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The Use of Niobium Based Catalysts for Liquid Fuel Production

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The catalytic properties of niobium based catalysts were investigated in the conversion of oleic acid to liquid fuels at atmospheric pressure and at 623 K. The catalytic tests were performed in a fixed bed and continuous flow reactor using an acid to catalyst ratio equal to 4 and N_2 as carrier gas. The reaction products were analyzed by gas chromatography and acidity measurements. NH_3 temperature programmed desorption, N_2 adsorption-desorption (BET method) and X-ray diffraction were also performed in order to determine the structural and acidic properties of the catalysts. From the catalytic tests, it was detected the formation of compounds in the range of gasoline, diesel and lubricant oils. Higher catalytic activity and selectivity for diesel fuel were observed for the catalysts $NbOPO_4$ and H_3PO_4/Nb_2O_5 that possesses higher acidities and surface areas.

Keywords: *niobium, oleic acid, bio-diesel*

1. Introduction

Diesel fuel plays an essential role in the economic activity of any country as it is used in different kinds of vehicles, electric generators, agricultural equipments, etc. Due to the worldwide expected growth rate of its consumption as well as the reduction of petroleum resources, the interest and researches for suitable alternative diesel fuels have increased in the last years[1].

An alternative to diesel must be economically competitive, easily available and acceptable from both technical and environmental viewpoints. Vegetal oils (constituted of 90-98% triglycerides) and their derivatives fulfill all of these requirements. Moreover, the comparison of petrodiesel and biodiesel shows that biodiesel presents many beneficial characteristics as its biodegradability, a high cetane number and the absence of sulfur and aromatics which contributes to reduce environmental pollutants.

In the exploitation of vegetable oil for substitution to diesel, three distinct routes are possible[2]:

- The direct use of pure vegetable oil. Although this route is economically attractive, it brings serious problems of adjustment as the physical and chemical properties of the vegetable oil, such as density, viscosity and flash point, are quite different from diesel. Another point to be considered is that the products obtained from vegetal oil combustion would be also different and this could not only compromise the metallic parts of the engine but also generate new pollutants in the atmosphere, possibly sufficiently toxic.
- The vegetable oil transesterification, which converts the natural triglycerides into monoesters of ethyl or methyl alcohol. This process improves the physical properties of the fuel approaching its characteristics to those of petrodiesel. However it brings some disadvantages as, for example, high ethyl or methyl alcohol consumption and the generation of a high amount of glycerin as by-product.

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- The catalytic degradation of the triglycerides with production of a mixture of hydrocarbons almost similar to diesel. Concerning the quality of the fuel, this route is the best one, since it would be necessary no modification or adaptation of the engines.

Although in the last years many catalytic systems have been investigated for the conversion of vegetal oils to fuel, their effective action is still little known[3-8].

The great amounts of raw materials in Brazil concerning both vegetable oils and niobium, as well as the knowledge that niobium based catalysts can be efficient in different industrial processes[9-10], have motivated us in our research. So, the aim of this work is to study the viability of the use of niobium as a catalytic agent in the conversion reaction of the oleic acid to hydrocarbons in the range of diesel oil (C_{14}-C_{18}). The oleic acid was chosen as reactant as it is the major constituent of the soy oil.

2. Experimental

2.1. Catalysts Preparation

The start materials were niobium phosphate ($NbOPO_4$) and niobic acid ($H_8Nb_6O_{19}$), which were donated by the Brazilian Company of Metallurgy and Mineration (CBMM). Three samples were prepared: $NbOPO_4$, Nb_2O_5 and H_3PO_4/Nb_2O_5. $NbOPO_4$ was submitted to calcination at 623 K. Nb_2O_5 resulted from the thermal treatment of $H_8Nb_6O_{19}$ up to 623 K and the third catalyst H_3PO_4/Nb_2O_5 was prepared by wetness impregnation of a 12% H_3PO_4 solution into the support Nb_2O_5.Then, this sample was dried overnight at 373 K and calcined in an oven at 623 K for 2 h.

2.2. Catalysts Characterization

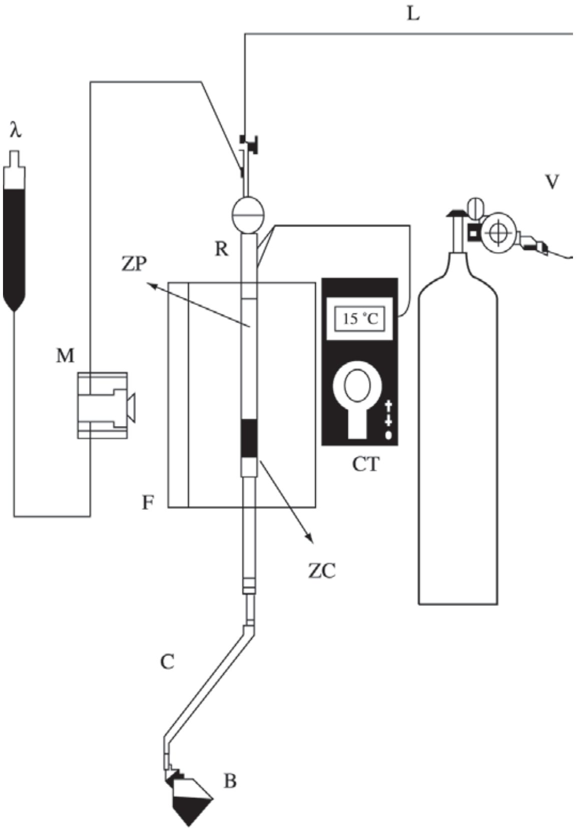
The textural properties of the samples such as specific area, average pore diameter and pore volume were determined by N_2 physical adsorption-desorption (BET method) at its normal boiling temperature (77 K) with an ASAP 2000 Micromeritics apparatus. Prior to the analysis, the catalyst was submitted to a preheating treatment at 423 K under vacuum of 15×10^{-6} mmHg. The BET isotherms were taken at pressures between 45-160 mmHg using super dry N_2.

The acid sites distributions were obtained with the NH_3 temperature programmed desorption technique (TPD-NH_3). Initially, the samples were treated for 0.5 h under pure He flow of 60 mL/min using a heating rate of 10 K/min up to 473 K. The chemisorption of 4%NH_3/He was carried out at room temperature for 0.5 h and the excess of fisisorbed molecules was removed by vacuum during 1.5 h at the same temperature. Finally, the ammonia termodesorption analysis was performed using a heating rate of 10 K/min up to 773 K.

Powder X-ray data for structural analysis were collected with a Siemens X-ray diffractometer using Cu Kα radiation over a 1h40min period from $2\theta = 3 - 80°$, with a 1.0 s step.

2.3. Catalytic Tests

The oleic acid conversion to hydrocarbons had been carried out at 623 K in a fixed bed and continuous flow reactor. A scheme of the catalytic unit is illustrated in Fig. 1. The catalytic bed was constituted by 5 g of catalyst and 5 cm of small glass balls. The catalyst was pre-treated *in situ* during 2 h under N_2 flow at 623 K. After this treatment, the reactant was introduced into the reactor inlet by a pump (reactant flow = 20.5 g/h). The liquid products were collected after passing through a condenser connected to reactor outlet. During the test, two samples were withdrawn from the reactor effluents at 30 min and 60 min for posterior acidity value determination (Ma) as well as for chromatographic analysis (GC). These analysis were performed in order to bring informations about the degree of acid descarboxilation



l = Soy oil reserver
M = Pump
B = Liquid product collector
C = Condenser
F = Oven
ZC = Catalytic zone
ZP = Pre-heating zone
R = Reactor
CT = Temperature controller
L = Carrier gas line
V = Valve for carrier gas control

Figure 1. Scheme of the catalytic unit.

and to obtain the hydrocarbon product distribution in the ranges of gasoline, diesel and lubricant oil. The material that remained in the reactor after the reaction was weighed and considered as a residue.

2.4. Acidity Measurements of the Liquid Products

A solution of ethyl alcohol and benzene (volumetric ratio equal to 1) was initially added to a weighed amount of the liquid product. Afterwards, it was titrated with an alcoholic solution of 0,1 mol/L KOH using phenolphtalein as indicator. The amount of free acid was obtained using the following expression:

$$\mathrm{Ma} = \frac{V_{KOH} M_{KOH} f_{KOH}}{Pa}$$

where:

Ma = acidity measurement
V_{KOH} = volume of KOH spent in titration
M_{KOH} = KOH solution concentration
f_{KOH} = correction factor for KOH solution concentration
Pa = weight of the sample product

3. Results and Discussion

3.1. Specific Area and Porosity

The results obtained from textural characterization of the samples are shown in Table 1. All catalysts had presented type IV adsorption-desorption isotherms according to Brunauer-Emmett-Teller classification, which increases the confidence of the method in the determination of porous properties.

The results obtained with the Nb_2O_5 catalyst are in good agreement with those reported in the literature[11]. Comparing the textural properties of Nb_2O_5 and $NbOPO_4$ catalysts, it is observed that both have practically the same specific areas. Nevertheless, $NbOPO_4$ catalyst has higher pore volume and pore diameter values. This behavior can be explained by the presence of a lamelar structure for the $NbOPO_4$ compound where the formed layers consist of octaedrons [NbO_6] connected in the equatorial plan by tetrahedrons [PO_4], as can be seen in Fig. 2[12]. Individual layer is electrically neutral and interacts by hydrogen bonding, allowing the occlusion of neutral molecules that increase the interlamelar distance and thus the volume of this solid[12].

Concerning the H_3PO_4/Nb_2O_5 catalyst, the impregnation of phosphoric acid to Nb_2O_5 support caused a decrease in its specific area value. This is probably due to the condensation of PO_4^{3-} ions on the surface of the Nb_2O_5 support and/or due to the bonding of these ions to niobium with formation of phosphate species, which would be also responsible for the increasing of the pore diameter value.

The pore volume distribution curves of the samples are presented in Fig. 3.

As appears from this figure, $NbOPO_4$ catalyst exhibits a monomodal pore distribution, with mesoporosity in the range of 40 Å to 100 Å and having 65 Å as a medium value. Both Nb_2O_5 and H_3PO_4/Nb_2O_5 catalysts presented a bimodal pore distribution in the ranges of 20 Å to 70 Å and 200 Å to 1000 Å, respectively. Comparing the curves of the H_3PO_4/Nb_2O_5 sample with that of the corresponding pure support, it is observed a slight narrowing of the peak in the 20 Å to 70 Å region, probably due to a partial blockage of the mesoporous caused by phosphoric acid incorporation to Nb_2O_5.

3.2. X-ray Diffraction

The X-ray diffraction patterns of the prepared catalysts are given in Fig. 4. The analysis of this figure demonstrates that both H_3PO_4/Nb_2O_5 and Nb_2O_5 catalysts are amorphous. However, for the $NbOPO_4$ sample, small peaks are detected corresponding to the crystalline plans 020 ($2\theta = 28^o$ (d~3,19)), 110 ($2\theta = 20^o$ (d~4,5)) and 130 ($2\theta = 45^o$ (d~2,02)), indicating that the material has a low cristallinity and is not totally amorphous as the other samples. The detected peaks are characteristics of the β-phase of $NbOPO_4$[13-

Table 1. Textural properties of the samples.

Catalyst	Specific Area (m^2/g)	Pore Volume (cm^3/g)	Medium Pore Diameter (Å)
Nb_2O_5	115	0.15	41.7
H_3PO_4/Nb_2O_5	78	0.13	51.5
$NbOPO_4$	119	0.31	71.0

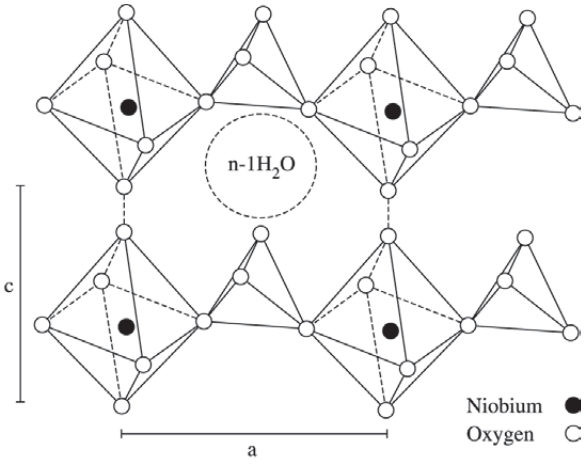


Figure 2. Fragment of $NbOPO_4.3\ H_2O$ structure on *ac* plane.

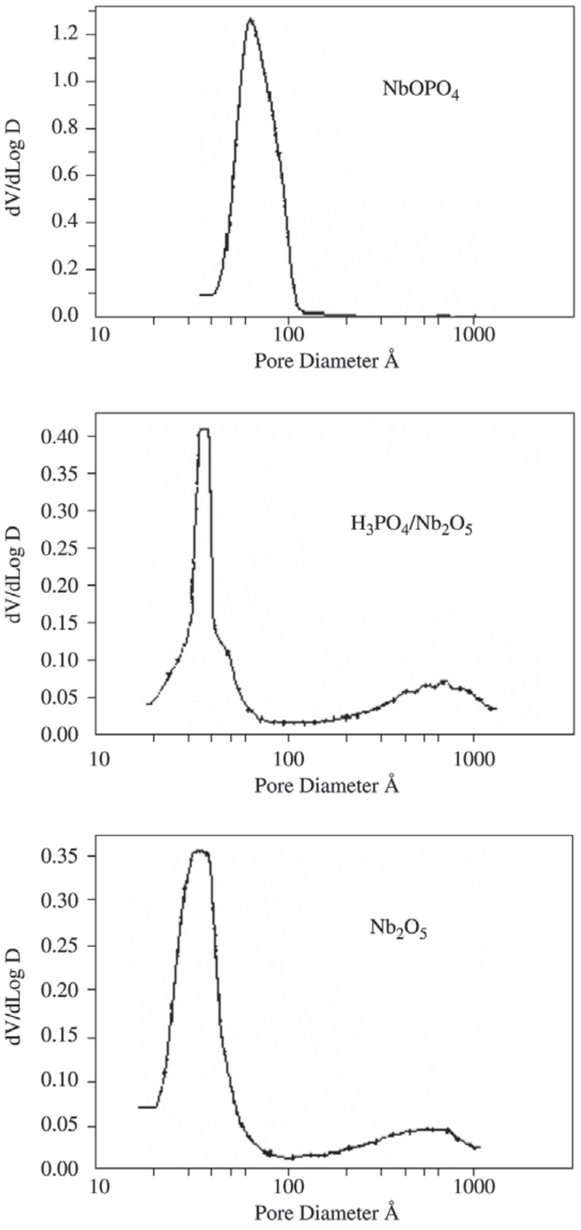


Figure 3. Pore size distribution of the different catalysts.

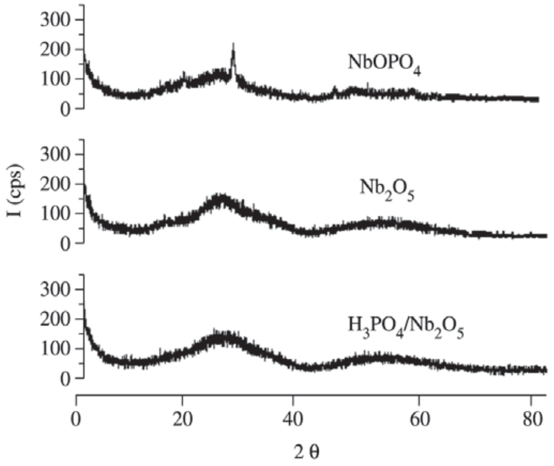


Figure 4. X-ray diffraction patterns of the samples.

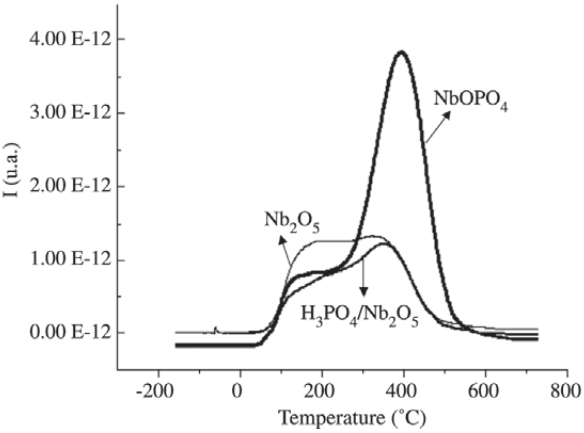


Figure 5. NH_3-TPD profiles of the prepared catalysts.

[14].

3.3. Ammonia Temperature Programmed Desorption

NH_3-TPD profiles are displayed in Fig. 5. From this figure, it is clear that the $NbOPO_4$ catalyst profile is shifted towards higher temperatures as compared to the other samples, indicating that stronger acid sites are present on its surface.

The peak areas values allowed us to obtain the total acidities of the catalysts expressed in mmols of NH_3/g of the catalyst. These informations are reported in Table 2. In order to make a semi-quantitative determination, the desorption curves were partitioned into chosen temperature ranges, assuming that the ammonia retained on stronger sites desorbs at higher temperatures as mentioned in the literature[15] and these results are also shown in Table 2.

As it can be noted, H_3PO_4/Nb_2O_5 catalyst exhibits the highest total acidity followed by Nb_2O_5 and $NbOPO_4$ catalysts. However, $NbOPO_4$ catalyst presented the highest strong acid sites distribution (T > 623 K) and this behavior must be probably caused by the loss of water in its structure, which promotes a strong NH_3 adsorption on the support.

3.4. Catalytic Tests

Table 3 presents the average results obtained from cata-

Table 2. Total acidity and acid strength distribution of the catalysts obtained from NH_3-TPD analysis.

Catalysts	Total acidity[μmol $NH_3.g_{cat}^{-1}$]	Relative acidity distribution [μmol $NH_3.g_{cat}^{-1}$]		
		T < 473 K	473 K < T > 623 K	T > 623 K
$NbOPO_4$	143	18	42	83
Nb_2O_5	529	142	245	142
H_3PO_4/Nb_2O_5	811	157	366	288

Table 3. Summary results from catalytic tests with oleic acid at 623 K.

Catalyst	Sample	% LP*	Ma**	Conversion (%)	Residue (wt. %)
None (pure reactant)	—	—	3.7	—	—
None (thermal cracking)	1	84.8	3.7	0	11.4
	2	90.8	3.5	5.4	
Nb_2O_5	1	85.2	2.5	32.4	7.4
	2	82.2	2.5	32.4	
H_3PO_4/Nb_2O_5	1	71.9	1.7	54.0	22.2
	2	90.2	2.0	45.9	
$NbOPO_4$	1	47.7	0.67	81.9	23.2
	2	78.5	1.0	73.0	

*%LP = weight percentage of liquid products from reactor outlet (liquid products generated + oleic acid not reacted).
**Ma = mmol acid/g product.

lytic conversion reactions at 623 K, where samples 1 and 2 correspond to the aliquots withdrawn after 30 min and 60 min of time on stream, respectively.

From this table, it is possible to assess the descarboxilation activity of the catalysts by comparing the products acidity measurement (Ma): the lower it is, the more efficient is the catalyst in the descarboxilation process. The acidity measurement of the reactant, oleic acid, was also included in Table 3 in order to provide data comparison.

The catalytic activities are compared as a function of the liquid products formation, that is, the ability of converting the oleic acid reactant to hydrocarbon products, using the following expression:

$$\text{Conversion (\%)} = \left(\frac{\text{Ma of oleic acid - Ma of products}}{\text{Ma of oleic acid}}\right)\times 100$$

The results from Table 3 suggest the occurrence of a thermal cracking process in the pre-heating zone of the reactor for the non-catalyzed reaction which resulted in a small amount of liquid products.

On the basis of experimental data, it is obvious that the presence of a catalytic agent substantially increases the oleic acid conversion. The catalytic activity of the pentoxide niobium sample was significantly enhanced by impregnating this support with phosphoric acid. As previously mentioned, the phosphoric acid incorporation to Nb_2O_5 leads to an increase of the total acidity but also to a decrease of the specific area value. Hence, the catalytic promotion effect may be attributed mainly to an increase of the acidic properties of the support.

A maximum of activity was found for $NbOPO_4$ catalyst that exhibits conversions up to 82%. The results of catalytic activity did not follow the same general trend as the TPD results. This is not surprising, since the TPD technique measures all sites capable of adsorbing ammonia and only a fraction of these is likely to be active in the acid oleic descarboxilation reaction. Based on these findings, it can be concluded that strong acid sites are required for catalyzing this reaction.

After all tests, it was observed a viscous residual product formation, mainly with H_3PO_4/Nb_2O_5 and $NbOPO_4$ catalysts.

3.5. Gas Chromatography

Table 4 presents the weight percentage of products obtained from the catalytic oleic acid conversion to hydrocarbons. The average products distribution was expressed taking into account the different hydrocarbon ranges and it was determined by using a standard chromatogram for comparison.

For the non-catalyzed reaction, no hydrocarbon product was detected. The presence of the catalyst promoted the formation of compounds in the range of gasoline, diesel oil and lubricant oil for all of the samples. The addition of phosphoric acid improved the performance of Nb_2O_5 catalyst.

Table 4. Products distribution expressed in hydrocarbon ranges (weight %).

Catalyst	C_6-C_{12} (gasoline range)	C_{14}-C_{18} (diesel range)	C_{19}-C_{22} (lubricant oil)
None (thermal cracking)	0	0	0
Nb_2O_5	0.11	4.56	91.29
H_3PO_4/Nb_2O_5	1.77	21.32	72.79
$NbOPO_4$	0.72	33.12	65.12

The best result concerning biodiesel selectivity was obtained with $NbOPO_4$ catalyst. The simultaneous analysis of the oleic acid descarboxilation with the chromatographic results allow us to conclude that the $NbOPO_4$ catalyst is the most efficient for the process, since it showed the highest conversion (73% and 82%) and selectivity values (33% of compounds in the range of diesel oil). This result is probably related to its particular properties: it is a solid with a lamelar phosphate structure with high pore volumes and a monomodal mesopores distribution. Moreover, this solid presents some crystallinity and a higher amount of strong acid sites in comparison to the other samples.

4. Conclusions

The addition of phosphoric acid to niobium pentoxide caused an increase of the total acidity resulting, however, in the partial blockage of the pores. The comparison between the H_3PO_4/Nb_2O_5 catalyst and the pure Nb_2O_5 support suggested that phosphoric acid impregnation improved the efficiency in the oleic acid descarboxilation. Nevertheless, $NbOPO_4$ catalyst was the most efficient in this process: it showed the best results in both activity and selectivity for diesel fuel. This is probably related to its strong acid sites and high specific area value. So, both textural and acidic properties play an important role in the catalytic performance of the conversion of oleic acid to liquid fuels. $NbOPO_4$ seems to be a promising catalyst for oil reform reaction.

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