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# Immersion Calorimetry for the Characterization of PD Catalysts Supported on Activated Carbon

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**Abstract:** Activated carbons obtained from coconut peel were oxidized using hydrogen peroxide. Superficial characteristics of these carbons were determined through N<sub>2</sub> and CO<sub>2</sub> isotherms and functional groups were characterized by TPD. Finally, the microcalorimetry technique was used in order to obtain the immersion enthalpies in diverse liquids and established the relation between them and the results obtained by the other characterization techniques. The results suggested that the immersion calorimetry allow establishing the difference between the supports and the catalysts.

**Keywords:** Catalysts, Activated carbon, Immersion calorimetry, Palladium.

## Introduction

The preparation of supported metallic catalysts is important for a great variety of chemical processes, in which the reactions of interest are facilitated and the energetic content of these processes is modified<sup>1-10</sup>. Mentioning a particular case, inquietudes as producing hydrogen with the lowest CO generation are still waiting for being solved. Here is where the catalyst selection is worthy of special attention. The metals that shall be used are required to undergo a dispersion process on a porous solid that preferably has a great superficial area to obtain a maximum of active phase. Generally, the highly dispersed catalysts possess a greater activity per gram of metal because they contain small metal crystals, allowing that a good proportion of the metal is available for the reactive molecules<sup>11-15</sup>.

The variables of interest during the catalysts preparation and which affect the properties of the final product are several. Among the most important are: (a) metallic precursor, (b) support,

(c) deposition technique of the metallic precursor on the support, (d) weight percentage of the metal on the catalyst, (e) catalyst activation procedure (reduction, sulphuration, *etc*) and (f) support chemical treatment. The palladium active sites are influenced by some factors, such as the particle size, support interaction and salts nature; among others. The present research study of palladium catalysts supported on activated carbon and the influence of the thermal and chemical treatment on the supports characteristics is analyzed.

## Experimental

For the preparation of the supports used in this study, activated carbon from coconut peel was employed by N<sub>2</sub> flux carbonization and posterior activation using water steam. From this material, diverse supports were obtained by different treatments. A portion of the carbon was left on its original state to be thermal and chemical treated (CA1-series). Another part of the carbon was purified with sulfuric acid for the reduction of the mineral ashes content and later was taken at 1273 K for four hours in nitrogen flux (100 mL min<sup>-1</sup>) to obtain the CA2 carbons.

The CA1 carbon was oxidized using 6 N hydrogen peroxide to introduce oxygen superficial groups. The procedure is as follows: 20 g of carbon were heated at mechanic vacuum at 453 K to be then cooled down at room temperature. 250 cm<sup>3</sup> of the oxidizing agent were added and the mixture was kept into contact during 72 hours with stirring at room temperature. Finally, the carbon was filtrated through a synerized glass plaque and washed with bidistilled water until peroxide absence. This way, the CA1OxP support was obtained. A part of the same carbon was later treated using a N<sub>2</sub> flux (100 mL min<sup>-1</sup>) during four hours at 780 K to eliminate the superficial groups that appeared to be less stable in order to obtain the CA1OxPT1 support.

The CA2 activated carbon suffered the same process than CA1, producing the CA2OxP and CA2OxPT1 carbons. The ashes content of the carbons CA1 y CA2 was determined by the standard method<sup>2</sup>.

The characterization of the carbons porous structure was carried out through the physical adsorption of N<sub>2</sub> at 77 K and CO<sub>2</sub> at 273 K using an automatic AUTOSORB 3B (QUANTACHROME). The superficial groups have been determined through the temperature desorption programmed technique (TPD) using a micromeritics equipment.

The samples (0,1 g aprox.) were set in a quartz microreactor and then treated with He flux (50 mL.min<sup>-1</sup>) for one hour. Afterward, they were heated at a velocity of 10 K min<sup>-1</sup> until 1273 K. The decomposition products (CO, CO<sub>2</sub> and H<sub>2</sub>O) were analyzed using a Balzers cuadrupolar mass spectrometer model MSC 200 bound to the reactor.

## Catalysts

Two different salts were selected for the preparation of the palladium catalysts on activated carbon: Pd(NO<sub>3</sub>)<sub>3</sub> and Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>. With the first precursor, the incipient impregnation method was applied, using an aqueous dissolution in the proportion of 0.5 mL per gram of support. For the Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>, the method of absorption in aqueous dissolution was employed. The supports were kept into contact with the dissolution during 12 hours and the supernatant was evaporated using a water bath.

In all cases, the dissolution concentration and volume was the appropriate for obtaining a palladium charge of approximately, 2% in weight. All catalysts were dried at 373-383 K overnight.

Four groups of catalysts were then obtained: one per each precursor, to which two series of supports correspond. The catalysts were called using the palladium symbol and the name of the support. The catalysts obtained by the palladium trinitrate(III) complex have been

distinguished by their symbol and oxidation state. So, Pd(III) CA2, shall be a palladium catalyst supported on the CA2 activated carbon and prepared from palladium nitrate and Pd(II) CA2 shall be a similar catalyst but prepared from tetraamminpaladio chloride(II).

The palladium dispersion on the catalysts has been carried out by the hydrogen chemical adsorption at 298 K; the samples previously degasified at vacuum at room temperature, were reduced in hydrogen atmosphere ( $50 \text{ mL}\cdot\text{min}^{-1}$ ) at 623 K for 12 hours. The catalysts were characterized through the physical adsorption of  $\text{N}_2$  at 77 K and of  $\text{CO}_2$  at 273 K using an automatic AUTOSORB 3B equipment and the programmed temperature desorption (DTP) with a micromeritics device.

For each catalyst, immersion calorimetries were determined; 0.1 g samples were desorbed at 383 K and at a vacuum of  $1 \times 10^{-5}$  mBar for 24 hours. Each sample was then put in a cell that contains the liquid in which the immersion was performed. Each measurement contains an electric calibration. In Figure 1, the general scheme of the microcalorimeter employed is shown<sup>16</sup>.

### Immersion enthalpies

The degasified sample in the glass ampoule was set inside the immersion microcalorimeter (Figure 1). Once the baseline becomes stable, the breakage of the ampoule inside the studied liquid takes place and an electric calibration was performed posterior to the generation of the thermal effect. The immersion enthalpies in NaOH and HCl were carried out using 1 N solution. Each determination was repeated five times. The immersion enthalpy in benzene,  $\Delta H_{\text{C}_6\text{H}_6}$ , was done controlling the samples interaction because this enthalpy shows superficial-type parameters.



Figure 1. Immersion calorimeter.

## Results and Discussion

The  $\text{N}_2$  and  $\text{CO}_2$  adsorption isotherms at 77K and 273 K respectively. The  $\text{CO}_2$  adsorption isotherms at 273K are shown in Figure 2.

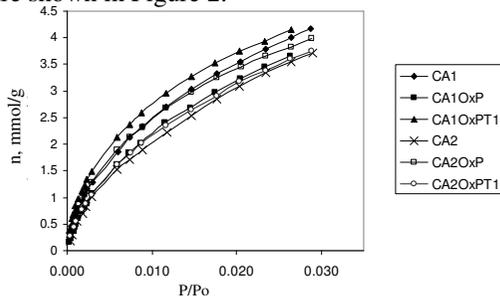


Figure 2. Carbon dioxide desorption isotherms at 273 K.

Table 1 summarizes the BET superficial areas and the micropores volume for each support obtained from the nitrogen adsorption isotherms and from the zone of relative low pressures of the N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms, respectively.

**Table 1.** Superficial areas and micropores volume corresponding to the employed carbonaceous supports.

Sample	N <sub>2</sub> at 77K		CO <sub>2</sub> at 273K
	SBET	VO(DR)	VO(DR)
CA1	820	0.37	0.30
CA1OxP	810	0.37	0.30
CA1OxPT1	887	0.40	0.21
CA2	950	0.43	0.29
CA2OxP	930	0.39	0.33
CA2OxPT1	980	0.39	0.30
Pd(III)CA1	567	0.27	0.22
Pd(III)CA1OxP	518	0.27	0.21
Pd(III)CA2	620	0.21	0.20
Pd(III)CA2OxP	600	0.20	0.15
Pd(II)CA1	510	0.18	0.14
Pd(II)CA1OxP	476	0.17	0.16
Pd(II)CA2	550	0.17	0.14
Pd(II)CA2OxP	510	0.16	0.16

As shown in Figure 2, the CA1 shows an inferior adsorption in the zone of relative low pressures, suggesting a narrow microporosity. Consequently, it presents the lowest micropores volume, as Table 1 illustrates.

The intermediate zone of the curve shows a quasi-horizontal slope, indicating a scarce mesoporosity. The CA2 support is found to be on the opposite side about both, the superficial area and the micropores volume, whereas an increase due to the purification process and thermal treatment appeared to take place. The posterior zone of the isotherm elbow, presents a more pronounced slope, indicating a greater development of the mesoporosity (pores widening). The augment of the micropores volume can be attributed to the impurities elimination (gasification).

The posterior treatment at 773 K of the oxidized CA1 carbon slightly increases the superficial area, at the same time that increases to some extent the micropores volume determined by the N<sub>2</sub> adsorption at 77 K. It is important to note the fact that the volume of the more narrowed micropores has considerably decreased as a consequence of the thermal treatment of this carbon. Also, the elbow of the isotherm seems to be wider. These facts are evidence of the greater porosity development, which is in accordance to the superficial area increase.

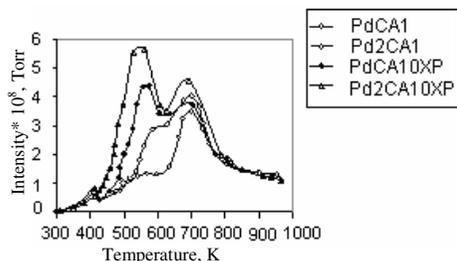
When the fixation of the palladium on the supports arises, the superficial area is modified and according to the ionic radii for both, the Pd<sup>3+</sup> and the Pd<sup>2+</sup> (0.0072 and 0.093 nm respectively), it may be observed that the area for the supports with Pd(III) is greater than their superficial area in relation with the catalysts obtained using Pd(II).

In general, the CA2 oxidation has the effect of diminishing both, the superficial area and the micropores volume without altering the most narrowed microporosity. A tendency to match between the isotherms may be seen in the final zone, indicating a similar macropores

distribution. The posterior thermal treatment of this material generates an isotherm extremely alike with the previous one. This same behavior can be observed with the CO<sub>2</sub> isotherms in Figure 2.

### Temperature programmed decomposition

The decomposition graphs at programmed temperature for the series CA1 catalysts are shown in Figure 3.



**Figure 3.** TPD Profiles for CO<sub>2</sub> of the CA1 supports.

The TPD results are summarized in Table 2.

**Table 2.** TPD of the catalysts on the activated carbons with different oxidation states.

Sample	CO, m mol g <sup>-1</sup>	CO <sub>2</sub> , m mol g <sup>-1</sup>	CO/CO <sub>2</sub>	O, m mol g <sup>-1</sup>
CA1	0.35	0.15	2.3	0.30
CA1OxP	1.12	0.28	4.0	0.53
CA1OxPT1	1.05	0.3	3.5	0.48
CA2	0.38	0.15	2.5	0.45
CA2OxP	1.45	0.55	2.6	0.60
CA2OxPT1	1.32	0.32	4.1	0.50
Pd(III)CA1	0.3	0.09	3.3	0.27
Pd(III)CA1OxP	0.93	0.22	4.2	0.36
Pd(III)CA2	0.35	0.09	3.9	0.37
Pd(III)CA2OxP	1.27	0.43	3.0	0.52
Pd(II)CA1	0.24	0.06	4.0	0.22
Pd(II)CA1OxP	0.86	0.17	5.1	0.28
Pd(II)CA2	0.2	0.06	3.3	0.31
Pd(II)CA2OxP	0.77	0.36	2.1	0.39

These results from TPD for the supports and catalysts. It may be seen that using the supports treated with hydrogen peroxide, the superficial groups containing oxygen, augment; as studies have previously reported. The same behavior may be seen for the catalysts obtained with Palladium. The relation CO/CO<sub>2</sub> particularly increases with the thermal treatment and the hydrogen peroxide

### Immersion calorimetry

In Table 3, the results of the immersion heats of each support and the catalyzed in benzene, water, sodium hydroxide and chloride acid are shown. It is important to remark that the immersion enthalpy does not become modified by the oxygen content of the material, which corroborates the observation that soft oxidation processes do not modify the structural properties of the original support, aspect confirmed by Barton<sup>17-18</sup>. There is a change in the

immersion enthalpies using benzene between the supports and the catalysts; which is coherent because the support structure changes once the palladium is fixed. This shows that the microcalorimetric technique allows establishing these differences.

**Table 3.** Immersion enthalpies for each catalyst.

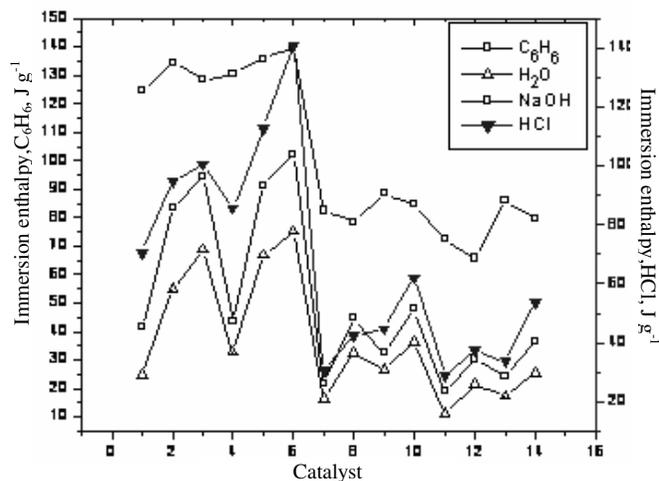
	$-\Delta H_{C_6H_6}$ , $J g^{-1}$	$-\Delta H_{H_2O}$ , $J g^{-1}$	$\Delta NaOH$ , $J g^{-1}$	$\Delta HCl$ , $J g^{-1}$	$\Delta Hi$ , $NaOH_{,net}$	$\Delta Hi$ , $HCl_{,net}$
CA1	124	24.9	41.5	70.5	16.6	45.6
CA1OxP	134	54.8	83.4	94.5	28.6	39.7
CA1OxPT1	128	68.7	94.6	100	25.9	31.8
CA2	130	32.7	43.5	85.7	10.8	53.0
CA2OxP	135	66.9	91.4	112	24.5	45.9
CA2OxPT1	139	75.2	102	140	27.1	65.6
Pd(III)CA1	82.5	16.5	21.6	30.5	5.10	14.0
Pd(III)CA1OxP	78.5	32.6	44.7	42.6	12.1	10.0
Pd(III)CA2	88.4	26.5	32.5	44.7	6.00	18.2
Pd(III)CA2OxP	84.6	36.5	47.9	62.1	11.4	25.6
Pd(II)CA1	72.7	11.2	18.9	28.7	7.70	17.5
Pd(II)CA1OxP	65.8	21.4	30.4	37.5	9.00	16.1
Pd(II)CA2	85.8	17.4	24.4	33.7	7.00	16.3
Pd(II)CA2OxP	79.5	25.3	36.7	53.6	11.4	28.3

In Figure 4 the immersion enthalpies are shown. Whether the behavior is carefully compared to the oxygen content ( $mmol g^{-1}$ ) reported in Table 2, it may be deduced that there is a direct correlation. The immersion enthalpies are greater in the three assayed molecules. The neutralization net enthalpy is the difference between the neutralization enthalpy and the immersion enthalpy in water,

$$\Delta Hi(NaOH)_{net} = \Delta Hi(NaOH) - \Delta Hi(H_2O) \quad (1)$$

and

$$\Delta Hi(HCl)_{net} = \Delta Hi(HCl) - \Delta Hi(H_2O) \quad (2)$$



**Figure 4.** Immersion enthalpies of the supports and catalysts.

It is shown that both, the net immersion enthalpies in NaOH that determine acid groups and the net enthalpies in HCl that establish basic groups, decrease in the catalysts, which is logical because part of the functional groups are used by the Palladium ions when these are fixed on the activated carbons.

This investigation shows that the microcalorimetry as technique may distinguish not only the functional groups, as previous studies by Moreno *et.al*<sup>18</sup> had already reported but the differences between the catalysts, and these results are complementary to the obtained through other techniques.

## Conclusions

The present study shows that the microcalorimetric technique is highly sensitive and that it can be used as a complementary method to establish changes in the chemical surface, not only of the supports for the catalysts according to their treatment, but for the same catalysts. The enthalpy values change according to the catalysts treatments.

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