STUDY OF THE APPLICATION OF Mo/SBA-15 AND Ni/SBA-15 CATALYSTS, PREPARED BY MICROWAVE HEATING, IN THE SYNTHESIS OF BIODIESEL

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ABSTRACT

This work aimed to produce 5% (w/w) molybdenum and nickel catalysts, supported in SBA-15 molecular sieve, and evaluate their application in the synthesis of biodiesel. The catalysts were prepared by physical dispersion and were characterized by X-ray diffraction, X-ray energy dispersion spectrophotometry, and N₂ adsorption-desorption. Transesterification reactions were carried out to evaluate the activity of the catalyst. The synthesis was effected by using a system comprised of a polytetrafluoroethylene batch reactor jacketed with a piece of stainless steel working at 600 rpm. The reactions were conducted at 473K for 4 hours, using a soybean oil/ethanol molar ratio of 1/12, and 5% of catalyst based on the mass of oil used. After characterization, the catalysts were subjected to catalytic tests to check the reaction conversion parameters obtained by gas chromatography. The kinematic viscosity and density of the biodiesel samples were then determined. The chromatography results were not satisfactory for the test with SBA-15 (pure silica). The conversion to esters obtained was 5%, which can be due to the formation of silanol groups (Si-OH) on the silica surface, which are considered Brönsted acidic sites. However, in terms of strength, the acidity of silanol is usually either low or moderate. Mo/SBA15 and Ni/SBA-15 catalysts yielded conversions to biodiesel as high as 96.57% and 84.67%, respectively.

KEYWORDS

SBA-15; molybdenum; nickel; biodiesel synthesis

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1. INTRODUCTION

Most of all energy consumed worldwide comes from fossil sources. However, these sources are limited. Thus, the search for alternative, renewable sources is strategically important (Cruz et al., 2011). Biodiesel consists of alkyl esters derived from either the transesterification of triglycerides or the esterification of free fatty acids with low molecular weight alcohols (Melero et al., 2012; Morales et al., 2011).

Potential feedstocks for the preparation of biodiesel are vegetable oils, such as soybean and sunflower oils. The use of algae or used cooking oils is particularly interesting for the preparation of second-generation biofuels considering that these products use a more sustainable production process. Therefore, the use of vegetable oils as biodiesel has become more attractive due to environmental benefits, and the fact that these oils are made from renewable resources. In the last decade, numerous heterogeneous solid acid catalysts have been developed for this reaction (Cruz et al., 2011; Melero et al., 2012; Morales et al., 2011).

After the discovery of the Mobil-41 Synthesis (M41S) family of mesoporous materials in 1992, several new types of mesoporous solids (MCM-48, SBA-15) have been prepared to provide new catalysts, such as zeolites. Moreover, the low acidity of mesoporous silica can be enhanced by impregnating metals such as molybdenum and nickel which create Lewis acid sites. Recently, the synthesis of a new periodic mesoporous silica, SBA-15, has been reported under acidic medium using triblock copolymers as structure-directing agents (Rodrigues et al., 2012). The SBA-15 has a high surface area (600–1000 m²/g) and is formed by a hexagonal array of uniform tubular channels with pore diameters ranging from 5 to 30 nm. These tubes are significantly larger than those of MCM-41. The SBA-15 also has thicker pore walls and a better hydrothermal stability than MCM-41 (Rodrigues et al., 2012; Xiong et al., 2010); a feature that can be relevant for biodiesel production.

The incorporation of metals such as molybdenum and nickel to the siliceous framework creates mesoporous solids with a great potential in acid-catalyzed reactions for large molecules (Xiong et al., 2008).

Jacobson et al. (2008) conducted detailed studies with molybdenum catalysts supported on silica by methyl route esterification from frying oil using a metal content of 5 % in weight. According to these authors, the reaction was held at 473 K, with 3 % catalyst, and a water/oil molar ratio of 1:6, for 10 hours. The results showed conversions as high as 79 %.

Serio et al. (2008) reported that Lewis acid catalysts are more active in transesterification reactions, while Brönsted acid catalysts are ideal in esterification reactions. Thus, the presence of acidic sites can be related to the efficient performance of the catalysts in the transesterification reaction. This may also be associated with the textural properties of the mesoporous molecular sieve, with uniform hexagonal channels ranging from 3 to 30 nm, very narrow pore size distribution, and high surface area (600–1000 m²/g).

The objective of this work is to describe the preparation of catalysts with 5% metal, such as molybdenum and nickel, supported in a SBA-15. It evaluates the influence of the type of impregnated metal supported on a mesoporous structure with favorable properties for catalysis, and evaluates their application in the transesterification reaction for the production of biodiesel using soybean frying oil.

2. EXPERIMENTAL

2.1 Preparation of SBA-15

SBA-15 was synthesized according to the procedure reported in the literature (Zhao et al., 1998). First, 2 g of Pluronic P123 (template, Aldrich) were dissolved in 15g of deionized water and 60g of 2 mol/L HCl solution while stirring. Then, 4.25g of tetraethyl orthosilicate (TEOS, 98 wt%, Sigma–Aldrich) were added to the solution while stirring. This mixture was stirred continuously for 24h, and then transferred to a microwave digestion system (model MS-3, Microwave Digestion System for COD Determination). The SBA-15 microwave synthesis was performed for 1h at 373K. The product was centrifuged at 1100 rpm, washed out with deionized water several times and dried at 373K. The material was calcined in static air at 823K for 2h to remove the polymer template and to obtain

the white powder SBA-15. The sample was synthesized with the following molar composition: 1.0 TEOS : 0.017 P123 : 5.7 HCl : 193 H₂O.

2.2 Preparation of catalysts

The deposition of metal with 5% (w/w) on the SBA-15 support was carried out by physical dispersion. The mixing proceeded for 30 min using mortar and pestle. Next, the material was calcined in static air at 550°C for 2 hours (Chen et al., 2011). The Mo/SBA-15 catalyst was impregnated with molybdenum oxide generated from ammonium molybdate [(NH₄)₆Mo₇O₂₄ · 4 H₂O] (Merck) as the source of molybdenum. For the preparation of the Ni/SBA-15 catalyst, nickel nitrate hexahydrate [Ni(NO₃)₂ · 6 H₂O] (Merck) was used.

2.3 Synthesis of biodiesel

The transesterification of vegetable oil with ethanol (98% purity and 2% water content) was performed in a system comprised of a batch reactor (autoclave stainless steel) with 600 rpm shaking. The reaction conditions were: temperature of 200°C and 4 hours of reaction, using a molar ratio oil/alcohol of 1/12 with 5% of catalyst related to the mass of oil used.

2.3.1 Characterization

X-ray energy dispersion spectrophotometer (EDX): An elemental analysis was determined through energy dispersive X-Ray spectrophotometry in a Shimadzu EDX-700 instrument.

X-Ray Diffraction (XRD): Powder diffraction patterns were measured on a Shimadzu XRD 6000. The operational conditions were: Copper K α radiation at 40 KV/30 mA, goniometer velocity of 2°/min with a step of 0.02° over the 2 θ -range from 2° to 80°. The average diameter of the sample crystallites was determined by the Scherrer equation.

Nitrogen Adsorption (BET method): The textural characteristics of the analyzed samples were investigated by isothermal gas adsorption/desorption of N₂ at 77K using a Micrometrics ASAP 2020 equipment. The adsorption and desorption N₂ isotherms were obtained in the range of relative pressure (P/P₀) between 0.02 and 1.0. The values of the average pore diameter and surface area (S_{BET}) were obtained by the proposed BET method.

Viscosity: The viscosity kinematic of the samples was determined using a Cannon Fenske viscometer. This equipment uses a bath at 313K with a capillary tube numbered 300 cSt (centistokes). The determination of the viscosity is a result of the total flow of liquid in the capillary tube, multiplied by the time spent for such disposal, according to equation 1:

$$V = k t \quad (1)$$

Where, $k = 0.2407 \text{ mm}^2/\text{s}^2$ is the constant inherent to the viscometer used and t (s) is the time of flow of liquid through the capillary.

Density: The density of the samples was determined at 20°C with a digital Anton Paar densitometer, model 30px. A 2-mL aliquot of biodiesel was added to the densimeter and the result was recorded.

Ester Content: The analysis of the methyl esters were determined by gas chromatography, using a Varian 450c gas chromatograph with flame ionization detector, Varian Ultimetal "Select Biodiesel Glycerides + RG" capillary column as stationary phase (0.32mm x 15m x 0.45 μ m). Sample preparation consisted of diluting 50mg of the product in 50mL of standard UV/ HPLC n-hexane (Vetec PA/ACS) and subsequently injecting 1 μ L of solution. The standard used was the internal standard provided by Varian, which was the same standard recommended for this analysis by the Brazilian Petroleum Agency and the European Standard EN 14214.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of sample (SBA-15 synthesized) is shown in Figure 1. It can be seen that the structure of the ordered hexagonal mesoporous molecular sieve SBA-15 is consistent with that reported on the literature (Chen et al., 2011; Ghampson et al., 2010; Khodakov et al., 2003). The SBA-15 showed diffraction lines due to the SiO₂ plane (1 0 0), indicating the P6-mm hexagonal symmetry structure. By dissolving the Pluronic P123 polymer template in water and hydrochloric acid under stirring and mild heating (35°C), interactions between copolymer and solvent occur. Upon addition of the silica source, other interactions between silica and the solvent

Figure 1. Diffractogram of synthesized SBA-15.

(a)

(b)

Figure 2. X-ray diffraction patterns of the catalysts after calcination and impregnation process: (a) Mo/SBA-15 and (b) Ni/SBA-15.

are formed causing silica/copolymer interactions. The obtained gel was subjected to aging for 24 hours under stirring, inducing the formation of siloxane phases by condensation of copolymer micelles on the silica, depending on solution conditions (temperature, pH). The gel was then subjected to a hydrothermal treatment to increase the silica wall thickness, forming the SBA-15 molecular sieve.

In the diffractogram shown in Figure 2, it is possible to visualize the main diffraction peak characteristic of SBA-15, indicating that no

significant changes occurred in the structure of the mesoporous sieve after metal impregnation process and calcination.

The values of parameters a_0 and mesoporous 2θ angles, with their respective interplanar spacings in the (hkl) plane for the SBA-15 samples, are shown in Table 1.

A contraction is observed after calcination of the support (SBA-15 before impregnating metal) (Figure 2), which is related to the reorganization of Si-O- ions and condensation of silanol groups ($\equiv\text{Si-OH}$) due to removal of the Pluronic P123 directing

Table 1. Values of the 2θ angles, their respective interplanar distances and mesoporous parameter a_0 for the (1 0 0) plane for SBA-15 and catalyst samples.

Sample	2θ	$d_{(hkl)} / \text{\AA}$	A_0 / nm
SBA-15	0.84	104.93	12.10
Mo/SBA-15	0.86	101.80	11.70
Ni/SBA-15	0.85	102.80	11.90

Table 2. Chemical composition of the SBA-15 and catalysts.

Sample	SiO ₂ / %	Mo / %	Ni / %	Other / %
SBA-15	99.3	-	-	0.7
Mo/SBA-15	91.4	4.9	-	1.0
Ni/SBA-15	92.3	-	5.0	0.7

Table 3. Textural properties of the SBA-15 and catalysts.

Samples	$S_{\text{BET}} / (\text{m}^2/\text{g})$	$VP_{\text{total}} / (\text{cm}^3/\text{g})$	e / nm
SBA-15	763	0.98	8
Mo/SBA-15	484	0.78	-
Ni/SBA-15	471	0.75	-

agent. The Pluronic P123 polymer template has the function of maintaining the material's structure. After it is extracted, an imbalance in the surface tension of the inner wall of the pore occurs, which tends to cause the system to physically contract. With the removal of Pluronic P123, the Si-O-groups are reorganized, thereby forming new siloxane linkages, and the Si-OH groups condense in order to restore balance. Thus, there is an increase in the ordering of the porous system and, consequently, an increase in the intensity of the peaks, and a contraction of the hexagonal lattice parameter, shifting the angle of the peaks to higher values (Silva, 2008; Umbarkar et al., 2006).

According to Selvaraj and Lee (2005), the increase in d_{100} and a_0 observed can be related to the fact that the length of Mo-O- and Ni-O- links with the support surface is greater than that of Si-O-. This behavior depends on how the catalyst is prepared as well as on the coordination number of the metal with the OH groups, and the length and angle between the metal ions binding to a silica surface. Table 2 presents the results of chemical analysis of the SBA-15 and catalysts. From the results of Table 2, one can see that the percentage of nickel and molybdenum is similar to the pre-established value (5 wt.%).

The textural properties of the calcined SBA-15 support and the catalysts obtained by N₂ adsorption are given in Table 3.

The combination of techniques (X-ray diffraction and BET adsorption) allowed calculating the thickness of the wall (e) (Beck et al., 1992). The specific area (S_{BET}) and total specific pore volume (VP_{total}) of the calcined SBA-15 molecular sieve, given in Table 3, are typical of SBA-15 structures synthesized under similar conditions (Zhao et al., 1998).

Analyzing the textural properties of the catalysts, it was found that the area and the total volume decreased significantly after impregnation and calcination of the catalyst. This may have been caused by the pore blockage of the SBA-15 molecular sieve by agglomeration of oxides (Ghampson et al., 2010; Prieto et al., 2009).

Figures 3 and 4 show the N₂ adsorption/desorption isotherms at 77K of the calcined SBA-15 and of the catalysts.

The isotherms for the calcined SBA-15 sample were of type IV and exhibited a well-defined H1 hysteresis loop according to the IUPAC classification relative to the mesoporous materials (Morales et al., 2011). The isotherms for the

Figure 3. N_2 adsorption/desorption isotherms at 77K for the calcined SBA-15.

Figure 4. Adsorption-desorption isotherms of N_2 , at 77K, for catalyst (a) Mo-SBA15 and (b) Ni-SBA15.

catalysts Mo/SBA-15 and Ni/SBA-15 also showed similar profiles, typically of type IV. The desorption curve for this catalyst also showed an H1 hysteresis loop for partial pressures (P/P_0) between 0.6 and 0.8, which can be attributed to capillary condensation and evaporation in the internal mesoporous structure of the tubes (Jacobson et al., 2008; Morales et al., 2011).

After the catalytic tests, the biodiesel was subjected to characterization parameters, kinematic viscosity and density, to check the conversion reaction. These parameters were and also important to determine the ester content by gas chromatography. The results are shown in

Table 4. ASTM D6751 standards specify limits for the density of diesel and biodiesel samples. The tests performed in this work showed that the density values are within the limit stipulated for diesel used as reference.

There is a high concentration of saturated fatty acids in the samples, so the viscosity found for biodiesel with Mo/SBA-15 and Co/SBA-15 catalysts used in this study were 5.09 and 5.35 mm²/s, respectively. These values are within the limits established by the ASTM D6751 viscosity for biodiesel. One factor that may contribute to an increase in the viscosity of biodiesel is the contamination with glycerin.

Table 4. Viscosity, Density, and Conversion of esters.

Samples	Viscosity (mm ² /s)	Density (kg/L)	Conversion (%)
SBA-15	-	-	5.01
Mo/SBA-15	5.09	0.855	96.57
Ni/SBA-15	5.35	0.875	84.67

The results of chromatography were not satisfactory for the test with SBA-15 (pure silica). The conversion to esters obtained was 5%. This was due to the formation of silanol groups (Si-OH) on the silica surface, which are considered Brönsted acidic sites. The surface silica (SiO₂) hardly produces Lewis acids. However, in terms of strength, the acidity of silanol is usually low or moderate (Crépeau et al., 2006). However, deposition of metal on the surface of the silica renders acidity to it, creating an efficient alternative to increase the acidity of solid catalysts. This can be checked by chromatography in the analysis of Mo/SBA-15 and Ni/SBA-15 catalysts, which provided satisfactory results such as the percentage of total esters. The conversion and yield in esters were high. The value obtained for the conversion of total esters in biodiesel was 96.57% with the Mo/SBA-15 catalyst, which is within the limit established by the EN 14214 ester content for biodiesel. Furthermore, a yield of 84.67% in biodiesel was obtained with the Ni/SBA-15 catalyst, which is not much lower than the value established by the EN 14214 (96.5%).

4. CONCLUSIONS

Patterns of X-ray diffraction showed the characteristic peaks of the structure of SBA-15. After impregnation with molybdenum and nickel, the structure of the molecular sieve was preserved. The analysis of N₂ adsorption indicated that a mesoporous material with high surface area was obtained. The EDX analysis indicated that the levels of impregnated metals were very close to the expected value. The transesterification reaction of soybean oil with ethanol showed in this work presented an efficient conversion of 96.57% with Mo/SBA-15 catalyst and 84.67% with the Ni/SBA-15 catalyst. The chemical and physical properties evaluated in this study showed that biodiesel had characteristics similar to diesel, in accordance with the limits established by the ASTM D6751 for

biodiesel. According to the analysis performed in this study, it is possible to say that the synthesized biodiesel showed satisfactory physicochemical properties. Therefore, Ni/SBA-15 and Mo/SBA-15 catalysts may be potentially useful for application in the transesterification reaction for the production of biodiesel.

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