Contents lists available at ScienceDirect

Applied Clay Science

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

Note

Raw halloysite as reusable heterogeneous catalyst for esterification of lauric acid

Leandro Zatta [a], José Eduardo Ferreira da Costa Gardolinski [b], Fernando Wypych [a],*

[a] CEPESQ — Research Center in Applied Chemistry, Department of Chemistry, Federal University of Paraná, Caixa Postal 19081, 81531-980, Curitiba, PR, Brazil
[b] LAMIR — Laboratory for Analysis of Minerals and Rocks, Department of Geology, Federal University of Paraná, Caixa Postal 19062, 81531-980, Curitiba, PR, Brazil

A B S T R A C T

The methylic and ethylic esterifications of lauric acid were investigated using raw halloysite as a catalyst, in heterogeneous media. The reactions were conducted with different molar ratios (alcohol:lauric acid) and proportions of catalyst, at 160 °C for 2 h in a pressurized steel reactor. Halloysite produced lauric acid conversion of 95.02% and 87.11% for the methylic and ethylic esterifications, respectively. These results were better than those obtained from thermal conversion (75.61% and 59.86% for methanol and ethanol, respectively). After four consecutive reaction cycles, halloysite was recovered and could be reused after washing and drying. The results showed that halloysite is a promising inexpensive and reusable material for esterification reactions involving fatty acids.

© 2010 Elsevier B.V. Open access under the Elsevier OA license.

1. Introduction

In recent years there has been great interest in the transesterification of triacylglycerols (TAG, triglycerides) and esterification of free fatty acids (FFA), these being the two major chemical processes for obtaining biodiesel (fatty acid alkyl monoesters) from animal fats, crude vegetable oils and wastes from industrial processing of those substances (Suwannakarn et al., 2009). Oils and fats are mainly composed of acylglycerols (AGs), which are esters of various fatty acids with glycerol (Knothe et al., 2005), and also contain different amounts of free fatty acids (Marchetti and Errazu, 2008).

Esterification reactions are commonly used in industrial processes. The ester products are mostly used as solvents, plasticizers, synthetic food odorants and scents, as well as precursors for various pharmaceuticals, agrochemicals and other compounds (Carmo et al., 2008). In recent years these reactions have gained importance due to the production of fuels from renewable energy sources, especially as an alternative for fossil diesel. The esterification process consists of a reaction between a carboxylic acid and an alcohol in the presence of a catalyst to obtain the corresponding esters (Carmo et al., 2008; Marchetti and Errazu, 2008).

The esterification of free fatty acids is an alternative process to transesterification because it enables the use of industrial wastes and byproducts such as crude and processed vegetable oils (including used frying oil from food processing plants), acid sludge, animal fats, suet and lard, all of which are rich in FFAs (Juan et al., 2007; Marchetti and Errazu, 2008; Xu et al., 2008). These materials usually cost less than those used in the transesterification processes (Cardoso et al., 2008).

Traditionally, strong Brønsted acids like H_2SO_4 are used as homogeneous catalysts in the esterification processes (Xu et al., 2008). The disadvantages of this approach are the slow reaction rates, corrosion problems (Barbosa et al., 2006) and the production of highly acidic wastes, implying environmental restrictions for their disposal, with the need for additional neutralization procedures (Carmo et al., 2008).

In this context, heterogeneous catalysis has been widely discussed in recent years as being a more viable industrial process than homogeneous catalysis to produce biodiesel by transesterification and esterification reactions. Heterogeneous catalysts usually solve various problems associated with homogeneous media and add advantages such as lower toxicity, the possibility of catalyst recovery and recyclability, minimized corrosion capacity, ease of handling and separation from the reaction medium (Xu et al., 2008; Zhou, 2010). For these reasons, they are often called "environmentally friendly" (Sejidova et al., 2005; Kirumakki et al., 2006). Within heterogeneous catalyst technologies, raw and modified clay minerals are already widely employed in many industrial processes due to their favorable properties, such as catalytic efficiency (often displaying product-, regio- or shape-selectivity), low cost, wide availability, ease of preparation and high thermal stability (Okada et al., 1998; Hart and Brown, 2004; Adams and McCabe, 2006; Murray, 2007; Ramesh et al., 2010; Zhang et al., 2010).

The great majority of these processes, however, use cationic exchanged clay minerals of the 2:1 group and derivatives, which usually present higher activities and catalyze a broader range of reactions than do other clay minerals (Adams, 1987; Adams and McCabe, 2006; Castellano et al., 2010). The use of 1:1 group clay minerals as catalysts is largely restricted to kaolinite, and even then its

use is also restricted as a support to the actual catalysts or as a precursor to other catalytic ceramic materials or zeolites (Murray, 2007). The use of halloysite as a catalyst in organic reactions is no exception, and references to its use are very scarce (Machado et al., 2008; Barrientos-Ramírez et al., 2009; Liu and Zhao, 2009).

Halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$), a dioctahedral 1:1 clay mineral of the serpentine–kaolin group, is a polymorph of the more common kaolinite, and can be regarded as a hydrated kaolinite phase, with water content depending on various factors, thus often being highly interstratified or completely dehydrated (Brigatti et al., 2006). The morphology of halloysite particles is highly diverse, but the most common shapes are elongated, curled kaolinite-like particles forming nanotube-analogue morphologies similar to polygonal spirals ("nano-rolls" or "nanoscrolls") (Robertson and Eggleton, 1991; Joussein et al., 2005; Brigatti et al., 2006; Guo et al., 2009).

The present work presents the application of raw halloysite as a heterogeneous catalyst in the methylic and ethylic esterification of lauric acid. The understanding of the synthesis techniques for the ester studied in the present work is the starting point for the development of technologies using the 1:1 group clay mineral for the production of biodiesel, especially fully renewable fatty ethylesters.

2. Experimental

2.1. Materials

Raw "premium grade" halloysite, supplied by New Zealand China Clays Limited (New Zealand, part of the Imerys Group), was dried at 100 °C for 24 h and used without any further treatment. For the esterification reactions, all chemicals were used as received (lauric acid – $C_{12}H_{24}O_2$ – Vetec – 98%, methanol – QEEL – 99.8% and anhydrous ethanol – Synth – 99.8%).

2.2. Methods

2.2.1. Esterification reactions

The lauric acid methylic esterification reactions were conducted at three different molar ratios (MRs) – 3.5:1; 6:1 and 12:1 (alcohol:fatty acid) – while the ethylic reactions were conducted at MRs of 6:1 and 12:1. The reactions were performed in a Cyclone Büchiglasuster miniclave drive reactor for 2 h with a stirring speed of 500 rpm and using 4%, 8% and 12% catalysts in relation to the mass of the fatty acid. The temperature, time and speed were optimized in preliminary experiments. The internal reactor pressure of 9 bar was defined by the vapor pressure of the alcohol at 160 °C. After the reaction, the catalyst was extracted from the reaction medium by centrifugation (3500 rpm), washed with 15 ml of ethanol:hexane mixture (1:1) and dried at 90 °C for 12 h. The excess alcohol was removed by rota-evaporation and the lauric acid conversion yield was determined through the American Oil Chemist's Society Official Method Ca-5a-40 (AOCS, 2002). This method consists of titrating the excess free fatty acid content with a standardized sodium hydroxide solution in the presence of phenolphthalein as indicator.

Scheme 1 shows the generic esterification reaction investigated in the present work.

2.2.2. Characterization

The samples for powder X-ray diffraction analysis were prepared by placing the powdered material onto a neutral glass slide with a thin film of silicon grease, oriented by hand-pressing. X-ray diffraction
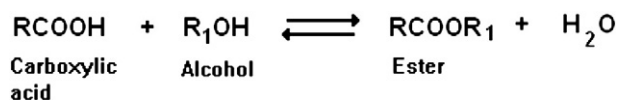
patterns were obtained using a Shimadzu XRD-6000 diffractometer with $CuK_\alpha = 1.5418$ Å radiation (30 mA and 40 kV) and a dwell time of $2° \, min^{-1}$.

The FTIR spectra were obtained by a Bio-Rad spectrometer, Model FTS 3500GX, using the KBr pellet technique. Measurements were obtained between 4000 and 400 cm^{-1}, with a resolution of 4 cm^{-1} and by the accumulation of 32 spectra.

Thermal analysis (thermogravimetry (TGA) and differential thermal analysis (DTA)) measurements were performed in 150 μL alumina crucibles with a Mettler-Toledo TGA/SDTA 851^e thermo-analyzer under a 50 mL min^{-1} oxygen flow. The heating rate was of 10 °C min^{-1} and the temperature range was 30–1000 °C.

3. Results and discussion

3.1. Catalyst characterization

In the TGA/DTA curves of raw halloysite (Fig. 1), a mass loss of 3.32% was observed and attributed to the loss to water (physisorbed and intercalated), associated with an endothermic peak at 66 °C. In the second thermal event, a mass loss of 14.27% was observed (dry basis), characteristic of the dehydroxylation of the matrix, also associated with an endothermic peak centered at 509 °C. This value is close to the theoretical mass loss of 13.96% for the ideal formula of dehydrated halloysite ($Al_2Si_2O_5(OH)_4$). The exothermic event near to 1000 °C was associated with the mullite crystallization (Kakali et al., 2001). The small deviation from the theoretical value was associated with the presence of remaining intercalated water, which was only slowly eliminated from the interlayer spaces of the halloysite (the TGA curve is not stable between ~100 and 400 °C). Small contaminations of the sample with calcium, titanium and iron were evidenced by X-ray fluorescence (data not shown). The X-ray diffraction pattern of the raw sample (Fig. 2a) indicated a basal distance of 7.4 Å, assigned to dehydrated halloysite (Rocha et al., 1990; Brigatti et al., 2006), with small contaminations of quartz and low temperature cristoballite (reflections indicated as "Q" and "CB" in the XRPD pattern) (Brindley and Brown, 1980; Díaz and Santos, 2001; Kakali et al., 2001). After the second (Fig. 2b) and fourth uses, shown in Fig. 2c, halloysite crystallinity was improved, as seen by the narrowing and better definition of the basal diffraction reflections. This lowering of the stacking disorder is associated with the effect of heat treatment and pressure during the esterification reactions. Additionally, it can also be caused by the lowering of the interstratification of the catalyst used in relation to the raw material (small amounts of water were still present, as discussed in the TGA/DTA results for the raw halloysite).

The TGA/DTA data of the catalyst after the fourth reaction cycle showed the same profile as the raw halloysite, attesting to the stability of the mineral (not shown).
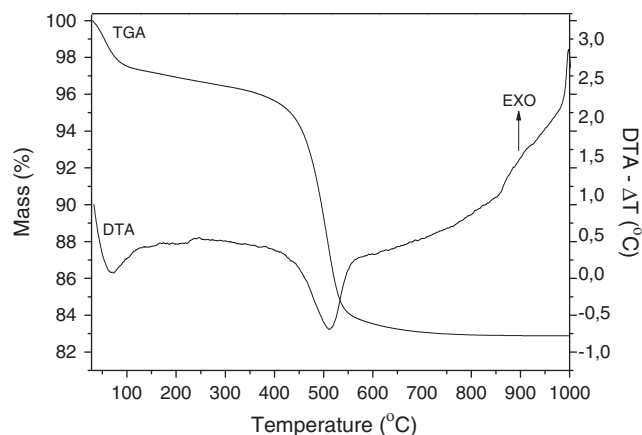

RCOOH + R₁OH ⇌ RCOOR₁ + H₂O

Scheme 1.

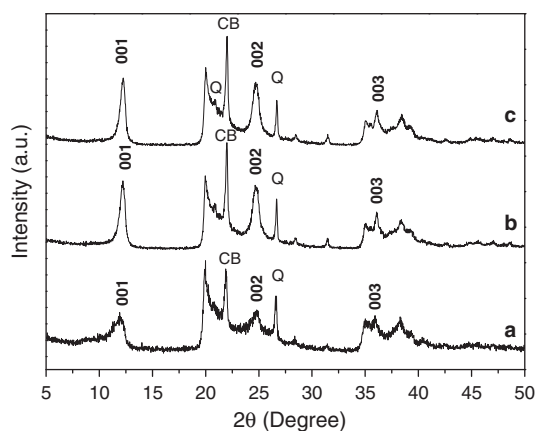**Fig. 1.** Thermal analysis (TGA/DTA) curves of raw halloysite.

Fig. 2. X-ray diffraction patterns of raw halloysite (a), after the first use (b) and after the fourth use (c), in the methylic esterification of lauric acid (MR = 6:1, 12% catalyst). The sequence of basal diffraction peaks are indicated as 001, 002 and 003. Q = quartz, CB = cristobalite (low temperature).

The positions of the indexed basal reflections (001, 002 and 003) for the above mentioned samples were determined as (7.42, 3.60 and 2.50 Å), (7.24, 3.61 and 2.49 Å) and (7.23, 3.60 and 2.49 Å), respectively. These observed differences are mainly due to the higher definition of the basal diffraction peaks of the samples used as catalysts. A complete indexation of the halloysite structure can be found in the literature (Brindley and Brown, 1980).

The FTIR spectra of raw halloysite (Fig. 3) presented the typical vibration modes for this mineral. The absorption bands at 3696 and 3622 cm^{-1} are assigned to the external and internal hydroxyl groups' stretching modes, respectively. Below 1500 cm^{-1} mainly the vibration modes of the skeletal bonds were observed (Madejová, 2003; Joussein et al., 2005).

An increase of the band near 3300–3500 cm^{-1} could be observed after one and four cycles of catalytic use (Fig. 3b and c) in the halloysite spectra, indicating the presence of physisorbed water (Madejová, 2003), which was generated in the esterification reaction. The hydrophilic character of halloysite is a positive aspect to remove water from reaction media, avoiding unwanted progress of the ester hydrolysis reaction (Scheme 1).

The appearance of bands at 2926 cm^{-1} and 2854 cm^{-1}, attributed to asymmetric stretching of C–H bonds in the methyl groups and asymmetric/symmetric stretching of C–H bonds in the methylene groups, respectively (Silverstein et al., 2005), suggest the presence of organic residues not completely removed by the catalyst washing
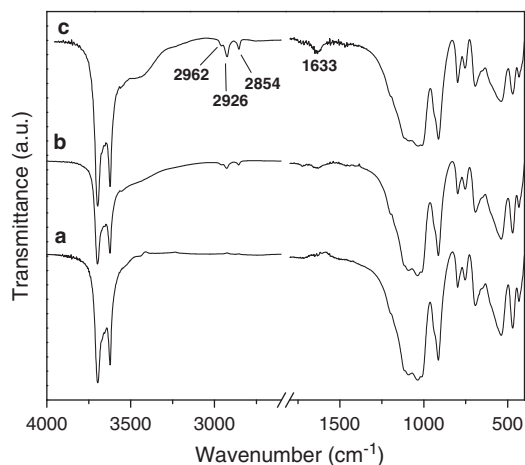
Table 1
Results obtained for the esterification of lauric acid. Thermal conversion (experiments 1 to 3, 13 and 14) and catalytic conversion using raw halloysite as catalyst (methylic esterification: experiments 4 to 12; ethylic esterification: experiments 15 to 20).

Experiment	[&]Molar ratio	Catalyst (%)	Acidity (%)	Conversion (%)
1[*]	3.5:1	–	22.12	77.88
2[*]	6:1	–	19.16	80.84
3[*]	12:1	–	24.39	75.61
4	3.5:1	4	15.63	84.37
5	3.5:1	8	12.28	87.72
6	3.5:1	12	11.53	88.47
7	6:1	4	8.40	91.60
8	6:1	8	6.32	93.68
9	6:1	12	5.21	94.79
10	12:1	4	15.74	84.26
11	12:1	8	5.60	94.40
12	12:1	12	4.98	95.02
13[*]	6:1	–	31.56	68.44
14[*]	12:1	–	40.14	59.86
15	6:1	4	26.91	73.09
16	6:1	8	25.71	74.29
17	6:1	12	15.42	84.58
18	12:1	4	36.89	63.11
19	12:1	8	33.38	66.62
20	12:1	12	12.89	87.11

[*] Thermal convertion.
[&] Molar ratio = alcohol:lauric acid.

process. As per the literature, the band at 1633 cm^{-1} was attributed to the bending mode of physisorbed molecular water (Madejová, 2003).

3.2. Esterification reactions

3.2.1. Methylic esterification

Table 1 and Fig. 4 show the results of the methylic esterification of lauric acid using raw halloysite as catalyst. The experiments marked with asterisks refer to thermal conversion in the absence of catalyst. The thermal conversion increased directly with the increase of the MR from 3.5:1 to 6:1, but when increasing the MR to 12:1, the ester conversion declined. This can be attributed to the shift of the equilibrium reaction towards the reagents with the presence of water generated in the reaction or to the effect of fatty acid dilution. Thermal conversion yields for the MRs of 3.5:1, 6:1 and 12:1 were 77.88%, 80.84% and 75.61%, respectively.

As the amount of the catalyst was increased (w/w in relation to the fatty acid) from 4% to 8% and 12%, maintaining the MR constant at 6:1,
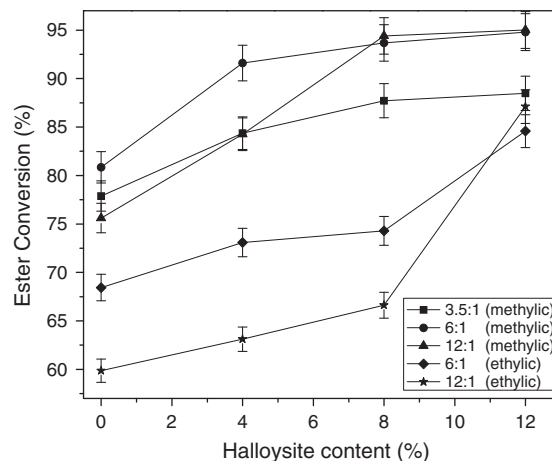

Fig. 3. FTIR spectra from raw halloysite (a), after first use as catalyst (b) and after fourth use as catalyst (c), in the methylic esterification of lauric acid (MR = 6:1, 12% catalyst).

Fig. 4. Ester conversion: methylic/ethylic esterification of lauric acid under various experimental conditions (zero catalyst content means thermal conversion).
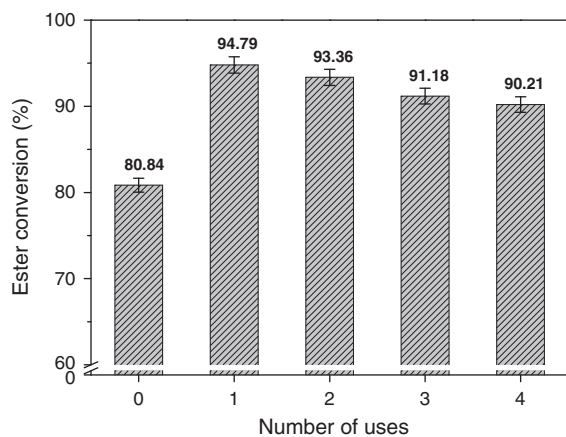
Fig. 5. Results from the recycling experiments (MR = 6:1; 12% catalyst; "zero uses" means thermal conversion value).

the ester conversion yields increased from 91.60% to 93.68% and 94.79%, respectively. This showed the positive effect of the catalyst concentration on the reaction media, an effect that can be attributed to the increase of the number of reactive sites present. This behavior was also observed when lower or higher MRs were used. When the MR was maintained at 12:1 and the catalyst concentration was increased from 4% to 8% and 12%, the ester conversion yields were 84.26%, 94.40% and 95.02%, respectively. Fig. 4 shows the compiled results obtained for different evaluation conditions.

For a MR of 6:1, a maximum conversion gain of 13.95% in relation to thermal conversion of methyl laurate was achieved by using 12% catalyst (experiment 9). The highest gain, 19.41%, was achieved for a MR of 12:1, also using 12% catalyst (experiment 12). The conversion gain was calculated by subtracting the catalytic conversion of the thermal conversion.

Experiment 12 also produced the highest absolute conversion to methyl laurate (95.02%) among the studied conditions. The conversions achieved with MRs of 6:1 and 12:1 were, however, very similar, which suggest that excess methanol did not have any significant effect, effectively qualifying the MR of 6:1 as a local ideal condition.

Halloysite reuse experiments were conducted to verify the reproducibility of the esterification procedure and sustained catalytic activity to the recycling of the catalyst, where a MR of 6:1 and 12% catalyst were used as the experimental conditions. The results for four use cycles are presented in Fig. 5. A gradual decrease in the lauric acid conversion was observed as the catalyst was reused, but the values still surpassed the thermal conversion under the same experimental conditions, even after four cycles, indicating that halloysite can act as a reusable catalyst under the investigated conditions. The partial loss of activity can be attributed to the increased particle size and lower surface area, as attested by XRD data (Fig. 2).

3.2.2. Ethylic esterification

As methanol is obtained from fossil sources, the objective to use ethanol as acylating agent aims to produce a fully renewable biofuel (Table 1, Fig. 4). Only the MRs of 6:1 and 12:1 were used in these experiments to compare the catalytic performance. By comparing the thermal conversion yields at MR 6:1 (reaction 13) with the experiments catalyzed by 4, 8 and 12% halloysite (reactions 15–17), the conversion gains were 4.56, 5.85 and 16.44%, respectively. When comparing the reactions at MR 12:1, these gains were 3.25, 6.76 and 27.25% (reaction 14 versus reactions 18–20).

Comparison of the gains obtained at MRs of 6:1 and 12:1 showed the positive effect of the catalyst concentration and of the molar ratio. These observations indicate that the best experimental condition was with MR 12:1 and 12% catalyst (27.25% gain, 87.11% ester conversion). In general, the conversion to ester decreased with the increase of MR

(increased concentration of alcohol) in the reaction mixture, the tendency was observed for both evaluated alcohols. The excess of alcohol hinders the esterification reaction, probably by blocking the active sites on the halloysite structure, as observed in the esterification of alcohols with acetic acid, using different zeolites (Kirumakki et al., 2006) and/or by diluting the reagents.

As halloysite has a heterogeneous surface charge and is able to function as both an electron acceptor and an electron donor, the esterification reaction mechanism is rather difficult to predict.

4. Conclusion

Raw halloysite solid catalyst was able to esterify lauric acid and produce fatty esters. The potential catalytic activity of the raw mineral was demonstrated by the reaction yields, which were higher than those achieved by thermal conversion. Experimental conditions such as molar ratio and catalyst content were evaluated and optimal conditions for achieving higher yields were also determined. The possibility of catalyst recovery and reuse were also tested successfully, by evaluating four reaction cycles. The obvious environmental advantages of the use of a natural product as a catalyst in a heterogeneously catalyzed process are also complemented by the fact that halloysite is fairly inexpensive, is readily available worldwide (at least in some degree of purity in local kaolin deposits), and even after the exhaustion of catalytic activity, it can be used as a raw materials for cement, ceramics or other industries, for example.

To the best of our knowledge, this is the first report of the catalytic activity of halloysite by itself instead of simply acting as a support for other catalysts.

References

Adams, J.M., 1987. Synthetic organic chemistry using pillared, cation-exchanged and acid-treated montmorillonite catalysts — a review. Appl. Clay Sci. 2, 309–342.
Adams, J.M., McCabe, R.W., 2006. Clay minerals as catalysts, In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science (Developments in Clay Science, Vol. 1), 1st edition. Elsevier, Amsterdam, pp. 541–581.
American Oil Chemist's Society — AOCS, 2002. Official Methods and Recommended Practices of the American Oil Chemist's Society. AOCS Press, Champaign.
Barbosa, S.L., Dabdoub, M.J., Hurtado, G.R., Klein, S.I., Baroni, A.C.M., Cunha, C., 2006. Solvent free esterification reactions using Lewis acids in solid phase catalysis. Appl. Catal. A. 313, 146–150.
Barrientos-Ramírez, S., Ramos-Fernández, E.V., Silvestre-Albero, J., Sepúlveda-Escribano, A., Pastor-Blas, M.M., González-Montiel, A., 2009. Use of nanotubes of natural halloysite as catalyst support in the atom transfer radical polymerization of methyl methacrylate. Microporous Mesoporous Mater 120, 132–140.
Brigatti, M.F., Galan, E., Theng, B.K.G., 2006. Structures and mineralogy of clay minerals, In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science (Developments in Clay Science, Vol. 1), first edition. Elsevier, Amsterdam, pp. 19–86.
Brindley, G.W., Brown, G., 1980. Crystal Structures of Clay Minerals and their X-ray IdentificationFirst edition. Mineralogical Society, London.
Cardoso, A.L., Neves, S.C.G., Silva, M.J., 2008. Esterification of oleic acid for biodiesel production catalyzed by SnCl₂: a kinetic investigation. Energies 1, 79–92.
Carmo Jr., A.C., Souza, L.K.C., Costa, C.E.F., Longo, E., Zamian, J.R., Filho, G.N.R., 2008. Production of biodiesel by esterification of palmitic acid over mesoporous aluminosilicate Al-MCM-41. Fuel 88, 461–468.
Castellano, M., Turturro, A., Riani, P., Montanari, T., Finocchio, E., Ramis, G., Busca, G., 2010. Bulk and surface properties of commercial kaolins. Appl. Clay Sci. 48, 446–454.
Díaz, F.R.V., Santos, P.S., 2001. Studies on the acid activation of Brazilian smectitic clays. Quim. Nova 24, 345–353.
Guo, B., Chen, F., Lei, Y., Liu, X., Wan, J., Jia, D., 2009. Styrene-butadiene rubber/halloysite nanotubes nanocomposites modified by sorbic acid. Appl. Surf. Sci. 225, 7329–7336.
Hart, M.P., Brown, D.R., 2004. Surface acidities and catalytic activities of acid-activated clays. J. Mol. Catal. A: Chem. 212, 315–321.
Joussein, E., Petit, S., Churchman, J., Theng, B., Righi, D., Delvaux, B., 2005. Halloysite clay minerals — a review. Clay Miner. 40, 383–426.

Juan, J.C., Zhang, J., Yarmo, M.A., 2007. 12-Tungstophosphoric acid supported on MCM-41 for esterification of fatty acid under solvent-free condition. J. Mol. Catal. A: Chem. 267, 265–271.

Kakali, G., Perraki, T., Tsivilis, S., Badogiannis, E., 2001. Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. Appl. Clay Sci. 20, 73–80.

Kirumakki, S.R., Nagaraju, N., Chary, K.V.R., 2006. Esterification of alcohols with acetic acid over zeolites Hβ, HY and HZSM5. Appl. Catal., A 299, 185–192.

Knothe, G., Gerpen, J.V., Krahl, J., 2005. Biodiesel HandbookFirst edition. AOCS Press, Champaign.

Liu, P., Zhao, M., 2009. Silver nanoparticle supported on halloysite nanotubes catalyzed reduction of 4-nitrophenol (4-NP). Appl. Surf. Sci. 255, 3989–3993.

Machado, G.S., Castro, K.A.D.F., Wypych, F., Nakagaki, S., 2008. Immobilization of metalloporphyrins into nanotubes of natural halloysite toward selective catalysts for oxidation reactions. J. Mol. Catal. A: Chem. 283, 99–107.

Madejová, J., 2003. FTIR techniques in clay mineral studies. Vib. Spectrosc. 31, 1–10.

Marchetti, J.M., Errazu, A.F., 2008. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. Biomass Bioenergy 32, 892–895.

Murray, H.H., 2007. Applied Clay Mineralogy: Ocurrences, Processing and Application of Kaolins, Bentonites, Palygorskite-Sepiolite, and Common Clays, First edition. : Developments in Clay Science, 2. Elsevier, Amsterdam.

Okada, K., Shimai, A., Takei, T., Hayashi, S., Yasumori, A., Mackenzie, K.J.D., 1998. Preparation of microporous silica from metakaolinite by selective leaching method. Microporous Mesoporous Mater 21, 289–296.

Ramesh, S., Prakash, B.S.J., Bhat, Y.S., 2010. Enhancing Bronsted acid site activity of ion exchanged montmorillonite by microwave irradiation for ester synthesis. Appl. Clay Sci. 48, 159–163.

Robertson, I.D.M., Eggleton, R.A., 1991. Weathering of granitic muscovite to kaolinite and halloysite and of plagioclase-derived kaolinite to halloysite. Clays Clay Miner. 39, 113–126.

Rocha, J., Adams, J.M., Klinowski, J., 1990. The rehydration of metakaolinite to kaolinite: evidence from solid-state NMR and cognate techniques. J. Solid State Chem. 89, 260–274.

Sejidova, F.T., Mansoori, Y., Goodarzi, N., 2005. Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition. J. Mol. Catal. A: Chem. 240, 186–190.

Silverstein, R.M., Webster, F.X., Kiemle, D.J., 2005. Spectrometric Identification of Organic CompoundsSeventh edition. John Wiley & Sons, New York.

Suwannakarn, K., Lotero, E., Ngaosuwan, K., Goodwin Jr., J.G., 2009. Simultaneous free fatty acid esterification and triglyceride transesterification using a solid acid catalyst with in situ removal of water and unreacted methanol. Ind. Eng. Chem. Res. 48, 2810–2818.

Xu, L., Yang, X., Yu, X., Guo, Y., Maynurkader, 2008. Preparation of mesoporous polyoxometalate-tantalum pentoxide composite catalyst for efficient esterification of fatty acid. Catal. Commun. 9, 1607–1611.

Zhang, L.X., Jin, Q.Z., Shan, L., Liu, Y.F., Wang, X.G., Huang, J.H., 2010. $H_3PW_{12}O_{40}$ immobilized on silylated palygorskite and catalytic activity in esterification reactions. Appl. Clay Sci. 47, 229–234.

Zhou, C.H., 2010. Emerging trends and challenges in synthetic clay-based materials and layered double hydroxides. Appl. Clay Sci. 48, 1–4.