

The Pd/Ni(110) Bimetallic System: Surface Characterisation by LEED, AES, XPS, and LEIS Techniques; New Insight on Catalytic Properties

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Pd deposits on Ni(110) have been studied by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), low-energy ion scattering spectroscopy (LEIS), and X-ray photoelectron spectroscopy techniques and their catalytic properties tested by the butadiene hydrogenation reaction at room temperature. Their catalytic activity is greatly enhanced by appropriate annealings. Superstructure indicative of a long range ordering of Pd atoms on Ni is evidenced for low Pd coverages neither before nor after annealing. For higher coverages, a LEED superstructure appears after annealing. AES and LEIS studies reveal a sharp Pd depth profile and the existence of a Pd–Ni surface alloy even at room temperature. The Pd 3d core level binding energy is shifted upwards by at least 0.4 eV with respect to pure Pd surface atoms and remains unchanged in the course of annealings. Hence geometrical rearrangements have to be taken into consideration to explain the activity enhancement.

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1. INTRODUCTION

In the field of heterogeneous catalysis, a particularly promising class of multicomponent catalysts belongs to bimetallic systems which are found to exhibit superior properties compared to their single metal counterparts in terms of activity, selectivity, stability, and poison resistance (1). The behavior of such catalysts is usually understood either in terms of a geometrical “ensemble-effect” (associated with the number of surface atoms needed for the catalytic process to occur) (1, 2) or of the so-called “ligand-effect” (associated with the electronic modifications induced by the system constituents (2, 3)). An additional “bi-site effect” (in which both components play a specific role with respect to the partners of the catalytic reaction) has also been suggested to understand synergetic effects on cata-

lysis by alloys (4). The knowledge of the uppermost layer electronic structure, composition, and atomic arrangement of such catalysts is of primary importance for the understanding of their catalytic properties. Another central concept, evolving out of all these studies, is that of the active site (5–8) which is also a key point for the understanding of the catalytic process. In the particular case of the butadiene hydrogenation reaction occurring on the Pd–Ni bimetallic surface, theoretical studies (8) have predicted that the butadiene is di- π adsorbed on an atom pair. It needs to be stressed that this adsorption mode (energetically more favorable than a di- σ or a mono- π mode) is consistent with experimental data (5, 6, 9), showing that the selectivity S towards butenes remains equal to unity until quasi-complete conversion ($S = P_{\text{butenes}} / [P_{\text{butenes}} + P_{\text{butane}}]$). As long as butadiene is present in the gas phase, it prevents butane formation by removing butenes from the catalytic surface. One can wonder whether the catalytic site is constituted by a homonuclear pair (Ni–Ni or Pd–Pd) or a heteronuclear one (Ni–Pd). There is much emphasis on identifying and characterising the catalytic site through theoretical and experimental studies employing model catalysts (7–9).

In a previous study (5, 6), we have shown that a small amount of Pd atoms deposited on Ni(111) (namely from 0.5 to 3 monolayer (ML) of Pd) leads to a slight activity enhancement compared to pure Pd(111), whereas the selectivity (S) towards butenes is not altered and remains equal to unity. The binding energy of the Pd 3d electrons, measured by XPS, is shifted upwards by at least 0.4 eV (compared to pure Pd surface atoms) (5) but is found to be *unchanged* upon annealing, whereas the activity was further and greatly enhanced. Therefore, the specific catalytic properties of the annealed sample cannot be explained solely in terms of electronic structure modifications. Geometrical changes (induced by the annealing) have to be considered, and it was considered that they induce more efficient catalytic sites for the hydrogenation reaction (5).

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For a better understanding of the role played by the surface morphology on the activity, we have now studied the properties of Pd atoms deposited onto the Ni(110) face. This particular face, exhibiting furrows along the (110) direction, is expected to generate linear Pd structures. STM (scanning tunnelling microscopy) studies have already shown that linear structures can be induced by fcc (110) faces. For example, the aggregation of long Cu mono-atomic chains on the Pd(110) (10) or Au on Ni(110) (11) have been evidenced at room temperature. In the case of Au/Ni(110), the authors have even identified the existence of a surface alloy at room temperature, although Au is completely nonmiscible with bulk Ni. A low density corrugated Ni surface like Ni(110) (1.1×10^{15} atoms cm^{-2}) therefore gives the opportunity to study the role played by substrate structural factors on the Pd growth and their consequences for the catalytic activity. Moreover, as the enthalpy of mixing of the Pd–Ni system is small with no gap for miscibility (12), one can expect to generate an intermetallic compound (a surface alloy) at low temperature and so have the opportunity to study its properties.

In this work we investigate the electronic properties, the surface composition, and the catalytic activity of Pd deposits on Ni(110) at room temperature and after annealing. The active site will be discussed in terms of (i) the surface electronic properties measured by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), (ii) the outermost surface composition measured by low-energy ion scattering spectroscopy (LEIS), and (iii) the surface organisation measured by low-energy electron diffraction (LEED).

II. EXPERIMENTAL

Pd is grown on a clean Ni(110) surface at 300 K and analysed by AES and LEED under ultrahigh vacuum conditions (UHV) in a system fully described elsewhere (13). Before any deposit is made, the surface is cleaned by repeated cycles of Ar^+ ion bombardment at 3 keV, followed by an annealing at 875 K. It exhibits then a (1 × 1) LEED pattern with very sharp spots. Pd is vapour deposited under 3×10^{-9} Torr using a Knudsen cell. The Pd deposition rate is 1.35×10^{13} at. $\text{cm}^{-2} \text{s}^{-1}$ and is controlled by a quartz microbalance. The deposited thickness is calibrated by Rutherford backscattering spectroscopy (RBS). The deposits can be annealed at controlled temperatures, under ultrahigh vacuum conditions, using an IR lamp. The UHV chamber is connected to a reactor (84 cm^3) operating in a static mode at room temperature only. The gas analysis during the reaction is realised by sampling through a leak valve in a quadrupole mass spectrometer. A UHV “suitcase” under dynamic vacuum allows the sample to be transferred without air exposure into an ESCALAB 200R machine

(from Fisons Instruments) where LEIS and XPS are carried out (base pressure 1×10^{-10} Torr).

III. RESULTS AND DISCUSSION

1. Catalytic Efficiency

Table 1 displays the catalytic activities, for the butadiene hydrogenation reaction, of various Pd coverages on Ni(110) compared with Pd deposits on Ni(111). The activities of the pure metals are also recalled for reference. Let us first study the activity of the nonannealed Pd/Ni(110) deposits: it increases with the Pd coverage and is greater than for pure Pd(110) (except for low coverage, namely $\theta = 0.25$ ML). For the annealed deposits on Ni(110), the same observation is valid but the activity magnitude is greatly enhanced by the 475 K annealing.

The activity of the deposits (nonannealed or annealed) on Ni(111) with the Pd coverage is quite different: it is smaller than for the Pd/Ni(110) cases (for a similar deposit amount) and an optimal value seems to be reached for a Pd coverage between 0.5 and 1 ML. This might not be surprising since the (110) face is supposed to generate a particular geometrical arrangement of the Pd atoms along the furrowed (110) direction which would lead to a quite different chemical activity.

It has to be emphasised that for each deposit, the variation of the activity versus Pd surface concentration does not increase linearly (5) and that in all cases, the selectivity (S) towards butenes remains near unity even for quasi-complete butadiene conversion.

The following sections are devoted to the interpretation of this noticeable catalytic activity behavior based on the analysis of different effects.

TABLE 1
Catalytic Activity ($\times 10^{15}$ Molecules $\text{cm}^{-2} \text{s}^{-1}$) for the Butadiene Hydrogenation Reaction on Pd/Ni(110) and Pd/Ni(111) ($P_{\text{H}_2} = 20$ Torr, $P_{\text{H}_2}/P_{\text{HC}} = 5$, and $T = 295$ K)

Catalyst	Catalytic activity				
	0.25 ML	0.5 ML	1.0 ML	3.0 ML	4.0 ML
Pd/Ni(110), 295 K	1.1	7.4	8.4	—	42.3
Pd/Ni(110), 475 K, annealed	2.2	68.6	46.0	—	142.0
Pd/Ni(111), 295 K	2.3	1.8	1.8	1.6	—
Pd/Ni(111), 475 K, annealed	3.1	12.0	15.4	8	—

Note. Results are given for various Pd coverages (monolayers, ML) on Ni(110) and Ni(111) at 295 K or after 475 K annealing. Values for pure metals, reported for comparison (units as in Table): Pd(110), 4.2; Pd(111), 0.9; Ni(110), 0.3; Ni(111), 0.2.

2. LEED Observations

The LEED technique is used to characterise the Ni(110) surface before and after Pd atom deposition. Owing to the hindrance of the UHV chamber equipments, no photography could be properly taken. Hence we are, up to now, unable to give quantitative information.

The LEED pattern background is greatly enhanced after the Pd atom deposits (from 0.25 to 1 ML) at room temperature; nevertheless, no superstructure is observed. After annealing, the contrast between the characteristic Ni(110) spots and the background becomes better, but again, no superstructure indicative of Pd overlayer long range ordering can be identified. However, the disorder encountered in the LEED observation indicates some departure from an ideal layering.

The 4 ML Pd deposit has a similar effect on the background to the above-mentioned Pd coverages *before* the annealing, leading to the vanishing of the Ni(1×1) pattern. After a 15-min annealing at 475 K, the Ni(1×1) primitive pattern reappears and the contrast between the characteristic Ni(110) spots and the background becomes better. Additional spots (Scheme I) develop: (i) in $1/2$ position along the (001) direction, (ii) offset from the primitive spots along the (110) direction. The latter spots might be associated with a large coincidence mesh which would be the consequence of the atomic radius mismatch between the nickel substrate and the outermost palladium atoms. This is not surprising since the topmost atoms are Pd (see LEIS measurements) which have a larger radius with respect to the underlying substrate atoms. The former spots would correspond to Pd adatom ordering and nucleation along the (110) furrows. Although the pure Pd surface is not known to be reconstructed, it has to be emphasised (in the case of the Pd-Ni bimetallic system) that the observed (1×2) structure suggests that the deposited Pd layers would be reconstructed either within a row-pairing or missing-row model. The driv-

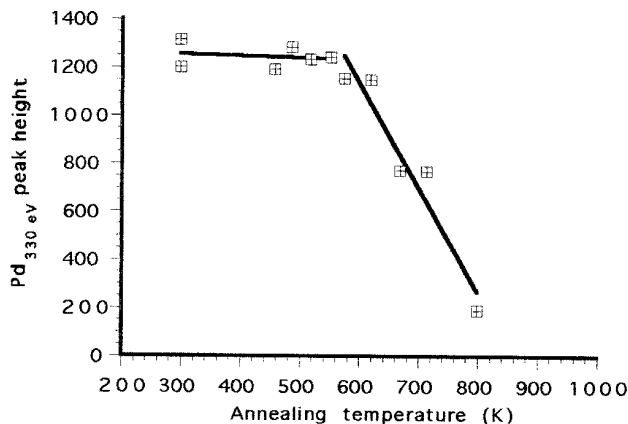
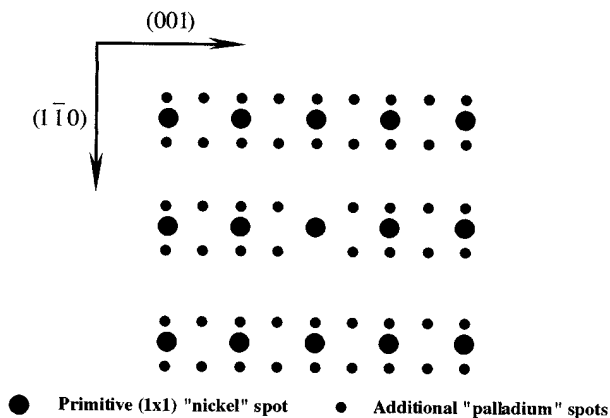


FIG. 1. Pd_{330 eV} AES peak height (arbitrary units) versus annealing temperature (K). ($E_p = 1500$ V, $V_{mod} = 10$ V_{pp}, $I_e = 10$ μ A).

ing force for this reconstruction could be the minimising of the surface free energy of the Ni(110)-supported Pd layers.

3. AES and LEIS Results

In previous work (9), we have shown that the AES measurements of the Pd_{330 eV} peak height at room temperature might be understood in terms of a Pd Stranski-Krastanov growth mode on Ni(110) for which Pd-3D islands are formed on a first Pd monolayer. The disorder encountered in the LEED observations indicates strong departure from an ideal layering. As in previous studies (5, 6, 9), Fig. 1 depicts the measured AES Pd_(330 eV) peak heights as a function of the annealing in the case of Pd(0.5 ML) deposited on Ni(110). It reveals that the Pd remains *near* the very surface as long as the annealing temperature is limited to 475 K. It has to be underscored that similar measurements and conclusions are valid for higher Pd coverages. Nevertheless, due to the rather high value of the mean free path of the electrons, AES gives information on the first few upper layers and does not allow a precise depth profile determination. Hence, for an accurate description of the outer shell composition of the deposits before and after annealing, we have performed LEIS analysis using 1 keV He⁺ ions with a 142° scattering angle, the analysis being performed along the normal to the surface. Two peaks (Fig. 2) are observed at 783 and 874 eV corresponding to backscattered ions from Ni and Pd surface atoms, respectively. Except for a slight amount of oxygen at 401 eV, no other impurity is detected. However, the noticeable background level at low kinetic energy attests to the presence of some contamination by residual gases during the transfer from the preparation chamber to the XPS machine. Despite a possible segregation induced by the contamination, we did not perform any cleaning of the surface before the LEIS measurements, as it could alter the surface structure and the Pd depth profile. The contamination was removed within



SCHEME I. Schematic picture of the LEED pattern appearing after annealing (15 min at 475 K) in the case of Pd 4 ML/Ni(110).

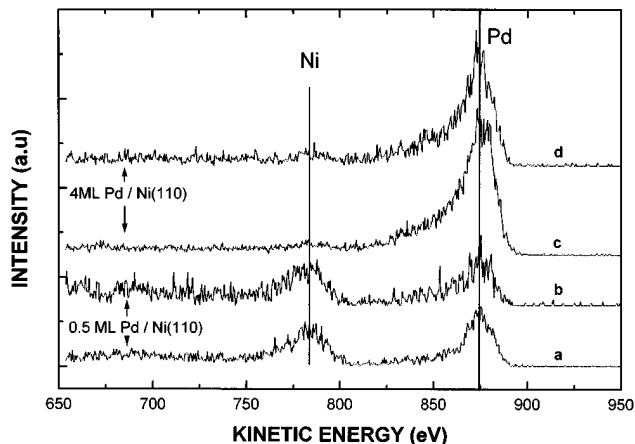


FIG. 2. LEIS spectra of: (a) Pd (0.5 ML) on Ni(110) as deposited at room temperature, (b) Pd (0.5 ML) on Ni(110) annealed at 475 K, (c) Pd (4.0 ML) on Ni(110) as deposited at room temperature, (d) Pd (4.0 ML) on Ni(110) annealed at 475 K (He^+ ions, 1 keV, primary current = 5 nA, spot size $\approx 0.1 \text{ mm}^2$, the sputtering time before acquisition is 60 s).

the Pd depth profile determination during the very early sputtering time.

In order to avoid important damage of the surface sample and to have a correct determination of the first layer composition and of the depth profile, a low ion current intensity is used (50 nA/mm^2) for a gentle sputtering of the surface sample. The Pd outermost layer concentration is determined from the corresponding Pd and Ni LEIS peak areas, corrected for the sensitivity factor of Pd with respect to Ni ($S_{\text{Pd}}/S_{\text{Ni}} = 2.3$). The result is compared with the calculated topmost Pd concentration (based on an extrapolation back to zero sputter time) using an adapted sequential layer sputtering model (14, 15) which is also able to provide the Pd depth profile.

The model is based on a sequential layer sputtering for which the number of atoms irradiated by the primary beam in each layer is assumed to be proportional to $\exp(-t/T)$ (15), where t stands for the sputtering time and T for the time span needed to remove the equivalent of one monolayer. This model was originally developed by Hofmann (15) in order to reach the depth profile from AES data. We have implemented it for LEIS to determine the depth profile of binary alloys. The preferential sputtering is taken into account. Though work has already shown the influence of the different ion beam mixing mechanisms on the interpretation of LEIS data (16), we have assumed, to a first approximation, that these effects are negligible since light ions of low energy during short sputtering time are used for the experiments. The experimental conditions are also chosen to prevent crater effect distortions. It is supposed that no further segregation phenomenon occurs, either induced by the sputtering effect or due to the thermodynamic reequilibration of the system. This last point can be ruled out as long as the temperature at which the measurements are

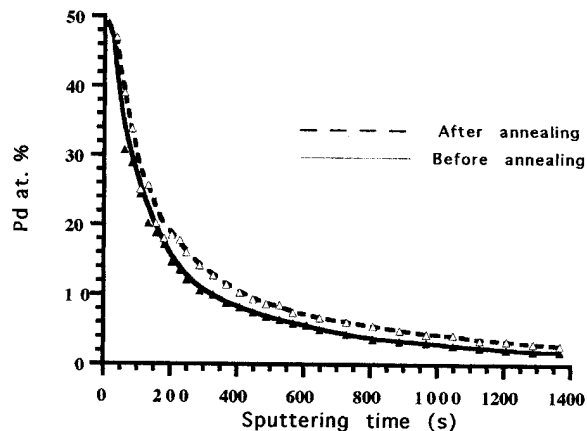


FIG. 3. LEIS experimental Pd at.% variation with sputtering time (s) before (solid line) and after annealing (475 K during 15 min, dotted line) in the case of 0.5 ML Pd deposited on Ni(110). The analysed depth is roughly 6 to 8 Å.

performed is low (room temperature) compared with the temperature for which the diffusion of atoms becomes appreciable (for transition metal alloys, the bulk diffusion allowing the possible reequilibration of the system, has been found to become appreciable only above 700 K). Owing to the approximations used, the physical significance and applicability of this model are therefore limited. Nevertheless, it can be successfully applied to the treatment of the first few atomic layers of transition metal alloys.

This treatment has already been applied to the determination of the composition of the outermost layer and depth profile of the well-known PtNi(111) bimetallic system (17, 18). The uncertainty in the determination of the composition of the different layers and the sensitivity of the model has allowed us to claim that the solution is determined with good reliability and to look promising for bimetallic systems (14).

Figure 3 depicts the experimental Pd at.% evolution of the Pd 0.5 ML/Ni(110) sample before and after annealing. It appears that the variations of the Pd at.% as a function of the sputtering time are similar for the nonannealed and annealed sample. The experimental determination of the outermost layer composition (of both nonannealed and annealed samples) leads to a Pd concentration of about 50 at.%. This is supported by the quantitative analysis of the Pd depth profile (Table 2). The Pd topmost layer

TABLE 2

Theoretical Pd Depth Profile for the Pd 0.5 ML/Ni(110) Sample

	0.5 ML/Ni(110), nonannealed (at.%)	0.5 ML/Ni(110), 475 K, annealed (at.%)
1st Layer	48 ± 2	45 ± 2
2nd Layer	2 ± 2	5 ± 2
3rd Layer	0 ± 2	0 ± 2

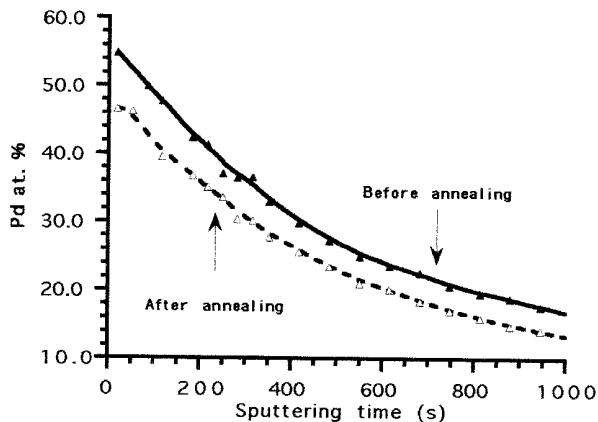


FIG. 4. LEIS experimental Pd at.% variation with sputtering time (s) before (solid line) and after (475 K during 15 min, dotted line) in the case of 1.0 ML Pd deposited on Ni(110). The analysed depth is roughly 6 to 8 Å.

concentration being roughly 50 at.%, no significant Pd diffusion in the bulk occurs, neither at room temperature nor in the course of annealings. Nevertheless, the LEIS technique (in *this* particular case) does not provide any evidence of a Pd–Ni surface alloy formation since the results are consistent with Pd atom location *on* or *in* the topmost Ni layer.

Figure 4 depicts the Pd at.% evolution of the Pd 1 ML/Ni(110) sample before and after annealing. The experimental variations of the Pd at.% with the sputtering time are rather similar, the annealed sample exhibiting a lower Pd topmost layer concentration, 48 at.% instead of 55 at.% for the nonannealed one. This is supported by the theoretical treatment which indicates that both depth profiles are very similar (Table 3). For both nonannealed and annealed samples, a Pd atom diffusion occurs towards the underlying Ni layers, giving rise to a surface alloy but is limited to the first two uppermost Ni layers, since the Pd atom concentrations are equal to roughly 55 and 45 at.% (in the first and second layers, respectively) for the nonannealed sample and 50 and 50 at.% (in the first and second layers, respectively) for the annealed sample. This is not surprising since the Pd–Ni system exhibits no gap for miscibility. The annealing would only lead to a reorganisation of the Pd atom arrangement and would generate more efficient catalytic sites at the very surface. This result is contrasting rather with Pd deposits on

TABLE 3

Theoretical Pd Depth Profile for the Pd 1.0 ML/Ni(110) Sample

	1.0 ML/Ni(110), nonannealed (at.%)	1.0 ML/Ni(110), 475 K, annealed (at.%)
1st Layer	55 ± 2	50 ± 2
2nd Layer	45 ± 2	50 ± 2
3rd Layer	5 ± 2	0 ± 2

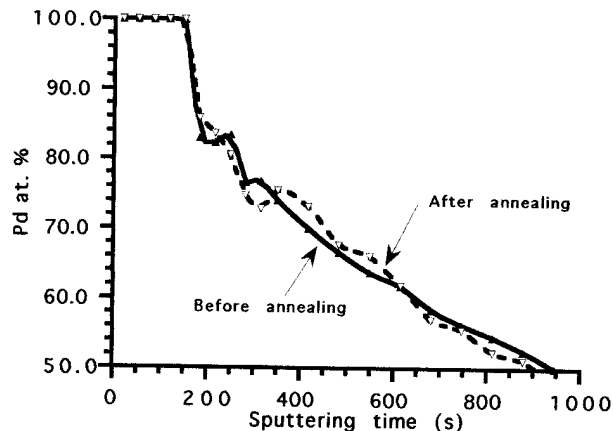


FIG. 5. LEIS experimental Pd at.% variation with sputtering time (s) before (solid line) and after (475 K during 15 min, dotted line) in the case of 4.0 ML Pd deposited on Ni(110). The analysed depth is roughly 6 to 8 Å.

Ni(111) for which the formation of a surface alloy occurs only after annealing (5, 6). The Ni(110) face being more open than the (111) face, the formation of a surface alloy on Ni(110) might be easier at room temperature.

The result concerning the Pd 1 ML deposited on Ni(110) gives insight on the Pd 0.5 ML/Ni(110) sample for which the formation of a surface alloy might also have occurred (even at room temperature) despite the fact that no LEIS evidence exists to support this assumption. The annealing would lead to the reorganisation of the Pd arrangement at the very surface, the Pd depth profile remaining unchanged.

Figure 5 depicts the LEIS study for the 4 ML Pd deposit. It appears that the Pd at.% variations as a function of the sputtering time are identical for both samples, suggesting that their Pd depth profiles are similar. This is supported by the theoretical treatment (Table 4). The first three top layers are constituted by Pd atoms only. In the fourth and fifth layers (Pd–Ni interface) a Pd–Ni intermixing seems to occur.

In conclusion it must be recalled that the formation of a surface alloy occurs at room temperature. The annealing would favour a geometrical reorganisation of the outermost layer leaving the depth profile unchanged. It has to be highlighted that this reorganisation is supported by the

TABLE 4

Theoretical Pd Depth Profile for the Pd 4.0 ML/Ni(110) Sample

	4.0 ML/Ni(110), nonannealed (at.%)	4.0 ML/Ni(110), 475 K, annealed (at.%)
1st Layer	100 ± 2	100 ± 2
2nd Layer	100 ± 2	100 ± 2
3rd Layer	100 ± 2	100 ± 2
4th Layer	57 ± 2	68 ± 2
5th Layer	38 ± 2	32 ± 2

LEED data which clearly show, subsequently to the annealing, the appearance of a Pd superstructure. Bearing in mind the particularly high catalytic activity of these samples (in particular for the four monolayer sample), one could think that a particular geometry is necessary for an optimal catalytic activity. However, electronic effects have also to be considered.

4. XPS Measurements

In order to provide evidence for electronic effects of the Ni environment on the Pd atoms, we have analysed the energy value and line shape of the Pd 3d signal, recorded using the $MgK\alpha$ radiation line and a low pass energy of 20 eV for various exit angles. For both nonannealed and annealed Pd deposits (0.5, 1, and 4 ML), the Pd 3d structures are *identical* in shape, but are shifted towards higher binding energy by 0.4 ± 0.1 eV with respect to those of pure bulk Pd (Fig. 6). Recalling that the LEIS measurements indicate that the Pd atoms remain at the very surface even after annealing, the Pd 3d binding energies have to be compared to those of pure Pd(110) surface atoms in order to evaluate the electronic modifications induced by the Ni neighbours with respect to pure Pd surface atoms. Forsell *et al.* (19) have determined a downwards core level shift of 0.4 eV for the (100) Pd surface atoms, but since our study concerns the (110) orientation, it is not possible to have a reliable value for this shift. However, the measured core level shift in the case of Pd atoms deposited on Ni(110) is expected to be greater than +0.4 eV compared with pure Pd surface atoms. Nevertheless, the shift in core-level binding energy must be interpreted with caution, since this effect includes contributions from other initial-state effects and final-state effects. The fact that the binding energies do not change

with increasing coverage suggests that they may be determined by a complex interplay of effects. Such a discussion mainly holds for low Pd coverages. For higher coverages, the presence of Pd(110) atoms in the underlying layers makes these conclusions more questionable.

Since the electronic properties remain unchanged in the course of the annealing, the Pd electronic characteristics seem to be established as soon as the Pd atoms are deposited on the Ni(110) surface.

The same observations have been made on the Pd atom deposits on Ni(111) (5) which showed no electronic modification after a moderate thermal treatment despite a huge catalytic activity enhancement.

5. The Active Site

Let us try to understand why the activity of palladium (the active metal) for the hydrogenation of butadiene is enhanced when associated with nickel. One of the key points for such a discussion is the study of the bond strength (which would be altered with respect to pure Pd) between the active site and the diene.

With respect to the diene, a theoretical study of butadiene adsorption on the surface of the Pd–Ni bimetallic system (8) has shown that the di- π adsorption mode on an atom pair is favoured compared with the di- σ one. Such an adsorption mode requires an *adjacent* atom pair. It has to be recalled that this result is consistent with experimental catalytic test data which indicate that the selectivity (*S*) of the bimetallic surface towards butenes is equal to unity. Hence, three basic catalytic sites can be suggested regarding the chemical nature of the active site of the Pd–Ni surface alloy: (i) Ni atoms only, (ii) both Pd and Ni atoms, (iii) Pd atoms only.

The activity of Ni atoms is poor for the hydrogenation of butadiene, compared to that seen in pure Pd (see Table 1). Moreover, the number of Ni–Ni sites is decreasing with increasing Pd coverage until total disappearance in the case of high Pd coverages (namely four monolayers). Therefore, sites involving only Ni surface atoms do not play a dominant role, and the “active site” involves inevitably Pd surface atoms. The possible action of mixed sites has already been ruled out (5) considering the decreasing number of mixed sites with increasing Pd coverage. This is supported by the study of the Ni(110)-supported four Pd monolayer sample which has no Ni atom in the first three upper layers but exhibits a particularly high catalytic activity. We therefore suggest that the active sites is a Pd pair. Recalling the XPS study, these Pd surface atoms are electronically modified by surrounding Ni atoms in such a way that the bond strength between Pd pairs and the diene would be modified, enhancing the Pd–Ni alloy activity. The Pd–Ni mismatch may also play a role in putting the Pd atoms at a particular distance favourable for the butadiene activation. We cannot as yet rule out the effect played by such a strain. STM experiments are currently in progress.

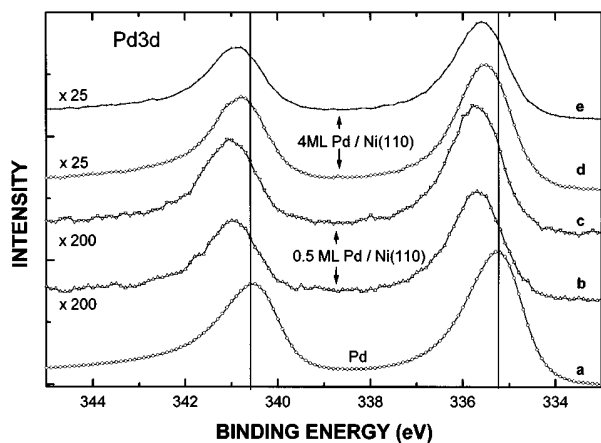


FIG. 6. XPS spectra of the Pd 3d core level for: (a) Pure bulk Pd, (b) Pd (0.5 ML) on Ni(110) as deposited at room temperature, (c) Pd (0.5 ML) on Ni(110) annealed at 475 K, (d) Pd (4.0 ML) on Ni(110) as deposited at room temperature, (e) Pd (4.0 ML) on Ni(110) annealed at 475 K ($MgK\alpha$, the analysis angle is 90°).

We have discussed the modification of the reactivity in terms of the butadiene adsorption sites solely. We are aware of the role of weakly held states (20) or of adsorbed hydrogen in the hydrogenation reaction. However, only a very slight difference in the isosteric heat of adsorption of H₂ on pure Pd(110) (21) and on pure Ni(110) (22) can be found. This inclines us to consider that the hydrogen may not be the key factor in the activity enhancement in the butadiene hydrogenation reaction. Some difference would be certainly found with respect to the *absorbed* hydrogen. It is known that adsorbed hydrogen generates Pd hydride with pure Pd while this is not the case with pure Ni. We cannot rule out, up to now, the formation of Pd hydride on the bimetallic surfaces.

IV. CONCLUSIONS

More effective catalytic materials can be generated by Pd–Ni bimetallic systems obtained by deposition technique. AES and LEIS data treatments reveal that the Pd atoms are located at the very surface of the samples and show a sharp Pd depth profile. In contrast with Pd deposits on Ni(111), the formation of Pd surface alloys occurs on Ni(110) at room temperature. Subsequent 475 K annealing allow one to enhance greatly the activity of Ni(110)-supported Pd layer(s) towards butadiene hydrogenation. As the result of a complex interplay of effects, XPS measurements reveal an upwards shift of the Pd 3d core level binding energy with respect to the surface of the pure metal. These electronic modifications are found to be established as soon as Pd is deposited on Ni(110) and remain unchanged in the course of annealing. Therefore, geometrical rearrangements are the key to explaining the enhanced catalytic activity of annealed samples. Such geometrical modifications are evidenced in the case of high Pd coverages since a LEED superstructure appears after annealing. Geometrical rearrangements are expected to occur even for lower Pd coverages despite the fact that no LEED superstructure indicative of a long range ordering could be detected. Assuming that the butadiene molecule is di- π adsorbed on an active site constituted by a Pd pair, both electronic and geometrical modifications would alter the “butadiene–bimetallic surface” bond (with respect to the pure Pd surface) and

would act in such a way that the active site is much more efficient than the same site located on a pure Pd matrix.

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