Characterization of Catalysts Pt / γ-Al2O3 Prepared by Incipient Wetness Impregnation Method

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ABSTRACT

A platinum catalyst supported on gamma alumina was prepared by incipient wetness impregnation method, using as a precursor Platinum II acetylacetonate salt. Because the precursor salt is not soluble in water, a variant of the method, consisting of a milling was applied by mixing boehmite and a platinum salt. Once the physical mixture was homogeneous, drops of a solution of nitric acid 1:16 were added, this was achieved by modifying the pH of the surface of the boehmite, thus achieving impregnation the salt. Then platinum particles were anchored. To obtain oxides of platinum the calcination method was utilized; finally, the catalysts of metal oxides were reduced by exposure to a flow of hydrogen at 400 °C, obtaining as a product a Pt /γ-Al_2O_3, which can accelerate and direct the hydrodeoxygenation reaction of oxygenated organic compounds to make them into second generation biodiesel departing from first generation biodiesel. The catalysts were characterized by Raman spectroscopy, X-ray diffraction, scanning electron microscopy, IR analysis and EDS. With the interpretation of the results, the effectiveness of the preparation process was guaranteed, also their catalytic action to accelerate and direct the reaction of hydrodeoxygenation.

Keywords: Pt/ γ-Al_2O_3; biodiesel, oxygenated organic compounds.

1. Introduction

At present, about 80% of world energy demand is obtained by burning fossil fuels. This leads to a depletion of fossil energy resources, which are limited. This, in turn, has led scientists to think that the use of fossil fuels is the main cause of global climate change: the emission of pollutants as a result of combustion [1].
One option to reduce the consumption of fossil fuels and their impact on the environment is the use of renewable biofuels based on biomass processing, because they have a huge energy potential and can contribute to the reduction of greenhouse emissions. Such is the case of Biodiesel. The method of application of biodiesel and its blends with diesel fuel based on oil can be used in diesel engines without the need to perform significant engine modifications in them [2]. Disadvantages encountered in the application of first generation biodiesel are: susceptibility to oxidation under low temperature and high emissions of NOx [3]. In order to solve these drawbacks, there has been an increasing interest on the part of investigators in the development of methods of preparation of Pt catalysts for their application in catalytic processes of hydrodeoxygenation of methyl esters from vegetable oils and animal fats, so that they can transform the biofuel molecules from polyunsaturated into monounsaturated. This new biodiesel is known as second generation biodiesel.

In different publications, several methods have been reported that help obtain catalysts of palladium, platinum and nickel, among which we can mention: sulfurized NiMo catalysts prepared by incipient wetness impregnation method; catalysts of Pd on SiO_2 deposited by incipient wetness impregnation method; Pd/ImS3-12 catalysts on γ-Al_2O_3 deposited by the method of adsorption of palladium nanoparticles. This paper presents an effective method of preparation of catalysts for Pt/γ-Al_2O_3 by the wet incipient impregnation method, also the results of the characterization of the catalyzers that guarantee their catalytic action to manage and accelerate the reaction of hidrodesoxigenacion.

2. Experimental

- The necessary amounts of boehmite and Platinum II acetylacetonate, in order to obtain the percentages of active metal phase sought (3%, 5% and 7%) are weighed.
- A physical mixing of the catalyst support and the precursor salt are blended and subjected to a fine grinding process by mixing quantities of boehmite and Platinum II acetylacetonate.
- A solution volume ratio of 1:16 (water : acid) nitric acid is prepared.
- Once the mixture has been produced, the solution of nitric acid is added through a dripping process, until a smooth paste is formed.
- The paste is allowed to dry at room temperature for 48 hours.
- Once the paste is dry, an extrusion process is performed in order to obtain pellets cut to the same size, making sure that they won't be pulverized, since if this happens, the catalyst cannot be recovered after hydrodeoxygenation process.
- Subsequently all pellets are calcined at 510 °C in the presence of oxygen. The purpose of the calcination of the catalyst is for the water to be removed from the boehmite in order to obtain γ-

Al_2O_3; another aim of this calcination is for the acetylacetonate and the nitric acid to burn, in order to obtain the end oxides of platinum on γ-Al_2O_3 deposited.

- Finally the catalysts are subjected to a reduction process with hydrogen flow at 400 °C, through this, the conversion the oxides of platinum is achieved, eliminating all oxygen from all platinum oxides, obtaining Pt deposited on γ-Al_2O_3, ready to be used in the process hydrodeoxygenation.

3. Results and discussion

The characterization of catalysts Pt/γ-Al_2O_3 with 3%, 5% and 7% weight active phase was performed through Raman spectroscopy, X-ray diffraction, scanning electron microscopy and EDS. Then the results of these characterizations and the interpretation and discussion of results obtained are here included:

Figure 1 shows Raman spectra, which were used to monitor the preparation process of the catalysts of platinum on γ-Al_2O_3. The blue spectrum is the one that corresponds to the precursor platinum salt (II platinum acetylacetonate, PTACAC). The green spectrum shows the Raman signal of the mix in coordination (PTACAC + Boehmite = PTACACBO5), corresponding to obtain a 5 wt% platinum on gamma alumina, this indicates that the process of deposition of the precursor salt by the incipient wetness impregnation method was adequate, and pH modification helped the impregnation of salt, a new mix in coordination was obtained with very different peaks to those showed by the single precursor salt. This clearly shows that the catalyst of platinum oxide on gamma alumina OPTGA5 (preparation to obtain 5% by weight of Pt) doesn't show Raman characteristic peaks; this is due to the fact that the amount of platinum oxide deposited on the γ-Al_2O_3 is very small. It was also demonstrated that the process of calcination at 510 °C is suitable, because the characteristic peaks disappeared from the organic components of the mixture in coordination. Finally, the spectrum of the catalyst 5% by weight of platinum on gamma alumina (PTGA5) which was reduced to 400 °C and a pressure of 20 bar of hydrogen, doesn't show the characteristic Raman peaks, this is because Raman doesn't detect pure metals, regardless of the percentage of metal that the substance may contain.

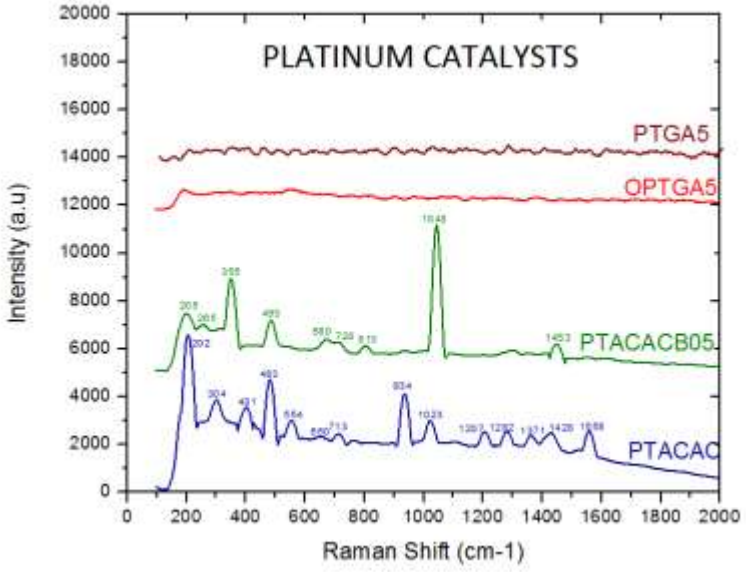

Figure. 1. Monitoring of the preparation process of platinum catalysts on γ-Al2O3 by Raman spectroscopy.

In Figure 2, the patterns of X-ray diffraction of the catalysts of platinum deposited on gamma alumina with 3% weight (PTGA3 display) show reflections in 2 θ of 32.6 °, in 37.2 °, in 39.8 °, in 46.25 ° and in 67.1 °. These reflections are characteristic of the gamma alumina phase (GA). Still an indication of the presence of metal particles of Pt can be noticed in the growth of the intensity of the reflections at 2 θ of 39.8 ° and 46.25 °. This phenomenon is consistent with several works published before [4], [5].

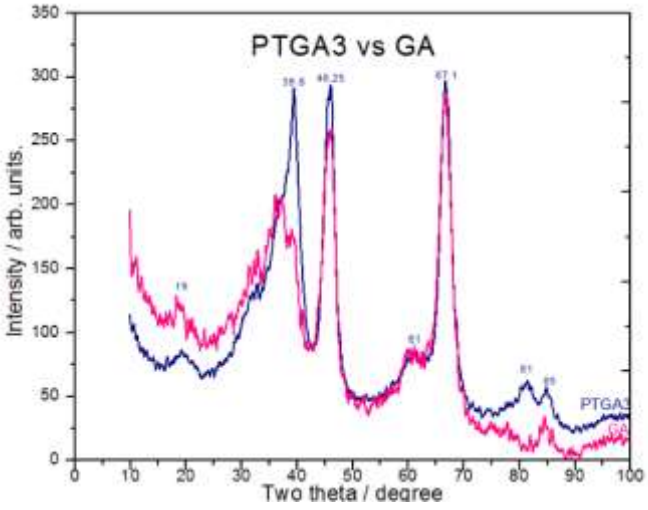

Figure 2. XRD patterns of the platinum catalyst on γ-Al_2O_3 with 3 wt% (PTGA3) and γ-Al_2O_3 catalyst support (GA).

Figure 3 shows the image of scanning electron microscopy of platinum catalysts deposited on gamma alumina with 3% weight. It is possible to observe crystals or clusters ranging in size from nanoscale and up to 7 μm.

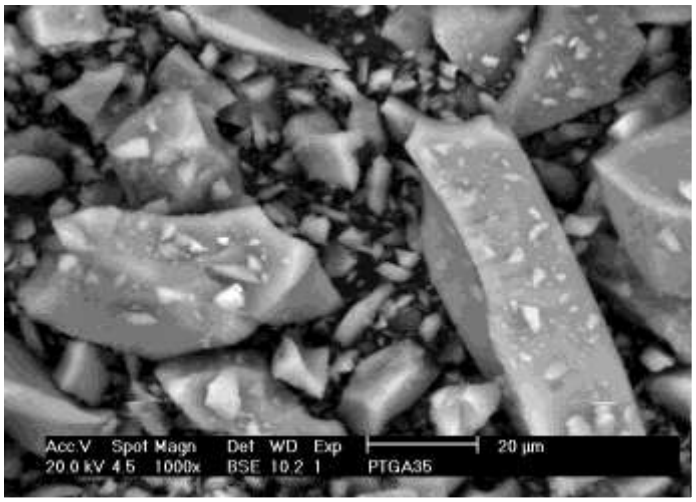

Figure 3. Image of scanning electron microscopy of platinum catalysts deposited on gamma alumina with 3% weight of active phase.

Table 1 shows the percentages of weight and the atomic percentage of platinum deposited on gamma alumina with a 3% weight of active phase. The data show that the amounts of reactants mixed and the preparation process of the catalysts were appropriate.

Table. 1. Average chemical composition by EDS for the platinum catalyst deposited on gamma alumina with 3% weight of active phase.

Catalyst	O		Al		Pt	
	Wt %	At %	Wt %	At %	Wt %	At %
PTGA3	38.995	53.465	56.59	46.035	4.41	0.495

4. Summary and perspectives

Through Raman spectroscopy it was found that the deposition process of the precursor salt of platinum carried out using the incipient wetness impregnation method was adequate; also the calcination process. Through the interpretation of patterns of X-ray diffraction, the presence of metal particles of Pt was proved, and the results of chemical composition by EDS showed that the amounts of reactants mixed and the preparation process of the catalysts were suitable.

With the results of characterization of the catalysts, it can be assured that these catalyzers will direct and accelerate the reaction of hydrodeoxygenation of oxygenated organic compounds in order to obtain second-generation biodiesel. The next stage of the project is to test the catalysts in a reactor containing first generation biodiesel, at controlled temperature and pressure of hydrogen, in order to determine the conditions under which the highest yield in the hydrodeoxygenation reaction can be obtained.

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6. References

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