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Structure and reactivity of Pd–Pt clusters produced by laser vaporization of bulk alloys

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Abstract. Pd–Pt nanoclusters are obtained by the focusing of an Nd:YAG laser onto rods of alloys. The aggregates, which are produced by plasma cooling via short helium bursts synchronized with the laser pulses, are collected on amorphous carbon or silicon substrates, in a UHV chamber. Transmission electron microscopy (TEM) experiments show that the diameters of the clusters range between 1.5 and 4.5 nm, and analytical microscopy indicates that they have the same composition as the vaporized rods. Low-energy ion scattering (LEIS) also shows that the surface of the obtained clusters is Pd enriched: the Pd concentration in the first atomic layer is found to be equal to 38% for a $Pd_{17}Pt_{83}$ rod composition and 87% for the Pd_{65} Pt_{35} alloy. The catalytic activity of these clusters in the hydrogenation of 1,3-butadiene to butenes and butane is measured in static mode, with mass spectrometry detection. The reactivity of the bimetallic clusters is explained by the atomic local order and low-coordination sites considered as "hot sites".

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 61.66.Dk Alloys

1 Introduction

Numerous associations of two metals are used as active phases in catalytic hydrogenation, oxidation or reforming reactions. In most cases, a noble metal like Pt, Pd, Ir, or Rh is alloyed to a less reactive one like Ag or Cu, either for increase in the selectivity of the catalytic reaction towards a desired product or to reduce the phenomenon of deactivation of the active phase. More unusual is the association of two noble metals like Pd and Pt. Actually, bimetallic catalysts based on the association of these two elements can show either a simple additivity of the reactivity of each component, as observed in the dehydrogenation of cyclohexane [1], or an enhancement of activity as compared to that of the pure metals, as in, for example, the isomerization and hydrocracking of alkanes [2] and in the hydrogenation of aromatics [3]. The latter reaction is now of primary economical importance, given the reinforcement of the regulation concerning car exhaust emissions that imposes a benzene concentration in gasoline lower than 2%. Pd and Pt are generally both active in hydrogenation reactions, but Pd is generally preferred because of its lower cost and its larger selectivity for partial hydrogenation, leading to molecules of interest. On the other hand, it is known that Pd–Pt bimetallic catalysts are more resistant than monometallic ones to sulfur poisoning, an element present at a level of 200 to 350 ppm in gasoline.

Most of the bimetallic catalysts prepared by chemical methods suffer from a lack of composition homogeneity, and, in some cases, one cannot even be sure that alloys are really formed; a new method of elaboration has been proposed for overcoming this difficulty [4, 5] that uses the laser vaporization of bulk alloys, a method that ensures a perfect homogeneity of composition of the particles.

2 Elaboration and characterization of the Pd–Pt clusters

2.1 Production of the clusters

A Nd:YAG laser is focused onto a metallic rod driven in a slow screw motion. Synchronized with the laser pulses, short intense helium bursts delivered by a fast pulsed valve cool the laser-induced plasma. Further cooling and cluster condensation occurs at the output nozzle of the source, because the instantaneous pressure in the source chamber rises high enough to produce an efficient supersonic expansion at the exit of this chamber. The deposit is made in a UHV chamber coupled to the source. We have used $Pd_{17}Pt_{83}$ and $Pd_{65}Pt_{35}$ bimetallic rods. Free clusters are analyzed in a perpendicular time-of-flight mass spectrometer (TOFMS). The clusters are deposited onto a thin amorphous carbon film evaporated on a copper grid to perform electron microscopy experiments. The pressure in the deposition chamber is about 10^{-10} mbar, and the equivalent deposited thickness is 2 Å. Once the samples are produced, they are either exposed to air and characterized in a transmission electron microscope (JEOL 2010)

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operating at 200 kV and allowing energy-dispersive X-ray analysis (EDX), or transferred in a UHV suitcase under dynamic vacuum (5×10^{-9} mbar) into an ESCALAB 200R machine (from Fisons Instruments) where low-energy ion scattering (LEIS) experiments are carried out (base pressure 1×10^{-10} Torr). To ensure a sufficient sensitivity in the measurements of reactivity, we perform deposits of an equivalent thickness of 8 Å on thin silicon wafers.

2.2 Size and composition distributions measured by TEM and EDX

The nucleation of deposited clusters is not a well-known process. In our case, deposits have been made on several different supports (pellets of Al_2O_3, pellets of graphite, and amorphous C). The mean size and standard deviation have been found identical whatever the support, indicating that cluster diffusion, and hence coalescence, must be very weak. Focusing our attention on amorphous-C systems: The observed dispersion (0.6) and mean size (2.5 nm) are similar for both alloys. However, in contrast with the vapor deposition technique, the mean cluster size is independent of the deposited thickness. EDX allows the determination of the composition of individual particles by reducing the probe area down to 1 nm^2; for both alloys, the composition homogeneity has been checked and found equal to that of the corresponding rod [6]. The homogeneity of composition ensures that LEIS would give reliable results with respect to surface versus bulk composition of the particles.

2.3 Surface composition measured by LEIS

In a catalytic process, the molecules involved are adsorbed on the surface; this implies that a first step in the understanding of an alloy's reactivity is the determination of the surface composition. LEIS is a surface-sensitive technique that selectively probes the outermost atomic layer.

Generally, this technique is used to study massive systems. Nevertheless, in a recent work [6], we have shown that it can be applied to our clusters. The main result is that the cluster surface is enriched in Pd for both alloys. More precisely, the Pd surface concentration reaches up to 38 at. % and 87 at. % for $Pd_{17}Pt_{83}$ and $Pd_{65}Pt_{35}$ alloys, respectively. In parallel with LEIS experiments, modeling of the segregation process has been done through the use of Monte Carlo simulations [6]. The deduced surface concentrations are in rather good agreement with experiments. In addition, these simulations show that the segregation is site dependent: the segregating element preferably occupies the low-coordination sites.

3 Reactivity in the hydrogenation of the 1,3-butadiene

The catalytic measurements were carried out in a UHV equipment composed of three vessels interconnected by line-of-sight valves [7]. The 73 cm^3 stainless steel reactor was connected to a mass spectrometer and to an introduction chamber onto which the transport suitcase can be fixed. The samples were transported with a linear drive into a preparation chamber or into a characterization chamber equipped with Auger and LEED facilities. To study the conversion of the 1,3-butadiene, 35 Torr of hydrogen and 7 Torr of C_4H_6 were introduced at 300 K in the reactor. The variations of pressure of butadiene, butenes, and butane were followed as a function of time by recording of the 39, 41, and 43 masses. This type of detection does not allow the determination of butenes isomers. Absolute rates of conversion of the reactants were thus determined and expressed as the number of molecules transformed per surface metal atom per second. The number of surface metal atoms was deduced from the thickness of the deposit and from the diameter distribution determined by TEM, assuming that the size distribution of clusters deposited on SiO_x is similar to the one observed on amorphous C. An important parameter is the selectivity for the formation of butenes expressed as: $\sum P_{\mathrm{butenes}}/\sum(P_{\mathrm{butenes+butane}})$.

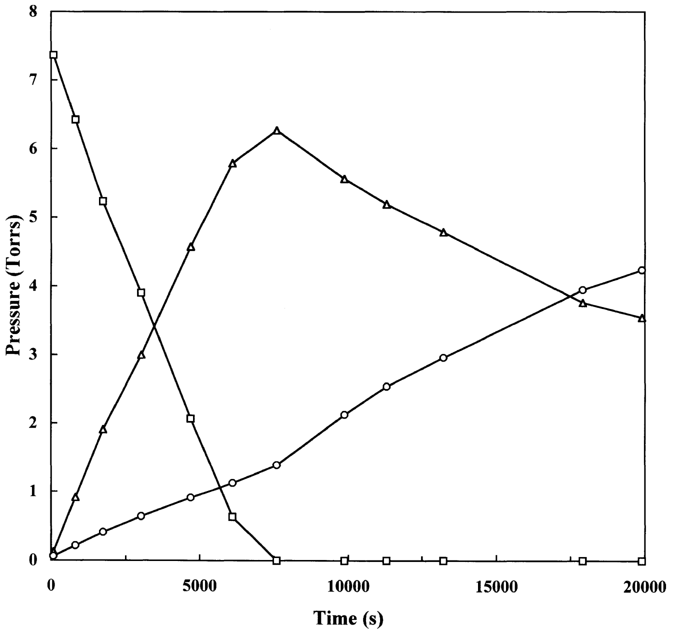

Fig. 1. Partial pressure variations of 1,3-butadiene (squares) butenes (triangles) and butane (circles) versus time for $Pd_{65}Pt_{35}$ alloy. Experimental conditions: hydrogen pressure = 35 torrs, 1,3-butadiene pressure = 7 torrs; $T = 300$ K.

The variations of the 1,3-butadiene, butenes, and butane partial pressures versus time, for the 1,3-butadiene hydrogenation reaction over the $Pd_{65}Pt_{35}$ and $Pd_{17}Pt_{83}$ samples, are reported in Figs. 1 and 2. First of all, one can notice that the decrease of the diene partial pressure versus time is linear: this agrees with a zero order of the reaction with respect to butadiene pressure. A first order with respect to hydrogen has been assumed for both studied systems, as in the case of pure Pd [8]. The activities and selectivities of the two alloys are summarized in Table 1 and compared with those of pure Pd [9] and pure Pt [10]. One can notice that the pure Pd catalyst, which has been prepared by ionic exchange with $Pd(NH_3)_4(OH)_2$, has a nar-

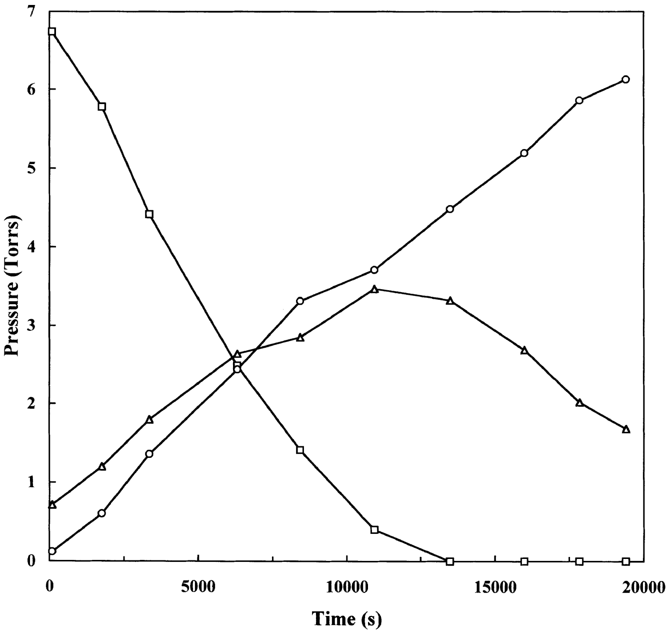

Fig. 2. Partial pressure variations of 1,3-butadiene (squares) butenes (triangles) and butane (circles) versus time for $Pd_{17}Pt_{83}$ alloy. Experimental conditions: hydrogen pressure = 35 torrs, 1,3-butadiene pressure = 7 torrs; $T = 300$ K.

row particle diameter distribution, like our clusters; however, its mean diameter is slightly smaller, close to 2 nm. The Pt activity is much lower than that of Pd. As seen in Figs. 1 and 2, the presence of butane at the very beginning of the reaction implies that the selectivities of the studied systems are lower (especially at low Pd content) than those of Pd after stabilization.

On the basis of these results, we have tried to explain the observed activities and selectivities of the alloys, compared to those of pure Pd. The selectivity of pure Pd clusters, observed at the beginning of the reaction, is poor compared to those of single-crystal faces (100% for the two close-packed (111) and (110) faces [11]); this has been explained [9] as a consequence of the electronic properties of "hot" atoms with low coordination numbers. Indeed, it has been shown [12] that corner atoms have a strongly modified density of states compared to atoms lying in the center of dense faces. Modifications of the chemical properties are thus to be expected, namely, an increase of bonding energies for unsaturated hydrocarbons and, consequently, an augmentation of the rate of hydrogenolysis reactions [13]. Since the platinum activity is low as compared to that of Pd, we are led to neglect Pt contribution in the following. For the $Pd_{17}Pt_{83}$ system, 38% of the surface is covered by Pd atoms and Monte Carlo simulations [6] (weighted by the size distribution and considering a cubo-octaedral shape) indicate that 20%, 44%, 11%, and 25% of Pd atoms are located at corners, edges, [100] faces, and [111] faces, respectively. As for the $Pd_{65}Pt_{35}$ system, 87% of the surface is covered by Pd atoms, which are located at corners (11%), edges (29%), [100] faces (10%), and [111] faces (50%).

Assuming that low coordination number (N) sites (i.e., corner $N = 6$, edges $N = 7$ and [100] faces $N = 8$), the so-called hot sites, have a mean activity A_h, and that highly coordinated sites (i.e., [111] faces $N = 9$), or "cold sites", have an activity A_c, we can write the following system of equations:

$$\frac{A_\mathrm{h} \times 75 + A_\mathrm{c} \times 25}{100} = 3.29 \tag{1}$$

(Mean activity per Pd surface atom for $Pd_{17}Pt_{83}$ system)

$$\frac{A_\mathrm{h} \times 50 + A_\mathrm{c} \times 50}{100} = 2.75 \tag{2}$$

(Mean activity per Pd surface atom for $Pd_{65}Pt_{35}$ system)

which lead to $A_\mathrm{h} = 3.83\,\mathrm{s}^{-1}$ and $A_\mathrm{c} = 1.67\,\mathrm{s}^{-1}$; this implies that hot sites are 2.3 times more active than cold sites.

In the absence of values for the activity of a Pd [100] face, one can also assume that the atoms located at sites with $N = 8$ ([100] faces of our clusters) are "cold atoms", and the above system of equations leads to $A_\mathrm{h} = 4.1\,\mathrm{s}^{-1}$ and $A_\mathrm{c} = 1.85\,\mathrm{s}^{-1}$, showing that hot sites are 2.2 times more active than cold sites.

These assumptions both show the same tendency: the low-coordination sites are 2 or 3 times more active than the high-coordination sites.

Going over to the pure Pd catalyst, one knows of course that all the surface sites are occupied by Pd atoms. Assuming the same size distribution as that of our bimetallic clusters, we calculate that 44% of atoms have a coordination of 6, 7, or 8, and that 56% have a coordination of 9. At the beginning of the reaction one can write:

$$\frac{A_\mathrm{h} \times 44 + A_\mathrm{c} \times 56}{100} = 3.95 \tag{3}$$

Table 1. Activities and selectivities of the bimetallic clusters, compared to those of pure Pd- and Pt-silica-supported catalysts and normalized to the same hydrogen pressure, 35 Torr.

Sample	Surface composition Pd (at.%)	Activity (molecule/surface atom/s)	Selectivity for the butenes formation (%)
Pd/SiO_2 [9]	100	$3.95^{*} \rightarrow 1.32^{**}$	$40^{*} \rightarrow 90^{**}$
$Pd_{65}Pt_{35}$	87	2.4	85
$Pd_{17}Pt_{83}$	38	1.25	50
Pt/SiO_2 [10]	0	0.1	60

* at the beginning of the reaction
** measured after stabilization

At the end of the reaction, i.e., after stabilization, it is seen that cracking reactions and the formation of cokes have occurred on the hot sites; this is attributable, as mentioned above, to an increase in the rate of hydrogenolysis reactions. This accounts for the large deactivation of the pure Pd catalyst. So, after stabilization, we can consider that only cold sites are still active and we can write:

$$\frac{A_{\mathrm{c}} \times 56}{100} = 1.32 \tag{4}$$

Values of $A_{\mathrm{h}} = 5.9$ and $A_{\mathrm{c}} = 2.35\,\mathrm{s}^{-1}$, for the activity of hot and cold, respectively, are extracted from (3) and (4). Once again, hot sites are found to be 2 or 3 times more active than cold sites. The slightly higher absolute activities of pure Pd clusters could be related to their smaller mean diameter, compared to bimetallic catalysts.

We thus show that by the consideration of only the distribution of the Pd atoms between hot and cold sites, our results can be explained.

Concerning the selectivity, the arguments developed above qualitatively explain our results. The selectivity observed for pure Pd clusters at the beginning of the reaction and after stabilization (see Table 1) indicate that cold sites have a selectivity of 90%, and that hot sites have a bad selectivity of close to 40%. This explains the low selectivity of the $\mathrm{Pd}_{17}\mathrm{Pt}_{83}$ clusters, where 75% of the Pd surface atoms are hot, and the better selectivity of the $\mathrm{Pd}_{65}\mathrm{Pt}_{35}$ clusters, for which a larger proportion of cold Pd atoms are expected. Finally, no electronic influence of the surrounding Pt atoms on Pd atoms has been evidenced; this is in agreement with the absence of atomic core-level binding energy shifts as shown by photoemission measurements [14].

4 Conclusion

Model-supported bimetallic clusters have been produced by laser vaporization of bulk alloys. The narrow size range and well-defined stoichiometry have been measured by TEM-EDX analysis. Low-energy ion scattering experiments, coupled with Monte Carlo simulations, show a strong Pd surface segregation exacerbated on low-coordination sites. The reactivity of these systems towards 1,3-butadiene hydrogenation has been studied and compared to pure Pd and Pt supported clusters. The determined Pd surface concentration and local order have allowed us to satisfactorily explain the catalytic behavior of our bimetallic clusters by assimilating the low-coordination sites to the "hot sites" described in the literature.

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