



Microwave-assisted preparation of a new esterification catalyst from wasted *flint* kaolin

Alex de Nazaré de Oliveira^a, Laura Rafaela da Silva Costa^a, Luíza Helena de Oliveira Pires^a, Luís Adriano S. do Nascimento^a, Rômulo S. Angélica^b, Carlos E.F. da Costa^a, José R. Zamian^a, Geraldo N. da Rocha Filho^{a,*}

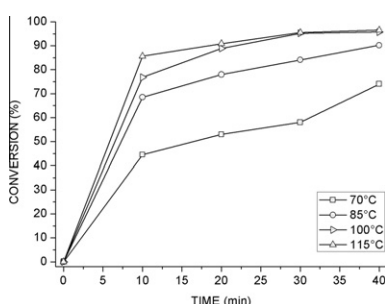
^aLaboratório de Catálise e Oleoquímica, Universidade Federal do Pará, Rua Augusto Corrêa, Guamá, CEP 66075-110, Belém, Pará, Brazil

^bLaboratório de Difração de Raios-X, Universidade Federal do Pará, Rua Augusto Corrêa, Guamá, CEP 66075-110, Belém, Pará, Brazil

HIGHLIGHTS

- Thermal activation at 850 °C made the *flint* kaolin more reactive to acid leaching.
- Catalysts prepared using microwaves decreased time and temperature of reaction.
- Metakaolin activated at 400 W by 15 min presented better performance.
- A more efficient and eco-friendly catalyst for production of biodiesel.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 3 April 2012

Received in revised form 3 July 2012

Accepted 5 July 2012

Available online 20 July 2012

Keywords:

Flint metakaolin
Microwaves
Acid catalysis
Esterification
Biodiesel

ABSTRACT

Amazon *flint* kaolin, considered useless from an economic and industrial point of view, was calcined at 850 and 950 °C to obtain metakaolin samples. These samples were subsequently treated with sulfuric acid (4 M) by assisted heating with microwave radiation. The prepared samples were characterized by X-ray diffraction, scanning electron microscopy and N₂ physisorption; the surface acidity was determined by titration with 0.2 M KOH. The materials obtained were used as catalysts in the esterification of oleic acid with methanol. Metakaolin that was calcined at 850 °C and activated at 400 W for 15 min presented a surface area of 187 m² g⁻¹, yielding acidic sites with a concentration of 4.32 mmol g⁻¹ and a conversion of 96.5% (115 °C, 40 min, molar ratio of oleic acid: methanol 1:60). In addition to a lower preparation time, the *flint* metakaolin activated by microwave radiation gave a catalytic performance equivalent or superior to the one prepared by reflux, as well as it showed considerably reduced reaction time and temperature.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Most of the energy consumed worldwide comes from oil, coal and natural gas. These sources are not renewable and are expected to be depleted in the near future. Moreover, fossil fuels are heavy pollutants that aggressively affect the environment. These reasons are just a few that demonstrate the importance of studying alternative energy sources [1].

* Corresponding author. Tel.: +55 9132017143.

E-mail address: narciso@ufpa.br (G.N. da Rocha Filho).

The production of biofuel as a substitute for fossil fuels has been a target of several studies in recent decades. Biodiesel can be produced by the catalytic esterification of oleic acid with methanol [2,3]. Traditionally, these reactions are carried out in the homogeneous liquid phase, where strong Brønsted acids, such as sulfuric acid, are usually used as catalysts. However, these acids need to be neutralized after the reaction, due to the consequent salt formation. This problem can be solved by the use of solid acids as catalysts such as Al-MCM-41 and heteropolyacids (PW) immobilized in silica [2–4].

Another possibility is the use of solid acid catalysts produced from clays, such as kaolin, which have been applied toward the esterification of oleic acid with methanol [4].

Natural clays have low catalytic capacity for reactions in polar or non-polar environments. Generally, the structural properties of these materials can be modified by acid activation [5–10]. Kaolin must be converted to metakaolin before acid activation because metakaolin is more susceptible to acid leaching. Acid activation of metakaolin increases the surface area and pore volume, and can generate Brønsted and/or Lewis acid sites. These are important characteristics for this catalytic transformation [4,11].

Acid activation under reflux requires high temperatures and long periods of time [12]. The use of microwaves, also known as dielectric heating, is an alternative to reflux heating and uses reduced reaction times and temperatures. Acid treatment using microwave radiation is a faster, cleaner, simpler, and in some cases, a more energetically efficient process than conventional heating. This method has the advantages of producing uniform volumetric heating, creating good quality materials, saving energy and providing a good cost–benefit ratio [13–15].

In recent publications from our research group, *flint* kaolin (considered a worthless material) has been presented as an interesting raw material for the production of an efficient catalyst (showing up to 98% conversion) for the esterification of oleic acid with methanol [4]. This catalyst also accomplishes a 92.8% conversion for the esterification of waste products from the deodorization of palm oil [7].

The objective of this paper was to prepare and characterize catalysts prepared by microwave-assisted acidic leaching of Amazon *flint* kaolin and to assess the performance of these solid acidic catalysts toward the esterification of oleic acid with methanol.

2. Experimental

2.1. Materials

The chemical products used in this experiment were oleic acid (synthetic grade, Vetec), methanol (AR grade, Nuclear) and sulfuric acid (98%, ISOFAR). *Flint* kaolin from the Capim River region (Pará-Brazil) used in this experiment was kindly provided by the Geosciences Institute of the Universidade Federal do Pará (IG-UFPa).

2.2. MF8 and MF9 metakaolin preparation by microwave-assisted acid activation

Flint kaolin samples were calcined at 850 and 950 °C for 2 h. These samples were designated as MF8 and MF9, respectively. The materials that were obtained were leached with 4 M H₂SO₄ using dielectric heating at 300 or 400 W for 8 or 15 min. Using the MF8S4M4W15 sample as an example, the identification codes for these samples are as follows: MF8 = *flint* metakaolin prepared by calcination at 850 °C; S4 = acid leaching with 4 M H₂SO₄; M4W = microwave heating at 400 W; 15 = 15 min. Following the acid treatment, all samples were washed, dried at 120 °C for 12 h and calcined at 400 °C for 2 h.

2.3. Characterization

The chemical compositions of the samples were obtained using a Shimadzu EDX-700 energy dispersive X-ray (EDX) spectrometer. X-ray diffractions (XRD) were obtained using a PANalytical XPERT PRO MPD (PW 3040/60) diffractometer using the powder method at $5 < 2\theta > 70^\circ$ intervals. Cu K α (40 kV and 40 mA) radiation was used. The 2θ scanning speed was $0.02^\circ \text{ s}^{-1}$.

N₂ adsorption–desorption isotherms were obtained at –196 °C using a Micromeritics TriStar II model 3020 V1.03 apparatus. Before

each measurement the samples were outgassed at 130 °C for 2 h. The specific surface area was determined according to the standard Brunauer–Emmett–Teller (BET). The microporous area and the microporous volume were obtained by the Barrett–Joyner–Halenda (BJH) method.

Scanning electron microscopy (SEM) images of the samples were taken with a ZEISS model LEO 1430 microscope operating at 10 kV and 90 mA. The samples were supported on carbon tapes and coated with gold under vacuum conditions.

The FTIR of adsorbed pyridine was the technique used to confirm the presence of Brønsted and Lewis acid centers in the catalysts [4]. A THERMO model IS 10 apparatus was used. The surface acidity was determined using acid–base titration as described by Moraes and coworkers [16]. In a typical measurement, 0.5 g of the solid was dispersed in 50 mL of 0.1 M KCl. The dispersion was stirred for 20 min and titrated with 0.2 M KOH in the presence of phenolphthalein.

2.4. Catalyst tests

Before the experiments, the catalysts were activated at 130 °C for 2 h. The catalyst tests were conducted in a PARR model 4843 reactor. In a typical experiment, the oleic acid was mixed with methanol and 5% m/m of the acidic solid catalyst was added (compared with the oleic acid mass). The reaction mixture was stirred (700 rpm) and heated from room temperature to 70, 85, 100 and 115 °C. As soon as the desired temperature was reached, the system was maintained for 10, 20, 30 and 40 min. This time was considered as the kinetic contact time. At the end of the reactions, the catalyst was separated by filtration. The percent conversion of oleic acid to the corresponding ester was estimated by an acidity measurement of the product by titration with 0.1 M sodium hydroxide.

3. Results and discussion

3.1. Characterization

3.1.1. Chemical compositions

The chemical composition of the *flint* kaolin and of the leached metakaolin was determined by the EDX technique (Table 1). The values obtained were compared with previously published theoretical values for kaolin [4,17].

The dehydroxylation of the octahedral layer of the *flint* kaolin calcined at 950 °C can lead to the combination of the SiO₄ groups with the AlO₆ groups, which would form primary mullite (Al₂O₃·SiO₂) and the Al–Si spinel phase; the latter phase appears at 920 °C and persists until 1150 °C [8,11,18]. With dielectric heating, the efficiency of this transformation was improved, making the metakaolinite resistant to leaching acid and presenting a total of 46.1% Al₂O₃. Metakaolinite calcined at 850 °C led to an octahedral layer that was highly susceptible to acid leaching, leading to a much lower percentage of Al₂O₃, 17.05%. Both metakaolins were treated with the same radiation intensity and for the same time (400 W for 15 min). The mass loss in the fire analysis revealed that the kaolin

Table 1
Percentage of chemical composition of kaolin and leached metakaolin.

SAMPLES	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	Loss on ignition ^a
Theoretical kaolinite [10]	46.54	39.50	–	–	13.96
<i>Flint</i> [4]	43.24	37.98	2.34	0.51	15.40
MF9S4M4W15	48.94	46.10	2.83	1.68	0.45
MF8S4M3W8	62.19	8.15	3.81	0.55	25.30
MF8S4M3W15	67.42	9.14	3.72	0.49	19.23
MF8S4M4W8	57.26	8.91	3.30	0.54	29.99
MF8S4M4W15	66.82	17.05	3.48	0.67	11.98

^a At 1000 ± 25 °C (wt%).

Download English Version:

<https://daneshyari.com/en/article/6643373>

Download Persian Version:

<https://daneshyari.com/article/6643373>

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