

Preparation and Characterisation of Dispersed Palladium Catalysts Supported on Carbon Previously Treated with Different Strong Oxidants

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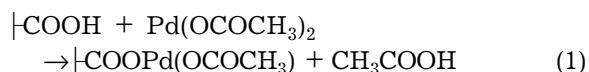
Abstract

Dispersed palladium catalysts supported on carbon were prepared using different strong oxidants for preliminary treatment of the support. The surface properties of carbon and its ability to give place to highly dispersed Pd were discussed. Oxidative pre-treatment was shown to promote the dispersion significantly increasing the catalytic activity.

INTRODUCTION

It is well known that carbon is a useful support to obtain well-dispersed palladium catalysts, because of its high surface area (500–1000 m²/g) and low costs. The interaction between the palladium precursors and the carbon surface occurs mainly through the oxygen containing surface groups, such as: lactones, carboxylic, carbonyl and phenolic groups. They are by far the most important groups influencing the surface characteristics and adsorption behaviour of activated carbon. Their amount is, in general, highly dependent on the way of preparation and can be strongly increased by oxidation with molecular oxygen at a temperature close to the ignition point (400–420 °C) [1, 2] or by contacting the carbon surface with an aqueous solution containing a strong oxidant, such as: KMnO₄, H₂O₂ or HNO₃ [3]. The precise nature of carbon-oxygen structures is not well established. However, a large number of methods exists in literature, such as Boehm titrations [1] which allow to evaluate the distribution of the different oxygenated surface sites by determining, for example, the concentration of the surface carboxylic and hydroxyl groups on the carbon surface.

In this work, a series of catalysts has been prepared *via* ion exchange by supporting palladium acetate on the surface of activated carbon, previously treated with an aqueous solution containing different oxidants, such as: potassium permanganate, nitric acid, sodium hypochlorite and hydrogen peroxide. All the prepared catalysts were submitted, first of all, to titration analyses in order to determine the concentration of the surface carboxyl and hydroxyl groups (mmol/g), respectively. The adsorption of palladium on the carbon surface occurs through an exchange reaction of the type:



Hydroxyl groups are more resistant to the exchange reaction. Then palladium is converted into the metallic state in a reduction step by flowing hydrogen. The palladium dispersion was determined by measuring chemisorbed hydrogen with a pulse chemisorption method [4]. All the prepared catalysts have been submitted to activity tests, consisting in the measurement of the reaction rate of cyclo-octene hydrogenation in a batch reactor. Finally, the properties and catalytic performances of the prepared supported Pd/

carbon catalysts were also compared with other catalytic systems, containing roughly the same Pd amount but prepared by using other palladium precursors and different metal oxide supports, such as: SiO₂, γ -Al₂O₃, and SiO₂-Al₂O₃. A detailed discussion about the surface properties of carbon and its ability to give place to highly-dispersed Pd catalysts, compared with the ones of the other considered metal oxide supports, was reported in the last section of the paper.

EXPERIMENTAL

Supports used

Both metal oxides and activated carbon have been used as supports for the preparation of the catalysts. They have been obtained as follows: carbon (CA) (CHIMET, Catalyst Division; specific surface area, 950 m²/g; specific pores volume, 0.74 cm³/g; average particle size, 25 μ m); SiO₂ (SI) (Sigma Aldrich, specific surface area, 289 m²/g; mmol_{OH}/g, 2.2); γ -Al₂O₃ (AL) (Dutral-Montedison, specific surface area, 180 m²/g; specific pore volume, 0.45 cm³/g); Silica-alumina (SA) (Akzo Chemie, specific surface area, 140 m²/g; specific pore volume, 0.52 cm³/g). Before being used, the activated carbon has been submitted to an oxidant pre-treatment and, then, dried at 100 °C under vacuum for 6 h, while the metal oxides have been calcined, at 500 °C for 3 h, in order to eliminate moisture without a significant decrease in the hydroxyl density [5, 6]. The main properties of the used supports different from carbon are reported in Table 1.

TABLE 1

Main properties of the used supports different from carbon

Type of support	Specific surface, m ² /g	I.E.P., pH units	OH densities, mmol/g, from	
			TGA	titration
γ -Al ₂ O ₃	180	7.2	1.00	1.05
SiO ₂	289	2.2	2.20	2.50
SiO ₂ -Al ₂ O ₃ *	140	4.5	1.10	1.08

*13.6 mass % of Al₂O₃.

TABLE 2

Concentration of acid groups on the surface of carbon

Carbon support pre-treatments	-COOH, meq/g	-OH, meq/g
Untreated carbon	0.16	0.05
Carbon + KMnO ₄ (0.1 M)	0.83	0.39
Carbon + KMnO ₄ (1.0 M)	1.21	0.88
Carbon + HNO ₃ (0.1 M)	0.27	0.15
Carbon + NaClO (8 mass %)	0.16	0.05
Carbon + H ₂ O ₂ (12 vol.)	0.16	0.05
Carbon + H ₂ O ₂ (120 vol.)	0.27	0.26

Oxidation pre-treatments of the activated carbon

In Table 2, the effect of the activated carbon oxidant pre-treatments on the surface concentration of -COOH and -OH, respectively, is reported. The method suggested by Boehm [1] consists in contacting 0.5 g of carbon with 50 cm³ of a basic solution 0.05 N for 18 h under stirring. The residual solution, after filtration, is titrated to evaluate the amount of the reacted base. Bases of decreasing strength must be used, such as: NaOC₂H₅, NaOH, Na₂CO₃, NaHCO₃, in order to discriminate the contribution of the different groups to the total surface acidity. In our case, for example, the titrations were performed by using NaOH and NaHCO₃ in order to separate phenolic and carboxylic groups.

As can be seen from Table 2, the oxidant pre-treatment conducted with KMnO₄ has been made by using solutions of two different concentrations of 0.1 M and 1 M, containing the same amount of carbon (5 g), but having different volumes (100 and 50 cm³, respectively).

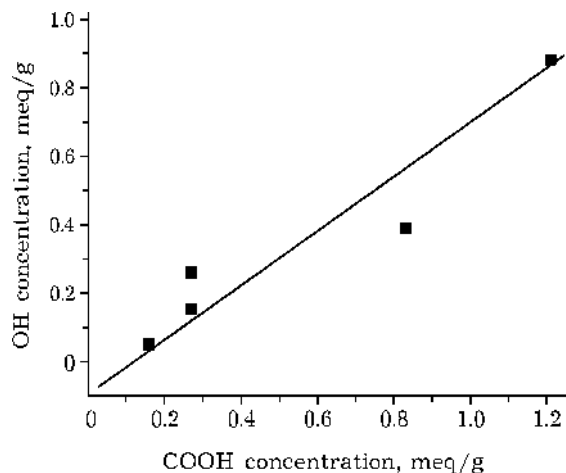


Fig. 1. Correlation between OH and COOH groups concentration obtained after different pre-treatments of the catalyst.

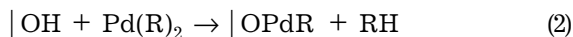
After filtration, the activated carbon was then washed with HCl 10 mass % to eliminate manganese. KMnO_4 has been already proposed as an efficient oxidant of the carbon surface by Semikolenov [7], and Gurevich [8]. The other oxidation pre-treatments, reported in Table 2, have been made by contacting a weighted amount of carbon (5 g) with 100 cm³ of the corresponding solution. The use of H_2O_2 at 120 vol. gives place to a vigorous reaction with a strong increase of the solution temperature, probably due to both surface oxidation and hydrogen peroxide decomposition.

It is interesting to observe that, independently of the method adopted for the oxidation of carbon, a linear trend between the OH and COOH surface concentration is obtained as it can be appreciated in Fig. 1.

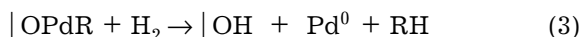
Catalysts preparation

All the tested catalysts have been prepared by contacting the support with a solution of the dissolved precursor. As mentioned above, different supports have been considered. Moreover, several precursors have been used, such as: palladium acetate (PdAC) (put in contact only with CA), palladium bis-allyl (PdAL), palladium bis-acetylacetonate (PdAA) and palladium allyl acetylacetonate (PdAAC). It should be noted that, in the case of the metal oxides used as supports (SI, AL, and SA), the

surface hydroxyl groups react with palladium complexes according to the following scheme:



The reduction of Pd^+ palladium is the following step, obtained also in this case in a flow of hydrogen, as shown by



in agreement with Yermakov *et al.* [10].

Preparation of supported Pd/carbon catalysts. As previously mentioned, $\text{Pd}(\text{OCOCH}_3)_2$ has been used as precursor only for the preparation of supported carbon based catalysts. The preparation was performed by contacting for 3 h a weighted amount of support (~2 g), with 50 cm³ of a solution of Pd acetate in benzene. Pd acetate concentration was arranged to obtain the desired Pd loading (~1 mass %). A total of six catalysts have been prepared according to this procedure, differing only for the type of the activated carbon oxidant pre-treatment. For a useful comparison, a carbon-supported Pd catalyst was also used without any carbon oxidant preliminary treatment.

Preparation of supported Pd/metal oxides catalysts. Catalysts supported on metal oxides have been prepared, on the contrary, by using precursors such as: palladium bis-allyl [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2$], palladium bis-acetylacetonate [$\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$] and palladium allyl acetylacetonate [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{C}_5\text{H}_7\text{O}_2)$]. It is largely known that the use of these precursors favours the obtaining of catalysts characterized by a very high Pd dispersion [7–10]. The synthesis of the three mentioned complexes will be described below.

The preparation of catalysts by using palladium bis-allyl [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2$] has been made by adding dropwise 50 cm³ a solution of the mentioned complex in *n*-pentane to a well stirred suspension of the support (5 g) in *n*-pentane (100 cm³) under N_2 atmosphere. The temperature was kept at -20°C during the impregnation. The addition of the complex solution occurred in about 1 h, but the solution was kept in contact with the support for other 2 h. A total of five catalysts has been prepared according to this procedure, by using different supports, in the range 0.5–1 mass % of palladium loadings.

Palladium bis-acetylacetonate [$\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$] seems to be less reactive than the previous one and consequently the wet impregnation based reaction is not complete. A similar procedure to the one described above was adopted with the unique difference of the impregnation temperature, kept at 50 °C. Three catalysts have been prepared in this way, differing for the used support. The amount of palladium loaded was about 1/3 of the expected value, that is, about 0.3–0.38 mass %.

Palladium allyl acetylacetonate [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{C}_5\text{H}_7\text{O}_2)$] has also been synthesized and used, because, it is much more stable than palladium bis-allyl [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2$], being the decomposition temperature about 75 °C and more easy to prepare and more reactive than palladium bis-acetylacetonate [$\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$]. In this case, impregnation has been made at room temperature. Benzene was used as a solvent (50 cm³) for both dissolving the complex and suspending the support (2 g). According to this preparation procedure, three catalysts have been prepared, differing in this case only for the type of support used.

In all the cases, grafted complexes have been reduced by contacting the catalyst with a gaseous flow of hydrogen. Acronyms easily recognizable have been adopted to indicate the different prepared catalysts in the text. The acronym reports in the order: (1) % of the metal, (2) acronym of the support, (3) acronym of the precursor, (4) type of oxidation pretreatment (this last one only for carbon). For example, 0.5-SI-PdAL means a catalyst containing 0.5 mass % of palladium supported on silica and prepared by using palladium bis-allyl complex, while 1-CA-PdAC-Mn0.1 means a catalyst containing 1 mass % of palladium supported on the carbon surface, pretreated with KMnO_4 (0.1 M), and prepared by using palladium acetate as precursor.

Methods, techniques and reagents

Precursor synthesis. Palladium acetate (PdAC) is commercially available and was not synthesized. On the contrary, all the other complexes were obtained by synthesis starting from the preparation of the dimer [$\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)_2$]. The preparation of this compound from

PdCl_2 is described by Tatsuno [11]. The product, extracted with CH_2Cl_2 and opportunely purified, has been obtained with a yield of 87 %.

Palladium bis-allyl [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2$] (PdAL) can be obtained in a relatively low yield (less than 50 %) by directly reacting PdCl_2 with allylmagnesium chloride ($\text{CH}_2=\text{CH}-\text{CH}_2\text{MgCl}$), as reported in [12]. Higher yields can be obtained by reacting the previously mentioned dimer [$\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)_2$] with magnesium allyl chloride at -50 °C in ethyl ether (yield obtained 70 %) [13]. Magnesium allyl chloride has been prepared as described by O'Brien *et al.* [14].

Two methods described by the literature for preparing palladium bis-acetylacetonate (PdAA) [15, 16] have been tested. The former one, developed by Barbieri [15], has given a yield of 50 %, while the yield obtained by following the method suggested by Grinberg [16] was 76 %. In the first case, PdCl_2 was previously reacted with potassium bicarbonate and then with acetylacetone, giving a yellow precipitate of palladium bis-acetylacetonate. In the second case, a solution of KOH was added to a mixture of PdCl_2 and acetylacetone in aqueous solution, giving also in this case the yellow precipitate.

At last, palladium allyl acetylacetonate [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{C}_5\text{H}_7\text{O}_2)$] (PdAAC) has been prepared starting from the dimer [$\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)_2$] complex. A weighted amount of the mentioned dimer (0.2 g), dissolved in 5 cm³ of benzene, was treated with 20 cm³ of a benzene solution of tallium acetylacetonate (a slight excess of 5 %), at 40 °C. A yellow precipitate of the desired product is formed with a yield of 50 %. In all the mentioned cases, the identification of the synthesized products has been made on the basis of the ¹H NMR spectra, by dissolving the purified complexes in deuterated chloroform.

Determination of palladium dispersion by hydrogen chemisorption. Palladium dispersion of the different catalysts has been determined by using a pulse technique developed by the authors [17], based on the evaluation of the amount of hydrogen chemisorbed on the surface of previously cleaned surface of palladium. Initially 0.5–1 g of the catalysts powdered were pre-reduced in a tubular reactor with a hydrogen stream fed, at 300 °C for 2 h. Then, the catalysts were cooled down to 150 °C in a flow of nitrogen and treated with 5–10

pulses of oxygen (each of about 0.15 cm^3). At 150°C oxygen reacts very fast with the chemisorbed hydrogen but very slowly with palladium. In this way, the surface is cleaned of the chemisorbed hydrogen without forming PdO. In the next step, the surface has been submitted, always at 150°C , to different pulses of hydrogen of the same volume used for oxygen (0.15 cm^3). The hydrogen at the outlet of the reactor was analysed online with a gas chromatograph. The amount of the chemisorbed hydrogen can be determined by counting the number of pulses fed but not emerged out of the reactor. By taking into account this amount, it is possible to evaluate: (i) the specific metal surface, (ii) the metal dispersion and (iii) the mean size of the palladium particles by assuming a surface stoichiometry $\text{H}/\text{Pd}_s = 1$, a palladium surface site density of $1.2 \cdot 10^{19} \text{ sites/m}^2$, in agreement with the suggestions of Aben [18] and, finally, by considering a spherical geometry for the particles.

Catalytic activity tests

Catalytic activity tests were performed by hydrogenating cyclooctene to cyclooctane in a well stirred slurry reactor operating under semi-batch conditions schematised in Fig. 2.

A determined amount of catalyst (200–600 mg) was charged on the reactor and reduced in situ by flowing hydrogen at the reaction temperature for 2 h and then washing with nitrogen. Then, 150 cm^3 of a solution of cyclooctene in *n*-hexane were introduced in the reactor by avoiding the contact with air by sucking the solution under vacuum. The reactor was heated at the reaction temperature and, then, filled with hydrogen without stirring. The reaction started when the slurry was stirred. The amounts of hydrogen consumed during the time were automatically recorded by using a flow-meter. Curves obtained for the hydrogen consumption were linear in the initial period, therefore, it was easy to evaluate the initial reaction rates in $\text{mol}/(\text{h} \cdot \text{g Pd})$ and to compare the activities. More details about the kinetic behaviour of this reaction are reported elsewhere [19].

RESULTS AND DISCUSSION

Catalysts dispersion and activity

As mentioned in one of the previous sections, all the prepared catalysts have been submitted to the evaluation of the metal dispersion by using the hydrogen pulse technique. The obtained results are reported in

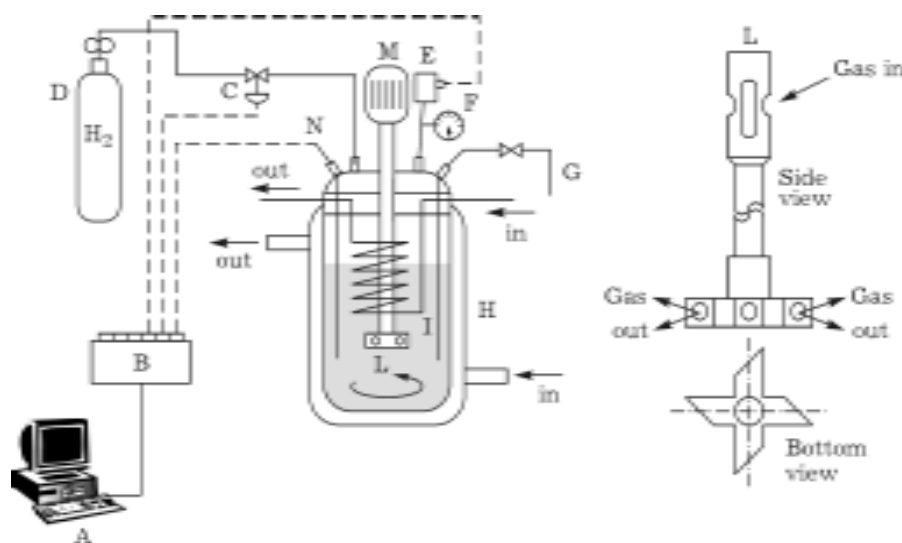


Fig. 2. Experimental apparatus for hydrogenation experiments. A - computer, B - data acquisition board, C - flow regulation device, D - hydrogen bomb, E - pressure transducer, F - pressure indicator, G - sampling line, H - jacketed reactor, I - cooling line, L - gaseous effect stirrer, M - magnetic drive motor.

TABLE 3

Dispersion of palladium evaluated for all the prepared catalysts: D is dispersion; S is specific metal surface area; d is mean particles diameter; r_1 and r_2 are initial reaction rate differently expressed

Catalyst	Amount, mg	D , %	S , m^2/g	d , nm	r_1 , cm^3/s	r_2 , $\text{mol}/(\text{h} \cdot \text{g Pd})$
1.0-CA-PdAC-no	400	56	264	1.90	0.28	12.24
1.0-CA-PdAC-N0.1	400	69	325	1.54	0.44	19.24
1.0-CA-PdAC-Na8	400	60	283	1.76	0.36	15.75
1-CA-PdAC-H ₂ O ₂ 12	400	72	340	1.47	0.46	20.12
1.0-CA-PdAC-H ₂ O ₂ 120	400	48	227	2.20	0.13	5.90
1.0-CA-PdAC-Mn0.1	400	56	264	1.90	0.44	19.24
3.0-CA-PdAC-Mn1	400	54	256	1.94	0.94	13.71
1.0-SI-PdAL	200	46	217	2.30	0.52	45.57
1.0-AL-PdAL	200	75	373	1.34	0.26	22.78
1.0-SA-PdAL	200	60	283	1.76	0.25	21.91
0.5-SI-PdAL	200	60	283	1.76	0.3	52.58
0.5-AL-PdAL	200	90	424	1.18	0.22	38.48
0.32-SI-PdAA	600	69	325	1.54	0.20	18.22
0.38-AL-PdAA	600	82	387	1.29	0.13	9.97
0.30-SA-PdAA	600	55	260	1.92	0.14	13.6
1.0-SI-PdAAC	600	34	160	3.12	0.17	4.92
1.0-AL-PdAAC	600	38	180	2.77	0.16	4.54
1.0-SA-PdAAC	600	26	122	4.01	0.13	3.87

Table 3. As reaction rates are very probably related to the palladium specific surface area, it is interesting to plot initial reaction rates expressed in $\text{mol}/(\text{h} \cdot \text{g Pd})$ as a function of the palladium specific surface area. As can be seen in Fig. 3, an exponential trend can be roughly recognised independently of both the used

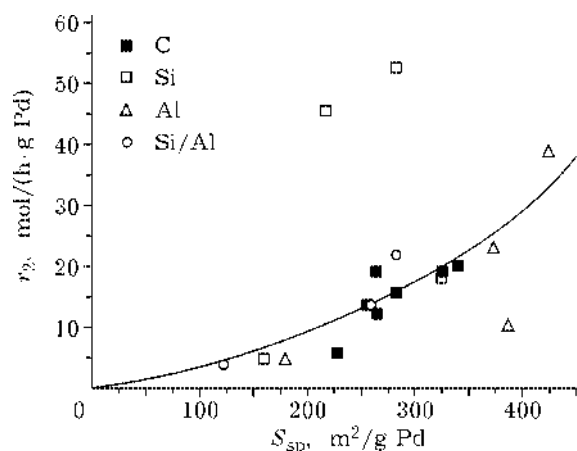


Fig. 3. Initial reaction rate (r_2) as a function of the metal specific surface area (S_{sp}) for different supports.

support and the precursor. This behaviour suggests, first of all, that the metal surface dispersion plays a fundamental role with respect to the nature of the support. Moreover, the exponential trend suggests that the reaction is “structure sensitive” [20] and the catalytic sites are probably located at the vertic of the palladium crystallites. At last, as expected, the activity is largely favoured by the dispersion. The high dispersion values, determined by using the chemisorption method with the pulse technique, have been confirmed for the catalyst 0.5-Al-PdAL, that was submitted to XRD analysis (35 and 50°) also. By comparing the spectra obtained for the catalyst and the corresponding support, respectively, no significant difference was observed. This means that the average size of the clusters, in this case, is certainly less than 1.5 nm which is the detectable limit for this technique. This observation is in agreement with the very high dispersion observed by pulse hydrogen chemisorption for the mentioned catalyst.

It is interesting to observe that, despite the apparently low effect of the carbon pre-treatments on the evaluated dispersions, considering the very high specific surface of the carbon support favouring in any case the achievement of a high dispersion, activities significantly change generally increasing by a factor 2 for the oxidations under mild conditions, and decreasing for more drastic conditions (H_2O_2 120 vol.). It is also interesting to compare the behaviour of the carbon catalysts, respectively untreated and pre-treated with $KMnO_4$ 0.1 M and 1 M. In all the mentioned cases, the dispersion measured resulted quite similar; on the contrary, the activities were different. In particular, despite the increase by a factor of 3 in the amount of supported palladium for the catalyst pretreated with $KMnO_4$ 1 M, the catalytic activity related to the palladium amount remained unchanged with respect to the untreated carbon catalyst but less by a factor of 2 than the catalyst pretreated with $KMnO_4$ 0.1 M. All this probably means that the evaluation of the dispersion for the carbon catalysts could be affected by errors as a consequence of the very high surface of the support, while the catalytic activities are more

representative of the achieved dispersion degree. As a consequence, we can also conclude that the oxidant pre-treatments promote the dispersion significantly increasing the catalytic activities.

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