Preparation of Pd/AC Catalyst by Ion Exchange

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Abstract

By choosing appropriate liquid oxidizing treatment, the carbonaceous surface of an activated carbon (AC) can be functionalised with carboxylic groups in a broad range of content. These carboxylic groups are necessary functions, in order to disperse, perfectly, palladium cations through exchange reactions: H^+/Pd^{2+} or $H^+/Pd(OH)^+$. Reduction in liquid phase of a 4 mass % Pd/AC whose carbonaceous surface was previously oxidized by NaOCl leads to palladium particles with a particle size of 1.5 nm which are much smaller than Pd particles obtained from a 4 mass % Pd/AC whose carbon surface was not oxidized. The well dispersed catalyst was tested in hydrogenation of cinnamaldehyde and exhibits quite a high hydrogenation efficiency as compared to activities reported in the literature.

INTRODUCTION

Noble metal catalysts supported on activated carbon (AC) are widely used in fine chemical industry. The chemical inertness and the possibility of recycling catalyst by recovery of the metal after burn off are the main advantages of carbonaceous materials [1]. Oxidizing treatments can be used to functionalise the carbon surface through the formation of surface oxygen groups (mainly carboxylic acids and phenolic groups). Gas phase oxidation mainly increases the content of hydroxyl and carbonyl surface groups, while liquid phase oxidation enhances especially those of carboxylic groups. This modification of the carbon surface will have a strong effect on metal adsorption which can occur through different interactions. Among them, ion exchange process may be written as follows:

$$M^{n+} + n[H^+]_{solid} \rightleftharpoons [M^{n+}]_{solid} + nH^+$$

This ion exchange process will have the advantage of dispersing perfectly the metal ions on the surface of the carbonaceous support. Therefore this work will deal particularly with the deposition of palladium on oxidized AC through this method of preparation. We will show that both the nature of the liquid oxidant and the treatment conditions are important in order to deposit the desired amount of palladium. Another point approached is the reduction the conditions of which will shape the size of the palladium particles.

Thus this study will be mainly focused on: (*i*) the characterization of an industrial support before and after oxidizing treatment, (*ii*) the adsorption of palladium in solution and (*iii*) the characterization of the palladium particles after exchange. Finally a Pd/AC with a required amount of noble metal will be compared to a catalyst prepared by impregnation of the initial support in the catalyzed selective hydrogenation of cinnamaldehyde.

EXPERIMENTAL

Supports and characterization

The starting material was an activated carbon L3S supplied by CECA. Carbon L3S was oxidized according to experimental conditions summed up in Table 1.

BET specific areas were determined by N_2 adsorption at 77 K with a Micromeretics ASAP

TABLE 1
Characteristics of the activated carbons before and after oxidation

Support	Oxidizing conditions	S_{BET}, m^2/g	V_{mic}, cm^3/g	S_{EXT}, m^2/g	pH_{PZC}	CO_2[a], mmol/g
L3S	–	901	0.24	391	8.2	0.07
L3S-NA1	HNO_3 1 M, reflux, 1 h	805	0.21	354	4.2	0.81
L3S-NA13	HNO_3 13 M, reflux, 1 h	790	0.21	350	3.9	1.68
L3S-B	NaOCl 30 mass %, 273 K, 5 h	820	0.23	334	4.0	1.13
L3S-OW	H_2O_2, 298 K, 4 days	749	0.19	337	4.3	0.76

[a]From thermodecomposition experiments.

2000 apparatus. Microporous properties and external surface area were estimated using the *t*-plot method with a carbon black reference [2].

The oxygen surface groups of the supports were characterized by temperature programmed desorption (TPDec–He) of the decomposition products. The supports (0.02 g) were heated (5 K/min) under helium flow (25 ml/min) from room temperature up to 1073 K. The effluent composition was continuously monitored by on line sampling by a quadrupole mass spectrometer (Pfeiffer Omnistar).

The pH values at the point of zero charge (pH_{PZC}) were measured using the so-called pH "drift" method [3].

Ion exchange experiments

The total sodium exchange capacity was determined by agitating activated carbon in NaCl/NaOH solution (m/V = 6.6 g/l) at 500 rpm for 48 h at room temperature. After extensive washing and filtering, the Na quantity was determined by elemental analysis.

Commercial $Pd(NH_3)_4(NO_3)_2$ solution (Strem Chemical) was added to Na-exchanged supports at room temperature (pH 6; m_{CA}/V = 6.5 g_{CA}/l). When equilibrium was reached, the suspension was filter, washed several times and dried at 353 K. The quantity of palladium adsorbed (q_e) was determined by the difference of the metal ion concentration before exchange (C_0) and after equilibrium and washing (C_e).

Catalyst reduction and characterization

The reducibility of the catalysts was determined by temperature-programmed reduction experiments (TPR) from 273 to 523 K in a H_2/Ar (3/97) mixture in the same apparatus than the TPDec–He experiments.

XRD powder patterns were collected on a Brucker AXS D8 Advance diffractometer using a CuK_α radiation (λ_{Cu} = 0.15401 nm) with a step size of 0.02°, on a 15–75° 2θ range.

TEM analysis were performed with a JEOL 1200 EX II instrument operating at 80–100 kV.

Catalytic test

The liquid phase hydrogenation of cinnamaldehyde was carried out in a sealed stainless-steel autoclave (Engineers Autoclave 0.1 l) at 333 K under 1 MPa H_2 pressure. The prereduced Pd/AC catalyst (0.05 g) was reactivated in solvent (cyclohexane) at 333 or 423 K under 1 MPa H_2 pressure for 2 h in the autoclave (1200 rpm). Samples were withdrawn periodically and analyzed on a gas chromatograph (HP-4890D) using an RTX S-Amine capillary column (30 m × 0.25 mm × 0.52 μm).

RESULTS AND DISCUSSION

Carbon supports

Textural properties. Figure 1 shows the N_2 adsorption–desorption isotherms of the original and modified activated carbons at 77 K. The nitrogen adsorption isotherms are Type I which corresponds to microporous solids. The hysteresis loop may be due to some interlayer space filling or to the contribution of some mesoporosity. The surface area and pore volume values obtained from these isotherms are summarized in Table 1. Support external surface area and

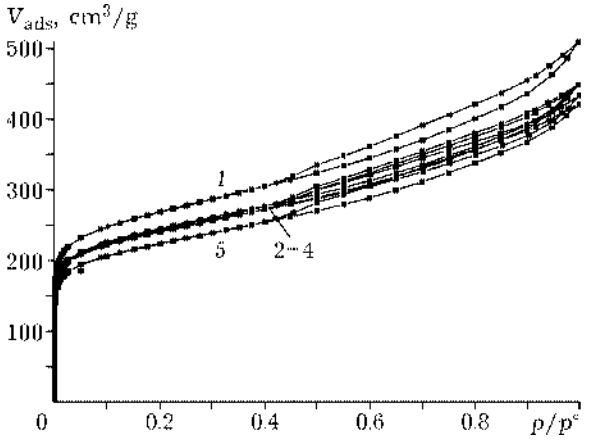

Fig. 1. N_2 adsorption–desorption isotherms: *1* – L3S; *2* – L3S-NA1; *3* – L3S-NA13; *4* – L3S-B; *5* – L3S-OW.

microporous volumes are not modified significantly after the oxidizing treatment. The loss of surface area and micropore volume is generally explained by the restricting pore volume available for N_2 uptake due to the formation of oxygen groups at the entrance and/or on the walls of micropores and by the potential destruction of micropore walls [4, 5]. Nevertheless, the H_2O_2 treatment leads to the highest change of the textural properties of L3S.

Quantification of the acidic functional groups by Temperature-Programmed Decomposition (TPDec–He). From the heating of activated carbons under inert atmosphere CO, CO_2 and H_2O vapours evolve [6]. Generally, CO_2 appears at lower temperatures than CO and results from the decomposition of carboxylic, anhydride and/or lactone groups. The CO_2 emission profiles of the different samples (not shown) have the same shape and have been coarsely divided into three parts. According to the literature [6], the two parts below 700 K correspond essentially to the decomposition of carboxylic acids, which represents, here, 80 % of the CO_2 evolved. The quantities of CO_2 corresponding to the decomposition of carboxylic acids for the different supports are reported in Table 1. These results show that a large range of concentration of carboxylic acid function can be formed at the carbon surface. Therefore, by using appropriate conditions, a determined value of acidic function can be reached. It is obvious that drastic conditions, like refluxing HNO_3 13 M, lead to the higher amount of carboxylic acid groups on the L3S surface. As shown previously, no significant change of textural properties was observed for this material.

Preparation and characterization of Pd supported oxidized L3S

Ion exchange experiments. The ion exchange experiment conditions were determined by measuring PZC. The pH_{PZC} of the starting L3S material is 8.2. After treatment, this value decreases in the range pH 3–5 depending on the oxidizing agent. Above the PZC value, the overall surface is negatively charged. The cationic exchange can therefore be achieved in an aqueous solution with a pH above 5.0, for oxidized samples, and 9.0, for the initial activated carbon.

Preexchange with sodium: exchange capacity measurement. A preexchange with sodium has been performed in order to determine the ion exchange capacity of the carbon sample. This H^+/Na^+ reaction of exchange is rather slow and requires an equilibrium time, from at least 48 h. The quantity of sodium introduced increases with the number of carboxylic functional groups (Table 2). Figure 2, *a* shows a good correlation between the sodium uptake and the number of acidic functions but the ratio Na^+/H^+ (mmol/mmol), 0.75, deduced from the linear curve fit, is inferior to the unit value. We may explain this lower value than the one expected by: *(i)* an overestimation of the exchangeable H^+ from the TPDec–He analysis and by *(ii)* a certain non-accessibility of the acidic functions to Na^+ cations since some acidic functions can be incorporated inside the microporous network.

TABLE 2

Cation uptakes of activated carbons before and after oxidation

Support	Na uptakes, mmol/g	Pd uptakes, mmol/g	Content of Pd, mass %
L3S	0.12	0.09	0.95
L3S-NA1	0.43	0.29	3.08
L3S-NA13	0.97	0.69	7.34
L3S-B	0.80	0.44	4.68
L3S-OW	0.39	0.27	2.87

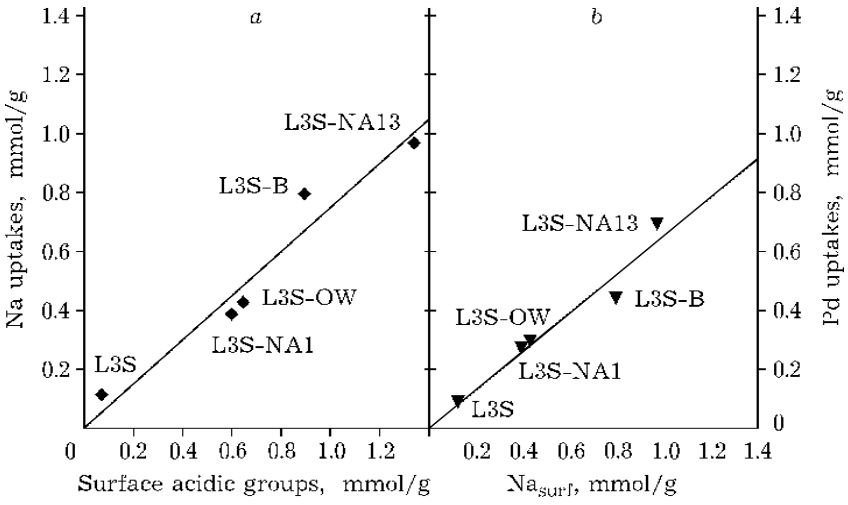

Fig. 2. Relationship between: *a* – Na uptakes *vs.* surface acidic groups; *b* – Pd^{2+}/Na^{+} exchange.

Sodium exchange by palladium cations. The Na-activated carbon sample are then exchanged with palladium cation from tetramine palladium nitrate aqueous solution. The preliminary kinetic studies assess that equilibrium is reached in 1 h but 5 h of contact were preferred. After washing, filtration and drying, the solids were back exchanged in HCl solution and more than 95 % of palladium was then released in the solution. Therefore, very few palladium elements remained trapped in the carbonaceous network. These results allow the assumption of an almost reversible adsorption of palladium through an ion exchange mechanism involving the acidic functional groups.

The palladium adsorption isotherms on oxidized carbons have been established (not shown). As expected, the adsorption capacities of palladium are enhanced with the oxidizing treated samples compared to the starting material.

Na released in the solution after total palladium adsorption is equal to the initial sodium capacity. The relation between initial Na content and Pd maximum uptake is described in Fig. 2, *b*. The Na^{+}/Pd^{2+} ratio, close to 1.5, is very inferior to 2.0. A Na^{+}/Pd^{2+} ratio equal to 2.0 corresponds to the following cation exchange reaction:

$$[Pd(NH_3)_4(H_2O)_2]^{2+} + 2Na^{+}...[^{-}OOCR]_2L3S \leftrightarrow [Pd(NH_3)_4(H_2O)_2]^{2+}...[^{-}(OOC)R]_2L3S + 2Na^{+}$$

Nevertheless, hydrolysis of $[Pd(NH_3)_4(H_2O)_2]^{2+}$ may occur with the formation, for example, of $[Pd(OH)(NH_3)_4(H_2O)]^{+}$ and may explain the lower Na^{+}/Pd^{2+} ratio observed. Similar observations have been noticed with other metals [7–9]. Jia and Thomas have studied the Na^{+}/Cd^{2+} exchange and they have found a ratio of 2 at low equilibrium concentration but noticed a slight decrease at higher concentrations [7].

The adsorption mechanism is not well known, nevertheless it is certain that acid carboxylic groups are involved in the palladium adsorption. Without these functions, the L3S activated carbon only adsorbs 0.09 mmol/g, eight times less than after treatment with HNO_3.

Metallic palladium particle size. Preparation by ion exchange of 4 mass % Pd/AC can be performed easily from L3S previously oxidized in liquid phase. The NaOCl oxidation was preferred for practical, safety and economical reasons. Moreover this procedure does not modified textural properties as some other oxidants do. Then, the sample was reduced either in formaldehyde solution at room temperature (L3S-B-F) or in hydrogen flow at 523 K (L3S-B-523) and, 773 K (L3S-B-773).

Reduction of palladium cations in liquid or in gas phase affects the particle size as shown on XRD patterns reported in Fig. 3. The liquid-reduced sample does not present any diffraction peak, demonstrating thus Pd particle size inferior to 2 nm, whereas reduction with hydrogen results in the presence of a diffraction peak indicating a particle size broadening. Reduction in H_2 flow at 523 and 773 K gives the same results. TEM analysis corroborate the particle sintering (not shown). The average metal

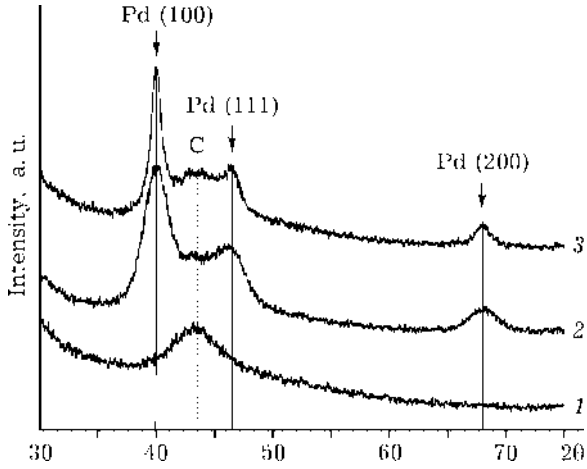

Fig. 3. XRD patterns of Pd/AC: *1* – L3S-B-F; *2* – L3S-B-523; *3* – L3S-IMP-F.

particle size shifts from 1.5 to 4.0 nm after reduction at 523 K which could be explained by acid carboxylic groups decomposition. To confirm this assumption, TPR experiment was monitored by mass spectroscopy. The CO_2 and CO emissions during reduction confirm carboxylic groups decomposition. The H_2/Pd ratio during reduction was superior to 1, which is the stoechiometric ratio to reduce Pd^{2+} in Pd^0. Dantas Ramos *et al.* observed the same behavior with carbon supported palladium catalysts. They attributed the hydrogen overconsumption either to (*i*) spillover phenomena, catalyzed by the surface oxygen groups: hydrogen that splits over the support could stay adsorbed onto the surface or to (*ii*) reduction of surface groups and hydrogasification reactions. This last point confirms the role of carboxylic anchoring groups to stabilize palladium cations.

A catalyst was prepared by impregnation on L3S support, which has no significant amount of carboxylic groups on the surface, with same amount of metallic precursor and with reduction in formaldehyde solution. In this case, an average particle of 11.4 nm was measured from XRD analysis. This ascertains the efficiency of the ion exchange technique to prepare well dispersed 4 mass % Pd catalyst.

Catalytic tests

Prior to the reaction, the pre-reduced catalyst was activated *in situ* at 333 or 423 K under the reaction hydrogen pressure. Typically, cinnamaldehyde (CAL) hydrogenation leads to a mixture of cinnamyl alcohol (COL), saturated hydrocinnamladehyde (HCAL) and phenylpropanol (PP). With palladium catalysts, the adsorption of cinnamaldehyde through C=C bond is favoured [11]. We also observe this property since no cinnamyl alcohol was detected. The final products are thus composed of hydrocinnamaldehyde and the fully hydrogenated product.

The reduction temperature decreases the initial rate of reaction by ten between reduction at room temperature by formaldehyde to 773 K in hydrogen flow (Table 3). The total hydrogenation rates are lower than those found by Giroir-Fendler *et al.* [12] with Pd ion-exchanged catalysts (4 mass % Pd/AC, d_{TEM} = 1.7 nm). However, the use of isopropanol/water as solvent compared to apolar solvent could explain this difference [11]. The HCAL selectivity of 76–87 at 40 % conversion is generally higher as compared to those found in the literature [13].

TABLE 3

Some properties of the catalysts in the hydrogenation of cinnamaldehyde

Catalyst	Activation temperature, K[a]	V_0, 10^4 mol/(s · g_{Pd})	HCAL selectivity, % mol[b]
L3S-B-F	333	78	87
	423	39	86
L3S-B-523	333	43	85
	423	15	87
L3S-B-773	333	8	76
L3S-IMP-F	333	36	80

[a]Temperature of *in situ* activation before the catalytic test.

[b]Determined at 40 % conversion.

The temperature of the *in situ* reactivation process before the catalytic test also influences the activity. There is a two fold decrease of the rate when the activation temperature goes up from 333 to 423 K. The decrease of rate can be assigned to an increase of Pd particle size. The XRD analysis of L3S-B-F shows a shift from 2 to 12 nm of the mean Pd particle size on the used catalyst after the catalytic run.

CONCLUSION

The carbonaceous surface can be functionalised with carboxylic groups in a broad range of content by modifying the conditions of the oxidizing liquid treatment. These carboxylic groups are necessary functions, in order to disperse, perfectly, palladium cations through exchange reactions: H^+/Pd^{2+} or $H^+/Pd(OH)^+$. Reduction under mild conditions, for example in formaldehyde solution at room temperature of a 4 mass % Pd/AC leads to the higher dispersion of the palladium phase by preventing sintering. The resulting catalyst contains palladium particles of 1.5 nm size which are much smaller than the particles of a 4 mass % Pd/AC the carbon surface of which was not oxidized.

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