Surface characterisation and reactivity of a Pd 0.5 monolayer deposit on Ni(110)

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An upward shift of 0.8 ± 0.1 eV is measured on the Pd 3d core levels of Pd atoms deposited on Ni(110) with respect to pure Pd surface atoms. These electronic properties are found to be unchanged in the course of a 475 K thermal treatment whereas the activity of the annealed deposit towards the butadiene hydrogenation reaction is largely enhanced. Consequently, electronic effects are not sufficient to explain the activity enhancement. The LEIS technique reveals that the Pd atoms remain at the very surface of the sample, the Pd concentration being roughly 48 at%. Therefore, some geometric effects have to be taken into consideration. The annealing would lead to a particular arrangement and would generate more effective catalytic sites.

Keywords: bimetallic catalysis; surface characterisation by LEED, AES, XPS, LEIS; butadiene hydrogenation; active site

1. Introduction

Bimetallic materials are widely used in heterogeneous catalysis because of their superior catalytic properties compared to those of their constituents (activity, selectivity, stability and poison resistance) [1–3]. Nevertheless, there is much emphasis on understanding the changes which occur in the structural, electronic and chemical properties of catalysts upon addition of a second metal through theoretical and experimental studies employing model catalysts. These phenomena on alloys are usually understood either in terms of a geometrical "ensemble effect" (associated with the number of surface atoms required for the catalytic process) [1,4] or of the so-called "ligand effect" (associated with the electronic modifications induced by the components of the system [3,4]). 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 alloy synergetic effects on catalysis [5]. An accurate understanding of the catalytic behaviour of bimetallic systems requires not only the precise knowledge of the local concentration and of the arrangement of both components at the very surface but also the knowledge of their electronic structure. The aim of this work is to give insights in such effects for the Pd–Ni bimetallic system. A direct consequence of such a study could be to improve the catalyst efficiency by generating an appropriate design for the arrangement of both components at the atomic scale.

A model alloy catalyst can be prepared by depositing an active metal onto another single-crystal metal substrate followed by annealing at an appropriate temperature. In a previous study [6,7], we have shown that an annealed 0.5 ML [#1] Pd atom deposit on Ni(111) exhibits a larger activity (for the butadiene hydrogenation reaction) compared with the one of pure Pd(111), whereas the selectivity 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 0.8 ± 0.1 eV (compared to pure Pd surface atoms) [7]. The core level shift is found to be *unchanged* by the annealing whereas the activity is enhanced. Hence, the specific catalytic properties of the annealed sample cannot be explained in terms of electronic structure modifications solely. Geometrical changes (due to the annealing) have to be taken into account and would induce more efficient catalytic sites for the hydrogenation reaction [7].

For a better understanding of the role played by the surface morphology of the catalyst on the activity, we have chosen to investigate the properties of Pd atoms deposited onto the Ni(110) face which is supposed to generate linear Pd structures. The STM (scanning tunnelling microscopy) technique has already shown that linear structures can be induced by fcc(110) faces, due to the presence of furrows at the very surface. For example, the aggregation of long mono-atomic chains of Cu on the Pd(110) [8] or of Au on Ni(110) [9] have been evidenced at 300 K. This low density corrugated Ni surface (1.1×10^{15} atoms cm^{-2}) gives the opportunity to study the role played by substrate structural factors on the Pd growth, and their consequences on the catalytic activity.

[#1] 1 ML is defined as the density of Ni atoms in the topmost layer i.e. 1.9×10^{15} atoms cm^{-2} for a Ni(111) surface. For the Ni(110) substrate, 1 ML = 1.1×10^{15} atoms cm^{-2}.

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Moreover, the mixing enthalpy of the Pd–Ni is small and there is no gap for miscibility [10]. Therefore one can expect to produce inter-metallic compounds at low temperature.

In this work, we have investigated the electronic properties and the modifications of the surface atomic composition (at room temperature and after a 475 K annealing) and studied their catalytic properties.

2. Experimental

Half a monolayer of Pd was grown on the clean Ni(110) surface at 300 K and analysed in situ by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) under UHV conditions in a system described in ref. [11]. Before starting the deposits, the (110) crystal surface is cleaned by repeated cycles of Ar^+ ion bombardment at 3 keV, followed by annealing at 875 K. It exhibits then a (1 × 1) LEED pattern with very sharp spots. Pd is vapor deposited at 3×10^{-9} Torr using a Knudsen cell. The Pd deposition rate is 1.35×10^{13} atoms cm^{-2} s^{-1} and is controlled by a quartz microbalance. The deposited thickness is calibrated by Rutherford backscattering spectroscopy. The deposits can be annealed at controlled temperatures, under UHV conditions, using an IR lamp. All samples are tested in the butadiene hydrogenation reaction in a small static reactor (84 cm^3) connected to the UHV chamber. During the reaction, gas analysis is performed using a quadrupole mass spectrometer by sampling through a leak valve. An UHV vessel under dynamic vacuum allows the sample transfer into an ESCALAB 200R machine (from Fisons Instruments) where low energy ion spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS) are carried out without exposure to air (base pressure 1.0×10^{-10} Torr).

3. Results and discussion

3.1. LEED observations

The LEED observations are performed in the preparation chamber on surfaces free from contamination before and after Pd deposition. The p(1 × 1) pattern of the clean Ni(110) substrate remains after the Pd 0.5 ML deposit at ambient temperature. Nevertheless, the background intensity is increased. No superstructure indicative of a long-range ordered Pd overlayer nor any surface reconstruction (row-pairing or missing row) can be identified, even after a 15 min annealing at 475 K. Nevertheless, the disorder encountered in the LEED observations indicates some departure from an ideal layering.

3.2. Auger analysis

The Auger analyses are performed using a RFA type detector, with a primary energy of 1.5 keV and the LEED gun as an electron source, for various Pd coverages at 300 K before and after the butadiene hydrogenation test reaction. The electron current, measured on the analysed sample is kept constant (10 μA) for each measurement. The $Pd_{330 eV}$ Auger peak-to-peak signal ($dN(E)/dt$ mode) is recorded for each Pd coverage and depicted on fig. 1a. A linear increase is measured until a coverage of about 0.92×10^{15} atoms cm^{-2} corresponding roughly to a Pd(110) surface density (0.92×10^{15} atoms cm^{-2}); after that, a slope break occurs on the curve. Subsequent depositions lead to a smoothly increasing signal. It seems that the first Pd layer is completed for a surface density slightly lower than that of the Ni(110) substrate, i.e. 1.1×10^{15} atoms cm^{-2}, which is not surprising since Pd atoms are 10% larger than Ni ones. The lack of a new break on the curve of fig. 1a for subsequent Pd deposition allows us to rule out the layer by layer growth mode. After the first layer completion, Pd atoms would agglomerate into 3D islands. Simultaneously, the $Ni_{60 eV}$ substrate signal is, on the opposite, linearly decreasing with increasing Pd coverage and then smoothly decreasing until the Pd coverage is roughly 2.5×10^{15} atoms cm^{-2}. For higher coverages, the $Ni_{60 eV}$ AES peak becomes irrelevant (fig. 1b). This may be con-

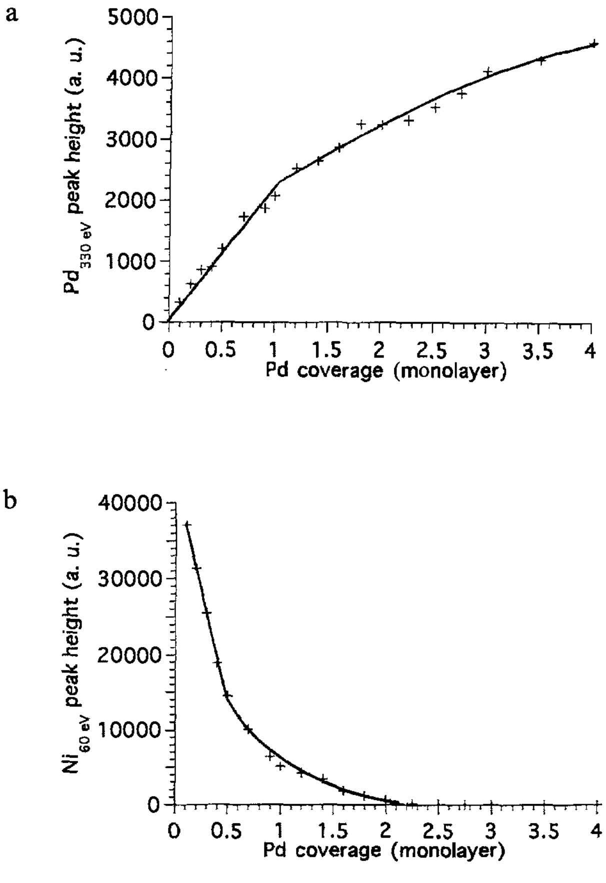

Fig. 1. (a) $Pd_{330 eV}$ AES peak height (arbitrary units) versus Pd coverage (in monolayer). (b) $Ni_{60 eV}$ AES peak height (arbitrary units) versus Pd coverage (in monolayer). (Ep = 1500 V, V_{mod} = 10 V_{pp}, I_e = 10 μA.)

sistent with a Stranski–Krastanov type growth mode [12].

A 0.5 ML Pd atom deposit (0.55×10^{15} atoms cm^{-2}) on Ni(110) is heated during 15 min at higher temperatures by increments. AES measurements are carried out after each annealing. The $Pd_{330\,eV}$ peak-to-peak signal versus annealing temperature is monitored and depicted on fig. 2. Despite a large contribution of the first layer to the signal, AES gives information on the first few top layers. No noticeable signal variation is recorded for temperature lower than 580 K, suggesting that Pd atoms remain *near* the very surface. For higher temperatures, the signal decreases significantly indicating a dissolution of the Pd atoms into the Ni matrix, evidenced by the segregation of the Pd atoms after a new annealing subsequent to an ion bombardment. In order to avoid bulk alloy formation, the Pd deposits under study are never annealed above 475 K.

In order to observe any modification of the electronic properties of the 0.5 ML Pd adlayer during the 475 K annealing, we have performed AES with increasing resolution (i.e. by decreasing the modulation voltage down to 5 V peak to peak). We have studied both the line shape and the energetic position of the M_4VV/M_5VV structures around 330 eV. Within the error of measurements, no changes of the peak shapes and of the energetic positions (330 ± 0.2 eV and 334.3 ± 0.2 eV for the M_5VV and M_4VV transitions, respectively) were observed. Although, for both annealed and non-annealed 0.5 ML Pd layer a downward shift of about 0.5 eV of the Pd Auger peak compared to pure Pd is observed. This suggests that the annealing might not alter the electronic properties of the Pd atoms and that the electronic modifications take place as soon as the Pd atoms are deposited on the Ni(110) surface.

AES analysis was also performed at the surface sample after the hydrogenation test reaction. Since the catalysed reaction involves hydrocarbons and hydrogen as reactants, the analysis reveals the presence of carbon or hydrocarbon fragments on the sample, in a similar amount, either on the non-annealed or annealed post-reaction sample surface. The ($Pd_{330\,eV}/Ni_{848\,eV}$) intensity ratio after hydrogenation is found to remain similar to the one measured before the test reaction suggesting that the Pd amount at the surface remains unchanged in the course of the butadiene hydrogenation reaction. A second hydrogenation reaction was performed after the first one. The similarity of catalytic efficiency suggests that the electronic and structural properties might be unchanged in the course of the reaction.

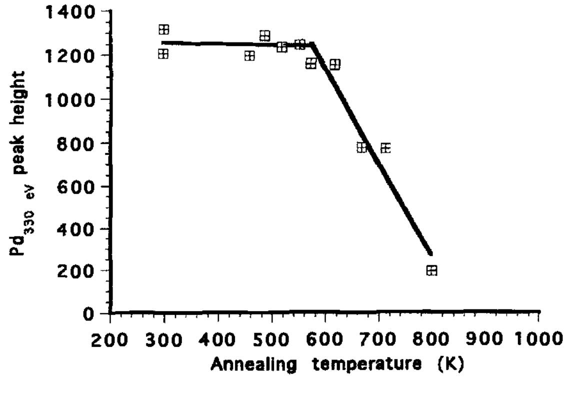

Fig. 2. $Pd_{330\,eV}$ AES peak height (arbitrary units) versus annealing temperature (K). ($E_p = 1500$ V, $V_{mod} = 10\ V_{pp}$, $I_e = 10\ \mu A$.)

3.3. LEIS analysis

For an accurate description of the 0.5 ML deposit outer shell composition deposit before and after annealing, we have performed LEIS analysis using 1 keV He^+ ions. The scattering angle was fixed at 142° and the analysis angle is along the normal to the surface. The acceptance angle of the spectrometer is limited to 15°.

Two peaks 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. Nevertheless, the noticeable background level at low kinetic energy attests the presence of a slight contamination (carbon monoxide) 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 which could alter the surface structure and the Pd depth profile. The contamination was removed within the Pd depth profile determination during the very early sputter time. In order to have an accurate determination of the first layer composition, the sample is gently sputtered by using a low ion current intensity (5 nA). The Pd and Ni uppermost concentrations are determined from the corresponding LEIS peak areas, taking into account the higher sensitivity factor for Pd with respect to Ni ($S_{Pd}/S_{Ni} = 2.3$). Based on an extrapolation back to zero sputter time using an adapted sequential layer sputtering model [7,13,14] they are found to be roughly identical before and after annealing (namely 48 Pd at%). Consequently no noticeable composition variation occurs in the course of the annealing.

The evolution of the Pd concentration as a function of the sputtering time is depicted on fig. 3 for both non-annealed and annealed samples. It appears that the Pd concentration decreases with time and that in both cases, the evolutions are similar. Assuming that there is no preferential contamination either of the Pd or the Ni atoms, this result agrees with a similar Pd depth profile for both samples and is consistent with a Pd atom location *on* or *in* the uppermost Ni layer. If Pd atoms remain on the Ni(110) surface, our results are consistent with the formation of Pd rows rather than a statistical Pd atom distribution for which the Ni masking would have been higher (i.e. the measured Pd concentration would have been higher) due to the shadowing–blocking effects.

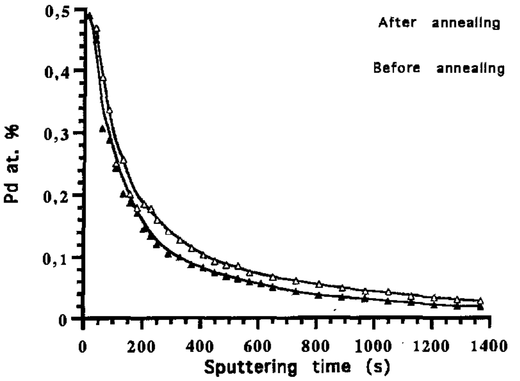

Fig. 3. Pd concentration evolution against sputtering time (s) for the non-annealed and annealed samples. The primary ions are $^4He^+$ with 1 keV kinetic energy. The ion current intensity is 5 nA.

3.4. XPS measurements

In order to evidence electronic effects of the Pd surface atoms, we have analysed the energetic positions and line shapes of the Pd $3d_{5/2}$ signals, recorded using a Mg K_α radiation line with a low pass energy of 20 eV. For both non-annealed and annealed Pd deposits, the Pd 3d structures are identical in shape to those of pure Pd, but are shifted upwards by $+0.4 \pm 0.1$ eV with respect to pure bulk Pd atoms. Recalling that the LEIS measurements indicate that Pd atoms remain at the very surface even after annealing, the Pd 3d binding energies have to be compared to those of pure Pd surface atoms, located 0.4 ± 0.1 eV lower in energy than Pd bulk atoms [15]. Hence, with respect to pure Pd surface atoms, a binding energy shift of about $+0.8 \pm 0.1$ eV has to be considered in the case of Pd deposits. These results indicate that Pd electronic modifications take place as soon as the Pd atoms are deposited on the Ni(110) surface. This core level shift is very close to the one measured on the contamination free Pd_5Ni_{95} bulk alloy [16] which exhibits also a Pd surface concentration of roughly 50 at%. Further thermal treatments do not alter significantly these electronic properties. This may be compared with Pd atom deposit on Ni(111) [7] which showed that, despite an alteration of the catalytic activity, no electronic modification was evidenced after a moderate thermal treatment.

The new electronic properties of Pd atoms deposited on Ni(110) can be understood in terms of orbital rehybridisations and/or charge transfer. A redistribution of Pd s and d electrons, induced by surrounding Ni atoms and/or a charge transfer between Pd and Ni may occur [17]. An electronic transfer from localised "4d" states to diffuse "5s" states of Pd and/or a Pd electronic depletion would lead to a decrease of the repulsive Coulomb interaction between core and valence electrons, and consequently to an increase of the Pd core-level binding energies [16–20]. The shift in core-level binding energy must be interpreted with caution, since this effect includes contributions from initial-state effects (charge transfer [21], orbital rehybridisation [21–24], volume renormalisation [25]) and final state effects (change in the screening of the core hole [21]).

3.5. Catalytic activity

The butadiene hydrogenation reaction is performed at 300 K with an excess of hydrogen (the $P_{H_2}/P_{C_4H_6}$ ratio is equal to five, with a total pressure of 24 Torr). For both samples (annealed and non-annealed) the selectivity towards butenes remains equal to the unity until quasi-complete butadiene conversion. The activities expressed as the number of C_4H_6 molecules transformed per cm^2 and per second for a hydrogen pressure of 20 Torr are given in table 1 (the reported values are initial rates) and compared to those of pure metals and to a Pd 0.5 ML deposit on Ni(111). These reported turnover frequencies (TOF) remain constant over a butadiene conversion range from zero to 100%.

It appears that:

– The activities of pure Ni(110) and Ni(111) are poor.

– The activity of a Pd 0.5 ML deposited at room temperature on Ni(110) is roughly twice larger than that of the pure (110) Pd face. Assuming that only Pd atoms are active for this reaction, one can consider the activity per Pd adatom (the Pd adatom concentration is determined from LEIS data): the turnover frequency of the Pd 0.5 ML deposited at room temperature sample is three times larger than that of a pure Pd(110) surface and seven times larger compared to a non-annealed Pd adatom on Ni(111).

– The activity per cm^2 of a Pd 0.5 ML on Ni(110) annealed at 475 K is nine times larger than that of the non-annealed sample, sixteen times larger than that of the Pd(110) surface. It is also six times larger than the activity of the annealed 0.5 ML deposit on Ni(111) for the similar surface Pd concentration. The activities per Pd surface atom are striking (see table 1). The annealed Pd 0.5 ML deposit on Ni(110) is much more active than every other sample.

Although these surfaces show quite different catalytic activities, the important synergetic effect cannot be explained by the modification of the electronic properties when the Pd atoms are in contact with the Ni matrix solely since no significant change of the electronic properties is observed in the course of the annealing. Moreover, Pd atoms deposited onto Ni(111) or onto Ni(110) exhibit identical electronic properties. Recalling the LEIS measurements which indicate that no Pd concentration modification occurs during the annealing, one has to consider the influence of geometric effects in addition to the electronic ones due to Ni ↔ Pd interaction. This geometric factor is probably crucial to explain the activity enhancement from non-annealed to annealed deposits, since Pd core-level binding energies or electronic properties are similar for both samples. Due to the

Table 1
Catalytic activity (molecules/(cm^2 s)) for the butadiene hydrogenation reaction (P_{H_2} = 20 Torr, P_{H_2}/P_{HC} = 5, 295 K). Results are given for 0.5 ML Pd deposits on Ni(110) and Ni(111) at 295 K or after 475 K annealing. The values for pure metals are reported for comparison

	Sample							
	0.5 ML Pd/Ni(110)		0.5 ML Pd/Ni(111)		pure Pd		pure Ni	
	295 K	475 K annealed	295 K	475 K annealed	Pd(110)	Pd(111)	Ni(110)	Ni(111)
activity (mol cm^{-2} s^{-1})	7.4×10^{15}	68×10^{15}	1.8×10^{15}	12×10^{15}	4.2×10^{15}	0.86×10^{15}	0.34×10^{15}	0.2×10^{15}
(1) Pd atom number on the first layer	0.53×10^{15} [a]	0.53×10^{15} [a]	0.9×10^{15}	0.9×10^{15} [a]	0.92×10^{15}	1.53×10^{15}		
(2) Ni atom number							1.1×10^{15}	1.88×10^{15}
turnover frequency TOF (s^{-1})	14	128	2	13.3	4.5	0.56	0.3	0.1

[a] These Pd concentrations are determined from the LEIS data.

Pd and Ni atom size difference, Pd surface atoms would be strained and/or protrude from the surface Ni plane. Geometrical effects have already been reported [8] by Röder et al. who have evidenced that two-dimensional islands of several atomic rows width are generated during a moderate annealing of a Cu deposit onto Pd(110). Once deposited at room temperature on Ni(110), Pd atoms might grow in linear chains above the Ni surface. Other geometrical arrangements which would occur in the course of the annealing and lead to the formation of a bidimensional surface alloy, cannot be ruled out up to now.

4. Conclusion

The catalytic activity (for the butadiene hydrogenation reaction) of a 0.5 ML Pd deposit on Ni(110) at room temperature is nearly similar to that of the pure Pd(110) surface. The activity is greatly enhanced after a thermal treatment at 475 K. This effect cannot be explained by an electronic factor only, since no significant Pd 3d electronic difference can be measured before and after annealing. The LEIS measurements indicate that no composition modification occurs in the course of the annealing at the very surface. Consequently, some geometrical effects have to be invoked. A particular arrangement might be generated and could be more efficient for the butadiene hydrogenation reaction.

Much remains to be done to put the light on the local Pd atom arrangement on the Ni surface. Some helpful UHV techniques such as STM, surface EXAFS, X-ray diffraction at grazing incidence have now to be implemented concomitantly with the study of the chemisorptive properties of this bimetallic system. Some adapted calculations would be helpful to gather information on the electronic structure of the Pd atoms and give trends on the adsorption mode of hydrogen and butadiene on the active site with respect to pure Pd.

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