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H_3PO_4/Al_2O_3 Catalysts: Characterization and Catalytic Evaluation of Oleic Acid Conversion to Biofuels and Biolubricant

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Al_2O_3 and H_3PO_4/Al_2O_3 catalysts were investigated in the conversion of oleic acid to biofuels and biolubricant at 1 atm and at 623 K. The catalytic tests were performed in a fixed bed and continuous flow reactor, using an oleic acid-catalyst ratio of 4 and N_2 as the carrier gas. The reaction products were analyzed by gas chromatography and acidity measurements. N_2 adsorption-desorption, X ray diffraction, ^{31}P nuclear magnetic resonance and FT-IR spectroscopy were also employed to evaluate the textural, structural and acidic properties of the catalysts. The results showed that phosphoric acid impregnation improved the alumina decarboxylation activities, generating hydrocarbons in the range of gasoline, diesel oil and lubricant oil. The best catalytic performance was achieved with the highest surface area alumina impregnated with H_3PO_4, which was the solid that allied high total acidity with a large quantity of mesopores.

Keywords: *H_3PO_4/Al_2O_3, oleic acid, biofuels, biolubricant*

1. Introduction

The enormous worldwide use of diesel fuel and the rapid depletion of crude oil reserves have prompted keen interest and exhaustive research into suitable alternative fuels. Biomass sources, particularly vegetal oils, have attracted much attention in recent years thanks to their wide availability and easy renewability. Moreover, biodiesel presents many advantages, such as a high cetane number and the absence of sulfur and aromatics, thus contributing to reduce the load of environmental pollutants[1]. Many investigations have focused on improving biofuel produced from vegetal oils and an extensive literature is available in this field[2-6]. Most of these researches use the transterification route, which consists of converting the natural triglycerides present in vegetal oils into ethyl or methyl alcohol monoesters. Though easy, this process has disadvantages, e.g., it requires large quantities of ethyl or methyl alcohol and generates large amounts of glycerin as a by-product, thus making the biofuel purification step difficult.

Alternatively, biofuels can be produced by the catalytic triglyceride degradation reaction, which generates a mixture of hydrocarbons very similar to petrodiesel. The catalyst must possess hydrodeoxygenation properties in order to complete the entire process in a single stage. Some catalytic properties such as surface area and acidity are also important[7,8]. As for the quality of the fuel, this route is better than the transterification one, since it does not require any engine modification or adaptation. This process can also generate biolubricant, which is a biodegradable fluid and an environmentally friendly product, as opposed to petrochemically derived lubricants.

This research purported to investigate the viability of using H_3PO_4/Al_2O_3 as catalytic agents in the conversion reaction of oleic acid into hydrocarbons in the range of diesel oil (C_{14} - C_{18}) and lubricant oil (C_{19} - C_{22}). Oleic acid was chosen as the reactant since it is one of the main constituents of many vegetal oils.

2. Experimental

2.1. Catalyst preparation

Two alumina samples donated by Petrobras Research Center (CENPES), one commercial, Pural 200 (Al_2O_3 - A) and one synthesized (Al_2O_3 - B), were used as support materials. The catalysts were prepared by wetting and impregnating the supports with a 12% (wt. (%)) phosphoric acid solution and these impregnated samples are symbolized by HP/alumina. After homogenization, the catalysts were dried overnight at 373 K and calcine d in a furnace at 623 K for 2 hours.

2.2. Catalyst characterization

The porous properties such as surface area (BET method), average pore diameter and pore volume (t-plot method) were determined by N_2 physical adsorption-desorption at the normal boiling temperature (77 K) using an ASAP 2000 Micromeritics apparatus. Prior to the analysis, the catalyst was subjected to a preheating treatment at 423 K under vacuum. The BET isotherms were measured at pressures between 6 and 21 kPa, using superdry N_2.

Powder X ray diffraction data for structural analysis were collected with a Siemens X ray diffractometer. A Cu Kα (35 kV) anode was used as the X ray radiation source, covering 2θ between 2° and 80°. For purposes of identification, the diffraction patterns obtained were compared against the standards of the American Society for Testing of Materials (ASTM).

Acidity measurements were carried out with a Perkin-Elmer 2000 FTIR analyzer at room temperature. The sample, in self-supporting disk form, was initially pretreated in an O_2 flow (30 $cm^3.min^{-1}$) at 723 K for 1 hour. After a vacuum treatment and cooling to room temperature, a preliminary IR spectrum was measured. The temperature was then increased to 423 K and the sample was exposed to pyridine

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vapor (4 Torr) under static conditions for 30 minutes. The IR spectrum was measured again after vacuum and cooling to room temperature. The absorbance spectra were obtained by using the interferograms of reduced samples as background references.

The interaction of phosphorous with the support was investigated by ^{31}P NMR analysis, using a Bruker DRX-300 Advance spectrometer operating in a resonance frequency of 121.5 MHz.

2.3. Catalytic reaction

The oleic acid conversion was performed at 1 atm and 623 K in a fixed bed continuous flow reactor. A scheme of the catalytic unit is illustrated elsewhere[9]. The catalytic bed comprised 5 g of catalyst and 5 cm of small glass balls. The catalyst was pretreated *in situ* for 2 hours under a N_2 flow at 623 K. After this treatment, the reactant was pumped into the reactor inlet (reactant flow = 20.5 $g.h^{-1}$). The liquid products were collected after passing through a condenser connected to the reactor's outlet. During the reaction, two samples were withdrawn from the reactor effluents at 30 minutes and 60 minutes to determine the acidity (Ma) and for a chromatographic analysis (GC). These analyses were carried out to evaluate the acid decarboxylation properties and the selectivities for biodiesel and biolubricant products.

2.4. Liquid products characterization

The liquid products were analyzed in a Hewlett Packard (HP) 5890 series II gas chromatograph using a PE-1 (100% methylsilicone) capillary column of 50 m and H_2 as the carrier gas. The column temperature was programmed to range from 323 K to 533 K, using a heating rate of 8 $K.min^{-1}$.

To measure the acidity, a solution of ethyl alcohol and benzene (volumetric ratio of 1) was initially added to a weighed amount of the liquid product. This mixture was then titrated with an alcohol solution of 0.1 $mol.L^{-1}$ KOH, using phenolphthalein as indicator.

3. Results and Discussion

3.1. Porous properties

Table 1 shows the results of the textural characterization of the samples.

As can be seen in Table 1, the microporous volumes of all the samples were almost negligible compared to their mesoporous volumes.

The results indicate that impregnation of phosphoric acid on the two aluminas reduced their surface areas considerably; therefore, this reduction cannot be attributed simply to an increase of the samples' densities due to the incorporation of acid, for both supports clearly underwent partial pore blockage.

As for the HP/Al_2O_3 - A catalyst, impregnation with acid markedly reduced the mesoporous volume, indicating that phosphoric acid may be located mainly on the inner surface of the Al_2O_3 - A mesopores. An increase in the average pore diameter of Al_2O_3 - A was also observed as a result of phosphoric acid impregnation.

Table 1. Textural properties of the samples.

Sample	S_{BET} (m^2/g)	$S_{external}$ (m^2/g)	S_{micro} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	$D_{average}$ (Å)
Al_2O_3 - A	48	40	8	0.44	0.0035	291
HP/Al_2O_3 - A	23	21	2	0.23	0.0005	381
Al_2O_3 - B	330	321	9	0.42	0.0009	41
HP/Al_2O_3 - B	120	108	12	0.30	0.0048	67

A comparison of the Al_2O_3 - B and HP/Al_2O_3 - B catalysts revealed a reduction of the total pore volume, but an increase in the mesoporous volume after the addition of acid to Al_2O_3 - B. One possible explanation may be the condensation of PO_4^{3-} ions on the external surface of the support, resulting in the formation of superficial phosphate species[10]. Similarly to the HP/Al_2O_3 - A catalyst, the average pore diameter also increased after H_3PO_4 impregnation on Al_2O_3 - B.

3.2. X ray diffraction

Figure 1 shows the XRD patterns of Al_2O_3 - A based catalysts. The Al_2O_3 - B based samples presented similar spectra, although the peaks displayed very low intensities, indicating the low crystallinity of these solids.

Figure 1 reveals typical peaks of gamma-alumina for all the samples. The H_3PO_4 impregnation of both supports hardly altered their XRD patterns. Only an extra peak at 2θ = 21.6° was observed, probably related to the formation of superficial aluminum phosphate[11].

3.3. Acidity measurements

Figure 2 shows the infrared spectra of adsorbed pyridine obtained in the wave range of 1300 and 2000 cm^{-1}.

The Al_2O_3 - A and Al_2O_3 - B based catalysts showed similar spectra, although the vibration bands of the Al_2O_3 - A samples were

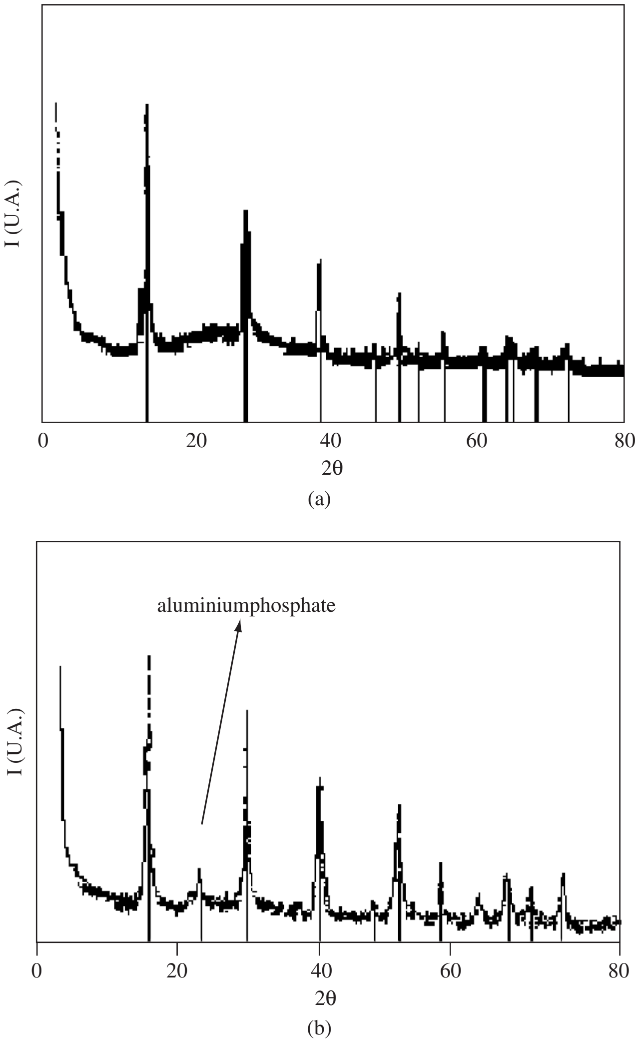


Figure 1. X ray diffraction patterns of Al_2O_3 - A based catalysts: a) Al_2O_3 - A; and b) HP/Al_2O_3 - A.

lower than those of Al_2O_3 - B. Pure alumina spectra presented bands at 1450, 1494, 1581 and 1615 cm^{-1}. The bands at 1450, 1494 and 1615 cm^{-1} are likely associated with pyridine bound coordinately to Lewis acid sites[12], while the band at 1581 cm^{-1} can be attributed to pyridine adsorbed on Brønsted acid sites[13].

The infrared spectra showed practically no change after the incorporation of phosphoric acid in the supports. Nevertheless, compared to the pure aluminas, most of the band intensities decreased, with a slight band shift occurring at 1615 cm^{-1} towards higher frequencies. The decrease in the peaks' intensities may be ascribed to the lower acid density of these impregnated samples, as evidenced by the strong reduction of surface area due to the phosphoric acid load in the alumina (textural analysis). With regard to the band at 1615 cm^{-1}, the higher the vibrational frequency the stronger the Lewis acid sites in the sample[12]. Therefore, the Lewis acid sites of impregnated samples were stronger than those of pure aluminas. This can be explained by the higher electronegative feature of phosphorous-alumina bonding and also by the decrease in the aluminum's electronic density, resulting in an increase of the acidity of the Lewis sites.

3.4. Nuclear magnetic resonance

Table 2 shows the chemical shifts obtained from the ^{31}P NMR analysis of the catalysts.

According to the ^{31}P-NMR data, no signal was detected at 0 ppm, indicating the absence of free phosphoric acid in these samples. The spectra signals were attributed to tetra-coordinated phosphorus species[14].

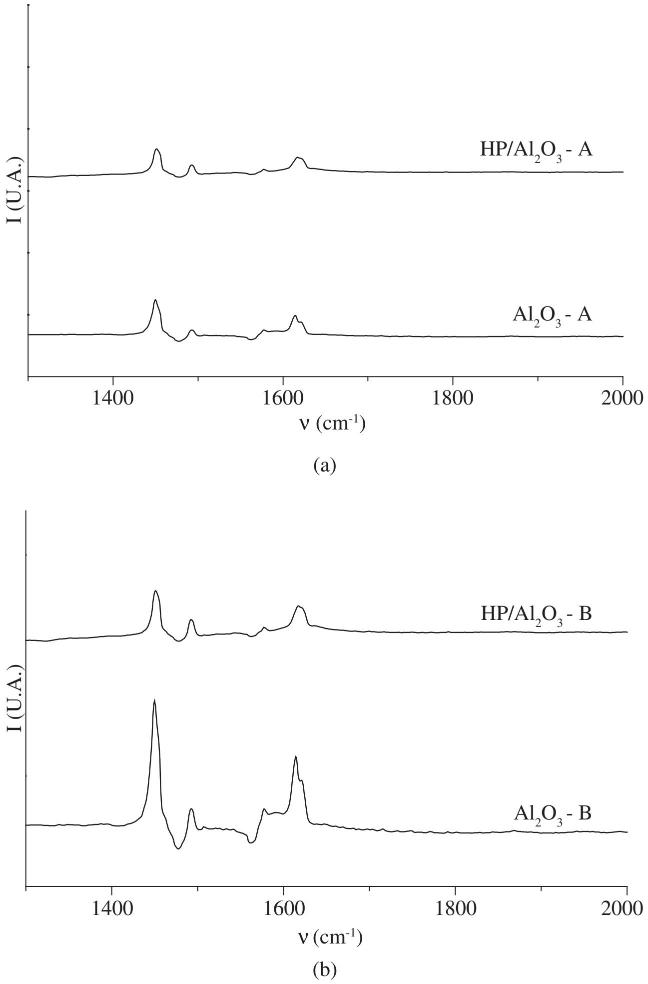
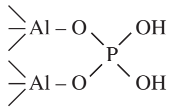
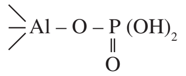


Figura 2. IR spectra after pyridine adsorption on a) Al_2O_3 - A; and b) Al_2O_3 - B based catalysts.

Signals were detected at - 18 and at - 28 ppm in the HP/Al_2O_3 - A catalyst, indicating different phosphorous and aluminum interactions in bridging structures[14], as depicted below:



The peak at - 12 ppm in the HP/Al_2O_3 - B catalyst was possibly related to linear phosphorous and aluminum bonding[14], based on the following simplified scheme:



$$\mathrm{Al-O-\overset{}{\underset{\underset{O}{\|}}{P}}(OH)_2}$$

3.5. Catalytic reaction

Table 3 presents the average results obtained from catalytic conversion reactions at 623 K, where samples 1 and 2 correspond to the aliquots withdrawn after 30 minutes and 60 minutes on stream, respectively.

This table reveals the decarboxylation activity of the catalysts by comparing the products' acidity measurements (Ma), in other words, the lower the acidity the greater the efficiency of the catalyst in the decarboxylation process. The acidity measure of the reactant, oleic acid, is also included in Table 3 for purposes of data comparison.

The catalytic activities are compared as a function of the generation of acidity in the liquid products, i.e., the ability to convert the oleic acid reactant into hydrocarbon products, using the following expression:

$$\text{Conversion (\%)} = \left(\frac{\text{Ma of oleic acid} - \text{Ma of products}}{\text{Ma of oleic acid}}\right) \times 100 \quad (1)$$

Table 2. Chemical shifts from ^{31}P NMR.

Sample	^{31}P-NMR chemical shifts (ppm)
Al_2O_3 - A	-
HP/Al_2O_3 - A	- 18.153 - 28.621
Al_2O_3 - B	-
HP/Al_2O_3 - B	- 11.846

Table 3. Summarized results of the catalytic tests with oleic acid at 623 K.

Catalyst	Samples	Ma (mmol acid/g product)	Conversion (%)
None (pure reactant)	-	3.67	-
None (thermal cracking)	1	3.66	0.27
	2	3.53	3.8
Al_2O_3 - A	1	0.36	90.2
	2	0.34	90.7
HP/Al_2O_3 - A	1	0.32	91.3
	2	0.32	91.3
Al_2O_3 - B	1	0.34	90.7
	2	0.33	91.0
HP/Al_2O_3 - B	1	0.15	95.9
	2	0.25	93.2

Table 4. Distribution of liquid products expressed in hydrocarbon ranges (weight %).

Catalyst	C_6 - C_{12} (gasoline range)	C_{14} - C_{18} (diesel range)	C_{19} - C_{22} (lubricant oil)	C_{22}^+
None	0	0	0	0
Al_2O_3 - A	0	0	100.0	0
HP/Al_2O_3 - A	2.6	15.0	78.7	3.7
Al_2O_3 - B	0	2.7	95.6	1.7
HP/Al_2O_3 - B	0	26.5	69.7	3.8

For the noncatalyzed reaction, the results suggest the occurrence of a thermal cracking process in the preheating zone of the reactor, which resulted in a small amount of liquid products.

Based on the experimental data, it is clear that the presence of a catalytic agent substantially increased the conversion of oleic acid. Comparing the pure supports, both aluminas presented the same catalytic activity (90% of conversion). The aluminas' catalytic performances were slightly enhanced by impregnating the supports with phosphoric acid, especially in the case of Al_2O_3 - B. As mentioned earlier, the incorporation of phosphoric acid in the aluminas increased their acidity but also decreased of their specific area. Hence, the catalytic promotion effect may be attributed mainly to an increase of the acidic properties of the support.

3.6. Gas chromatography

Table 4 presents the distribution of hydrocarbon products obtained from the catalytic conversion of oleic acid. Quantification of the liquid products was expressed taking into account the different hydrocarbon ranges, which was determined by using standard chromatograms for comparison.

No hydrocarbon product was detected in the noncatalyzed reaction. The presence of the catalyst promoted the formation of compounds in the range of gasoline, diesel oil and lubricant oil (mainly). The addition of H_3PO_4 to Al_2O_3 improved the selectivity for diesel oil.

The best biodiesel selectivity was achieved with HP/Al_2O_3 - B catalyst. The simultaneous analysis of the oleic acid decarboxylation (Table 3) with the chromatographic results allow us to conclude that the HP/Al_2O_3 - B catalyst is the most efficient one for the process, since it showed conversions of up to 96% and 26 w% of diesel oil production. This performance is probably related to its particular properties: it is a solid with a relatively high surface area, with a large quantity of mesopores and strong acid sites. Moreover, the linear phosphorous-aluminum interaction may be inferred to be a beneficial structure for promoting oleic acid decarboxylation.

4. Conclusions

The impregnation of both aluminas with phosphoric acid caused partial blockage of the pores due to the formation of aluminum phosphate, which was detected by XRD. The phosphoric acid was located mainly on the inner surface of the Al_2O_3 - A mesopores and preferentially on the external surface of Al_2O_3 - B support. The phosphorous-aluminum interaction was also dependent on the surface area: in the case of the Al_2O_3 - A support, the predominant interaction was through bridge-type bonding, while the Al_2O_3 - B showed linear phosphorous-aluminum linking. With regard to the catalytic tests, the impregnation of phosphoric acid improved the aluminas' decarboxylation properties. It can be concluded that both textural and acid properties play an important role in the catalytic performance of the conversion of oleic acid into biofuels and biolubricants. The HP/Al_2O_3 - B catalyst, which associated high total acidity with a large quantity of mesopores, presented a better catalytic performance in the oleic acid decarboxylation reaction.

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