ISSN 2321-807X
Volume 12 Number6
Journal of Advances in Chemistry

Synthesis, characterization and application of [CTA$^+$]MCM-41 in the catalytic conversion of soybean oil to fatty acid methyl esters

Vinícius Kothe[1], Helton José Alves[2], Marcos Henrique Luciano Silveira[1], Luiz Pereira Ramos[1,3*]

[1]Research Center in Applied Chemistry (CEPESQ), Department of Chemistry, Federal University of Paraná,
P.O. Box 19032, Curitiba, Paraná 81531-980, Brazil
kothe.vinicius@gmail.com, mlhsilveira@gmail.com, luiz.ramos@ufpr.br*

[2]Laboratory of Catalysis and Biofuel Production (LabCatProBio), Biofuels Technology Course, Federal University of Paraná (UFPR – Campus Palotina)
helton.alves@ufpr.br

[3]INCT Energy & Environment (INCT E&A), Department of Chemistry, Federal University of Paraná, Brazil

ABSTRACT

The transesterification of vegetable oil and/or animal fats in homogeneous alkaline medium is still the most widely used method for the production of biodiesel. However, this process requires raw materials with low acidity and moisture content to prevent undesirable side reactions such as saponification, which leads to emulsification and promotes losses in the reaction yield. Many solid compounds can be used in catalytic processes to reduce these limitations. Heterogeneous catalysts allow easy separation of the reaction media and have the possibility of reuse in several cycles. In this work, [CTA$^+$]MCM-41 molecular sieves were synthesized and characterized by several methods (XRD, SEM, TGA and BET) to be applied in the methanolysis of soybean oil. The resulting materials were characterized as mesoporous solids of type IV with similar textural properties and thermal stability. The catalytic activity of [CTA$^+$]MCM-41 in soybean oil methanolysis was analyzed by gel permeation chromatography (GPC) and the best solid catalyst was applied in a factorial design that was validated by Analysis of Variance (ANOVA). The oil:methanol molar ratio and the catalyst concentration were the variables with the highest statistical effects, with the latter showing a quadratic profile in relation to the response function. The best conversion was achieved at 343 K, 30 min and 3.75 wt % catalyst, which corresponded to a product with 99.2% in fatty acid methyl esters. Calcination caused a total loss in catalytic activity due to the removal of CTA$^+$ cations from the mesoporous solids. Hence, such activity was associated with the formation of (SiO$^-$)(CTA$^+$) ion pairs at the surface of the solid catalyst.

Keywords

Biodiesel, methanolysis, heterogeneous catalysis, molecular sieves, [CTA$^+$]MCM-41

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

Catalysis

TYPE (METHOD/APPROACH)

Biodiesel production by heterogeneous catalysis

INTRODUCTION

The production of diesel fuels from renewable resources has increased considerably over the last decades because of environmental issues related to greenhouse gas emissions and to the dependence of developing countries on the use of fossil fuels in their energy matrix (Demirbas, 2009). Biodiesel is a renewable, nontoxic and environmentally friendly fuel whose properties are suitable for fuel applications in the transportation sector without the need for major adjustments in the current technology of diesel engines. Besides that, there are other social and environmental advantages such as its contribution to regional development and its role in promoting fuel safety, better air quality in largely populated areas and other favorable externalities in local economies (Ren et al., 2015; Sharir et al., 2015; Silva et al., 2013).

Conventionally, biodiesel is produced by alkaline transesterification of triacylglycerides in homogeneous media using low molecular mass primary alcohols, usually methanol or ethanol, releasing glycerol and the corresponding fatty acid alkyl esters as the reaction coproducts (Choedkiatsakul et al., 2015). This process is catalyzed by alkaline metal alkoxides or by alkali metal hydroxides that are able to generate alkaline metal alkoxides in situ (Silva et al., 2013). Although highly efficient to produce fatty acid alkyl esters in high yields, this technology requires several purification steps to produce biodiesel of suitable fuel quality and to recover a glycerin stream in good conditions for its subsequent use directly as a chemical or as a carbon source or building block for other industrial applications (Ramos and Wilhelm, 2005). By contrast, heterogeneous catalytic processes usually facilitate or even eliminate such purification steps by allowing an easy removal of the solid catalyst and offering the possibility of its reuse in several reaction cycles, therefore reducing the environmental impact of handling process streams and improving the overall economics and/or sustainability of the entire production process.

Among the various materials used in heterogeneous catalysis, a specific class of molecular sieves has been widely studied (Grün et al., 1999). The term molecular sieve was created by McBain in 1932 and it applies to solids that are capable of adsorbing molecules selectively. According to the International Union of Pure and Applied Chemistry (I.U.P.A.C.), the molecular sieves can be classified according to the pore size as (a) microporous (pore diameter <2 nm), (b) mesoporous (pore diameter between 2-50 nm), and (c) macroporous (pore diameter> 50 nm) (Luna and Schuchardt, 2001; Sing et al. 1985). Since the discovery of the M41S molecular sieves, MCM-41 has been identified as a prominent catalyst for transesterification due to its appropriate structural features such as high thermal stability, pore diameters between 2 and 50 nm and surface area at around 1500 m^2 g^{-1} (Fabiano et al., 2010; Grün et al, 1999; Ranucci et al., 2015).

The synthesis of molecular sieves takes place in aqueous medium and involves four reagents: the mineralizing agent, water, a structure-directing surfactant (CTABr) and a silicon source. The mineralizing agent is responsible for converting the silicon source into an inorganic polymeric structure. Usually, the structure-directing surfactant contains nitrogen and has a hydrophobic chain of 6 and 20 carbon atoms ($C_nH_{2n+1}(CH_3)_3N^+$). The silicon source has the function of serving as the mesoporous wall construction units and, for that, pyrolyzed silica, tetraethyl orthosilicate (TEOS) or sodium silicate may be used, among others (Cheng et al., 1997; Grün et al., 1999; Kresge et al., 1992).

After their synthesis, these materials are usually calcined in order to remove the structure-directing agent that is occluded in the mesopores, generating materials that are composed only by silica which, at first, has no catalytic activity (Fabiano et al., 2010). The catalytic activity can be obtained by functionalization of the solid surface with amines, metals such as titanium and aluminum and alkali metal oxides. However, the use of high pH during this process may damage the structure of the solid catalyst (Grün et al., 1999; Martins and Cardoso, 2007).

Kubota et al. (2004, 2006) reported the use of MCM-41 without calcination, that is, with the surfactant still occluded in the mesopores, as a solid catalyst for optimizing the Knoevenagel condensation. These authors suggested that the basicity of this silicate-organic composite is related to the interaction of siloxy anions ($\equiv SiO^-$) with CTA^+ cations and that their active sites resided at the pore mouth of the solid catalyst. This interpretation was confirmed by the observed loss in catalytic activity when the surfactant was leached out from the catalyst structure. Fabiano et al. (2010) obtained conversions of 65 to 96% when using uncalcined catalysts from the M41S family in the transesterification of canola oil with methanol and ethanol.

The objective of this study was to synthesize the $[CTA^+]$MCM-41 catalysts by modifying the synthesis conditions in order to obtain materials with different textural properties. These catalysts were characterized and subsequently employed in the methanolysis of soybean oil for its conversion to fatty acid methyl esters.

MATERIAL AND METHODS

Synthesis of the $[CTA^+]$MCM-41 according to Grün et al. (1999)

Initially, the molecular sieve $[CTA^+]$MCM-41 was produced by the method described by Grün et al. (1999). The reaction medium was composed by Cetyl Trimethyl Ammonium Bromide (CTABr 99 %, Sigma-Aldrich®) as the structure-directing agent, ammonium hydroxide (NH_4OH 29 % FMAIA®) as the mineralizing agent, tetraethyl orthosilicate (TEOS 98 %, Acros Organics®) as the silica source, absolute ethanol as the TEOS co-solvent, and ultrapure water.

For the $[CTA^+]$MCM-41 synthesis, 2.28 g of CTABr were solubilized in 34.2 mL of ultrapure water and mixed for 15 min at 303 K. Then, 30.84 mL of NH_4OH and 64.2 mL of ethanol were added to the mixture and stirred until a clear solution was obtained. Finally, 4.6 mL of TEOS were added and the mixture remained under stirring for 2 h at 303 K. After this, the gel was filtered, washed with 200 mL of ultrapure water and dried for 24 h at 343 K.

Modification on the $[CTA^+]$MCM-41 synthesis

To produce $[CTA^+]$MCM-41 materials with different textural properties, the experimental conditions of the Grün's method were modified according to Table 1. The molar ratio between CTABr and TEOS was varied between 0.30 and 0.55. In addition, the molar ratio of ethanol and water was varied between 0.40 and 0.52. The reason for these was to change the availability of structure-directing agent and to increase the solubility of TEOS in the reaction medium.

Table 1. Conditions used for the synthesis of $[CTA^+]$MCM-41 materials with different textural properties.

Experiment	CTABr:TEOS molar ratio[a]	EtOH:H2O molar ratio[b]
E1	0.55	0.40
E2	0.30	0.40
E3	0.30	0.52
E4	0.55	0.52

[a] Cetyl Trimethyl Ammonium Bromide:tetraethyl orthosilicate molar ratio;

[b] Ethanol:water molar ratio.

Characterization of the solid catalysts

The synthesized catalysts were analyzed before and after calcination. X-ray diffraction analysis (XRD) was carried out in Rigaku Geigerflex X-ray diffractometer (Tokyo, Japan) within the range of 1.5° < 2θ < 40° with CuKα (45 mV, 25 mA) and 1° min^{-1} of scanning speed. Surface area and pore radius were evaluated by nitrogen sorption in a Quantachrome Instruments Nova 2000e (Boynton Beach, USA) analyzer. Samples were pretreated for 4 h at 383 K and the specific surface area (S_{BET}) was calculated by the BET (Brunauer, Emmett, Teller) equation. Thermogravimetry was performed in a TA Instruments Q-500 (New Castle, USA). About 10 mg of the sample was heated from 298 K to 1073 K under nitrogen flow (40.0 mL min^{-1}) at a heating rate of 10 K min^{-1}. Scanning electron microscopy (SEM) images were collected by a FEI Quanta 400 Microscope (Hilsboro, USA) to evaluate the morphology and the size of the catalyst particles.

Catalytic tests for the methanolysis of soybean oil

All synthesized solid catalysts were applied in transesterification using food grade soybean oil (Liza®) and methanol to produce fatty acid methyl esters. The tests were performed in a 60 mL homemade stainless steel reactor that was immersed in an oil bath. The reaction was carried out at 343 K for 60 min under magnetic stirring using an oil:alcohol molar ratio of 1:12 under autogenous pressure with 5% of catalyst (w/w). After this, the reactor vessel was cooled down to room temperature in 20-30 min and the mixture was centrifuged to remove the solid phase, which was washed with a 1:1 ethanol:hexane mixture and dried at 333 K for 24 h. The organic phase was separated, the excess of the solvent was removed by rotatory evaporation, and the reaction products were analyzed by gel permeation chromatography (GPC) without any further treatment to calculate the conversion of soybean oil to methyl esters. Thus, the catalyst that presented the best reaction performance was selected to be used in a 3^{n-1} factorial design (n = 3) with four replicates at the center point that were performed randomly. The experiments were organized and interpreted using the software Statistica 10.

GPC analysis were carried out in Waters HPLC Empower 3 workstation (Milford, USA) containing an isocratic chromatographic pump (model 1515), an autosampler (model 2707), a column heater module, and a refractive index detector (model 2414). Analyses were carried out in two Progel–TSK columns (1000 and 2000 HXL, 30 cm x 7.8 mm) placed in tandem after a suitable pre-column. Elution was performed with tetrahydrofuran (THF) at a flow rate of 0.8 mL min^{-1}. The quantitative analysis was carried out by external calibration using 1-stearoyl-rac-glycerol (monostearin), 1,2-distearoyl-rac-glycerol (distearin), glyceryl tristearate (tristearin) and stearic acid methyl ester (methyl stearate) as standards (Sigma-Aldrich®), which were prepared in THF in concentrations ranging from 0.156 to 5.0 mg mL^{-1}. The ester content in reaction products was determined according to Equation 1,

$$E_c\,(\%) = W_E/\sum_{WC} \times 100 \qquad \text{(Equation 1)}$$

where E_c gives the total methyl ester content, whereas W_E is to the total amount of methyl esters and $\sum_{WC}$ is the total amount of detectable components in the reaction mixture, including acylglycerides, and glycerol. Both W_E and $\sum_{WC}$ were obtained by GPC analysis as described above.

Calcination of [CTA^+]MCM-41

A sample of the [CTA^+]MCM-41 was calcined at 793 K for 4 h to produce a mesoporous structure after complete removal of the surfactant molecules. The resulting material was characterized as described in section 2.3 and applied as a solid catalyst for the methanolysis of soybean oil.

RESULTS AND DISCUSSION

All [CTA^+]MCM-41 syntheses resulted in the recovery of around 2 g of the solid catalyst after drying and this was in agreement with the amount of reactants used in the experimental procedure.

The XRD profiles of the synthetic [CTA^+]MCM-41 (Figure 1) showed the presence of peaks in 2θ between 1.5 and 8.0, typical of MCM-41 molecular sieves. The peaks related to the 100, 110 and 200 diffraction planes were indexed between 1.5° < 2θ < 5° and these seem to be due to the formation of a hexagonal phase of ordered mesopores (Grün et al., 1999; Martins and Cardoso, 2007). Interestingly, the peak indexed to the 100 diffraction plane was shifted to the right in sample E4, revealing the structure of a less organized synthetic material having small pore diameters and the smallest interplanar distance *d*.

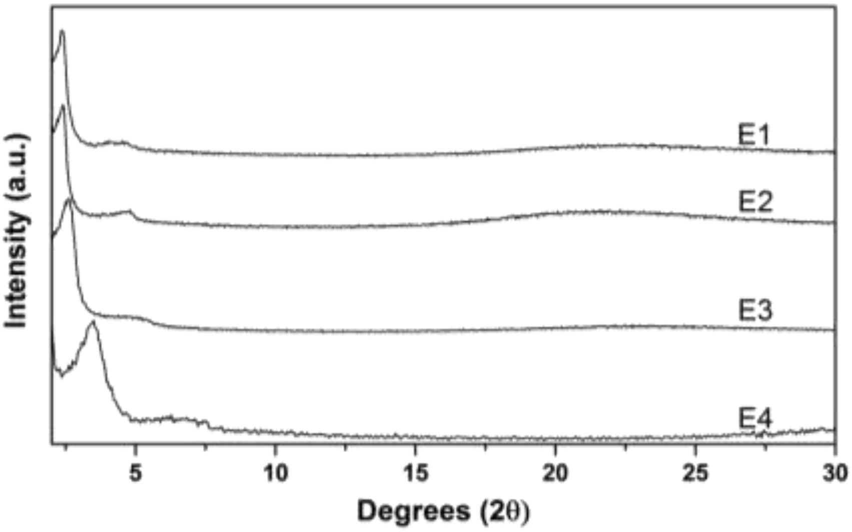

Figure 1. X ray analysis of the [CTA$^+$]MCM-41 solid catalysts.

The scanning electron microscopy images (SEM) of the synthesized solid catalysts showed spherical particles with homogeneous distribution and average diameter lower than 1 µm, typical of the [CTA$^+$]MCM-41 (Figure 2) (Grün et al., 1999). Figure 2B (sample E2) shows that the use of low levels of CTABr associated with low levels of reaction co-solvent resulted in the malformation of the solid particles. Figure 2D (sample E4) also reveals the occurrence of filamentous particles in the form of needles, which were probably formed due to the excess of surfactant in the reaction media.

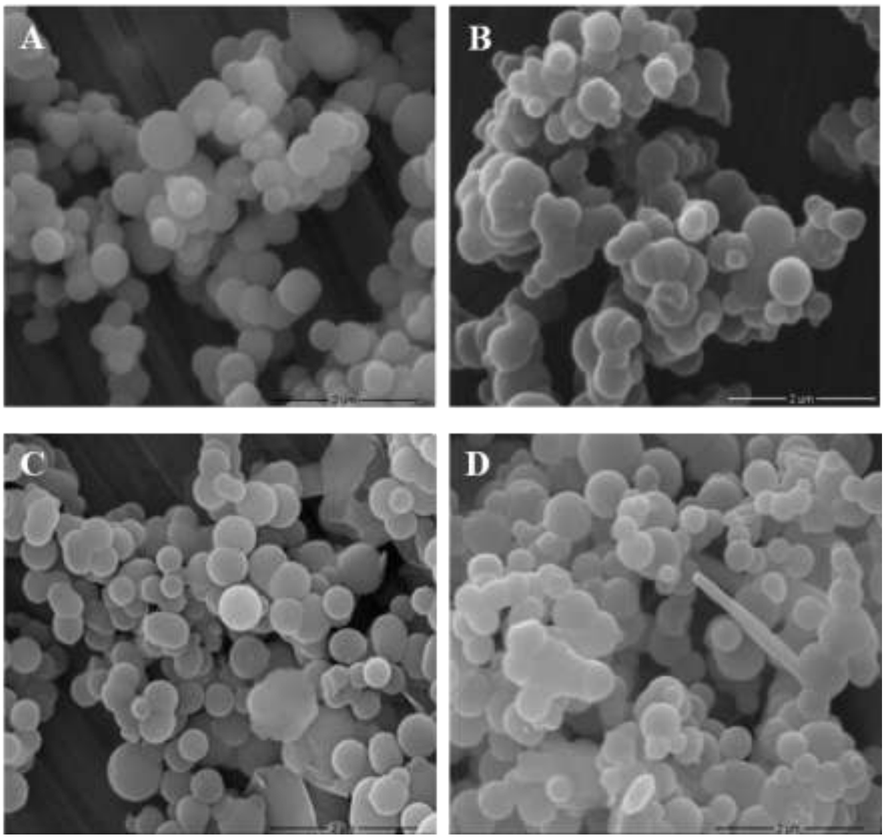

Figure 2. SEM micrographs of the [CTA$^+$]MCM-41 solids that were synthesized according to the factorial design described in Table 1 (A, sample E1; B, sample E2; C, sample E3; D, sample E4).

The surface area of the synthesized [CTA$^+$]MCM-41 solids is given in Figure 3. A wide variation ranging from 8.6 to 39.4 $m^2\ g^{-1}$ was observed among these catalysts, indicating that the use of different amount of reactants in the reaction media (Table 1) promoted the formation of catalysts with different textural properties. The relatively high surface area of the E1 catalyst was attributed to the use of a high reactant concentration during its synthesis, which resulted in solids with a higher porosity. However, the same was not observed for E4 probably due to ethanol acting as a TEOS dispersant.

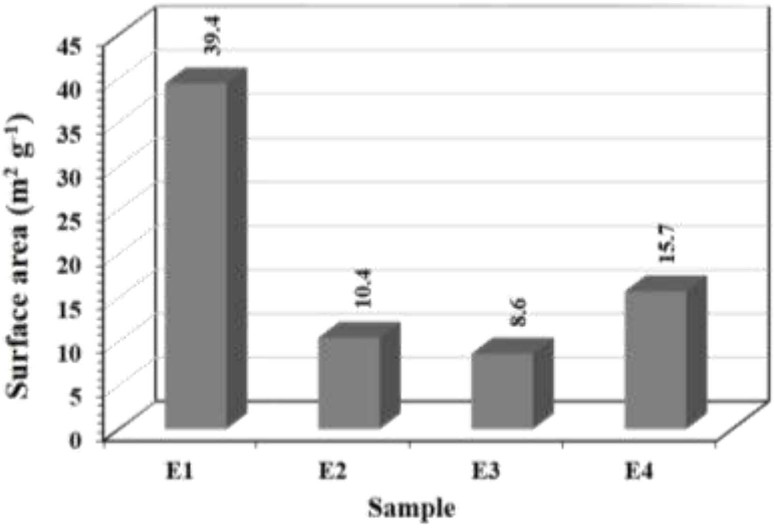

Figure 3. Textural properties of the [CTA$^+$]MCM-41 solids that were synthesized according to the Grün method with modification.

The thermal stability of the solid catalysts was evaluated by thermogravimetric analysis (Figure 4). For all samples, three mass loss regions were observed. The first region corresponds to the loss of adsorbed water (up to 423 K), while the second region between 423 and 573 K represents the decomposition of CTA+ cations and the third region (above 673 K) is attributed to the decomposition of silanol groups that are interacting with the CTA+ cations in the pore surface. The behavior of samples E1, E2, E3 and E4 were similar, suggesting that the synthesis variables did not influence the thermal properties of the resulting solids.

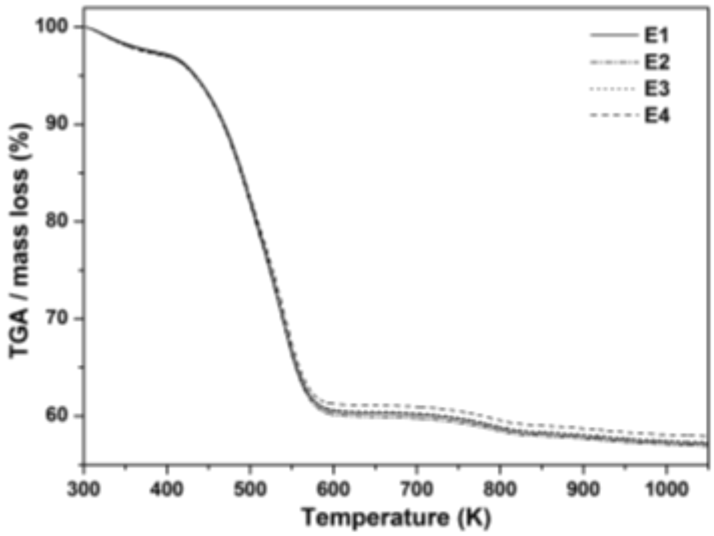

Figure 4. Thermogravimetric analysis of the [CTA$^+$]MCM-41 synthesized solids.

The catalysts described in Table 1 showed conversion rates in methyl esters of 97.2, 92.9, 97.1 and 99.3% for E1, E2, E3 and E4, respectively. By contrast, no conversion was observed when the calcined catalysts were used for soybean oil methanolysis, suggesting that the CTA$^+$ cations are required for developing the observed catalytic activity (Fabiano et al., 2010).

The poor catalytic performance of sample E2 (Table 1) can be associated to the use of lower amounts of both surfactant and co-solvent in the synthesis of the solid catalyst. These conditions seemed to reduce the solubility of TEOS in the reaction mixture and to compromise the formation of (CTA$^+$)(≡SiO$^-$) ionic pairs, which were critical for the catalytic activity of the solid material. By contrast, the superior catalytic activity of sample E4 was attributed to the use of higher amounts of CTA$^+$ and ethanol in the catalyst synthesis. Besides, sample E4 displayed the highest surface area among all synthesized materials, probably with a higher availability of active sites for the catalytic conversion. On the basis of these, sample E4 was selected for pre-optimization using a 3^{n-1} factorial design with four replicates at the central point as shown in Table 2.

Table 2. Reaction conditions used in the factorial design and the ester content of their final products.

Test	Catalyst (%)[a]	Time (min)	MR[b]

A1	5.0	45	1:6
A2	2.5	60	1:9
A3	2.5	30	1:6
A4	5.0	60	1:12
A5	2.5	45	1:12
A6[c]	3.75	45	1:9
A7[c]	3.75	45	1:9
A8	3.75	60	1:6
A9	3.75	30	1:12
A10[c]	3.75	45	1:9
A11	5.0	30	1:9
A12[c]	3.75	45	1:9

[a] Amount of catalyst in relation to the mass of soybean oil;

[b] Oil:methanol molar ratio;

[c] Center Point (standard deviation of 3.28%).

The standard deviation of measurements made at the center point was only 3.28% for an average value of 75.9%. This result was important for the statistical analysis and validation of the [CTA$^+$]MCM-41 catalyzed conversion of soybean oil to fatty acid methyl esters. Figure 5 shows the GPC profile of the methyl esters that were obtained at the conditions of the center point, in which unreacted triacylglycerides and partially reacted mono- and diacylglycerides are observed together with fatty acid methyl esters. This figure also shows the GPC profile of the best methyl ester preparation obtained in this work, which was derived from the reaction carried out with sample E4 from Table 1.

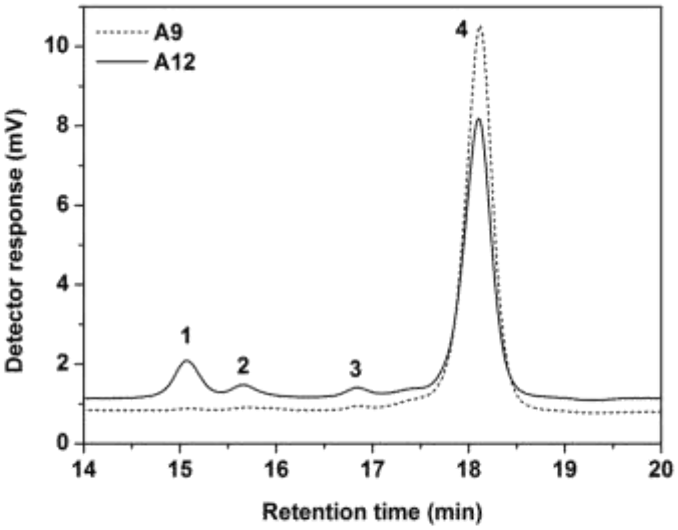

Figure 5. Gel permeation chromatography of the reaction products that were obtained at the center point (A12) and at the best reaction condition (A9), where peaks 1 to 4 correspond to triacylglycerides, diacylglycerides, monoacylglycerides, and fatty acid methyl esters, respectively.

The conversion data shown in Table 2 were submitted to a multiple linear regression and a mathematical model was developed to correlate the experimental with the theoretical data. A quadratic model was built and the coefficients of this model are given in Table 3, where the importance of the catalyst concentration is clearly seen from the high value of the Cat^2 term (-21.15 points percent).

Table 3. Mathematical parameters found by multiple linear regression.

Parameters	Effect (p.p.)*	Parameters	Effect (p.p.)*
Interaction	75.90	Interaction	75.90
Cat	16.62	Cat	16.62

T	8.25	T	8.25
MR	19.38	MR	19.38
Cat x t	-8.90	Cat x t	-8.90
Cat^2	-21.15	Cat^2	-21.15
t^2	4.75	t^2	4.75
MR^2	-1.05	MR^2	-1.05

* p.p., points percent.

The quadratic model of Table 3 was subsequently validated by Analysis of Variance (ANOVA). The higher F-value obtained for regression in relation to the corresponding tabulated F-value [F_{tab}(0.95;7.4)] indicates that the experimental data are not in the range of experimental error according to the Fischer distribution (Table 4). On the other hand, the low F-value for the residue (lack of fit and pure error) in relation to the corresponding F_{tab}(0.95;1.3) indicates that residues between the experimental and the theoretical data are mostly due to the pure error (experimental error) and not to limitations of the model.

Table 4. Analysis of Variance (ANOVA) of the soybean oil conversion to fatty acid methyl esters using [CTA$^+$]MCM-41 as the solid catalyst.

SOURCE	SS[1]	DF[2]	MS[3]	F[4]	Ftab
R^2 = 0.9276; % Var = 92.78%					
Regression	5920.00	7	845.72	7.32	6.09
Residual	462.29	4	115.57		
Lack of fit	1.36	1	1.36	0.0089	10.13
Pure error	460.93	3	153.64		
Total	6382.30	11			

[1] SS = sum of squares
[2] DF = degrees of freedom
[3] MS = mean square
[4] F = variance

After the statistical validation of the model, response surfaces were generated as shown in Figure 6. In general, the proximity of experimental data (white bullets) with the response surface reveals the good fit between the theoretical and the experimental data. The highest levels for all of the three process variables (molar ratio, catalyst concentration and reaction time) led to highest conversions. For variations in the catalyst concentration, the response surfaces showed a parabolic profile (Figures 6A and 6B), indicating that this variable has a quadratic behavior within the sampling space analyzed in this study. By contrast, both the molar ratio and the reaction time showed a linear correlation with the response function (see Figures 6B and 6C).

The trends in molar ratio, catalyst concentration and reaction time that were observed in the response surfaces were also evaluated within a 95% confidence and the corresponding Pareto chart was generated to reveal the individual and synergistic effects of the process variables (Figure 7).

The molar ratio had the most evident positive effect on the reaction conversion (4.42 p.p.) as observed in experiments A4 and A9. Another positive effect on the reaction conversion was the catalyst concentration (3.79 p.p.) but this effect was much lower than that of the molar ratio. No interaction effects between process variables were statistically relevant, indicating that there is no synergy between the variables. In addition, the quadratic effect of the catalyst concentration (3.05 p.p.) confirmed the curvatures that were observed in Figures 6A and 6B.

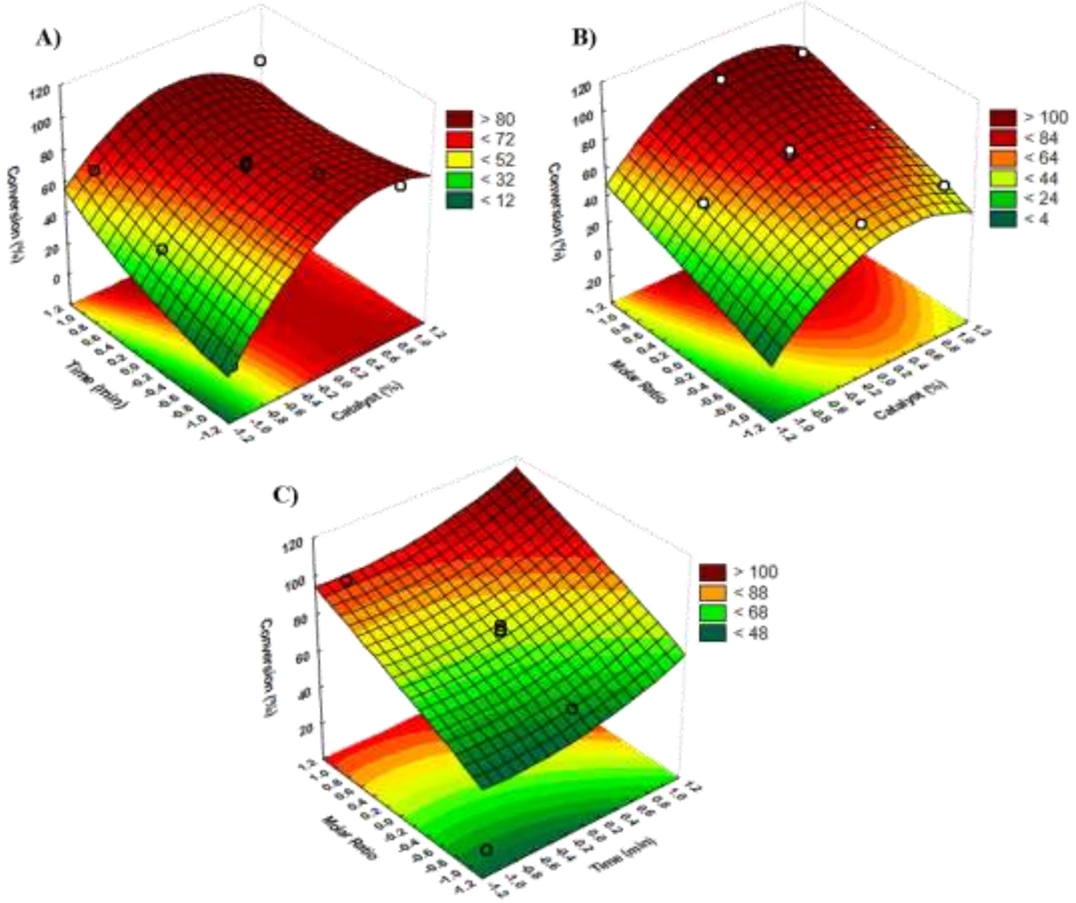

Figure 6. Response surfaces describing the soybean oil conversion to fatty acid methyl esters using [CTA$^+$]MCM-41 as the solid catalyst (axes X and Y in orthogonal range).

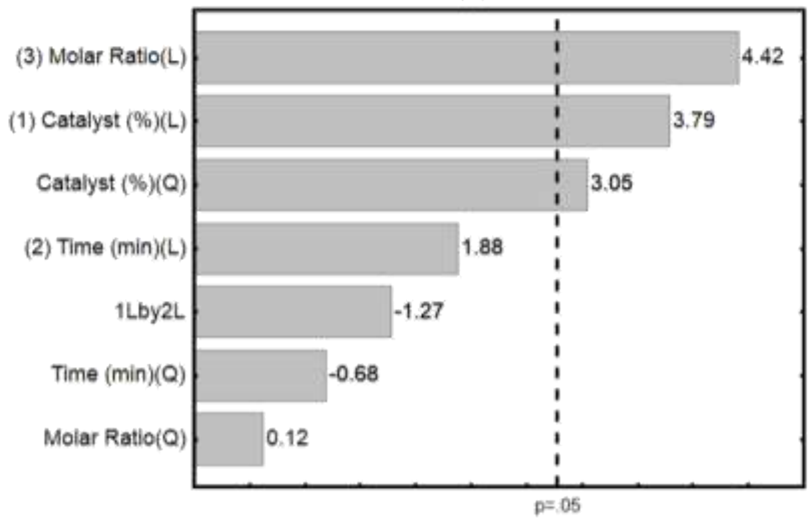

Figure 7. Pareto chart for the soybean oil conversion to fatty acid methyl esters using [CTA$^+$]MCM-41 as the solid catalyst.

The nitrogen sorption isotherms of the best [CTA$^+$]MCM-41 catalyst (sample E4) before and after calcination are given in Figure 8. The uncalcined material was classified as a type IV mesoporous solid according to the I.U.P.A.C. standards (Figure 8A) (Sing et al., 1985). By contrast, the isotherms of the calcined solids show an increase in the surface area up to 1249.0 $m^2\ g^{-1}$ due to the removal of the surfactant that was occluded in the mesopores. Such observation was in good agreement with the data available in the literature about this type of solid material (Fabiano et al., 2010; Grün et al., 1999; Kresge and Roth, 2013).

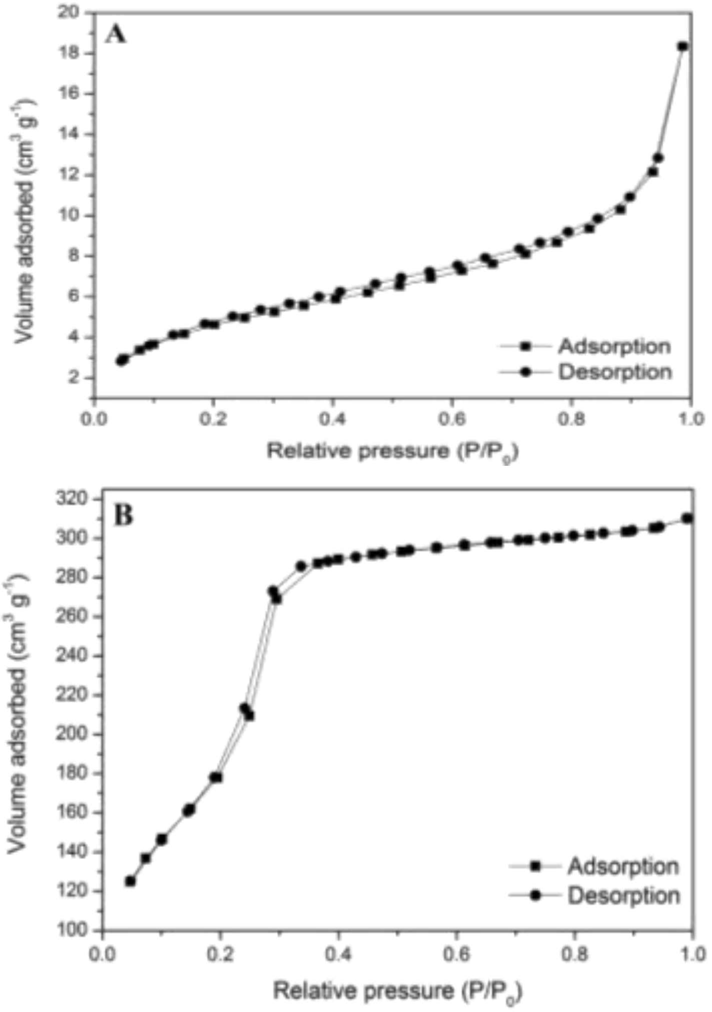

Figure 8. Nitrogen sorption isotherms of the best [CTA$^+$]MCM-41 catalyst (A) before and (B) after calcination.

The catalyst stability was evaluated by tests of reuse. The solid used in central point was recovered and applied in two cycles in the same reactional conditions. In these cases, the ester content was lower than 5%, indicating that the catalyst lost catalytic activity. This can be explained because the cation CTA$^+$ is leached to the reactional media, consequently promoting delocalization of the negative charge across the silica network decreasing the power of the catalyst. Another reason to explain the loss of activity is the formation of hydrogen bonds between methanol and SiO$^-$ anions, leading to deactivation of the solid catalyst.

To confirm that the catalytic activity was associated with the CTA$^+$/SiO$^-$ ionic pair, one additional reaction control was carried out in which [CTA$^+$]MCM-41 was replaced by the corresponding amount of untreated CTABr. The reaction conditions were the same as those described in section 2.4 and the analysis was carried out by GPC. Only 2% of esters was found after a complete reaction course, indicating that the surfactant alone had no catalytic activity in the methanolysis of soybean oil.

CONCLUSION

The [CTA$^+$]MCM-41 solids that were synthesized in the presence of a higher amount of surfactant and co-solvent (sample E4 in Table 1) displayed the best catalytic performance in the methanolysis of soybean oil and this was associated with the presence of more active sites in its chemical structure. On the other hand, the lower structural organization of this catalyst, as observed by XRD analysis, does not seem to have any influence on its catalytic activity. The oil:methanol molar ratio and the catalyst concentration were the variables that most affected the synthesis of fatty acid methyl esters. All of the synthesized catalysts were active in transesterification using mild conditions and relatively short reaction times. The formation of the (CTA$^+$)(≡SiO$^-$) ionic pair was associated with the catalytic activity since the calcined catalyst had a very poor performance in the conversion soybean oil into fatty acid methyl esters.

ACKNOWLEDGMENTS

The authors are grateful to CNPq and CAPES (Brazil) for the financial support to carry out this study in the form of research grants (CNPq Grants # 558836/2010-0 and 306920/2013-1) and scholarships for our graduate students (V.K. and M.H.L.S.), respectively.

REFERENCES

1. Demirbas, A. 2009. Progress and recent trends in biodiesel fuels. Energy Conversion and Management. 50:14-34.
2. Ren, J., Tan, S., Yang, L., Goodsite, M.E., Pang, C., Dong, L. 2015. Optimization of emergy sustainability index for biodiesel supply network design. Energy Conversion and Management. 92:312-321.
3. Shahir, V.K., Jawahar, C.P., Suresh, P.R. 2015. Comparative study of diesel and biodiesel on CI engine with emphasis to emissions - A review. Renewable Sustainable Energy Reviews. 45:686-697.
4. Silva, F.R., Silveira, M.H.L., Cordeiro, C.S., Nakagaki, S., Wypych, F., Ramos, L.P. 2013. Esterification of fatty acids using a bismuth-containing solid acid catalyst. Energy Fuels. 27:2218-2225.
5. Choedkiatsakul, I., Ngaosuwan, K., Assabumrungrat, S., Mantegna, S., Cravotto, G. 2015. Biodiesel production in a novel continuous flow microwave reactor. Renewable Energy. 83:25-29.
6. Ramos, L.P. and Wilhelm, H.M. 2005. Current status of biodiesel development in Brazil. Applied Biochemistry and Biotechnology. 121-124:807-819.
7. Grün, M,. Unger, K.K., Matsumoto, A., Tsutsumi, K. 1999. Novel pathways for the preparation of mesoporous MCM-41 materials: control of porosity and morphology. Microporous and Mesoporous Materials. 27:207-216.
8. Luna, F.J. and Schuchardt, U. 2001. Modificação de zeólitas para uso em catálise. Química Nova. 24:885-892.
9. Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquérol, J., Siemieniewska, T. 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure and Applied Chemistry. 57:603-619.
10. Ranucci, C.R., Colpini, L.M.S., Monteiro, M.R., Kothe, V., Gasparrini, L.J., Alves, H.J. 2015. Preparation, characterization and stability of KF/Si-MCM-41 basic catalysts for application in soybean oil transesterification with methanol. Journal of the Environmental Chemical Engineering. 3:703-707.
11. Fabiano, D.P., Hamad, B., Cardoso, D., Essayem, N. 2010. On the understanding of the remarkable activity of template-containing mesoporous molecular sieves in the transesterification of rapeseed oil with ethanol. Journal of Catalysis. 276:190-196.
12. Cheng, C-F., Park, D.H., Klinowski, J. 1997. Optimal parameters for the synthesis of the mesoporous molecular sieve [Si]-MCM-41. Journal of the Chemical Society, Faraday Transactions. 93:193-197.
13. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartulli, J.C., Beck, J.S. 1992. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. Nature. 359:710-712.
14. Martins, L. and Cardoso, D. 2007. Influence of surfactant chain length on basic catalytic properties of Si-MCM-41. Microporous and Mesoporous Materials. 106:8-16.
15. Kubota, Y., Nishizaki, Y., Ikeya, H., Saeki, M., Hida, T., Kawazu, S., Yoshida, M., Fujii, H., Sugi, Y. 2004. Organic-silicate hybrid catalysts based on various defined structures for Knoevenagel condensation. Microporous and Mesoporous Materials. 70:135-149.
16. Kubota, Y., Ikeya, H., Sugi, Y., Yamada, T., Tatsumi, T. 2006. Organic–inorganic hybrid catalysts based on ordered porous structures for Michael reaction. Journal of Molecular Catalysis A: Chemical. 249:181-190.
17. Kresge, C.T. and Roth, W.J. 2013. The discovery of mesoporous molecular sieves from the twenty year perspective. Chemical Society Reviews. 42:3663-3670.

Author' biography with Photo

LPR is Full Professor in Analytical Organic Chemistry at the Federal University of Paraná (UFPR – Curitiba, PR, Brazil). He graduated in Chemistry (1982) at the Catholic University of Paraná in 1982, obtained his Master's in Biochemistry from UFPR in 1988 and his Ph.D. in Applied Biology from the University of Ottawa in 1992. His research activities involve wood and carbohydrate chemistry, second and third generation biofuels, biomass fractionation using advanced pretreatment technologies, heterogeneous catalysis and several other topics within the main concept of sustainable biorefineries. Currently, he is one of the Associate Editors of the ACS journal Energy & Fuels (since 2012), participates in the Editorial Advisory Board of the Bioethanol Journal (edited by De Gruyter) and BioResources (Raleigh, USA) and has acted as ad-hoc consultant for several companies, leading international science journals and both national and international funding agencies.