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ELECTRONIC PROPERTIES OF SUPPORTED Pd AGGREGATES IN RELATION WITH THEIR REACTIVITY FOR 1,3-BUTADIENE HYDROGENATION

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XPS, binding energy, FWHM, supported Pd, aggregates 1,3 butadiene, hydrogenation reaction, TOF.

The electronic and catalytic properties of supported Pd particles have been studied by measurements of XPS core level shifts and activity for 1,3-butadiene hydrogenation reaction respectively. For samples prepared by atom beam deposition on carbonaceous supports the TOF at steady state decreases rapidly with decreasing particle size in the range of particle diameter 2.8 nm–1.2 nm. For these small particles, the Pd 3d core level shows an upwards shift and a larger half width compared to the values for massive Pd samples. For the Pd/SiO_2 particles of similar size, both the 3d core level energy and the TOF are comparable to these of the massive Pd systems.

1. Introduction

The size effect is one of the most important problems in catalysis by metals. Indeed, the commonly used noble metals are very scarce and expensive. Therefore, high dispersion of these metal particles on supports is a desired criterion for the preparation of industrial catalysts. This necessitates preparation of very small metal particles. But size effect may influence the intrinsic catalytic properties of the materials. For example, let us consider the hydrogenation reactions of alkynes and conjugated dienes where a high selectivity towards alkenes is required. It is generally considered that the Pd-based catalysts are the most active and selective catalysts for these selective hydrogenation reactions. But controversies exist on the Pd size effect for such catalytic hydrogenations. On Pd/Al_2O_3 and Pd/SiO_2 catalysts prepared by impregnation of the support with tetramine palladium nitrate ($Pd(NH_3)_4(NO_3)_2$), Boitiaux et al. [1–3] found large decrease of activity

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for the 1-butyne as well as for the 1,3-butadiene hydrogenation reactions. But, from the work of Sarkany et al. [4] no such direct correlation between the particle size and the activity/selectivity of Pd/Al_2O_3 could be established for the acetylene hydrogenation reaction. The latter authors prepared their samples by impregnation with ($PdCl_2$, $Pd(NH_3)_4Cl_2$) salts. Again, it was found by Ouchaïb [5] that 1,3-butadiene hydrogenation reaction is insensitive to the particle size for Pd/SiO_2 catalysts prepared by exchange of $Pd(NH_3)_4(OH)_2$ with function-labelled silica.

In order to have a better understanding of the possible size effect, the role of supports and the method of preparation etc. on the catalytic reactivity we made some investigations. In this letter we present our results which throw some light on the above effects. Our samples were Pd particles supported on SiO_2 as well as on both graphitic and amorphous carbon. The reaction studied was 1,3-butadiene hydrogenation and the electronic properties were investigated by measurements of Pd 3d core levels and their full width at half maximum (FWHM).

In the next section (section 2) we discuss briefly the experimental procedures and in section 3 we present our results and discuss them critically.

2. Experimental procedures

For the preparation of catalyst samples we used different methods as described below:

(A) Massic Pd single crystals were obtained by cutting the crystals along the (111) and the (110) orientations [6]. For the (111) orientation there is a close-packed arrangement of Pd atoms, the number of nearest atoms for a surface atom being $N = 9$. For the (110) orientation, however, the surface is more "open" and the number of nearest neighbours is $N = 7$.

(B) Pd/SiO_2 catalyst samples were prepared by exchange of $Pd(NH_4)^{++}$ $2(OH)^-$ with silica support pretreated by NH_4OH. Then it was decomposed under flowing oxygen up to 575 K using a slow temperature increase (2 $K.mn^{-1}$) and reduced at 500 K under a H_2–N_2 flow.

Two different contents were considered: 2.05 and 0.41 weight % Pd. The specific diameters ($d_{sp} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$), determined by small angle X-ray scattering, were 1.5 and 1.2 nm respectively [5]. Chemisorption and transmission electron microscopy (TEM) measurements also give the same values.

(C) Pd/C model catalysts were prepared by atomic beam deposition techniques [7,8]. Two supports were considered; namely, pyrolitic graphite and amorphous carbon outgassed at about 700 K under vacuum conditions. The Pd was evapored under ultrahigh vacuum from a Knudsen cell and the amount of metal deposited was determined using a quartz micro-balance [8].

XPS data were registered on two different spectrometers both using the AlK_α X-ray excitation source ($h = 1486.6$ eV). The resolution of the spectrometers is better than 1 eV and therefore the determination of the energy values is better than 10% of the spectrometer resolution, i.e. 0.1 eV. The spectra of Pd/SiO_2 catalysts were recorded without monochromatization of the primary photon beam on an ESCA II VG spectrometer coupled with a high pressure treatment cell. For these particles supported on an insulator, the silica, the XPS binding energy of Pd $3d_{5/2}$ level was determined from the Si 2p binding energy, 103.4 eV, used as a reference. Before analysis, samples were pretreated under hydrogen flow for four hours at 500 K, the temperature increase rate being 2 $K.mn^{-1}$.

The Pd/C aggregates were analysed using a HP5950A spectrometer equipped with a photon monochromator. On these more conducting samples, the Pd $3d_{5/2}$ level was referenced from the Au $4f_{7/2}$ level at 83.9 eV. These samples were studied after the course of a 1,3-butadiene hydrogenation reaction. The reaction appeared to passivate the sample and prevent further oxidation. It was checked that the three hour hydrogen treatment at 530 K and 50 Torr H_2 pressure (conditions which are known to be quite sufficient to reduce palladium oxides) does not affect notably our main XPS data like the energetic position of the Pd $3d_{5/2}$ photoemission line. However, the small contributions on the high binding energy side of the main peaks (which correspond probably to some trace palladium oxide) disappeared.

The turnover frequencies (TOF) of Pd were measured at 300 K and at a H_2 pressure of 100 Torr for the 1,3-butadiene hydrogenation reaction [6,8]. The given values correspond to measurements in the steady state regime. In order to avoid hydride formation, for Pd single crystals the experiments have been performed at 5 Torr and results have been extrapolated to a H_2 pressure of 100 Torr assuming an order one with respect to H_2.

3. Results and discussions

XPS spectra of the palladium samples are given in figs. 1–4. In figs 1–3 we have presented the rough data (denoted by ‘a’) as well as the data after appropriate smoothed and nonlinear background subtraction (denoted by ‘b’). In fig. 4, however, we have presented only the smoothed and background-subtracted data. The precise determinations of the XPS $3d_{5/2}$ energy level and its FWHM were done from these smoothed and background-subtracted data. The values are presented in table 1. The XPS $3d_{5/2}$ binding energy of massive Pd samples was found to be 335.6 ± 0.1 eV from both the spectrometers after proper calibration (i.e. by correcting their contact potential differences) with respect to the XPs Au $4f_{7/2}$ photoemission line at 83.9 eV. The FWHM values given in table 1 were determined from the spectra obtained with the photon source monochromator facilities. The observed binding energy shifts and FWHM variations with the particle size and the preparation method are effectively associated to an effect on the metal. Indeed, the C1s line on C supported samples and O1s line on silica supported samples stay unvaried with the calibration method used.

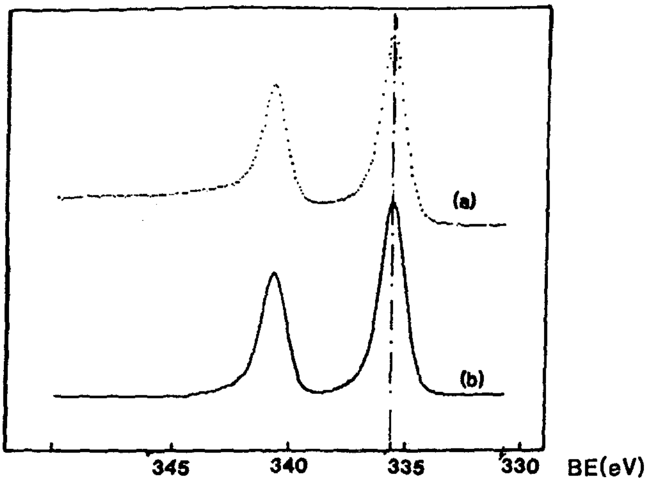

Fig. 1. XPS 3d spectra of massic Pd samples (a): the rough data; (b) after smoothing and background subtraction.

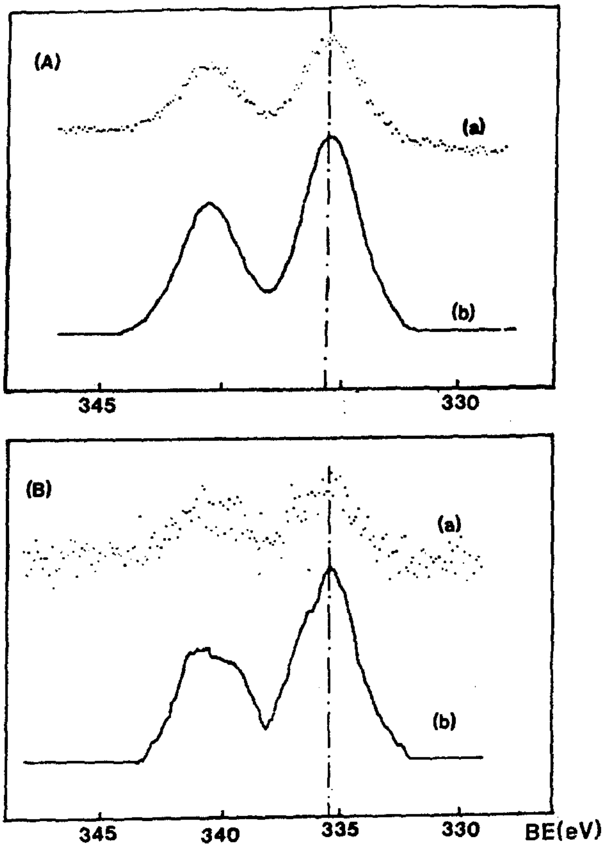

Fig. 2. XPS 3d spectra of (A) Pd 2.05%/SiO_2 and (B) Pd 0.41%/SiO_2 samples (a): the rough data; (b) after smoothing and background subtraction.

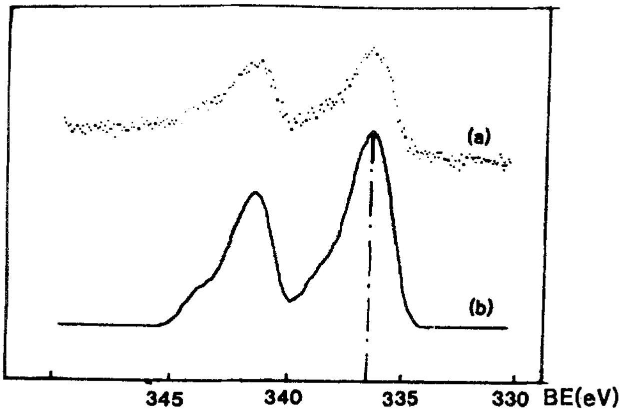

Fig. 3. XPS 3d spectra of Pd/graphite sample (a): the rough data; (b) after smoothing and background subtraction.

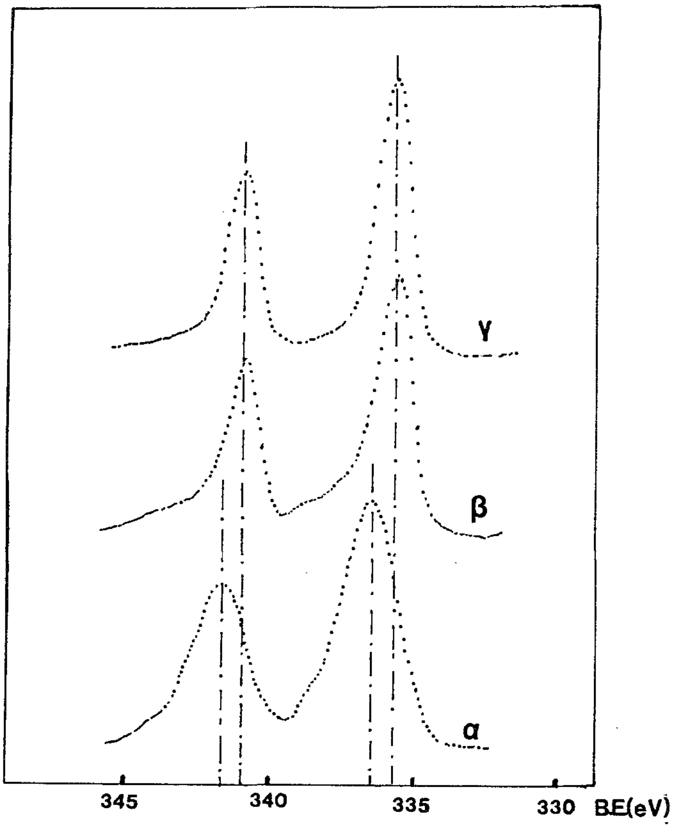

Fig. 4. XPS 3d spectra of Pd/amorphous carbon samples after smoothing and background subtraction (α): for particle size ≈ 1.4 nm) (β): for particle size ≈ 2.8 nm (without H_2 treatment); (γ) for particle size ≈ 2.8 nm with hydrogen treatment at 530 K.

Table 1

Specific diameters, XPS data and catalytic activity for the 1,3-butadiene hydrogenation reaction on different Pd catalysts (the TOF are given for 100 Torr hydrogen pressure and at 300 K, the reaction being performed in large excess of hydrogen).

Samples	Specific diameter dsp (nm)	XPS binding energy of $3d_{5/2}$ (eV)	FWHM (eV)	TOF (S^{-1})
Pd(111)				3
Massic		335.6 [a]	1.25	
Pd(110)				24
Pd 2.05%/SiO_2	1.5	335.6 [b]		3
Pd 0.41%/SiO_2	1.2	335.4 [b]		2.6
Pd/graphite (2.8×10^{14} at. cm^{-2})	–	336.5 [c]	1.9	0.03
Pd/am. C				
(α) (4×10^{14} at. cm^{-2})	1.4	336.4 [c]	2.2	0.01
(β) (5×10^{15} at. cm^{-2}) without treatment	2.8	335.7 [c]	1.5	16.4
(γ) (5×10^{15} at. cm^{-2}) H_2 treated	2.8	335.7 [c]	1.35	16.4

[a] Calibration with respect to Au $4f_{7/2}$ binding energy at 83.9 eV.

[b] Calibration with respect to Si 2p binding energy at 103.4 eV.

[c] Calibration with respect to C 1s is binding energy at 284.5 eV.

It may noticed that a correlation exists between the XPS Pd $3d_{5/2}$ binding energy and the catalytic activity for the hydrogenation reaction. The catalysts exhibiting an upward shift of the $3d_{5/2}$ cove level are less reactive. The shift reaches up to 0.9–1.1 eV for the smaller particles obtained by atomic beam deposition on carbonaceous supports. It may also be noticed that there is a sizable increase of the FWHM of the 3d lines for these systems. The upward binding energy shift as well as the increase of the FWHM with decreasing size of the Pd aggregates obtained by atomic beam deposition technique, have also been reported by others [8–11]. In those studies, the particles had the size in the range of 1–3 nm; and the observed results were the same irrespective of the nature of supports, namely SiO_2 or Al_2O_3 or amorphous/graphitic carbon.

The broadening of the XPS $3d_{5/2}$ line observed for small particles obtained by atomic beam deposition with respect to large particles and massive Pd, could reflect a change in the density of states of both filled and empty states near the Fermi level.

As to the possible causes of the upward shift of the energy levels on highly dispersed Pd catalysts there are different explanations put forward by different workers. Noack et al. [12] proposed that there could be some solid solution of oxygen on Pd characterized by a 3d level shift of about 0.4 eV. The concept of

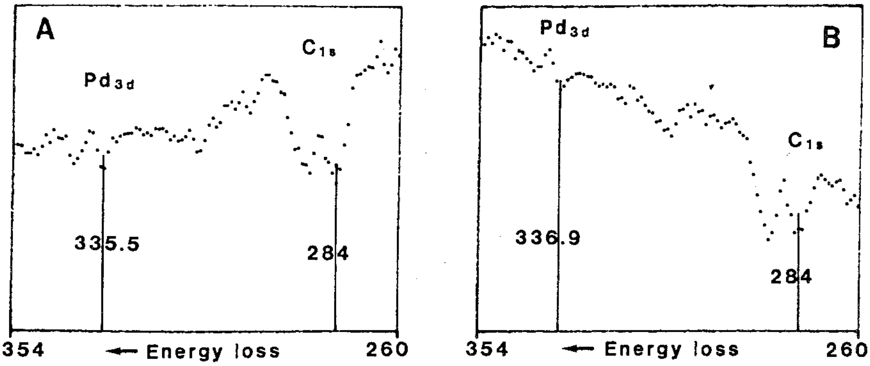

Fig. 5. Ionisation loss spectra (ILS) of Pd/amorphous carbon: (B): for particle size ≈1.4 nm, (A): for particle size ≈ 2.8 nm. (Primary energy of the impinging beam: 1.5 keV.)

intrinsic initial state or the final state (relaxation processes) electronic effects have also been invoked [9–12]. In order to get some complementary information and to have better understanding of these effects we have measured the energetic position of the threshold of the Pd 3d levels for the two Pd/C samples by ionisation loss spectroscopy (ILS). Unlike the photoemission process, where the final state is an ionised state, the ILS final state is an excited but neutral state. By the ILS studies, thus, the extra-atomic relaxation part in the energy shift is avoided, assuming that the empty orbital implied in the process is localized at least partially. The results are shown in fig. 5a and 5b. The $3d_{5/2}$ threshold is shifted from 335.5 eV for the larger Pd particles to 336.9 eV for the very small aggregates. The shift is comparable to that measured in XPS experiments. Therefore the intrinsic initial state effect would be the main cause of the observed shifts with particle size. By coupling X-ray absorption spectroscopy (XAS) and XPS measurements Mason also reached to the same conclusions [10].

For Pd aggregates on SiO_2 and carbonaceous support prepared by atomic beam deposition, the decrease in activity of 1,3-butadiene hydrogenation reaction with decreasing particle size has also been previously observed [7,8]. Not much information, however, are available for highly dispersed Pd catalysts prepared by more classical ways, for example, by impregnation or exchange with Pd salts followed by calcination and reduction procedures. Hub et al. [13] reported a decrease in reactivity for the 1-butyne hydrogenation reaction with the particle size and an upward shift of the Pd 3d level on Pd/Al_2O_3 catalysts prepared by impregnation method.

From our results given in table 1, it can also be seen that depending on the method of preparation, the Pd particles in the small size region (e.g. 1.2 nm for Pd $0.41\%SiO_2$ catalysts and 1.4 nm for Pd/C catalysts) behave differently. This would result of a modification of intrinsic chemical properties of these small particles including an increase of deactivation due to stronger metal-reactant bonds. This deactivation more or less important according to the sample has been evidenced on the different catalysts. From the results given in table 1, a relationship can be drawn between the steady state activity and the Pd $3d_{5/2}$ XPS shift. But not one to one relation exists between the particle size and the electronic and reactivity parameters. Consequently, besides the size effect, other parameters have also to be considered such as structure, epitaxial strain, morphology and support effect etc, which depend upon the method of preparation. However, for Mason et al. [10] the nature of the support does not significantly modify the Pd 3d binding energy on the samples prepared by vapor deposition.

In conclusion, Pd particle with size larger than 2.5 nm behave similar to the massive Pd, both in respect of their catalytic reactivity and electronic properties. For smaller particles, correlation can be drawn between their loss in activity for the 1,3-butadiene hydrogenation reaction and some of their electronic properties. These effects depend upon the preparation method, and seems to be more pronounced on Pd model aggregates prepared by atomic beam deposition techniques than on Pd catalysts prepared by more classical methods, Metal vapor deposition on a support is no doubt an important and useful method for preparing new materials; but further experiments have to be performed for a better knowledge of these new catalysts.

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