Sizeable deactivation effect for the 1,3-butadiene hydrogenation on vapor-deposited Pd aggregates on graphite

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The catalytic activity of Pd aggregates vapor-deposited on graphite has been measured in the 1,3-butadiene hydrogenation. It is generally decreasing with particle size. But, such a decrease is largely depending upon the hydrogen and the hydrocarbon pressure. Indeed, with low hydrocarbon pressure (about 1 Torr) and in presence of large excess of hydrogen ($p_{H_2}/p_{C_4H_6} = 100$) the activity of the smaller aggregates is comparable to that of larger particles. The different behaviour is consequently attributed to a size dependent deactivation. Such a deactivation could be due to carbon deposits generated by dehydrogenation of the diene admolecules. This behaviour is tentatively related with marked differences observed by XPS on the smaller aggregates, both with respect to the core level energies and to the density of states into the valence band.

Keywords: Deactivation; supported Pd; vapor-deposited aggregates; 1,3-butadiene; hydrogenation reaction; XPS; binding energy

1. Introduction

Many hydrogenation reactions of alkynes and alkadienes on Pd supported catalysts appear to be sensitive to the metal dispersion [1–4]. The catalysts having a low dispersion ($d \geqslant 4$ nm) show an approximately constant specific catalytic activity, whereas for the highly dispersed catalysts (4–1 nm) the specific activity is reduced by one order of magnitude at least. It has often been proposed that the low specific activity of highly dispersed palladium would be the consequence of a stronger chemisorption of the unsaturated hydrocarbons on the smaller particles. If so, the very strong chemisorption of hydrocarbons on the highly dispersed metal could entail a more or less important dissociation of the admolecules, which could induce a possible deactivation of small aggregates by carbonaceous deposits.

The aim of this study is to verify if the smaller reactivity observed for small particles in the 1,3-butadiene hydrogenation reaction is appearing via deactivation processes or if it is associated to modifications of intrinsic properties with respect to the considered hydrogenation reaction.

In order to do so we have first checked the behaviour of the samples for successive reactions performed without one further cleaning between consecutive runs. Secondly, we have measured reactions with different conditions for the hydrogen to hydrocarbon pressure ratio. The marked difference in behaviour of small with respect to larger particles will be discussed in the light of some electronic properties measured by X-ray photoemission spectroscopy (XPS) and of the possible hydrogen dissolution into the tridimensional aggregates during the reaction.

2. Experimental

Pd aggregates of different sizes were prepared by atomic beam deposition techniques [3], under ultrahigh vacuum using a Knudsen cell source. The substrate was pyrolytic graphite (PGCCL, Le Carbone Lorraine) previously cleaved in air and then outgassed at about 700 K for many hours under vacuum conditions. For each preparation the metal flux was controlled by a quartz microbalance and was fixed at 1.35×10^{13} Pd atoms cm^{-2} s^{-1}. The deposition time was varied between 10 and 210 s.

After deposition, the sample was transferred under UHV conditions to a 73 cm^3 reactor. The butadiene hydrogenation reaction was performed at room temperature under static conditions. The evolution of the reaction mixture during the reaction was analyzed by mass spectroscopy, by periodic sampling through a leak valve. The catalytic activity A for each sample was measured by following the C_4H_6 pressure decrease versus time. Two different reactive mixtures were prepared separately in a large volume cell and introduced through a valve in the reactor. The first one is prepared with 35 Torr H_2 and 3.5 Torr hydrocarbon, the second one with 100 Torr H_2 and 1 Torr C_4H_6. The catalytic activity values of vapor-deposited Pd samples are compared to those of Pd(111) and Pd(110) monocrystalline samples [5]. In order to avoid hydride formation in the case of Pd single crystals, the experiments have been performed at 5 Torr hydrogen and results have been extrapolated to a H_2 pressure of 35 Torr assuming reaction order equal to one with respect to this reactant.

To reveal the deactivation phenomenon, several batch reaction runs were repeated without any sample treatment between successive exposures to the reactive mixture.

Pd particles were exposed to nitrogen and to air before observation with a XPS spectrometer (Fisons-Instruments ESCALAB 200R) using a monochromatized Al Kα primary photon beam ($h\nu = 1486.6$ eV). The energy values are given at ±0.1 eV and are referenced to the C 1s value in graphite (284.5 eV).

3. Results and discussion

3.1. INFLUENCE OF THE REACTION CONDITIONS

Four deposits have been chosen as samples to work with, of respective amount: 1.5×10^{14}, 4×10^{14}, 15×10^{14} and 28×10^{14} Pd atoms/cm^2. The mean size of such particles, as deduced from transmission electron microscopy (TEM) observations is 0.8, 1, 1.2 and 2.4 nm respectively. In the following conditions, 300 K, 35 Torr for the hydrogen pressure and 3.5 Torr for the 1,3-butadiene, it appears that the activity A_1 measured in the first run (expressed in s^{-1} per Pd metal atom deposited) increases with the Pd particle size. The results are reported in fig. 1, as well as those obtained on the Pd(111) and Pd(110) single crystal faces, for comparison [5]. One can see that the reaction has proceeded with a lower rate on the smaller aggregates corresponding to 1.5 and 4×10^{14} Pd atoms/cm^2 deposits than on the larger (15 and 28×10^{14} Pd atoms/cm^2); those latter have behaved like the more open Pd(110) surface. It is to specify that the selectivity towards butenes remains near unity up to a very high conversion level whatever the Pd concentration of the studied samples.

The activity A_2 measured for a consecutive reaction is more or less decreased towards the first one A_1, depending upon the particle size (fig. 1, dashed rectan-

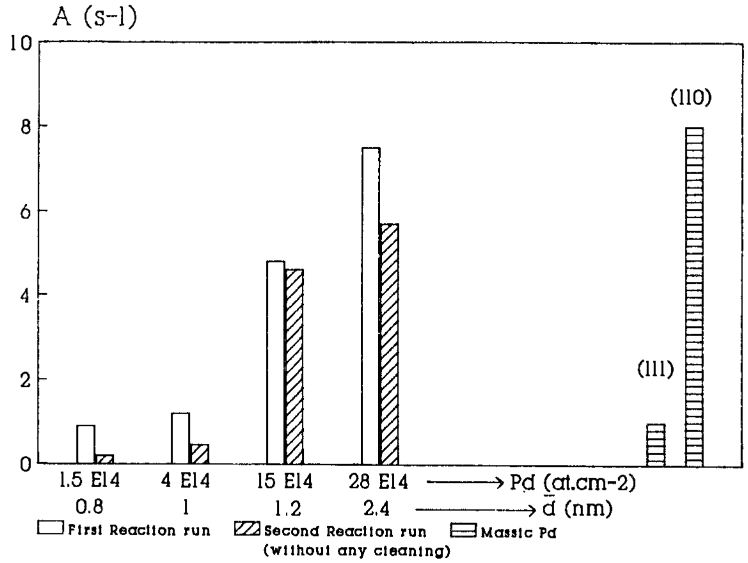

Fig. 1. Activity A (in s^{-1} per deposited Pd atom) of different Pd deposits on graphite for the 1,3-butadiene hydrogenation at 300 K, $p_{H_2} = 35$ Torr, $p_{C_4H_8} = 3.5$ Torr. For single crystals, the measurements have been performed at 5 Torr hydrogen. Reported values correspond to extrapolation at a hydrogen pressure of 35 Torr and are relative to surface atoms. (☐) First reaction run; (▤) massic Pd; (▨) second reaction run (without any cleaning).

gles). The activity is largely reduced for the smaller particles ($A_2/A_1 = 0.25$ for the 1.5×10^{14} Pd atoms/cm^2 deposit) while it stays rather constant for larger particles ($A_2/A_1 = 0.75$ for the 2.8×10^{14} Pd atoms/cm^2 deposit). Such results suggest that deactivation has occurred, its amplitude depending upon the particle size.

In order to confirm this conclusion, experiments have been performed using a reaction mixture with very large excess of hydrogen and a lower hydrocarbon pressure ($p_{H_2} = 100$ Torr, $p_{HC} = 1$ Torr); several consecutive reaction runs have been made for the two samples showing a noticeable deactivation: 1.5×10^{14} and 4×10^{14} Pd atoms/cm^2. In these conditions ($p_{H_2} = 100$ Torr), the activity measured on the two samples is 10 s^{-1}, i.e. if one assumes a reaction order equal to unity (as commonly admitted for the considered reaction when it is working out of deactivation), it corresponds to 3.5 s^{-1} at $p_{H_2} = 35$ Torr. Therefore, the reaction proceeds at a larger rate than for the previous reaction mixture. Moreover the decrease of activity for a second run is much less important: $A_2/A_1 \approx 0.6$ for the two samples considered.

In conclusion, a deactivation process is evidenced for the small amount of deposited Pd; it is the mean reason for the size dependent reactivity.

Vibrational EELS measurements on these Pd samples having undergone a batch reaction support such a conclusion. Indeed, features characteristic of hydrocarbon residues are only evidenced on the larger particles [3]. No vibrational structures have been observed after reaction on the smaller aggregates ($d \leqslant 1$ nm). The non observation of molecular vibration modes can be interpreted as a completely dissociative adsorption of the hydrocarbon molecules on the smaller particles. So during the 1,3-butadiene hydrogenation the very small Pd aggregates would be covered by carbon and thus could become inactive.

3.2. EVIDENCE OF DIFFERENT ELECTRONIC PROPERTIES

The XPS spectra of the 3d core levels of Pd relative to the studied samples have been registered. Many of them are reported in fig. 2, in comparison with that measured on a Pd foil. The spectrum of the 28×10^{14} Pd atoms/cm^2 deposit is very similar to that of the massic Pd; it is not shown on the figure for clarity. The 15×10^{14} Pd atoms/cm^2 deposit exhibits also a spectrum very close to that of massic Pd; only a very small upward shift of the 3d binding energy is evidenced. On the contrary, the two samples composed of very small particles and showing deactivation at a large extent (1.5 and 4×10^{14} Pd atoms/cm^2) have spectra broadened and largely shifted towards higher binding energies. Such electronic effects have been previously reported for small Pd clusters produced by vapour deposition, and seem to be a general trend whatever the substrate: graphite, amorphous C, Al_2O_3, SiO_2, ... [6,7] but the increase of the core-electron binding energy is controversially discussed as an initial or final state effect [8].

More promising appear to be the modifications measured in the valence band near the Fermi level (fig. 3). For the smaller Pd deposit, 1.5×10^{14} atoms/cm^2, it

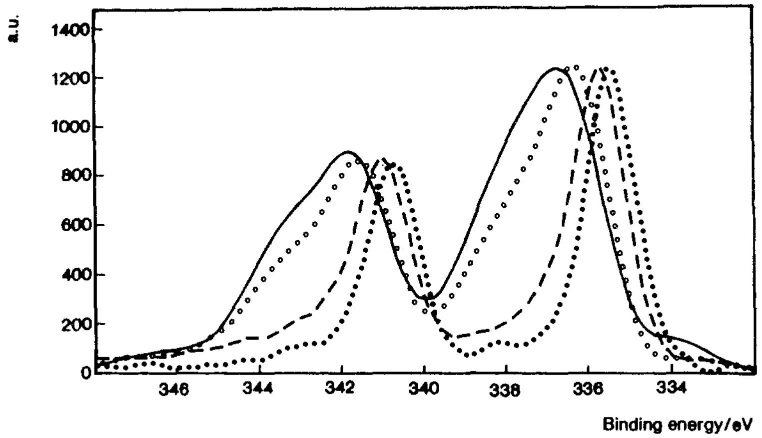

Fig. 2. XPS Pd 3d core level spectra for different amounts of metal deposited on graphite, as compared to massic palladium. (Monochromatized Al Kα X-ray source; $h\nu = 1486.6$ eV.) (• • •) Massic Pd; (- - -) 1.5×10^{15} Pd atoms/cm^2; (o o o) 4×10^{14} Pd atoms/cm^2; (——) 1.5×10^{14} Pd atoms/cm^2.

has not been possible to separate the Pd contribution from that of the graphite substrate. However, it is again clear that the BDV XPS spectrum for the larger deposits, i.e. the larger clusters, is very similar to that of the bulk Pd while it is notably changed for the small aggregates. The main change is a large diminution of the density of states (DOS) near the Fermi level. This indicates a real change of the electronic structure of the metal when the cluster size is varied.

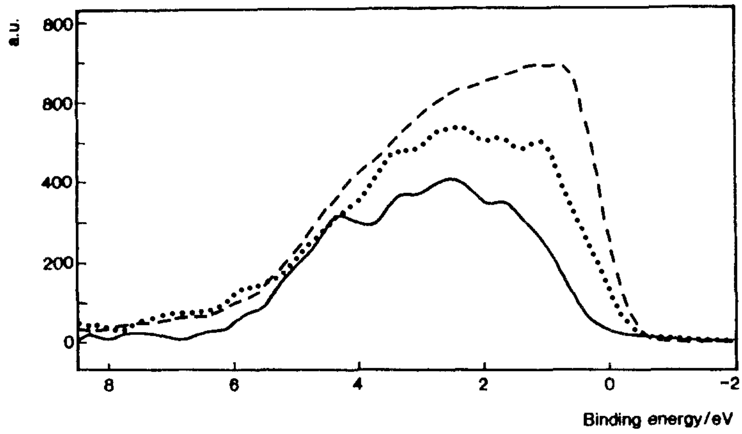

Fig. 3. XPS valence band for different amounts of Pd deposited on graphite, as compared to massic palladium. (Monochromatized Al Kα X-ray source; $h\nu = 1486.6$ eV.) (- - -) Massic Pd; (• • •) 1.5×10^{15} Pd atoms/cm^2; (——) 4×10^{14} Pd atoms/cm^2.

In conclusion, the larger deposits (which allow the formation of particles larger than 1 nm) present similarities with massic Pd with respect to both their reactivity for the 1,3-butadiene hydrogenation reaction and their electronic properties, as well as if one observes the energetic position of core level and the line shape of the BDV. The smaller deposits (which allow the formation of small particles, $\leqslant 1.1$ nm) show large deactivation when the hydrogen/hydrocarbon ratio is not very high and modifications of the line shape and energetic positions of both the core levels and the BDV. The shift upwards of the energy of the core levels could be tentatively assigned to an electron deficit of the Pd atoms via electronic interactions with the graphite substrate, and/or to intrinsic modifications of the density of states (DOS) of valence electrons associated to the low coordination of Pd atoms for the very small aggregates. Such conclusions hold only if the chemical shift can be attributed to an initial state effect, which seems reasonable if one takes into account the results given from the combined use of XPS and Auger electron spectroscopies [7] on conductive substrates.

The changes observed with respect to the reactivity could therefore be associated to a larger ability to accept electrons from the unsaturated hydrocarbon molecules, i.e. to couple more strongly these admolecules by electronic transfer from their bonding orbitals. Such a scheme of the chemical bond is further coherent with the low DOS near the Fermi level, which would induce again a large ability to accept electrons, i.e. to couple more strongly the molecule via electron transfers from the filled bonding π (and possibly σ) states to the empty level near E_F. In order to make a more complete correlation between the electronic properties of the Pd samples and the coupling of the molecules, more has now to be known about the DOS of the empty states of the reacting samples.

Another explanation to these more or less important deactivation phenomena could be the hydride formation for the larger particles, which could not be possible for the bidimensional aggregates. Indeed, Jobic and Renouprez have shown, by inelastic neutron spectroscopy, that hydride formation is still possible even for very small Pd particles ($d \approx 15$ Å), at 300 K and some Torr hydrogen pressure [9]. Keeping in mind the fact that the smaller Pd deposits lead to quite flat (2D) aggregates, which increase in height with further Pd deposition to give 3D like particles [10], it can be supposed that in our experimental conditions (hydrogen pressure ranging between 35 and 100 Torr) the 3D particles, even small in size, can dissolve hydrogen and form hydrides while the 2D shaped aggregates do not. In such a hypothesis, the hydrides formed with the 3D particles could play the role of a hydrogen reservoir which would act as a source of hydrogen for the surface as the hydrogen partial pressure does during the reaction. Therefore, for a given hydrogen partial pressure, less dissociation of the hydrocarbonated molecules, and consequently less deactivation, would occur on the 3D clusters as compared to the rather flat aggregates.

References

[1] J.P. Boitiaux, J. Cosyns and S. Vasudevan, Appl. Catal. 6 (1983) 41.

[2] V. De Gouveia, B. Bellamy, Y. Hadj Romdhane, A. Masson and M. Che, Z. Phys. D 12 (1989) 587.

[3] B. Tardy, C. Noupa, C. Leclercq, J.C. Bertolini, A. Hoareau, M. Treilleux, J.P. Faure and G. Nihoul, J. Catal. 129 (1991) 1.

[4] Yu.A. Ryndin, M.V. Stenin, A.I. Borinin, B.I. Bukhtiyarov and V.I. Zaikovskii, Appl. Catal. 54 (1989) 277.

[5] J. Massardier, J.C. Bertolini and A. Renouprez, *Proc. 9th Int. Congr. on Catalysis*, Vol. 3, eds. M.J. Phillips and M. Ternan (Chem. Inst. of Canada, Ottawa, 1988) p. 1222.

[6] M.G. Mason, Phys. Rev. B 27 (1983) 748.

[7] S. Kohiki and S. Ikeda, Phys. Rev. B 34 (1986) 3786.

[8] W.F. Egelhoff, Surf. Sci. Rep. 6 (1987) 253.

[9] H. Jobic and A. Renouprez, J. Less, Common Met. 129 (1987) 311.

[10] L. Porte, M. Phaner, C. Noupa, B. Tardy and J.C. Bertolini, Ultramicroscopy 42–44 (1992) 1355.