ECLÉTICA química
Volume 39
Artigo/Article

Evaluation of the Na/Nb_2O_5 system in the transesterification of soybean oil for biodiesel production

Carlos Eduardo Garção de Carvalho[a], *Nelson Consolin-Filho*[*,b], *Anelise Maria Regiani*[a], *Rogerio Antonio Sartori*[a], *Andréa Maria Duarte de Farias*[c], *Edilson Simões Cadaxo Sobrinho*[a], *Luiz Eduardo Pizarro Borges*[d], *Wilma de Araújo Gonzalez*[d]

[a]Center for Biological and Natural Sciences, Federal University of Acre, 69915-900 Rio Branco, AC, Brazil
[*,b]Federal Technology University of Paraná, Chemistry Coordenation, 87301-006 Campo Mourão, PR, Brazil
[c]LACAT, National Institute of Technology, 200081-310 Rio de Janeiro, RJ, Brazil
[d]Department of Chemical Engineering, Military Institute of Engineering, 22290-270 Rio de Janeiro, RJ, Brazil

*Corresponding author: consolin@utfpr.edu.br
Tel.: + 55-44-3518-1451; + 55-44-9949-4827

Abstract

Biodiesel is considered an important substitute of diesel oil. Traditionally, it is obtained by the transesterification of vegetable oils with methanol or ethanol, catalyzed by NaOH or KOH. Heterogeneous catalysts have been studied with the aim at facilitating and diminishing costs with purification stages. In the present work, the Na/Nb_2O_5 system was evaluated on the reaction of soybean oil with ethanol. It was verified, by DRX and IR, that the niobia calcined at 500ºC and impregnated with sodium underwent greater structural alterations than that treated at 300°C. These modifications allowed the generation of basic properties on niobia surface (Hammett and CO_2 adsorption /IR). This catalyst showed the highest conversion (30%) among the used materials. The method chosen for evaluating the catalysts yield was the ^1H NMR spectroscopy.

***Keywords**:* biodiesel, transesterification, heterogeneous catalysis, niobium.

Introduction

Increasing development in the area of renewable energy has led to innumerable researches aimed at the use of biodiesel as a substitute for petroleum-derived diesel fuel. This biofuel is obtained mainly through catalytic transesterification (alcoholysis) of vegetable oils or animal fats. The alcohols normally used in this reaction are methanol and ethanol, which are catalyzed by both bases and acids. Homogeneous base catalysis is widely adopted, mainly with strong bases such as NaOH and KOH, due to the high levels of conversion achieved in this process [1-8]. However, some limitations such as the difficulty in the stages of purification and their high relative cost, especially in the ethylic route, have led to research into heterogeneous catalysts [9-11]. Many of these attempts have been restricted to the methylic route, which allows for facilities such as separation and identification of the reaction products, as well as greater availability of the methanol. The search for solid base catalysts has followed many paths, such as the use of base zeolites (by ionic exchange/impregnation of alkaline cations) [12, 13]; guanidine-based compounds [14]; the use of alkaline metal oxides or carbonates [15, 16] or their immobilization on oxide supports [17-20]. Basicity or superbasicity traditionally involves the use of alkaline metals [21]. Alumina (Al_2O_3) has been chosen as a support because it possesses adequate superficial and structural characteristics that allow for the occupation of its cationic vacancies by the metal, donating electrons to the surface oxygen atoms, which enables its basicity to be increased [22]. In this context, Kim *et al*. [23] studied the Na/NaOH/γ-Al_2O_3 system in the methanolysis of soybean oil.

Mixed oxides containing niobium have been studied as catalysts and supports in several heterogeneous reactions [24, 25]. Niobium oxides have a tendency to form structural defects and to present acid properties. However, by means of heat treatment above 500ºC, surface sites become neutral due to the elimination of OH groups or the loss of water absorption capacity [26]. In this work, the generation of basicity on the surface of niobium was investigated through the addition of NaOH with the purpose of using it as a catalyst of the transesterification of refined soybean oil with ethanol.

Experimental

Preparation of the catalysts

The niobium acid ($Nb_2O_5.nH_2O$, ref. HY-340) used in this work was supplied by CBMM. The heat treatment of the samples started with a 2-hour drying stage at 120ºC. Two calcination temperatures were adopted: 300ºC and 500ºC in a muffle furnace for 10h, at a heating rate of 10ºC/min. Sodium was added to the niobium by dry impregnation using NaOH solution at a concentration suitable to obtain an Na/Nb ratio of 0.5. After impregnation, the catalysts were treated at 120ºC for 16h, followed by 350ºC for 5h, under a N_2 flow (40mL/min).

Transesterification conditions

Mixtures of refined soybean oil, absolute ethanol P.A. (VETEC) and solid catalyst were prepared in two types of systems: *1)* by reflux (78.5ºC) for two hours under magnetic agitation, and *2)* in a closed system (Parr reactor) for 4h at 120ºC and mechanical agitation at 250 rpm. The indices of acidity and saponification of the oil were first determined by the IUPAC method, which showed insignificant results. The catalyst concentrations adopted were 3% and 10% of the mass of oil.

Blank tests were performed using only the claimed supports. The molar ratio of ethanol to oil was 30:1

- ***NMR¹H***

The conversion into biodiesel was determined by NMR spectroscopy (VARIAN UNITY 300 spectrometer, 300 MHz). Aliquots of reaction products were diluted in reiterated chloroform prior to recording the spectra. The analysis of the spectra was concentrated in the region of 4.0 - 4.4 ppm, using the same approach as that used previously in transesterification reactions with methanol [27]. However, in this work, the calculations of conversion of oil into biodiesel (CBIO) were based on the integration of the peaks corresponding to the protons highlighted in Figure 1.

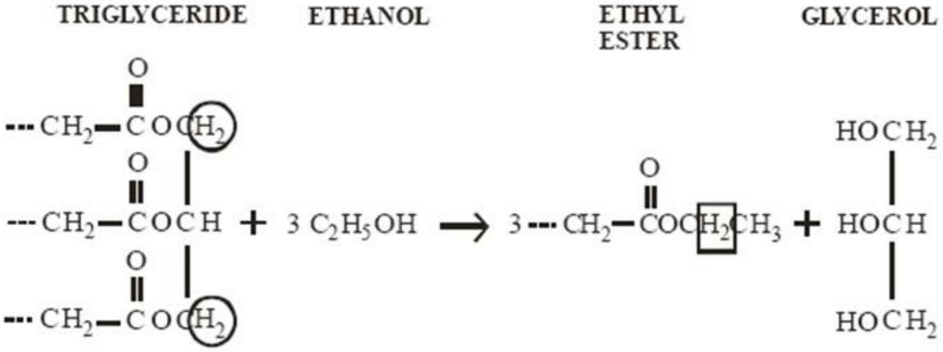


Figure 1 – Scheme of the transesterification reaction of oils with ethyl alcohol. O = glyceric protons (G), □ = ethyl protons (E).

Thus, the relationship between the G and E protons was considered (Eq. [1]).

$$C_{Bio} = \frac{\frac{4\cdot A_3}{3}}{\left(\frac{4\cdot A_3}{3}+\frac{A_1}{2}\right)}\cdot 100 \qquad \text{Eq. [1]}$$

In Eq. 1, areas A_1 and A_3 refer to the ones illustrated in Fig. 2 (a) and (c). The peaks corresponding to areas A_1 and A_3 were chosen for their good resolution and because they were not disturbed by overlapping. Figure 2 (c) highlights the relationship between areas A_2 and A_3, which follows the proportion of 1:8 that is typical for this type of NMR.

- ***Spectroscopy in the IV region***

The formation of biodiesel was confirmed qualitatively by spectroscopy in the IV region using a KBr window. Solid samples (catalysts) were also analyzed. In this case, pellets (1% KBr) were prepared. A Perkin Elmer 2000 FTIR spectrometer was used. CO_2 thermodesorption assays were monitored by spectroscopy in the IV region to evaluate the basic properties of the catalysts, using a Nicolet Magna 560 IR spectrometer. Self-supported pellets (~20 mg) were treated at 350ºC for two hours under high vacuum (10-7 Torr), and then placed in contact with air for 30 min. Adsorption was carried out at room temperature, at 10 Torr for 1 h, and desorption was performed at 25ºC and 100ºC for 1 h under high vacuum.

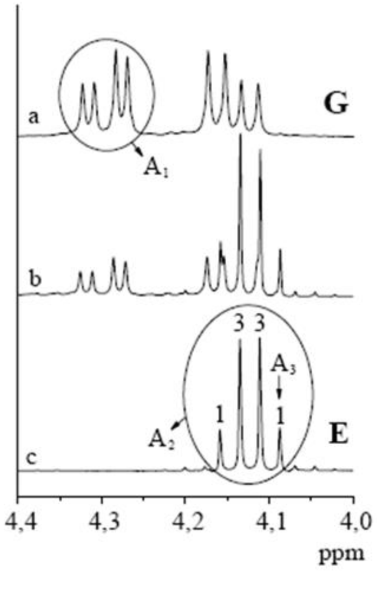


Figure 2 – NMR 1H spectra, illustrating the stages of a transesterification: (a) refined soybean oil, (b) Standard mixture of 40% biodiesel in soybean oil, (c) Standard biodiesel.

- ***Hammett basicity***

The basicity of the solids was also determined by the method of Hammett indicators [28]. Approximately 5 mL of cyclohexane P.A. (VETEC) and 3 drops of indicator were added to 0.05 g of sample. The indicators used were: phenolphthalein, thymolphthalein, alizarin, 4-nitroaniline and 4-chloro-2-nitroaniline, all at a concentration of 0.1 % m/v in cyclohexane. The systems were then mechanically shaken for 8 hours. Lastly, they were titrated with a solution of 0.05 mol/L of benzoic acid in cyclohexane, duly factored.

- ***XRD***

X-ray diffraction analyses were performed in a Rigaku Denki diffractometer (CuKα). The operating conditions were as follows: a 0.04º step and count time of 1s/step.

- ***BET***

The specific areas of the catalysts were determined by the N_2 adsorption/desorption method (BET), using a Micromeritics ASAP 2000 chemisorptions system.

Results and Discussion

Catalytic evaluation of ethanol transesterification of soybean oil to biodiesel

Fig. 3 shows spectra in the IV region of liquid samples (reaction products). For comparison, spectra if the soybean oil used as reagent and a spectrum of a standard biodiesel are shown (obtained by homogeneous reaction and NaOH as catalyst). A qualitative analysis of the spectrum of the sample of interest (Fig. 3 (b)) reveals the appearance of a band at 1037 cm^{-1}. This vibration is characteristic of stretching of the C-O bond of primary alcohol esters, which allows for the identification of the presence of ethyl ester, the main constituent of biodiesel. Similarly, for the other liquid samples obtained through several reaction conditions and with both catalysts (NaNb500 and NaNb300), it was also possible to detect the existence of biodiesel in the products.

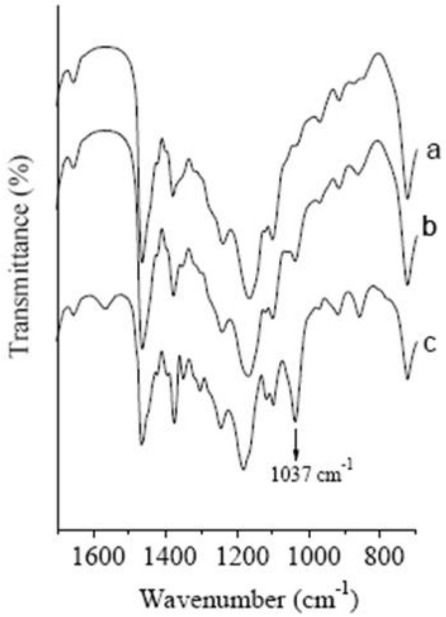
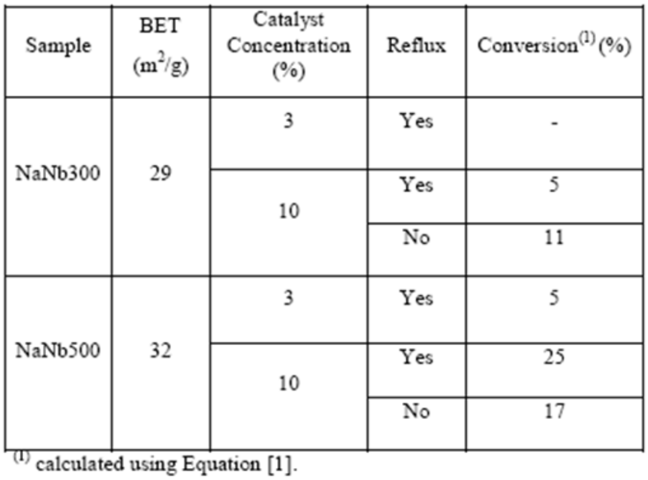


Figure 3 – Spectrum in the IV region of Biodiesel: (a) soybean oil; (b) biodiesel obtained with 10% of NaNb500 catalyzer (reflux); (c) standard biodiesel.

Table 1 summarizes the various reaction conditions adopted for the production of biodiesel. Note that the two catalysts have equivalent surface areas and that the maximum conversion achieved was 25% for the NaNb500 catalyst using a 10% concentration, atmospheric pressure (760 mmHg) and ethanol reflux temperature (~78,5ºC). It is interesting to note that the most severe conditions (Parr reactor) resulted in a lower conversion (17%). The blank assays using Nb300 and Nb500 supports as catalysts did not result in conversion to biodiesel.

The conversion levels achieved were well below the values traditionally obtained in homogeneous reactions, which approach 100%. Two factors should be highlighted because they are directly correlated to the activity of the catalysts: the surface area and the basic strength. The first case is explained by the preparation process of these materials: simple impregnation. This led to a significant reduction of the surface area of the Nb500 sample used as support (~50m^2/g), as well as that of the original niobium (~100m^2/g). The higher conversion of the NaNb500 sample is therefore due to its basic properties, which are analyzed in the next section.

Table 1 – Conversion and reaction conditions employed to obtain biodiesel from the NaNb300 and NaNb500 samples.



Sample	BET (m^2/g)	Catalyst Concentration (%)	Reflux	Conversion$^{(1)}$ (%)
NaNb300	29	3	Yes	-
		10	Yes	5
			No	11
NaNb500	32	3	Yes	5
		10	Yes	25
			No	17

$^{(1)}$ calculated using Equation [1].

Physicochemical characterization of the solid catalysts

The structural complexity of Nb_2O_5 is due to the polymorphism related to the preparation method and the calcination temperature [29, 30]. Three crystalline phases are formed as a function of increasing temperature [31]. The T form, which is present in the orthorhombic system, is found at low temperatures (550°C) [32] the pseudo-hexagonal form is found at 450°C and is classified by Schäffer [33] as the TT form. To understand the modifications Nb_2O_5 undergoes after thermal treatments and the subsequent addition of sodium, X-ray diffraction analyses were carried out (Fig. 4).

A comparison of the diffractograms of the samples reveals that non-calcined niobium (Nb) and the materials calcined at 300ºC have amorphous structures. The impregnated sample (NaNb300) has little crystallinity due to the post-impregnation treatment (350°C/5h). However, the diffractograms of the solids calcined at 500ºC have good crystallinity, showing a primary phase of Nb_2O_5 consisting of a hexagonal system (JCPDS 28-0317), the aforementioned TT phase. The niobium impregnated with sodium (NaNb500) shows the possible formation of one phase of sodium niobate (Na_3NbO_4 – JCPDS 22-1391), the width of whose peaks indicates a certain degree of disorder. This sample was the only one to exhibit evidence of the presence of sodium; however, no other crystalline phase containing this element was detected by XRD. It should be pointed out that the diffractogram of the NaNb500 catalyst recovered after the reaction was the same as that of the initial sample, indicating that there was no loss of crystallinity or sodium during the reaction.

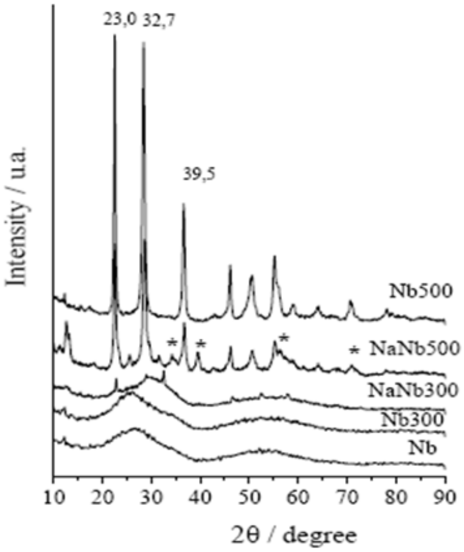


Figure 4 – Diffractograms of the impregnated catalysts (NaNb300 and NaNb500); Nb300 and Nb500 supports. Nb = commercial Nb_2O_5; * = Na_3NbO_4 phase (22-1391).

Other forms of preparation for the addition of sodium and other metals alkaline to niobium likewise commonly lead to the formation of niobates [34, 35]. Basically, the appearance of these compounds is related to the atomic ratio adopted.

Several authors have studied the Na/Al_2O_3 system, which, analogously, exhibits characteristic reflections of sodium aluminates. The basicity of this material originates from the increase of the electron-donor capacity of surface oxygen atoms in response to the insertion of sodium. This modification depends on the structure of the alumina employed [22]. To better investigate the structure and the types of Na-Nb bonds possibly formed, spectra were recorded in the IV region of the catalyst samples (Fig. 5).

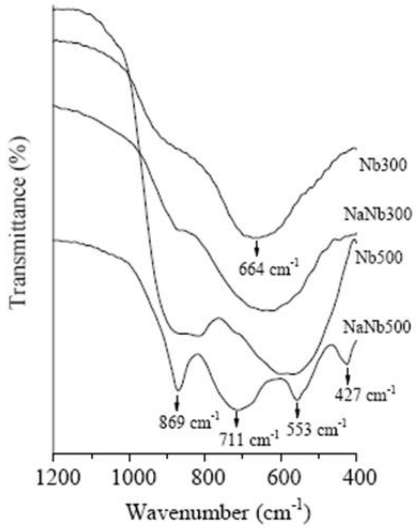


Figure 5 – Spectrum in the IV region of the catalysts.

These spectra revealed the presence of a broad band in the region of 500 to 1000 cm^{-1}, which is characteristic of niobium and niobate oxides. As can be seen, sodium impregnation of the solids calcined at 300ºC did not cause changes in this region, which shows a maximum at 664 cm^{-1} and a shoulder at 869 cm^{-1}, suggesting the presence of Nb-O bonds of [NbO_6] type octahedral units bound by both the vertices and the angles [36].

A comparison of the materials calcined at 500ºC against the previous ones indicates an increase in the region of 869 cm^{-1} and a decrease in the band at 664 cm^{-1}.

The spectrum of the impregnated sample (NaNb500) shows characteristics that are markedly distinct from the others, with the appearance of four bands with maxima at 869 cm^{-1}, 711 cm^{-1}, 553 cm^{-1} and 427 cm^{-1}. This may indicate that distortions occurred in the niobium structure due to the presence of Na. [NbO_6] units bound by the vertices are not strongly distorted, while the [NbO_6] units bound by the angles exhibit major distortions, resulting in significant variations in the Nb-O bond distance [37]. Similarly, in comparisons between $LiNbO_3$ and H-Nb_2O_5, the bands at 700 and 620 cm^{-1} were attributed to v_3 mode vibrations in octahedral

$[NbO_6]$ units bound by the vertices, and the bands at 850 and 500 cm^{-1} to octahedral $[NbO_6]$ units bound by the angles [36]. Therefore, the NaNb500 sample seems to have developed distortions in the Nb-O bonds that do not appear in the Nb500 support, particularly in relation to the bands at around 700 and 430 cm^{-1}.

The characteristic that was sought in these preparations was the creation of basic sites on the niobium surface. It should be kept in mind that niobic acid displays high acidity ($H_o \leq -5.6$) if calcined at temperatures of up to 300ºC and that the surface becomes practically neutral if treated at 500ºC [28]. This neutrality allowed for the development of a certain degree of basicity in the Nb500 solid by the addition of the alkali. This property can be visualized in CO_2 thermodesorption assays monitored by spectroscopy in the IV region (Fig. 6).

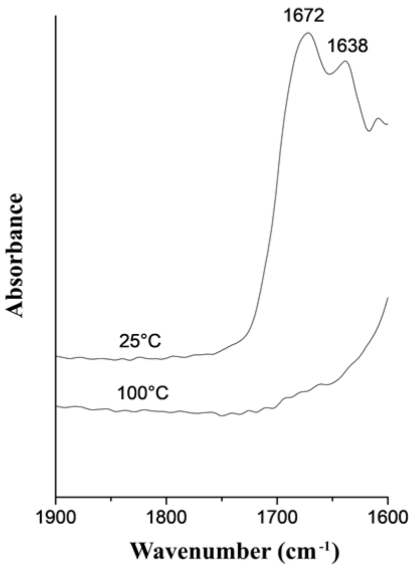


Figure 6 – Spectra in the IV region after CO2 adsorption of the NaNb500 sample.

The natural acidity of untreated niobium prevents the adsorption of CO_2, as already investigated and reported by Kus *et al.*[38] in TPD assays. In alumina, CO_2 adsorption leads to the appearance of a band, among others, at ~1650 cm^{-1} [39]. In the NaNb500 sample, note the appearance of two bands 1672 and 1638 cm^{-1} after CO_2 adsorption. These bands can be attributed to bidentate and monodentate carbonate species bound to the niobium surface (O^{2-} type sites) and/or to Na^+

cations. In this experiment, it was not possible to visualize the region below 1400 cm^{-1} due to the vibrations resulting from the niobium structure. Therefore, it is not possible to confirm the presence of hydrogen carbonate species (~1200 cm^{-1}). The bands shown in Fig. 6 remain at room temperature, but practically disappear when the temperature increases to 100ºC. This behavior denotes the emergence of weak- and medium-strength basic sites. This conclusion can be confirmed by the experiments with Hammett indicators. The NaNb500 solid presented a basicity equivalent to pH = 10.5. Among the tested indicators, this material reacted only with phenolphthalein (8.2 – 9.8) and thymolphthalein (9.3 – 10.5). The titration carried out with 0.05 mol/L benzoic acid recorded a number of basic sites of 0.6 meq/g in the range of phenolphthalein and of 0.4 meq/g for thymolphthalein.

Conclusions

The method employed in the preparation of the catalysts led to a significant reduction of the surface area (~50 m^2/g). However, the addition of Na to the niobium calcined at 500ºC (TT phase) caused structural changes, with the formation of a sodium niobate phase (XRD), without loss of crystallinity after the reaction. For this material, it was possible to obtain a weak to medium surface basicity (Hammett e CO_2/IV), translating into better results of conversion to biodiesel, principally when used at 10% in a reflux system (25%). This leads to the conclusion that, besides the importance of generating basicity in catalysts, the reaction conditions can still be optimized.

Acknowledgements

The authors are indebted to Prof. Stefano Caldarelli of the University of Marseille, France, for his invaluable discussions about catalytic evaluation via NMR ^1H spectroscopy, and to technician Magali Freitas, of the Instituto Nacional de Tecnologia, for the CO_2 / IV adsorption assays. The authors also wish to express gratitude for financial supporting to CNPq (process 302756/2009-4) and FUNTAC/MCT/CNPq/CT-INFRA (process 9267-6/08 and 31402-1 TO 022/09).

References

[1] B. Freedman, E. H. Pryde, T. L. Mounts, J. Am. Oil Chem. Soc. 61 (1984) 1638.
[2] B. Freedman, R. O. Butterfield, E. H. Pryde, J. Am. Oil Chem. Soc. 63 (1986) 1375.
[3] U. Schuchardt, R. Sercheli, R. M. Vargas, J. Braz. Chem. Soc. 9 (1998) 199.
[4] A. C. Pinto *et al.,* J. Braz. Chem. Soc. 9 (2005) 1313.
[5] J. R. O. Lima, *et al.,* Quim. Nova 30 (2007) 600.
[6] C. C. Enweremadu, M. M. Mbarawa, Renewable and Sustainable Energy Reviews 13 (2009) 2205.
[7] Z. Helwani, M. R. Othman, N. Aziz, W. J. N. Fernando, J. Kim, Fuel Process. Technol. 90 (2009) 1502.
[8] A. P. Vyas, J. L. Verma, N. Subrahmanyam, Fuel 89 (2010) 1.
[9] M. Zabeti, W. M. A. W. Daud, M. K. Aroua, Fuel Process. Technol. 90 (2009) 770.
[10] M. J. Dabdoub, J. L. Bronzel, M. A. Rampin, Quim. Nova 32 (2009) 776.
[11] C. C. S. Macedo *et al*., J. Braz. Chem. Soc. 17 (2006) 1291.
[12] K. Noiroj, P. Intarapong, A. Luengnaruemitchai, S. Jai-In, Renewable Energy (2009) 1145.
[13] G. J. Suppes, M. A. Dasari, E. J. Doskocil, P. J. Mankidy, M. J. Goff, Appl. Catal. A 257 (2004) 213.
[14] G. Gelbard, F. Vielfaure-Joly, C. R. Acad. Sci. Paris 3 (2000) 563.
[15] X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, Fuel 87 (2008) 216.
[16] S. Bancquart, C. Vanhove, Y. Pouilloux, J. Barrault, Appl. Catal.*,* A 218 (2001) 1.
[17] K. S. Kim, S. J. Song, J. H. Kim, G. Seo, J. Catal. 205 (2002) 244.
[18] S. Gryglewicz, Bioresour. Technol. 70 (1999) 249.
[19] S. Gryglewicz, Appl. Catal. A, 192 (2000) 14.

[20] V. A. Ivanov, A. Piéplu, J. C. Lavalley, P. Nortier, Appl. Catal. A 131 (1995) 323.

[21] G. Suzukamo, M. Fukao, M. Minobe, Chem. Lett. (1987), 585.

[22] K. Tanaka, H. Yanashima, M. Minobe, G. Suzukamo, Appl. Surf. Sci. (1997) 461.

[23] H. J. Kim, B. S. Kang, M. J. Kim, Y. M. Park, D. K. Kim, J. S. Lee, K. Y. Lee, Catal. Today 93 (2004) 315.

[24] K. Tanabe, Catal. Today 78 (2003) 65.

[25] K. T. G. Carvalho *et al*., Quim. Nova 32 (2009) 1373.

[26] K. Tanabe, Chem. Lett. (1984) 1085.

[27] G. Knothe, J. Am. Oil Chem. Soc. 77 (2000) 489.

[28] T. Ushikubo, T. Lizuka, H. Hattori, K. Tanabe, Catal. Today 16 (1993) 291.

[29] H. Schäfer, F. Schulte, R. Gruehn, Angew. Chem., Int. Ed. 3 (1964) 511.

[30] H. Schäfer, F. Schulte, R. Gruehn, Angew. Chem., Int. Ed. 5 (1966) 40.

[31] G. Brauer, Z. Anorg. Allg. Chem. 248 (1941) 1.

[32] A. Reisman, F. Holtzberg, J. Am. Chem. Soc. 81 (1959) 3182.

[33] M. W. Shafer, R. Roy, Z. Kristallogr. 100 (1958) 241.

[34] I. C. M. S. Santos, L. H. Loureiro, M. F. P. Silva, A. M. V. Cavaleiro, Polyhedron 21 (2002) 2009.

[35] C. H. Lu, S. Y. Lo, Y. L. Wang, Mater. Lett. 55 (2002) 121.

[36] M. Tatsumisago, A. Hamada, M. Tanaka, J. Non-Cryst. Solids 56 (1983) 423.

[37] A. A. McConnell *et al*., Spectrochim. Acta, Part A 32 (1976) 1067.

[38] S. Kus, M. Otremba, M. Taniewski, Fuel 82 (2003) 1331.

[39] A. M. D. Farias, A. L. E. Esteves, F. Ziarelli, S. Caldarelli, M. A. Fraga, L. G. Appel, Appl. Surf. Sci. 227 (2004) 132.