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

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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
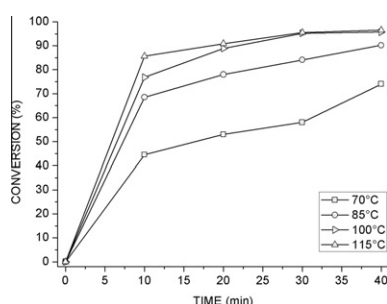
ABSTRACT

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 N_2 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 $m^2\,g^{-1}$, 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.

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1. Introduction

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

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 homogenous 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 H_2SO_4 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 H_2SO_4; 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 PANalyticalXPERT PRO MPD (PW 3040/60) diffractometer using the powder method at 5 < 2Θ > 70° intervals. Cu Kα (40 kV and 40 mA) radiation was used. The 2Θ scanning speed was 0.02° s^{-1}.

N_2 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 SiO_4 groups with the AlO_6 groups, which would form primary mullite ($Al_2O_3.SiO_2$) 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% Al_2O_3. Metakaolinite calcined at 850 °C led to an octahedral layer that was highly susceptible to acid leaching, leading to a much lower percentage of Al_2O_3, 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.

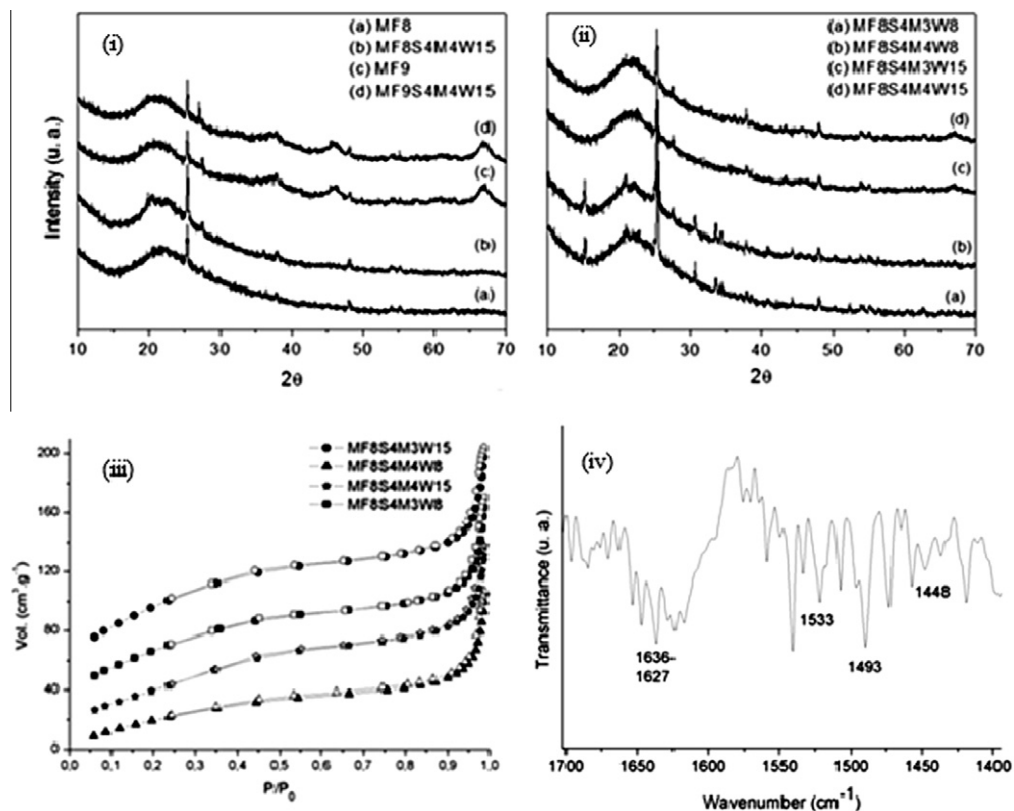| SAMPLES	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Loss on ignition[a]
Theoretical kaolinite [10]	46.54	39.50	–	–	13.96
Flint [4]	43.24	37.98	2.34	0.51	15.40
MF9S4M4W15	48.94	46.10	2.83	1.68	0.45
MF8S4M3W8	62.19	8.15	3.81	0.55	25.30
MF8S4M3W15	67.42	9.14	3.72	0.49	19.23
MF8S4M4W8	57.26	8.91	3.30	0.54	29.99
MF8S4M4W15	66.82	17.05	3.48	0.67	11.98

[a] At 1000 ± 25 °C (wt%).

Fig. 1. (i) MF8, MF8S4M4W15, MF9 and MF9S4M4W15 X-ray diffractograms. (ii) X-ray diffractograms of the metakaolins activated by dielectric heating. (iii) N_2 adsorption–desorption isotherms of the samples leached by microwaves. (iv) IR spectra in the region 1700–1400 cm^{-1} of MF8S4M4W15 with adsorbed pyridine.

treated at 950 °C had a mass loss of 0.45%, whereas the sample calcined at 850 °C presented a mass loss of 11.98%. This result can be explained by the increased hydrophilicity of the calcined material at 850 °C, which raises the amount of adsorbed water in the materiaĺs surface, elevating the cation interaction with the water molecules that act as Brønsted acid sites [4].

3.1.2. X-ray diffraction

The XRD for the samples calcined at 850 °C and 950 °C for 2 h (Fig. 1i) shows the absence of characteristic peaks for kaolinite. The lack of these characteristic peaks is due to the dehydroxylation of the external hydroxyl of the $Al(O,OH)_6$ moieties of the octahedral layer as the material becomes more susceptible to acid leaching during the thermal treatment [11,18]. These data also present evidence of an amorphous SiO_2 phase that diffracts in the broad range $2\Theta = 15–35°$ [4,6,11]. Additionally, there are three intense peaks with $2\Theta = 25.5°, 37.9°$ and $48.2°$, which could be due to the formation of anatase or rutile TiO_2, which are frequently found as accessories to the kaolins in the Capim river region [4,17].

The XRD diffractograms of (c) and (d) in Fig. 1i have peaks at high angles which could be related to the beginning of particle sintering of the kaolinite at 900 °C; an additional possibility is the transformation of the kaolinite into primary mullite (or the spinel phase), although this process normally occurs at temperatures above 980 °C [8,11]. At 950 °C, after the dehydroxylation of the octahedral layer, the SiO_4 groups combine with the AlO_6 groups, forming an Al–Si spinel phase. This phase emerges at 920 °C and persists until 1150 °C [18]. The acid treatment by dielectric heating resulted in almost no changes to the MF9S4M4W15 leached metakaolin structure, which was confirmed by the similarity between the (c) and (d) diffractograms (Fig. 1i).

In contrast to MF9S4M4W15 (d), MF8S4M4W15 (b), which was thermally treated at 850 °C, showed a more amorphous structure

following acid leaching by microwave radiation (Fig. 1i). When compared with metakaolin (a), the MF8S4M4W15 (b) sample also did not exhibit significant alterations.

The X-ray diffractograms of the MF8 sample after acid leaching by microwave radiation at different intensities (300 and 400 W) and for different times (8 and 15 min) are seen in Fig. 1ii. The diffractograms are practically identical, indicating that the microwave radiation did not modify the basal spacing of the crystals but nevertheless led to changes in the samples' structures [15]. Therefore, the chemical treatment by this procedure caused partial dissolution of Al^{3+} cations responsible for the relative increase of the peak at $2\Theta = 25°$. The X-ray diffractograms confirm that microwave intensities of up to 400 W did not affect the component structure of the metakaolin to a perceptible extent.

The crystalline properties of the minerals (anatase or rutile) that compose the samples remained unaltered because they are thermally stable under conditions of microwave radiation conditions [19]. However, in diffractograms (a) and (b) (Fig. 1ii), in which the microwave power was 300 and 400 W for 8 min, respectively, peaks at $2\theta = 15°$ due to crystalline $Al_2(SO_4)_3$ were seen [11]. In diffractograms (c) and (d) (Fig. 1ii) these peaks are absent, indicating the low crystallinity of the of $Al_2(SO_4)_3$ in these samples.

3.1.3. N_2 adsorption–desorption

The N_2 physisorption isotherms of the leached samples are shown in Fig. 1iii. According to the IUPAC classification, these isotherms can be classified as being of Type II, typical of mesoporous materials. The values for the specific surface area, microporous area and the pore volume of the leached samples (Table 2) are superior to the MF8 metakaolin. Of these, the specific surface area and the microporous area were the values most affected by the power and time of exposure of the materials to the microwaves. However, the pore volumes had very similar values for materials

Table 2
Specific surface area, microporous area, microporous volume, acid capacity and conversion values.

SAMPLES	SA[a] ($m^2\,g^{-1}$)	$A\mu$[b] ($m^2\,g^{-1}$)	$V\mu$[c] ($cm^3 g^{-1}$)	mmol $H^+\,g^{-1}$	Conv.[d] (%)
MF8	17	17	0.09	0.04	
MF8S4M3W8	246	114	0.21	0.57	13.5
MF8S4M3W15	284	126	0.22	1.44	83.3
MF8S4M4W8	150	76	0.17	0.84	56.4
MF8S4M4W15	187	130	0.21	4.32	95.2

[a] SA = BET specific surface area.
[b] $S\mu$ = microporous area calculated by BJH method.
[c] $V\mu$ = microporous volume calculated by BJH method.
[d] Conv. = Conversion values for esterification of oleic acid and methanol (1:60) after 30 min at 100 °C. Conversion without catalyst = 9.0%.

exposed to the same treatment conditions. This result is very interesting from the catalyst point of view because the pore volume facilitates reagent diffusion into the interior of the micropores in addition to facilitating access to the acidic sites [2,15].

The microwave radiation time was a key factor in determining the specific surface area of the catalysts. When exposed to an intensity of 300 W for 8 and 15 min, the specific surface areas had values of 246 and 284 $m^2\,g^{-1}$, respectively. However, with an increase in microwave radiation intensity to 400 W and using the same times (8 or 15 min), the surface area values dropped to 150 and 187 $m^2\,g^{-1}$, respectively (Table 2). This behavior is similar to that observed by Toukoniitty et al. [21], who reported specific surface areas of 233, 248 and 218 $m^2\,g^{-1}$ for Pt/Al$_2$O$_3$ when it was treated with microwave radiation at 100, 300 and 500 W, respectively. It is observed that, although materials with different chemical structures were used, the applied microwave radiation power was a key factor in obtaining higher specific surface area values. The presence of microwaves influenced the textural properties of the samples in this manner.

3.1.4. Scanning electron microscopy (SEM)

Fig. 2 shows that the *flint* kaolin and the leached metakaolin prepared by conventional heating (activated under reflux) have particles smaller than 1 μm. As seen in the micrograph, *flint* kaolin consists of scaled particles of pseudo-hexagonal morphology, whereas the conventionally leached metakaolin consists of particle clusters, indicating a rough surface and a characteristic porosity related to the spaces between these clusters [4].

In the images of the MF8S4M4W8 and MF8S4M4W15 samples (Fig. 2), it is possible to observe that the particles are smaller than 1 μm, and have even smaller spaces between the clusters. It is also evident that the morphology of both samples is very different from the morphology of sample MF9S4, confirming that the structure of the material was altered as a result of varying the time of dielectric heating with constant microwave intensity [19,20]. With the use of microwave radiation, there was a reduction of the spaces between the particle clusters of the activated metakaolin, possibly due a surface restructuring of this material [21].

3.1.5. Acidity of activated metakaolin

The results of the acidity analysis of the materials are presented in Table 2. The amount of cations present in the samples was correlated with hydroxyl consumption during titration [16]. Catalysts prepared from raw materials, such as clays, have a heterogeneous distribution of active sites (Al^{3+}) in the surface [12]. Thus, it was expected that the acid activation of the metakaolin provided a better distribution of these cations in the internal structure, because the acid treatment of metakaolinite results in the process of exsolving
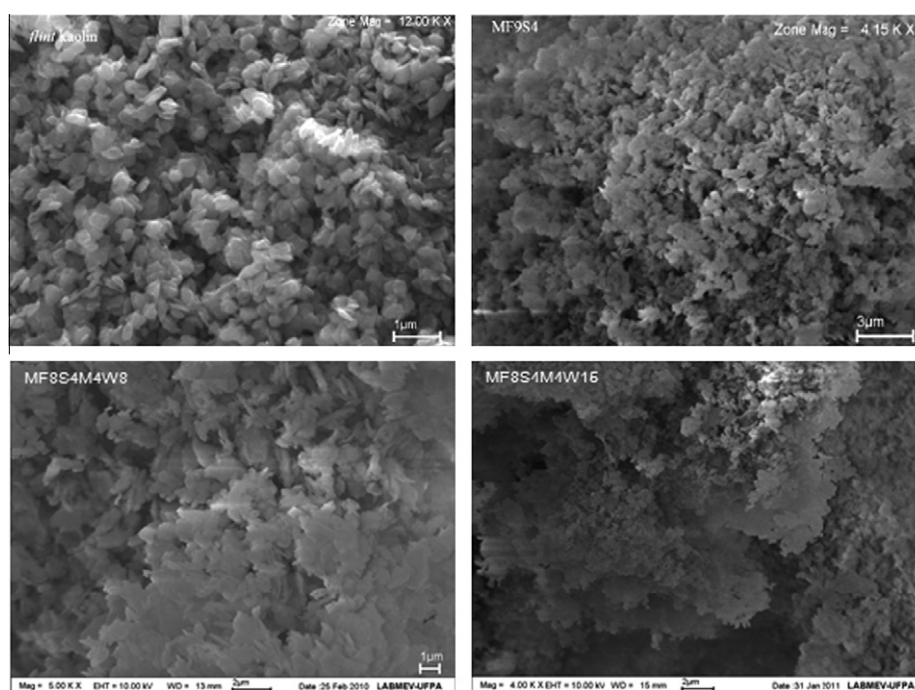

Fig. 2. SEM micrographs for *flint* kaolin (upper left), MF9S4 (upper right), MF8S4M4W8 (lower left) and MF8S4M4W15 (lower right).

of a large number of Al(III) cations and to a limited extent Fe(III) cations from the structure and their partial relocation in newly created pores, which, in the presence of water, act as Brønsted acid centers [22] (represented by a SiOH group influenced by the nearest Al cation, causing an increase in bond length of the OH group, which enhances acid strength of the proton [23,24]) and as Lewis acid centers in anhydrous conditions [22].

The nature of the acid sites of the prepared catalysts was proved by the presence of absorption bands of pyridinium ion at 1533 and 1636 cm^{-1} according to the experiments of pyridine adsorption accomplished by FTIR. According to the literature, these bands are related to the presence of Brønsted sites in the catalysts [4,25].

The infrared spectra in the region from 1700 to 1400 cm^{-1} samples with adsorbed pyridine (Fig. 1iv) showed typical bands that can be assigned to Lewis (at approximately 1448 and 1627 cm^{-1}) and Brønsted (at 1533 and 1636 cm^{-1}) sites-bonded pyridine. There is also a band at approximately 1492 cm^{-1} that can attributed to the pyridine molecules associated with both Brønsted and Lewis acidic sites, and this profile agrees with that presented by other leached metakaolins [4,25]. The MF8S4M4W15A sample presented a greater quantity of acidic sites (4.32 mmol H$^+$ g^{-1}). This result must be related directly to the preparation conditions of the samples; this sample was treated at a higher radiation intensity and for a longer time. The samples with greater specific surface areas (MF8S4M4W15 with 187 m^2 g^{-1} and MF8S4M3W15 with 284 m^2 g^{-1}) were also those that presented the highest concentrations of cations. According to the chemical composition analysis (Table 1), these characteristics are related to the percentage of Al$_2$O$_3$ present in the materials.

3.2. Catalyst tests

The catalytic activity of the metakaolin after acid activation by microwave radiation was assessed in the esterification of oleic acid with methanol with a molar ratio of acid:alcohol of 1:60.

In a preliminary test at 130 °C and lasting 30 min, catalysts MF8S4M4W15 and MF9S4M4W15 presented conversion percentages of 96.5% and 14%, respectively.

Flint kaolin calcined at 950 °C and activated under microwave radiation was observed to be resistant to acid leaching, in contrast to the results obtained by Do Nascimento et al. [4,6,7]. The difference between these results could be related to the fact that the dielectric heating favored the transformation of the metakaolin into primary mullite or spinel, which both begin to crystallize at 920 °C [11,18]. The possible sintering of the metakaolin into mullite was a determinant in the low catalytic activity of the MF9S4M4W15 during the reaction.

Therefore, the kaolin calcined at 850 °C was chosen as a starting point for the preparation of materials by varying both the microwave intensity (300 and 400 W) as well as the exposure time (8 and 15 min). After preparation, the catalytic activity of these materials was tested in the focus reaction.

Table 2 shows the catalytic performance in the esterification reaction of oleic acid with methanol at 100 °C for 30 min. The results obtained show that the catalyst performance was directly related to its chemical composition and to the number of acidic sites. For example, the MF8S4M4W15 sample, which presented a 95.2% conversion, has the highest acidity, efficiently promoting the transformation of the reactants into products at the superficial Al^{3+} sites.

3.2.1. Influence of temperature

It is known that catalytic yields are significantly increased when the reaction temperature is raised [4]. For these studies, the performance of the MF8S4M4W15 catalyst was assessed in the esterification of oleic acid with methanol, using a molar ratio of oleic acid:

Table 3
Conversion values for esterification of oleic acid with methanol (molar ratio 1:60) versus time.

T (°C)	Catalyst	10 min	20 min	30 min	40 min
70	–	1.4	4.6	6.5	7.5
70	MF8S4M4W15	44.5	53.0	58.0	74.0
85	–	2.3	6.9	8.2	10.7
85	MF8S4M4W15	68.4	78.0	84.2	90.2
100	–	5.6	6.3	9.0	10.8
100	MF8S4M4W15	76.8	88.9	95.2	95.7
115	–	8.5	9.4	11.6	12.6
115	MF8S4M4W15	85.5	90.8	95.5	96.5

methanol of 1:60 at 70, 85, 100 or 115 °C for 30 min. As expected, the increase in temperature was fundamental toward the conversion of the acid into the methyl ester in the presence of the MF8S4M4W15 catalyst. When the conversions were performed at 70 and 100 °C, for example, the percent conversion increased from 58 to 95.2%. However, it was observed that at reaction temperatures of 100 °C and above, the role of temperature is less significant; in reactions wherein the temperature varied from 100 to 115 °C, the conversion values were practically the same (95.7% and 96.5%, respectively).

3.2.2. Influence of reaction time

The effect of reaction time on conversion values was also studied. The results in Table 3 show that the reaction occurred more rapidly in the interval of 10–30 min and between 70 and 85 °C. The gradual increase in conversion rate with time was expected for this reaction. Under the experimental conditions used here, the reaction equilibrium was achieved at 40 min at 115 °C, revealing the high efficiency of the MF8S4M4W15 catalyst. As the reaction equilibrium is reached, water produced as a byproduct of the reaction can be adsorbed in the active catalytic sites [25]. The adsorbed water can favor a reaction inversion [4,25], possibly leading to a reduction in ester content.

On the basis of these results, it is possible to affirm that the use of MF8S4M4W15 as an esterification catalyst is very attractive because it showed conversion values equivalent to those obtained by Do Nascimento et al. [4,6,7] for leached metakaolin prepared under reflux. However, these materials, which were prepared using microwaves, achieved these results in much less time and at a much lower reaction temperature. As an example, using MF9S4, 98.9% of conversion was obtained at 160 °C and 240 min [4], whereas the MF8S4M4W15 catalyst reached 96.5% conversion at 115 °C and 40 min.

In this work, we have determined the order of the esterification reaction of oleic acid with methanol using the classical definitions of chemical kinetics and considering oleic acid as the limiting reagent, whose transformation into esters is followed by the acidity index [3,4]. To determine the order of the reaction by elementary kinetic theory, we proposed a complete conversion of the acid. According to the data from Table 3, it is possible to conclude that there is a first-order dependence between the reaction rate and the concentration of oleic acid, as the fitting shows a linear relation between all experimental data (when (-ln(1-conversion)) is plotted as a function of the reaction time). The regression coefficients of the straight lines show good fits to first-order kinetics. Using the esterification conversion data for MF8S4M4W15 catalyst we plotted (-ln(1-conversion)) versus the reaction time (not shown) to calculate the rate constants. The obtained values were of 0.0297 at 70 °C, 0.0534 at 85 °C, 0.0787 at 100 °C and 0.0802 at 115 °C. With these values we have plotted the Arrhenius of ln(k) versus 1/T and calculated the activation energy (Ea) and the frequency factor (A)

from the Arrhenius equation, which were 27.97 kJ mol^{-1} and 585.4 L mol^{-1} min^{-1}, respectively.

4. Conclusions

The thermal treatment of kaolin at 850 °C made metakaolin more susceptible to microwave activation. Metakaolin activated by microwave radiation presented specific surface areas with values that varied with the intensity and exposure time to the radiation. The experimental tests demonstrated that kaolin treated at 850 °C and activated with 4 M sulfuric acid for 15 min (MF8S4M4W15) was the most efficient catalyst, reaching a conversion rate of 96.5% for the esterification of oleic acid with methanol (molar ratio 1:60), at 115 °C and 40 min. The superior performance of this catalyst was also directly related to the density of the acidic sites on the surface, 4.32 mmol H$^+$ g^{-1}. When compared with the preparations employing reflux, the acid activation of *flint* metakaolin by microwave radiation achieved a catalytically more active material for the production of biofuels in less time and at a lower reaction temperature, making this methodology highly practical.

Acknowledgements

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