄²⁻ structure containing negatively charged oxygen basic sites.

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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–CeO₂ [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 TiO₂ [13], KOH/bentonite [14] and K⁺/chrysotile [15].

In this work, serpentinite Mg₃Si₂O₅(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 CO₂ storage [17,19]. Serpentinite can be a very versatile precursor to produce Mg based materials since under controlled thermal treatment, the Mg₃Si₂O₅(OH)₄ phase dehydrates to produce different Mg containing phases such as dispersed MgO, Mg₂SiO₄ besides other SiO₂ based phases. A simplified equation can be used to represent the serpentinite decomposition:

Here on, it is described the reaction of serpentinite with KOH to produce the phase K₂MgSiO₄ with basic properties, where K⁺ ions are trapped in the cavities formed by the SiO₄ and MgO₄ structural tetrahedra (Fig. 1).

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Fig. 1. Schematic representation of the thermal decomposition of serpentine KOH/ $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ to form the phase K_2MgSiO_4 .

Fig. 2. TG/DTG curves for serpentine (SER) and serpentine samples impregnated with K⁺ after thermal treatment at 500, 700 and 900 °C (20K₅₀₀, 20K₇₀₀ and 20K₉₀₀).

Fig. 3. XRD patterns of serpentine samples SER, and 20K₅₀₀, 20K₇₀₀ and 20K₉₀₀.

2. Experimental

2.1. Catalysts synthesis

Pulverized serpentine 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 20K₇₀₀, 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 20K₇₀₀, 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 N₂ atmosphere (50 mL min⁻¹) at 500 °C for 1 h, followed by treatment at 50 °C under CO₂ 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 N₂ at 77K using an Autosorb1-MP Quantachrome. The samples were degassed at 200 °C for 24 h before the analyses.

Fig. 4. SEM images of serpentinite before and after impregnation with KOH (20K) thermally treated at 500, 700 and 900 °C.

The absorption spectroscopy measurements for diffuse reflectance in the infrared region with Fourier transform (FTIR) were performed on a Bruker equipment, Alpha model. Spectra were collected in the range of 400–4000 cm^{-1} region, with 64 accumulations.

The influence of carbonation and hydration in the activity of the catalyst were studied during 30 days by exposing the catalyst to atmosphere. The catalyst was characterized by infrared spectroscopy, thermogravimetric analyses, TPD-MS and transesterification reactions after the 1, 5, 10, 20 and 30 days of air exposure.

2.3. Biodiesel synthesis

Biodiesel syntheses were carried out using soybean oil, methanol, and the catalysts based on serpentinite impregnated with K (0, 5, 10 and 20 wt%) treated at 700 °C/3 h. The catalyst concentration in the reaction were adjusted to 1, 5 or 10 wt%. The reactions were conducted at 60 °C, in a two necked glass reactor, under reflux and mechanical stirring for different times. The oil:methanol molar ratios used were 1:6, 1:9 and 1:12.

Fig. 5. Total basicity of serpentinite samples impregnated with KOH before and after thermal treatment.

Fig. 6. TPD-MS CO₂ curves: 0K₇₀₀, 5K₇₀₀, 10K₇₀₀ and 20K₇₀₀.

2.4. Catalyst reuse

The catalysts reuse reactions were performed under optimized conditions of 5 wt% and 10 wt% of the catalyst 20K₇₀₀, with oil:methanol molar ratio of 1:6 at 60 °C/2 h. After the reaction, the liquid phase was separated from the catalysts, and the recycling experiments were done by:

- simple reuse of the catalysts without any treatment,
- the catalyst was washed with 3 portions of 3 mL of solvent (acetone, hexane or methanol), centrifuged, and used for a new reaction,
- the catalyst was washed once with methanol and treated at 700 °C in air for 1 h.

Fig. 7. Effect of catalyst 20K₇₀₀ concentration with different soybean oil/methanol ratios and KOH homogeneous catalyst in the biodiesel production (60 °C, 180 min).

2.5. Biodiesel quantification

The biodiesel was separated and analyzed by ¹H NMR on a Bruker DPX 200 spectrometer for conventional reactions and in Bruker DPX 400 equipment for reuse reactions.

In order to calculate the yield of the transesterification reaction, ¹H NMR technique was used [20]. Mixtures of pure biodiesel and soybean oil were used to build a calibration curve (Supplementary material).

3. Results and discussion

The serpentinite used as precursor for the catalysts preparation showed a chemical composition of SiO₂ 40 wt%, MgO 30 wt% typical for the phases lizardite and antigorite Mg₃Si₂O₅(OH)₄, associated with talc (Mg₃Si₄O₁₁H₂O), with a significant concentration of iron (Fe₂O₃ 10 wt%).

Thermogravimetric analysis of pure serpentinite (SER, Fig. 2) showed a weight loss of ca. 1% until 300 °C, related to adsorbed water [21]. In the temperature range 500–800 °C, serpentinite

Fig. 8. Recycling reactions of the catalysts, using 5 and 10 wt%, 1:6 and 1:12 oil:methanol(60 °C, 120 min), and different recoverable methods.

decomposes by dehydroxylation with a weight loss of 10% to form new phases. Based on this result, the thermal decomposition of serpentinite was investigated in more detail at 500, 700 and 900 °C. XRD patterns showed, for the pure serpentinite treated at 500 °C, 0K₅₀₀ no significant change in phase composition. On the other hand, the material gradually dehydroxylates (Eq. (2)) at 700 and 900 °C and the new phases forsterite Mg₂SiO₄ and olivine (MgFe)₂SiO₄ are formed (Supplementary material).

Similar results have been observed for the thermal decomposition of chrysotile [15].

In order to prepare the K₂MgSiO₄ based catalysts, serpentinite was impregnated with KOH at 5, 10 and 20 wt% potassium, and each material was treated at 500, 700 and 900 °C. Fig. 2 shows the TG profiles of the catalysts containing 20% K after thermal treatment (all the other TG profiles are shown in Supplementary material).

It can be observed that the weight loss of 10% observed for the pure serpentinite precursor gradually decreased as SER was impregnated with KOH and pretreated at 500 and 700 °C. After pretreatment at 900 °C no significant weight loss was observed.

XRD data of the material 20K₅₀₀ (Fig. 3) suggests that KOH promoted the thermal decomposition at 500 °C which was not observed for the pure serpentinite precursor. It was also observed the formation of the new main phase K₂MgSiO₄ (JCPDS Card No. 39-1426) with small amounts of forsterite Mg₂SiO₄ (JCPDS Card No. 4-768) and olivine (MgFe)₂SiO₄ (JCPDS Card No. 2-1326). Similar results were observed for the materials treated at 700 and 900 °C. The XRD patterns of the samples 5K₇₀₀, 10K₇₀₀ and 20K₇₀₀ (see Supplementary material) clearly showed that the formation of the phase K₂MgSiO₄ was strongly favored as the concentration of K⁺ increased.

It is interesting to observe the absence of the diffraction peak at 43° related to MgO, which suggests that if MgO was formed it is likely very disperse. It can also be envisaged that the MgO was consumed in the formation of the main phase K₂MgSiO₄ (Eq. (3)).

The formation of this phase K₂MgSiO₄ has been reported by the ternary solid state reaction of K₂O–MgO–SiO₂ at high temperatures [22]. Detailed investigation of the K₂MgSiO₄ structure [23] sug-

gests a network of SiO₄ tetrahedra connected to Mg²⁺O₄ tetrahedra where the K⁺ ions are located in the interstitial space between the tetrahedral [23].

SEM images suggest that serpentinite is a bulky compact surface, but after thermal decomposition, with or without KOH, the material becomes more fragmented (Fig. 4). BET surface area analyses showed 12 m² g^{−1} for serpentinite, which after thermal treatment at 700 °C slightly increased to 27 m² g^{−1}. On the other hand, the samples containing potassium (5K₇₀₀, 10K₇₀₀ and 20K₇₀₀) showed a decrease to 7, 5 and 11 m² g^{−1}, respectively, suggesting that the KOH has an effect on the texture of the final material produced.

The different catalysts were analyzed for the total basicity by simple reaction with HCl (Fig. 5).

It can be observed that pure serpentinite showed a total basicity of 3.3 mmol OH[−] g^{−1}. This basicity is likely related to the Mg(OH)₂ layer solubilization by HCl. The treatment of pure serpentinite at 500 °C (0K₅₀₀) did not show any significant increase on the basicity. On the other hand, the basicity strongly increased to 7.2 mmol OH[−] g^{−1} after treatment at 700 °C, likely related to the decomposition of serpentinite with the segregation of MgO. It is interesting to observe that at 900 °C the basicity decreases probably by the reaction of MgO with SiO₂ to form the neutral magnesium silicates. As potassium was added to the serpentinite and treated at 500 °C, the basicity went to 6.5, 7.5 and 9.9 mmol OH[−] g^{−1} for the samples 5K, 10K and 20K, respectively. After treatment at 700 °C the basicity slightly increased whereas at 900 °C a decrease was observed. Based on these results the samples treated at 700 °C were selected for further characterization and used as heterogeneous catalyst for biodiesel synthesis.

The presence of surface basic sites of the catalysts was investigated by CO₂ TPD-MS technique (Fig. 6). The samples were pre-treated at 500 °C in a N₂ flow, and then exposed to CO₂ at 50 °C for subsequent TPD-MS analyses.

It can be observed that pure serpentinite (SER) and the sample 0K₇₀₀ showed no significant adsorption/desorption of CO₂, which indicates very low concentration of surface basic sites. These results suggest that the MgO produced during the serpentinite decomposition is not readily available on the surface for interaction with CO₂. The samples 5K₇₀₀ and 10K₇₀₀ showed low intensity desorption peaks. On the other hand, the TPD-MS for the catalyst 20K₇₀₀ showed the presence of 3 desorption peaks (Fig. 6): weak

Fig. 9. SEM images and EDS analyses of the catalysts (20K₇₀₀, direct reuse and acetone washing reuse) after 4 uses.

basic sites (up to 200 °C), medium basic sites (200–500 °C) and peaks above 500 °C. According to literature, peaks below 200 °C are related to CO₂ weakly adsorbed on the catalyst surface, corresponding to hydroxyl groups on the surface [24] whereas the peaks near 350 °C can be assigned to CO₂ desorbed from medium basicity, for example magnesium oxide [25,26] and Mg²⁺ and O²⁻ pairs [24]. Above 500 °C, the CO₂ is likely due to carbonate decomposition [27]. Studies with the mineral chrysotile showed similar results [15]. Shen et al. also detected medium strength basic sites, which were assigned to K_xMgO/SiO₂ [28].

The biodiesel synthesis was investigated with the different prepared catalysts. The series SER, 0K₅₀₀, 0K₇₀₀ and 0K₉₀₀, showed

yields lower than 20% indicating that the presence of potassium is critical for a more active catalyst. The best results were obtained for the catalysts 20K₇₀₀ and 20K₉₀₀. More detailed investigation was carried out with the catalyst 20K₇₀₀ in different reaction conditions. The effect of catalyst concentration and oil/methanol ratios in the conversion of soybean oil is presented in Fig. 7.

It can be observed that the reaction reached good conversion (>80%) using only 1 wt% of the catalyst at the oil:alcohol molar ratio of 1:9. For 5 and 10 wt%, conversions near 95% were obtained for all oil:methanol ratios.

Simple test in the biodiesel reaction using the classical homogeneous KOH at 0.5% (Fig. 7) showed ester yields of 95 ± 2%. Similar

Fig. 10. Quantification of groups of CO₂ in the catalysts.

results were obtained with the heterogeneous 20K₇₀₀ present in the reaction at 5%. Considering the K content in the catalyst 20K₇₀₀ is nearly only 20%, similar TON of 30 mol_{Me-ester} mol_K⁻¹ were obtained for both catalysts. These results suggest that the K presence in both, homogeneous and heterogeneous catalysts have similar activities.

The catalysts stability was investigated by consecutive reuses (Fig. 8). When reactions were carried out with 10 wt% catalyst with oil:methanol ratio of 1:12, a decrease of 21% on the conversion was observed after three consecutive reactions. The recyclability of the catalyst was also studied in a more limiting condition (i.e., 5 wt% catalyst and a 1:6 oil: methanol ratio, at 60 °C for 2 h) (Fig. 8).

After the reaction, the catalyst was completely agglomerated due to the impregnation with the organic phase. The second use of this catalyst without any treatment still showed very good conversion. Also, by washing the catalysts to remove the organic phase (different solvents were used, i.e., hexane, acetone, methanol) fairly good conversions were obtained. On the other hand, thermal treatment at 700 °C caused a significant decrease on the conversion, i.e., from 85 to ca. 45% (not shown). After the third use, the conversion decreased to less than 40% especially after thermal treatment at 700 °C. The obtained results suggest that potassium is lost after the first reaction and nearly 40% was lost after 4 reactions.

The fresh 20K₇₀₀ and the used catalysts (direct reuse and acetone washing reuse), in the more limiting condition, (after 4 uses) were analyzed by SEM/EDS (Fig. 9) and XRF (X-ray fluorescence).

Simple calculation of the EDS signal ratio K/Si and XR fluorescence measurements suggested that after the first use, the catalysts lost ca. 10–15% of the K content. The catalysts stability is an important factor to industry, in this sense, 20K₇₀₀ catalyst was exposed to air and investigated during 30 days by TG/DTG, FTIR and TPD-MS analyses. TG analyses (Supplementary material) showed that exposed catalysts (1, 5, 10, 20 and 30 days) presented small weight losses in two temperature ranges, up to 500 °C related to the loss of water and dihydroxylation processes [29] and between 600–800 °C likely related to carbonate decomposition. Carbonation on catalysts surfaces has also been observed before for different mineral oxides and basic catalysts [17,30]. The carbonates thermal decomposition is well known to take place in the temperature range 600–800 °C [31].

FTIR spectra for the materials exposed to air up to 30 days (Supplementary material) confirmed a gradual hydration at 3300 cm⁻¹ referred to –OH stretching and at 1659 cm⁻¹ (–OH bending) [32] and carbonation (CO₃: 862 (out-of-plane bending)), 1440 cm⁻¹

Fig. 11. Schematic representation of the K-trapped in the K₂MgSiO₄ structure (adapted from Ref. [21]).

(symmetric bending) and 1655 cm⁻¹ (antisymmetric bending) [33] of the catalyst.

The CO₂ desorption was measured by TPD-MS after catalyst exposure for 1, 5, 10, 20 and 30 days (Fig. 10). The presence of three desorption groups was observed: surface basic sites, carbonates and especially physisorbed CO₂ (up to 1.7 mmol g⁻¹).

The catalyst 20K₇₀₀ exposed to air for 1, 5, 10, 20 and 30 days was then tested for biodiesel production at 5 wt% catalyst, methanol:oil ratio of 1:6 at 60 °C. The obtained results (Supplementary material) showed no significant deactivation due to the exposure of the catalyst to air.

Although the catalyst nature is not clear, one can consider that the main crystalline phase K₂MgSiO₄ is likely involved in the reaction. There is only one report suggesting that this phase is a basic catalyst for the reaction of hexoses to hydroxymethylfurfural (HMF) [28]. In this report, the K₂MgSiO₄ was produced from pure K₂CO₃, MgO and SiO₂ at very high temperatures.

The structure of K₂MgSiO₄ has been described as a “stuffed” crystalite polymorph of SiO₂ [26], where a three-dimensional array of corner-sharing SiO₄ tetrahedra form large open cavities. Some fraction of the Si atoms can then be replaced with Mg²⁺ and the K⁺ ions are “stuffed”, i.e., trapped inside the cavities [23]. A very simple representation of this structure is shown in Fig. 11.

The compound K₂MgSiO₄ can also be viewed as a negatively charged solid matrix [MgSiO₄]²⁻ containing K⁺ trapped in the structure. Although the nature of the basic sites for the biodiesel reaction is not clear, it might be related to the surface and structural oxygens containing the negative charges. More detailed studies are necessary to further investigate the nature of the catalytic sites.

4. Conclusions

Serpentine proved to be a very interesting precursor to produce the special catalytic phase K₂MgSiO₄ which is apparently very active for the production of biodiesel. This new catalytic phase seems to be based on K⁺ ions trapped in the cavities of the MgSiO₄²⁻ structure containing negatively charged basic oxygen sites. The cat-

alyst 20K₇₀₀ at 10 wt% can be reused for three consecutive times without significant decrease on the reaction yield. Experiments using catalyst at 5% showed potassium leaching and a decrease on the conversion after the second reaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2016.02.006>.

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