

ACTIVITY ENHANCEMENT OF Pd/C CATALYSTS THROUGH OXIDATION OF ACTIVATED CARBON SUPPORTS

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Introduction

Activated carbon is an interesting material for the preparation of catalytic supports due to its high specific surface, high porosity and low reactivity. The porosity and surface chemistry of the supports can be controlled during the manufacture of the activated carbon and by further thermal or chemical treatment providing materials with tailor made properties. In addition to this, activated carbon supports have also been reported to play an important role in certain catalytic processes providing an efficient path for the reaction [1].

The performance of activated carbons as catalytic supports has been found to be determined by both their textural properties and surface chemistry [2]. In the case of metallic active phases supported on activated carbons, the surface chemistry is one of the determining factors in the metallic dispersion and the resistance to sintering, being of importance the role of surface oxygen groups [3]. The surface oxygen groups are considered to act as anchoring sites that interact with metallic precursors and metals increasing the dispersion, with CO evolving complexes significantly implied in this effect [3,4]. On the other hand, CO₂ evolving complexes, mainly carboxylic groups, seem to decrease the hydrophobicity of the support improving the accessibility of the metal precursor during the impregnation step.

Several methods based on reactions with oxidizing gases and oxidizing solutions have been described in literature to generate oxygen surface complexes in activated carbons [5]. In general, gas phase treatments require high temperatures, which can produce important changes in the textural properties and the loss of part of the surface oxygen. Liquid phase treatments can be applied at variable severity causing changes of different grades in the textural properties and the content of oxygen surface complexes [6,7]. The predominant type of surface groups generated is highly dependent on the oxidation method employed. Thus, it has been shown that gas oxidation with N₂O increases mainly the concentration of hydroxyl and carbonyl surface groups [8]. On the contrary, the treatment with a stream of gaseous ammonia enhances the basic properties of carbons at the expense of their acidic properties, giving rise to the occurrence of structures like pyridine after this treatment [9]. The oxidation in the liquid phase with nitric acid and hydrogen peroxide increase especially the concentration of carboxylic

acids and also fix, to a much greater extent, CO evolving-groups as ketones, quinones and phenols [10].

As a consequence of the modification on the surface chemistry of carbon supports enhancement of the activity of Pt/C in the hydrogenation of benzene has been reported [4]. Likewise, evidences of enhancement of the activity of Pd/C in the hydrodechlorination of 4-chlorophenol by nitric acid oxidation of the supports were found [11]. Thus, the pretreatment of active carbon supports is an important variable in the preparation of hydrogenation catalysts.

This work deals with the study of the influence of oxygen surface groups on the behavior of Pd/C catalysts. Several oxidative treatments were applied to active carbon supports in order to obtain supports with different amount and distribution of functional groups. The activity of the catalysts prepared from these supports were tested in the hydrodechlorination of 4-chlorophenol in aqueous phase.

Experimental

The catalytic hydrodechlorination of 4-chlorophenol with hydrogen was studied in aqueous phase in a trickle bed reactor provided with control of temperature, pressure, liquid flow and gas flow. A simplified scheme of the reaction set-up is shown in Figure 1. The hydrodechlorination reactions were carried out at 2.4 bar and 50-75°C. The starting concentration of 4-chlorophenol was 100 mg/L with a flow rate of 0.5 mL/min. Hydrogen was fed to the reactor diluted with nitrogen (50%, vol.) at a total flow rate of 100 NmL/min. The concentration of reaction products was determined by HPLC/PAD (Prostar, Varian) using a C₁₈ as stationary phase and a mixture of acetonitrile and water (1:1, vol.) as mobile phase, and by GC/MS (Saturn 2100 T, Varian) using a 30 m long x 0.25 mm i.d. capillary column (Meta X5 Tracsil 5). Previous to GC/MS analysis the aqueous samples were extracted with solid-phase cartridges (C₁₈, Waters), which were eluted with acetonitrile.

The Pd/C catalysts were prepared by incipient wetness impregnation of activated carbon of 1-2 mm particle size. The impregnation solution consisted on PdCl₂ dissolved in 0.1 N HCl. All catalysts were prepared with a palladium load of 0.5% (w) from a solution volume exceeding by 30% the pore volume of the support. After impregnation the catalysts were dried overnight at 100°C. Finally, the catalysts were reduced with hydrogen at 100°C for 1.5 h. Additional *in situ* reduction was carried out in the reactor at 100°C and 2.4 bar. Before the reaction the catalyst was saturated in 4-chlorophenol to minimize the effect of adsorption and reduce the time required to reach a steady state. The reactions were carried out with 0.5 g of catalyst.

Two series of supports, made in the laboratory from active carbons supplied by Chemviron (Centaur 1400) and Merck, were studied. The active carbons were subjected to oxidative treatments with nitric acid, hydrogen peroxide and ammonium persulfate. Nitric acid treatment was carried out by boiling 1 g of active carbon in 10 mL

of a 6 N solution for 20 min [3]. Oxidation with ammonium persulfate was performed by treating 1 g of active carbon in 10 mL of 1 M solution at room temperature [12]. In the peroxide treatment 1 g of active carbon was placed in 10 mL of 35% (w/v) hydrogen peroxide for 24 h at room temperature [13]. After all treatments the samples were washed with distilled water until neutrality and dried overnight at 100°C. All supports were characterized by N₂ adsorption at 77 K (Quantachrome, Autosorb-1) by applying the BET equation to the N₂ adsorption isotherm. The chemical nature of the surface of active carbons was studied by X-ray photoelectron spectrometry (XPS) and temperature-programmed desorption (TPD). XPS measurements were made with a Physical Electronics model 5700 equipment with a Mg-K α X-ray excitation source (1253,6 eV). TPD experiments were carried out by heating the samples up to 900°C in He flow at a heating rate of 10 K/min and recording the amounts of CO and CO₂ evolved with a GC (Siemens, model Ultramat 22).

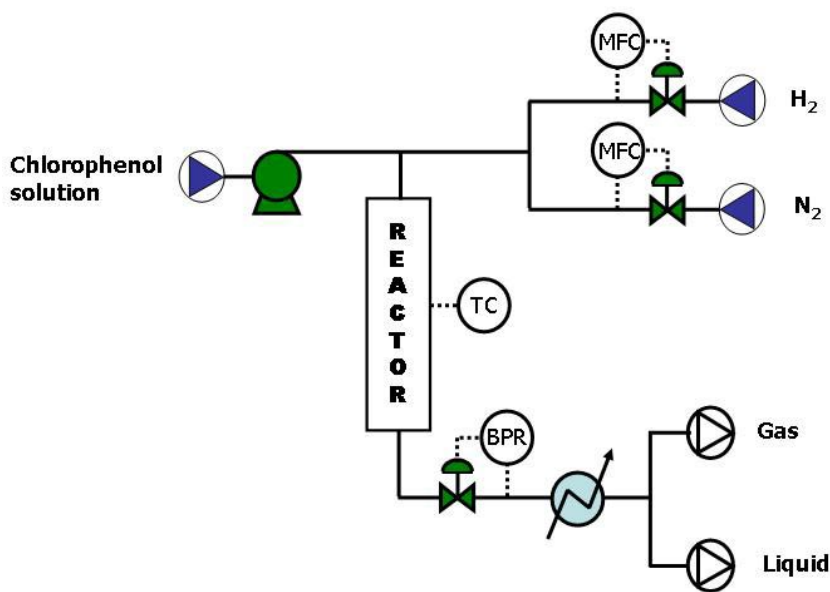


Figure 1. Scheme of the reaction set-up

Results and Discussion

The study was based on the use of active carbons of different characteristics as catalytic supports. The untreated active carbons employed had different textural properties as it can be seen in Table 1. Chemviron carbon showed a BET area and pore volume 50% higher than those of Merck carbon. The unmodified active carbons also exhibited differences in surface chemical nature, as it can be appreciated from the XPS results summarized in Table 2. The atomic O/C ratio was slightly higher for Merck carbon (0.066) than for Chemviron carbon (0.056), being especially relevant the higher content in phenolic and ether group. On the contrary, Chemviron carbon showed a significantly higher amount of carboxylic acid.

The treatment with nitric acid did not lead to an important modification in the textural properties of none of the active carbons. In the case of Merck carbon, both hydrogen peroxide and ammonium persulfate gave rise to a noticeable reduction in BET area and pore volume. However, for Chemviron carbon only the treatment with ammonium persulfate modified the pore structure. In all cases the decrease of surface area can be mainly attributed to the breakage of micropore walls [14].

Table 1. Textural properties untreated and treated activated carbons

Sample	Treatment	BET area (m ² /g)	External area (m ² /g)	Micropore vol. (cm ³ /g)	Mesopore vol.* (cm ³ /g)
ChU	None	1392	110	0.549	0.044
ChN	HNO ₃	1320	102	0.525	0.041
ChHP	H ₂ O ₂	1386	114	0.542	0.049
ChS	(NH ₄) ₂ S ₂ O ₈	716	71	0.270	0.030
MkU	None	917	119	0.332	0.041
MkN	HNO ₃	932	126	0.330	0.046
MkHP	H ₂ O ₂	748	93	0.267	0.037
MkS	(NH ₄) ₂ S ₂ O ₈	494	85	0.158	0.033

* 20 < D < 80 nm

Table 2. XPS results for the C 1s and O 1s peaks of activated carbons

Sample	C (%)	O (%)	O/C	Deconvolution O 1s peak (% of peak)		
				Carbonyl, quinone	Phenol, ether, lactone, carboxylic anhydride	Carboxylic acid
ChU	93.8	6.2	0.066	25.8	33.1	26.1
ChN	90.3	8.7	0.096	32.2	26.8	18.7
ChHP	93.4	6.5	0.069	28.3	36.0	18.4
ChS	78.7	18.9	0.240	31.7	41.8	16.9
MkU	94.5	5.3	0.056	25.1	26.6	22.3
MkN	89.9	9.5	0.106	27.4	32.8	20.5
MkHP	93.7	6.1	0.065	20.8	19.1	36.1
MkS	79.1	18.8	0.238	40.6	21.1	15.6

The XPS results, shown in Table 2, indicate an important modification in the chemical nature of the carbons surface as a consequence of the oxidation treatments. The higher rise in surface oxygen groups was observed for the oxidation with ammonium persulfate, which provided an atomic concentration of oxygen close to 19% for both activated carbons. Likewise, this treatment increased the O/C ratio up to 0.238 and 0.240 for Chemviron and Merck carbon, respectively. During the oxidation with nitric acid the surface oxygen content increased by 40-80% and the O/C ratio by 45-89% in spite of the low loss of textural properties observed for this treatment. The lower rise in oxygen content was observed for the hydrogen peroxide oxidation.

The oxidative treatments also modified the distribution of oxygen surface groups (Table 2). All the treatments increased the content in carboxylic and ester group. An especially significant increase in phenolic, ether, carboxylic anhydride, lactone and carboxylic acid was observed for ammonium persulfate oxidation; these groups amounted for more than 63% of the O 1s peak. These results are in agreement with the TPD profiles shown in Figure 2 and data summarized in Table 3, where it can be seen that a higher amount of CO and CO₂ is evolved from the carbons treated with ammonium persulfate and nitric acid. After these treatments the increase of evolved CO₂ was higher than that for CO, which is indicative of the generation of a higher proportion of acidic groups. Likewise, relevant peaks are observed between 175-250°C and around 400°C for the CO₂ evolution profile, which can be attributed to carboxylic acids and carboxylic anhydrides, respectively. The amount of CO₂ evolved is also significantly higher above 600°C for the Chemviron carbon oxidized with nitric acid. For both carbons the treatment with nitric acid increased the amount of CO evolved above 700°C.

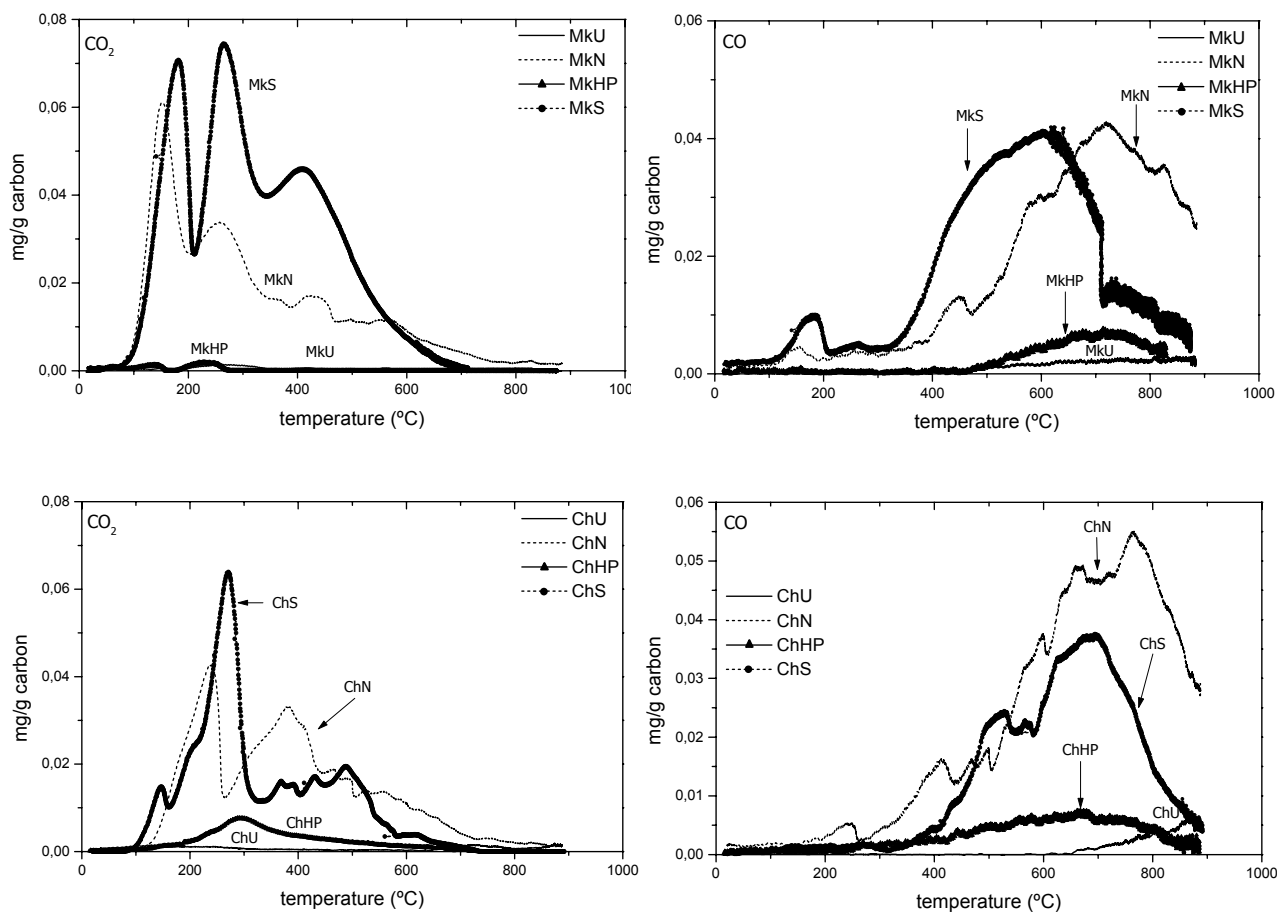


Figure 2. TPD profiles for untreated and treated activated carbons

Table 3. Data from the deconvolution of TPD profile for evolved CO and CO₂

Sample	CO ₂ evolved (mg/g)	CO evolved (mg/g)	CO/CO ₂ ratio
ChU	6	10	1.7
ChN	65	163	2.5
ChHP	8	24	3.0
ChS	62	85	1.4
MkU	1	10	10
MkN	55	123	2.2
MkHP	1	17	17
MkS	116	176	1.5

The characterization of the catalysts made from the different supports indicated that no significant modifications in the amount and distribution of oxygen surface groups took place during the catalysts preparation procedure. Only a slight loss of BET area and pore volume took place during impregnation. The results of the activity experiments for the hydrodechlorination of 4-chlorophenol are shown in Table 4. In general the oxidative treatments enhance the activity, although some deviations can be observed; the oxidation with hydrogen peroxide of Merck carbon resulted in a loss of activity, whereas this treatment provided the highest activity for Chemviron carbon series. The lower activity for nitric acid treated Chemviron carbon can be considered as non significant. The textural properties of the supports cannot explain the different behavior of the catalysts. For instance, the catalyst made with the support oxidized with ammonium persulfate shows the highest activity within the Merck series in spite of the fact that this catalyst has the lowest BET area and pore volume. These results evidence the important role of surface functional groups on the catalytic activity.

Table 4. Results of the catalytic activity experiments

Catalyst	Conversion (%)		Selectivity at 75°C*		
	50°C	75°C	phenol	cyclohexanone	cyclohexanol
ChU-Pd	96.0	99.0	0.213	0.308	0.479
ChN-Pd	95.7	98.3	0.015	0.023	0.963
ChHP-Pd	99.9	100	0.217	0.274	0.509
ChS-Pd	98.7	99.9	0.562	0.404	0.034
MkU-Pd	85.4	86.8	0.426	0.338	0.236
MkN-Pd	96.9	97.5	0.186	0.447	0.366
MkHP-Pd	78.7	80.2	0.430	0.166	0.404
MkS-Pd	98.8	99.6	0.350	0.482	0.168

* mass/total mass of organic compounds

The activity results obtained for the Merck series show that in general a high O/C ratio of the support leads to enhanced activity, although there are some deviations such as the low activity of the catalyst prepared from the support oxidized with hydrogen peroxide. This deviation can be explained in terms of the nature of the functional groups generated during the oxidation. Thus the occurrence of acid groups seems to be of importance for the activity. In the oxidation with nitric acid and ammonium persulfate the CO/CO₂ ratio is lowered by 78 and 85%, respectively, showing a drastic increase in the acidity of the support. On the contrary, the treatment with hydrogen peroxide increased the CO/CO₂ ratio, which can explain the loss of activity with respect to the catalyst of untreated support. For the Chemviron activated carbon, the untreated support already exhibit a lower CO/CO₂ ratio than untreated Merck support, which is responsible for the higher activity of the catalyst from untreated Chemviron carbon, although the textural properties of Chemviron carbon can also be determinant. Within the Chemviron series all the supports have low CO/CO₂ ratios and the conversion provided for all the catalysts is well above 95%. For this series the activity do not show a clear dependence on CO/CO₂ ratio. This may indicate that below a certain CO/CO₂ ratio other factors can also be of importance for catalytic activity. Thus, the catalyst of higher activity within the Chemviron carbon series, ChHP-Pd, has a less degraded structure than ChS-Pd catalyst.

The catalysts of higher activity showed in general a higher selectivity towards cyclohexanone and cyclohexanol, the less toxic products of the reaction chain. An exception to this trend can be found for the catalyst prepared from supports oxidized with ammonium persulfate, in spite of the very high activity of these catalysts. On the other hand, the reactions carried out with the catalysts from supports treated with nitric acid yield the lowest proportion of phenol in the reaction products. These facts can be indicative of the important role of functional groups in the reaction pathway, which requires further work to be elucidated.

Conclusions

The treatment of activated carbons with nitric acid, hydrogen peroxide and ammonium persulfate led to a higher content in surface oxygen groups. The nitric acid and hydrogen peroxide treatments resulted in higher oxygen content and acidity of the support. Nitric acid only modified slightly the textural properties, in contrast to ammonium persulfate. The increase in the activity of the supports was found to improve the activity of the catalysts prepared. Thus, for Merck carbon nitric acid and ammonium persulfate enhanced the activity whereas hydrogen peroxide decreased the activity. Within the Chemviron series all the supports showed an important acidity and very high activities were observed, being of importance the differences in textural properties in order to interpret the differences in activity.

Acknowledgements

We greatly appreciate financial support from the Spanish Ministerio de Ciencia y Tecnología (project PPQ2000-1763-CO3-01) and the Comunidad Autónoma de Madrid (project 07M/0039/2002), and the samples of Chemviron carbon provided by Aguas de Valencia, S.A.

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