

Catalytic Esterification of Oleic Acid over $\text{SO}_4^{2-}/\text{MCM-41}$ Nanostructured Materials

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ABSTRACT

This paper deals a study concerning the synthesis and catalytic application of a series of $\text{SO}_4^{2-}/\text{MCM-41}$ catalysts with different $\text{SO}_4^{2-}/\text{Si}$ ratios, in the catalytic esterification of oleic acid, aiming biofuels production. The catalysts were characterized by XRD and FT-IR. The catalytic tests were carried out in a batch reactor and the obtained results showed good catalytic activity with high degrees of conversions of oleic acid.

Keywords: MCM-41, Sulphate, Esterification, Oleic Acid

1. Introduction

The esterification is a reaction that occurs between the carboxylic acids of vegetable oils with methanol or ethanol with the production of esters and water [1,2] is a widely used route for the production of biofuel. Esterification reactions are classic examples of reversible reactions and typically are catalyzed by acids. Heterogeneous catalysts such as mesoporous M41S (Classical types Mobil Mesoporous materials) with acidic properties, have been studied in the literature and used successfully in reactions involving molecules of high molecular weight [3,4]. The silica based MCM-41 (Mobil Composite of Matter) is the main mesoporous material of the M41S family, discovered by researchers in Mobil Oil Corporation [5]. The formation of the MCM-41 phase occurs according to the liquid crystal template (LCT) mechanism, in which SiO_4 tetrahedra react with the surfactant template under hydrothermal conditions [5,6]. A typical preparation of the MCM-41 hexagonal array needs basically a solvent, a template (surfactant molecule) and a silica source. These materials present larger pores compared to other catalysts and is appropriate with the structure of the fatty acid, which need a larger area of contact.

The number of acid sites on the surface of the catalyst can be modified in large quantities by ion exchange or by treatment with acids. The MCM-41 has typically low

surface acidity. This acidity is important to catalyze the reactions of esterification. Thus, it is an important route to the esterification reactions to acidify the surface of the material. Some papers are found in the literature concerning the surface modification of mesoporous materials with acid treatment [3]. In this work, the MCM-41 was impregnated with different concentrations of sulphate in order to obtain acid catalysts. These catalysts can be applied in the acid organic reactions as esterification.

2. Experimental

The MCM-41 was synthesized starting from silica gel (VETEC), sodium silicate (VETEC), cethyltrimethylammonium bromide (CTMABr, vetec) and distilled water. The pH level was performed by Micronal pHmeter and after adjusted in a range of 9.5 - 10 using a 30% acetic acid solution. The chemicals were mixed in order to obtain a gel with the following molar composition: $4.58\text{SiO}_2 : 0.437\text{Na}_2\text{O} : 1\text{CTMABr} : 200\text{H}_2\text{O}$. The procedure used to obtain ca. 1.6 g of calcined MCM-41 was: 1) 0.911 g of silica, 0.705 g of sodium silicate and 8.34 g of water were placed into a 100 mL teflon beaker and stirred at 60°C for 2 h in order to obtain a clear solution; 2) a solution prepared from 1.743 g of cethyltrimethylammonium bromide and 8.34 g of distilled water was added to the above mentioned mixture and aged for 30 minutes at room temperature. The hydrogel was placed

into 70 mL teflon-lined autoclave and heated at 100°C for three days. Their pH was measured each day and adjusted to 9.5 - 10. The as-synthesized material was calcined at 450°C for 2 h in static atmosphere. The temperature was increased from room temperature to 450°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ [5]. XRD measurements were carried out, using CuK_α radiation in 2θ angle range 1 to 10° with step of 0.02° , on a Shimadzu XRD 6000 x-ray equipment. FT-IR analysis were carried out in a Perkin Elmer Equipment using tablets of ca 2% of each sample in the range of $400 - 4000\text{ cm}^{-1}$.

In order to obtain sulphated samples of MCM-41, ca. 0.3 g of pure MCM-41 was impregnated by insipient wetness with slow addition of 2 mL of aqueous solutions of sulfuric acid with different concentrations of 0.2, 0.4, 0.6 and 0.8 M. After this, the samples were dried at 110°C for 1 h.

The esterification reactions were conducted on a batch reactor of 250 mL, starting from 50 mL of oleic acid, 30 mL of absolute ethanol and 0.25 g of catalyst (previously dried in an oven at 110°C for 1 hour). The reactions were carried out varying the temperature at 30°C , 45°C and 60°C by vigorous stirring, until stabilization of the conversion. Aliquots of 1 mL were collected at intervals of 5 minutes for determination of the conversion degree via titration with NaOH standard solution.

3. Results and Discussion

XRD analysis of the MCM-41 and sulphated MCM-41, as presented in **Figure 1**, revealed characteristic diffraction peaks for this material, namely (100), (110), (200) and (210) [From the main interplanar distance (d_{100}), it was possible to obtain the hexagonal structure parameter a_o . The value of a_o represents the sum of the pore diameter (D_p) and the silica wall-thickness (W_s) [5,6]. The sulphated samples presented lower intensity than pure MCM-41, but with preservation of the hexagonal structure.

FT-IR analyses were useful to provide information about the efficiency of the calcination process where occurs the elimination of the CTMA+ groups from MCM-41 materials [7]. **Figure 2** shows the FT-IR analysis of the MCM-41 materials before and after the calcinations. Can to be observed that the CTMA+ was fully removed in the samples obtained. This can be verified by the absence of the functional groups of the CTMA+ species after a heat treatment under dynamic flow conditions. **Figure 3** shows the infrared spectra of the sulphated samples of MCM-41. The **Table 1** shows the FT-IR data and its respective attributions.

Figures 4, 5 and 6 show the curves of conversion degree of oleic acid as function of reaction time with several

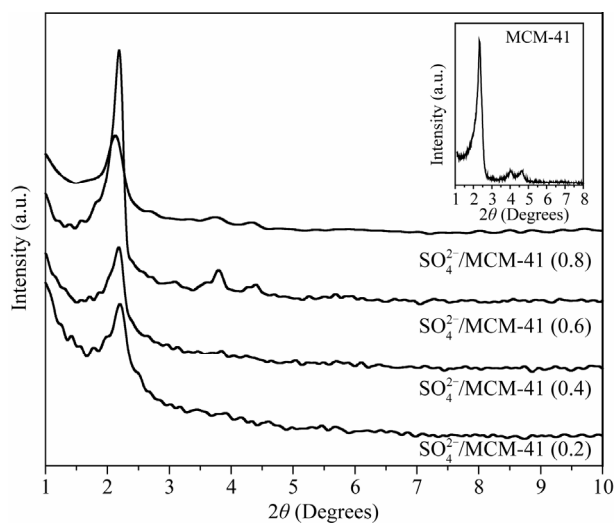


Figure 1. XRD of the MCM-41 samples.

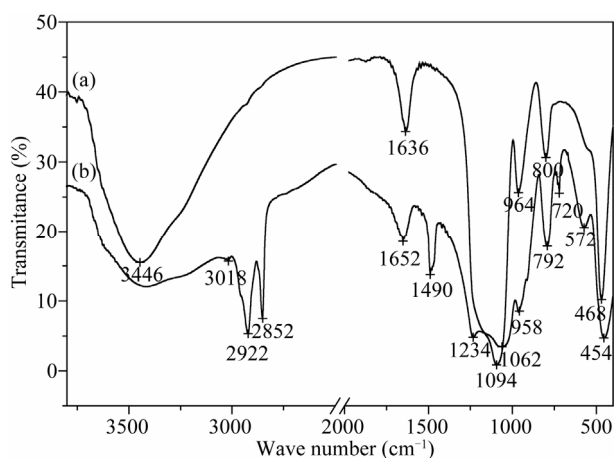


Figure 2. FT-IR of MCM-41 sample calcined and uncalcined.

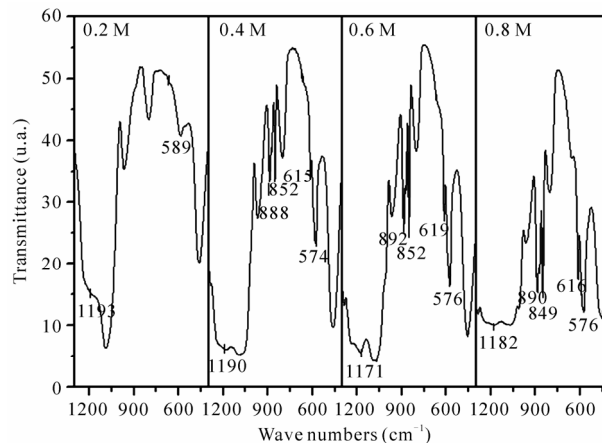


Figure 3. FT-IR of MCM-41 samples treated with solutions of different concentrations of sulphuric acid, where (a) calcined and (b) uncalcined.

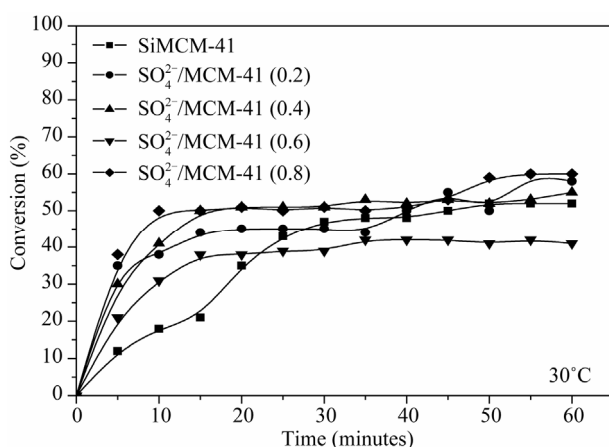


Figure 4. Conversion as functions of the time of the oleic acid esterification over MCM-41 samples sulphated with different sulphuric acid concentrations at 30°C.

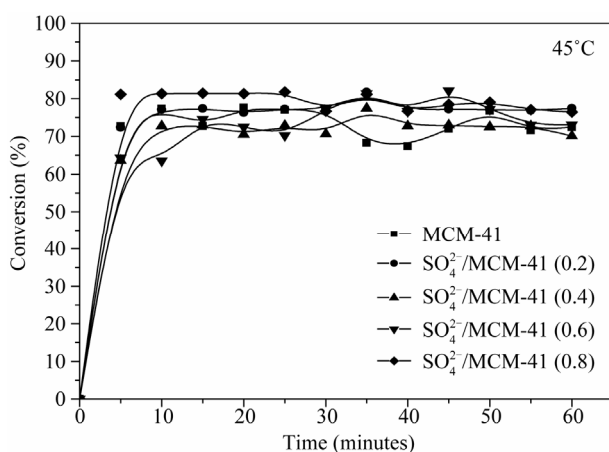


Figure 5. Conversion as functions of the time of the oleic acid esterification over MCM-41 samples sulphated with different sulphuric acid concentrations at 45°C.

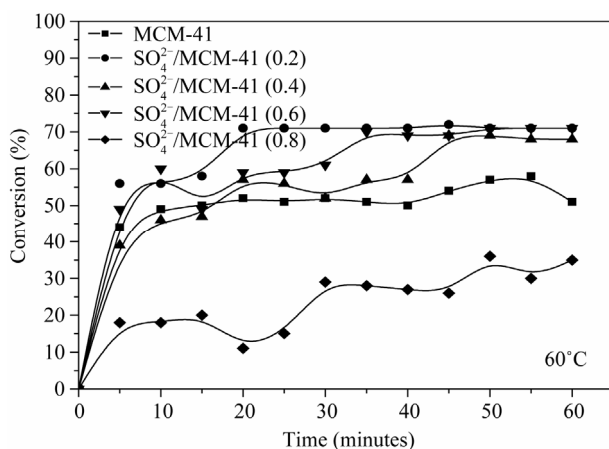


Figure 6. Conversion as functions of the time of the oleic acid esterification over MCM-41 samples sulphated with different sulphuric acid concentrations at 60°C.

Table 1. Vibrational bands and its respective attributions observed in the MCM-41 samples.

Vibration bands (cm^{-1})	Attribution
3750 - 3250	Hydroxyl groups on mesoporous structure
3000 - 2850	Stretching of C-H bonds of CH_2 and CH_3 groups on CTMA+ species
1700 - 1550	Water physically adsorbed
1466 - 1460	Asymmetric deformation of CH_3 -R bond
1475 - 1470	Deformation of CH_2 bond
1490 - 1480	Asymmetric deformation of head group methyl (CH_3 -N+)
1260 - 1240	Asymmetric Si-O stretching
965 - 955	Asymmetric CH_3 -N+ stretching
850 - 800	Symmetric T-O (T = Si, Al) stretching

sulphate concentrations at temperatures of 30°C, 45°C and 60°C. As observed in the **Figure 4** the conversion of oleic acid with the sulphated catalyst occurred during the first minutes of reaction, with a higher percentage of conversion. Were observed that the curves of conversion of the oleic acid showed similar behaviors for all concentrations and reaching 60% of conversion in the final minutes of reaction. **Figure 5** shows the curve of conversion versus time of oleic acid at 45°C. Can be observed a high conversion of oleic acid, around 75% with catalyst without sulphate. It was observed that the sulphated catalyst with solution 0.8 M presented larger conversion of the oleic acid along the reaction, with approximately 80% of acid converted. In the **Figure 6** was observed higher conversion of oleic acid along the reaction, with conversion of the oleic acid around 70%, maintaining stable conversion after 20 minutes of reaction. The catalyst with sulphate concentration of 0.8 M presents to smallest conversion of the oleic acid along the time, with approximately 25% conversion, at 60°C. The best results of conversion occurred at a temperature of 45°C, with the catalyst in sulphate concentration of 0.8 M, with conversion of oleic acid along the reaction in approximately 80%.

4. Conclusions

Through XRD analysis it was observed that the MCM-41 materials were obtained with a high degree of hexagonal ordering. XRD analysis showed that acid treatment did not provokes destruction on the hexagonal mesoporous structure. Based on the FT-IR analysis it was possible to identify the vibrational frequencies and its attributions of to the organic and inorganic functional groups present in

the catalysts. The esterification reactions were very efficient taking in consideration that were happened at ambient pressure and low temperatures, reaching relatively high conversions.

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