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Surface restructuring of palladium particles induced by CO adsorption

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In order to characterize chemisorption induced reconstruction the surface of supported palladium particles (model catalyst) has been investigated during CO adsorption by SSIMS (static secondary ion mass spectrometry). The SSIMS signal ratio Σ_n Pd_nCO^+/Pd_n^+ has been used to monitor the CO adsorption kinetics. The relative occupancy of linear and bridged CO sites has been determined by the value of $PdCO^+/(\Sigma_n\ Pd_nCO^+)$ and the variation of the Pd–Pd next neighbour distance by plotting Pd_2^+/Pd^+ during CO exposure. It has been shown that CO chemisorption induces a surface restructuring by increasing the Pd–Pd distance in the particle surface. This phenomenon has the features of a cooperative phenomenon. On the reconstructed particle one bonding state has been identified which appeared to be a precursor of the CO dissociation.

Keywords: Model catalysts; palladium; CO chemisorption; surface reconstruction; cooperative phenomenon; SSIMS analysis

1. Introduction

The chemisorption of foreign atoms or molecules on a metal surface frequently induces surface restructuring. Such a phenomenon has been extensively investigated on bulk single-crystal surfaces and the structures have been discussed in a widely documented article by Somorjai and Van Hove [1]. On palladium a CO induced reconstruction of the (110) face has been interpreted with the missing-row model involving a change in number density of atoms in the first layer [2,3]. Many examples describe the reshaping of metal particles upon chemisorption [4] and it has been shown that small metal clusters tend to distort upon addition of CO thereby reducing their compactness [5]. Then there is a growing evidence that the metal particle surface may undergo changes during surface chemical processes. Recently, restructuring models of bond dissociation or catalytic reaction have been proposed [6–9]; however, experimental evidence is not provided so far. On the contrary, supported metal particles are viewed as being cuboctaedra more or less truncated with well defined (111), (100) or (110) facets and the active sites involved in surface reaction analysis are face sites and edge sites by reference to stepped single-crystal surfaces [10–13]. This point of view is supported by a lot of studies of model catalysts by electron microscopy (TEM and HREM) [14–17], but until now the surface structure of metal particles has not been probed during chemisorption or under steady state reaction condition. Static secondary ion mass spectrometry (SSIMS) has been shown to be a suitable surface analysis method to provide local structural information [18,19]. In a recent experimental study using SSIMS we have evidenced a correlation between the C–O bond breaking, the size and the roughness of Pd particles [12,20]. These results have motivated the present work, which provides experimental verification and characterization on the surface restructuring during CO adsorption on supported Pd particles.

2. Experimental

The experiments are performed in a home built UHV apparatus combining two chambers which can be isolated from each other [11]. The main chamber is equipped with a 1–600 amu mass spectrometer (QMS) for SIMS analysis. Low primary ion currents (< 1 nA cm^{-2} Ar$^+$ at 1 keV, incident angle = 45°) and fast recording times are used such that the surface layer integrity is maintained during the period of the study. The optimum conditions for the QMS are chosen following the recommendations in adsorption experiments [21,22]. Palladium particles are grown in situ by vapor deposition on a heated single crystal α-alumina substrate ($T \approx 600$ K). The metal source is a calibrated Knudsen cell fitted to give a flux of $(1-2) \times 10^{13}$ atoms cm^{-2} s^{-1}.

The cleanliness of the alumina surface is checked by SIMS before palladium deposition. The SIMS spectrum reveals various hydrate and carbonate ions which disappear after heating the sample for 2 h at 700 K under vacuum. After deposition electron microscopy and diffraction provide information on size distribution, density and morphology of the particle population. Some time ago it has been demonstrated [11] that adsorbate coverage and structure can be studied on small metal particles by static SIMS by monitoring the species M_nCO^+ and M_n^+ ($n = 1, 3$) [1]. In the present work the SSIMS ion ratio Σ_n Pd_nCO^+/Pd_n^+ (I) is used to monitor CO adsorption kinetics under CO exposure (at a low pressure of the order 10^{-7} Pa). The adsorbate stucture, i.e. the relative occupancy of linear and bridged CO sites, as a function of CO coverage is determined by the ratio $PdCO^+/(\Sigma_n\ Pd_nCO^+)$ (II). The justification of the choice of relations (I) and (II) is given in ref. [23]. The effect of CO–surface bonds on the cohesive energy in the particle surface and therefore on the surface roughness and crystallography is investigated by the variation of Pd_2^+/Pd^+ ratio.

When the SSIMS study is completed the sample is transferred to the second chamber for a parallel TPD (thermo programmed desorption) experiment using a VG 1–120 amu QMS which follows CO desorption after the particles have been exposed to increasing doses of CO at 300 K.

3. Results and discussion

3.1. SIZE AND MORPHOLOGY OF PALLADIUM PARTICLES

Palladium particles are prepared on (1012) or (0001) bulk sapphire surfaces (Crystal-Tec-Grenoble). Therefore TEM and TED observations are realized using the transfer replica method. Fig. 1 shows an example of the palladium particle population studied in this work. The mean size of the particles is around 3 nm for 5×10^{11} cm^{-2} in number density; they have a morphology of truncated cuboctaedra with (111) or (110) planes in contact with the substrate [12–16]. The particles expose mainly (111), (100) and some (110) facets and the shapes that are observed can be considered as equilibrium shapes at the temperature of deposition.

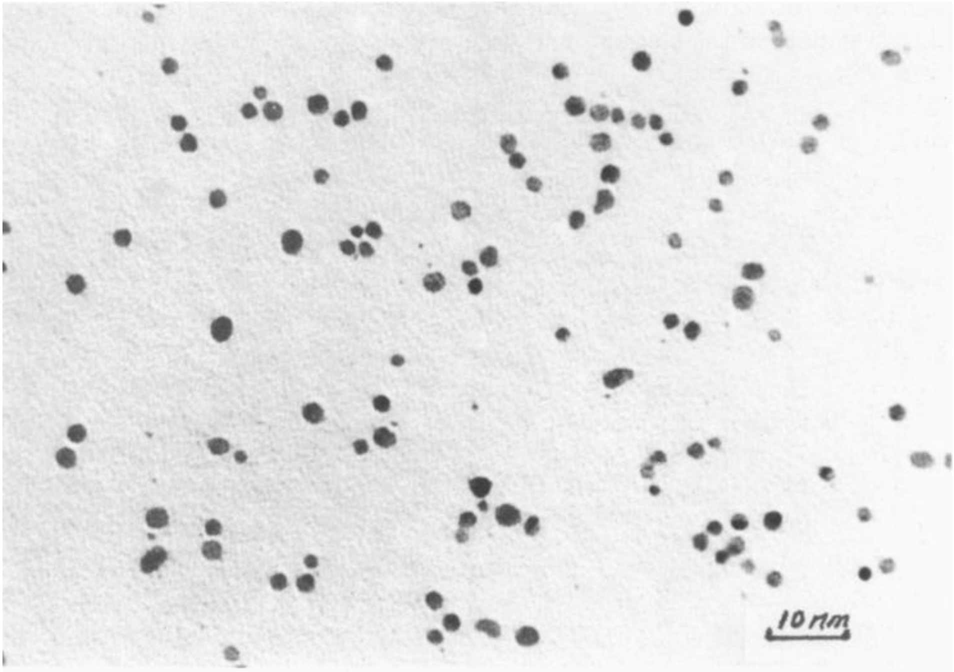

Fig. 1. Electron micrograph of particles deposited on α-Al_2O_3. After SSIMS and TPD analysis the particles are taken off the substrate by carbon transfer replica.

3.2. ADSORPTION KINETIC MEASUREMENTS AND ADSORBATE STRUCTURE AT ROOM TEMPERATURE

The clean annealed particles are exposed to a low pressure of CO ($\approx 10^{-7}$ Pa) such that the coverage saturation is obtained in a time less than 20 min at 300 K. The SSIMS spectra are recorded continuously during exposure with a frequency of one ion signal each 10 s. Fig. 2 shows the variation of the relative coverage deduced from the SSIMS signals as a function of exposure. On the same figure is plotted the relative coverage $\theta/\theta_{\mathrm{Max}}$ measured by TPD analysis. The two curves coincide, which confirms the linear relationship between SIMS ratio and coverage on small Pd particles in the whole coverage range. The same result had been also obtained for Pd particles deposited on mica [24]. Moreover, fig. 2 shows that the adsorption kinetics determined by the two methods are the same and, therefore, that the SIMS analysis is a true static SIMS. No gradient change is observed in the Σ_n $\mathrm{Pd}_n\mathrm{CO}^+/\mathrm{Pd}_n^+$ versus coverage plot, as is the case on single crystal Pd surface [25]. Fig. 3 shows the thermo desorption spectrum obtained at saturation coverage, it presents two peaks which have been commonly interpreted by CO adsorption in two states [11,26,27]. It has been found that the abundance of CO adsorbed molecules in the high energy state increases when the particle size decreases and that the low energy state (peak 1) begins to appear for an absolute coverage of about 0.2. These results seem to be denied by analysis of the data of fig. 2, which evidences one adsorption state. Unfortunately, on metal particles vibrational spectroscopies did not provide information

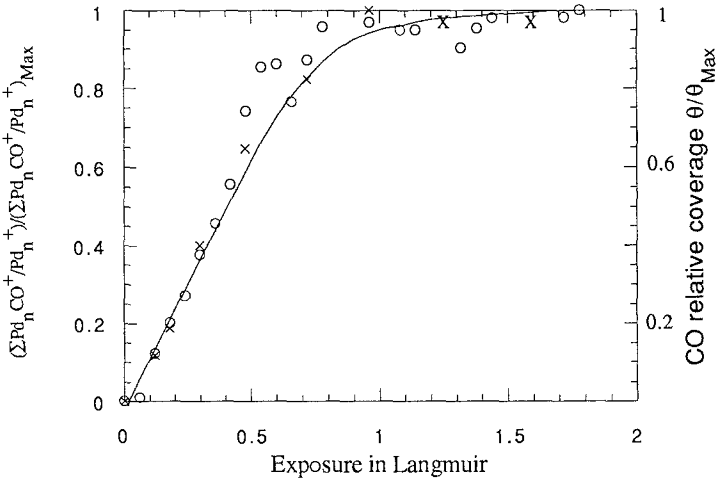

Fig. 2. (○) Variation of the relative ion ratio $(\Sigma_n\ \mathrm{Pd}_n\mathrm{CO}^+/\mathrm{Pd}_n^+)/(\Sigma_n\ \mathrm{Pd}_n\mathrm{CO}^+/\mathrm{Pd}_n^+)_{\mathrm{Max}}$ ($n = 1, 2$) as a function of exposure in Langmuir (1 L $= 10^{-6}$ Torr s). (×) Values of the relative CO coverage $\theta/\theta_{\mathrm{Max}}$ determined by TPD analysis. The absolute coverage at saturation calculated by using TPD and TEM data is estimated at $\theta_{\mathrm{M}} = 0.6$ (in molecules of CO adsorbed by Pd surface atom).

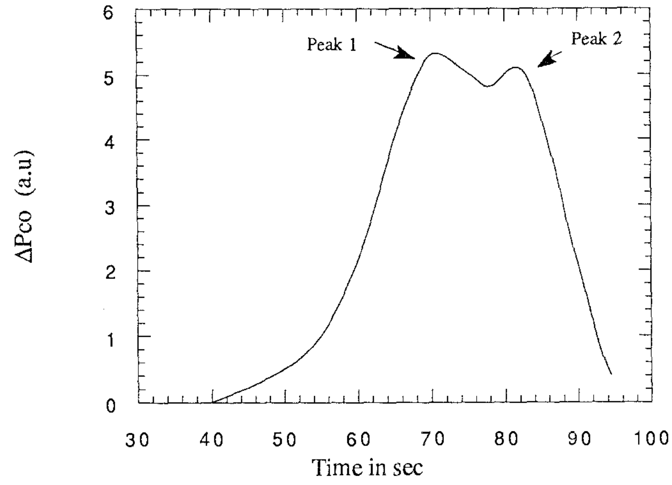

Fig. 3. Thermodesorption spectrum obtained at saturation coverage on the sample of fig. 1 with a temperature rate of 7 K s^{-1}.

to confirm if there are two CO bonding states on the particles as they did on single-crystal surfaces.

Examination of the SSIMS spectra reveals that Pd_3CO^+ ions are not present. This suggests that linear and/or two-fold coordination predominate. On the other hand the PdC^+ and Pd_2C^+ cluster ions are observed in the early stages of CO adsorption and they increase with coverage. Thus it can be inferred that the bonding state of CO on Pd particles is the precursor of CO dissociation. This state is characterized by specific relative yields of $PdCO^+$ and Pd_2CO^+ and fig. 4 shows the variation of the ion fraction $PdCO^+/(PdCO^+ + Pd_2CO^+)$ as a function of relative coverage. At very low coverages ($\theta/\theta_M < 0.25$) the $PdCO^+$

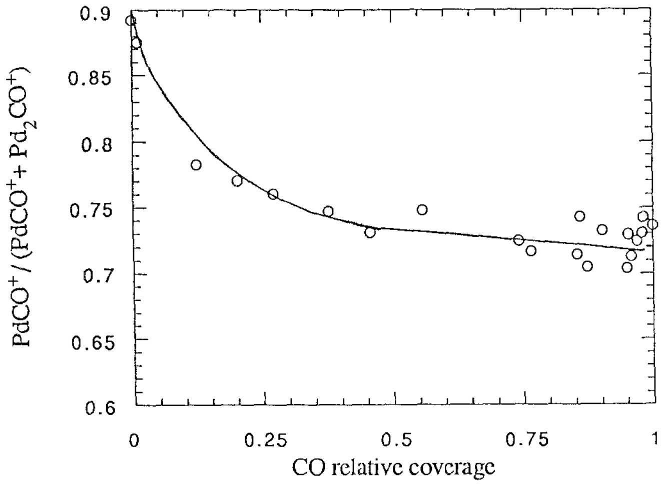

Fig. 4. Variation of the ion fraction $PdCO^+/\Sigma_n\ Pd_nCO^+$ during the experimental run of fig. 1.

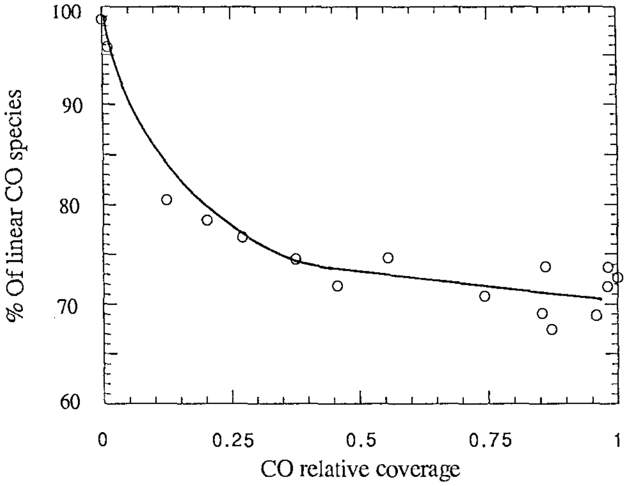

Fig. 5. Relative amount of linear Pd–CO bonds deduced from the data of fig. 4 by using the fragmentation patterns found on bulk single surfaces (see text).

fraction falls from 0.9 to 0.76 and remains to a steady state value of ≈ 0.74 for $\theta/\theta_{\mathrm{M}} \geqslant 0.5$. This variation is quite different to that observed on Pd (111) and Pd (100) [4,28], where the PdCO^+ relative intensity keeps a constant value (≈ 0.3) when the CO coverage increases. Assuming that Pd particles are limited by facets which have similar adsorption properties as Pd single-crystal surfaces we have deduced from fig. 4 data the relative amount of linear bonding sites. The results are plotted in fig. 5 as a function of $\theta/\theta_{\mathrm{Max}}$ and suggest that CO adsorbs linearly at low coverage and predominates at high coverage. Such an interpretation is implausible because it is well known that high energy bonding state (i.e. two or three fold coordinated CO) adsorbs first [29,30]. On the contrary, by comparing the data of figs. 2 and 5 one could suggest a continuity in the adsorption process inducing one adsorption state. Therefore it appears that the concept of the adsorption site on various facets does not seem pertinent to interpret the above results, which must be considered from another point of view: the particle surface restructuring. If such is the case the data indicate that the restructuring process occurs rapidly within the time scale of adsorption and does not need adsorption at adjacent sites. In effect it is shown in figs. 4 and 5 that the CO bonding readily changes as soon as the first molecules adsorb, the structure of the CO overlayer becoming steady at an absolute coverage value of $\theta \approx 0.2$.

The SSIMS analysis allows us to provide experimental verification of the surface restructuring induced by CO chemisorption. In effect the variation of $\mathrm{Pd}_2^+/\mathrm{Pd}^+$ ratio is able to probe the local atomic surface structure during CO exposure [22,25]. It is shown in fig. 6 that $\mathrm{Pd}_2^+/\mathrm{Pd}^+$ readily falls from 0.15 during the CO adsorption and remains at the constant value of 0.05 for $\theta/\theta_{\mathrm{M}} \geqslant 0.5$. This variation, parallel to the variation of $\mathrm{PdCO}^+/(\mathrm{PdCO}^+ +$

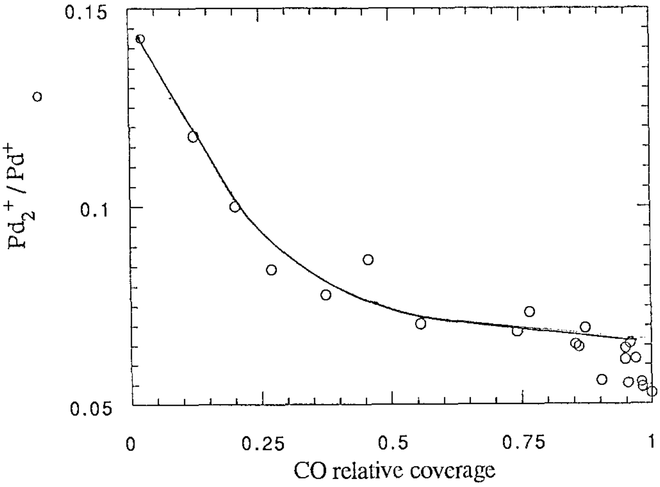

Fig. 6. The Pd_2^+/Pd^+ variation plotted during CO adsorption indicates a fast decrease of the cohesion in the metal particle surface in the coverage range $\theta/\theta_{Max} < 0.25$.

Pd_2CO^+) plotted in fig. 4, is a consequence of an increase of the Pd–Pd next neighbour distance, i.e. of the surface roughness, as a function of CO coverage. This phenomenon, which starts at a small coverage value, cannot be interpreted by direct interaction between the adsorbed molecules but by a through surface interaction. Moreover, we have verified that the surface structure returns to its clean state upon desorption by checking the ion yields obtained for two successive adsorption–desorption cycles. One can see in fig. 7 that CO coverage (a plots) and particle cohesion (b plots) are correlated and that the surface structure returns to its clean state after adsorption–desorption runs. Then, if a particle reshaping occurs, the phenomenon is reversible.

The above features are consistent with a cooperative behavior. In the model that is proposed by Oppenheim, Levine and Somorjai [7–9] the reconstruction starts with a small finite coverage. When CO chemisorbs it induces a local strain by a rearrangement which forms the “adsorption site”. This strain can be alleviated by CO induced reconstruction several sites away and so on.

The picture of fig. 8 is deduced from a previous work, which has shown that upon heating there exists a dissociation probability of CO at low coverage on Pd particles [31,32]. A correlation has been experimentally established between the degree of surface roughness [12] and the CO dissociation appearance. These characteristic features are taken into account in the CO chemisorption induced surface restructuring presented in fig. 8. A CO molecule adsorbs firstly in a low energy state E_0 and converts to a higher energy state E_1 after local restructuring. The next CO has then a probability to adsorb on a reconstructed surface as E_1 species and so on. There is no need for the E_1 states to be dissociated but, on the basis of the forward and back donation model for CO–metal bonding

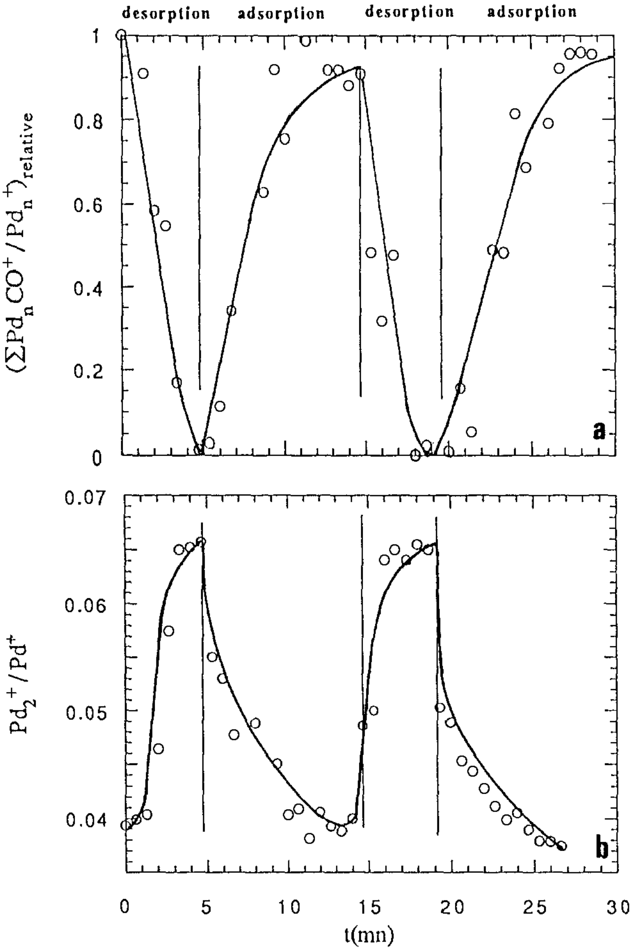

Fig. 7. SSIMS ratios variation for two successive adsorption–desorption cycles: (a) $(\Sigma_n \mathrm{Pd}_n\mathrm{CO}^+/\mathrm{Pd}_n^+)_{\mathrm{rel}} \propto \theta_{\mathrm{CO}}/(\theta_{\mathrm{CO}})_{\mathrm{Max}}$; (b) $\mathrm{Pd}_2^+/\mathrm{Pd}^+$.

[33,34], one can predict that the changes in the forces between the palladium atoms in the reconstructed area come with changes in the electronic structure of the surface atoms and with a weakening of the C–O bond.

The CO in E_0 state has been identified by SSIMS as linear bond species, the E_1 state is a precursor of the dissociated state E_2 which appears upon heating. The E_1 state is characterized by a high relative yield of PdCO^+ in the SSIMS fragmentation pattern because of a loss of cohesion between Pd next neighbour atoms. It is clear that the reaction kinetics determined on the basis of such unidimensional models are not realistic. In the case of small particles the rearrangement of metal atoms under the surface must be also considered and a size effect can be predicted. Other important parameters to take into considera-

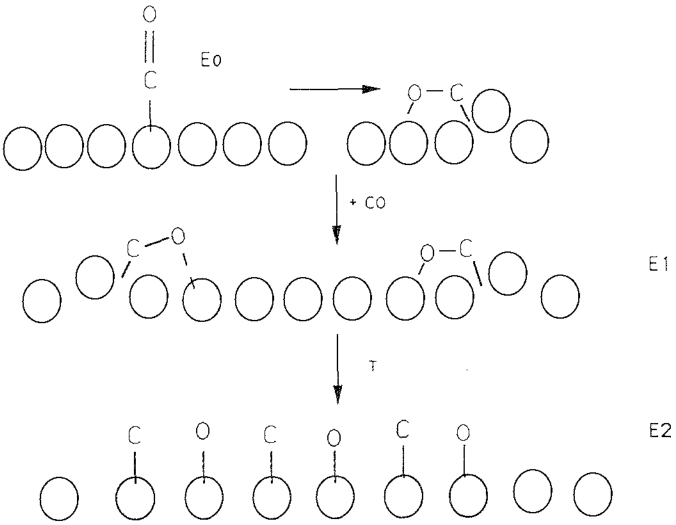

Fig. 8. Tentative one-dimensional model of the CO chemisorption–restructuring cooperative phenomenon on Pd particles (see text). The open circles are Pd atoms.

tion are the nature of the equilibrium shape of the bare particle and the interaction between the substrate and the metal particle.

4. Conclusions

(i) There is clear experimental evidence for a concomitance between CO chemisorption and surface restructuring of Pd particles.

(ii) The SSIMS and TPD data are consistent with an increase in the surface roughness and paradoxally in the homogeneity of the adsorption site coordination. That can be interpreted by an isotropic dilatation of the Pd–Pd bond and may be under the surface in a cooperative phenomenon which induces a CO bonding state (E_1) precursor of the dissociated state. In the E_1 state there is a Pd–C and a Pd–O interaction which give more than 70% of $PdCO^+$ species in the SSIMS fragmentation pattern.

(iii) In this model the CO molecules are adsorbed in only one bonding state. Hence the TPD spectrum of fig. 3 would be interpreted either by a kinetic effect due to E_1–E_2 conversion upon heating or by different reconstruction structure of the particle facets. Such an analysis of the TPD data is in progress in our group.

In a next paper, we intend to present coverage and thermal aspects of the CO adsorption. The influence of the particle size on the ability for the surface to restructure will be also studied.

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