Reactivity of O₂ on Pd/Ru(0001) and PdRu/Ru(0001) surface alloys

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The reactivity of a Pd monolayer epitaxially grown on Ru(0001) toward O₂ has been investigated by molecular beam techniques. O₂ initial sticking coefficients were determined using the King and Wells method in the incident energy range of 40–450 meV and for sample temperatures of 100 K and 300 K, and compared to the corresponding values measured on the clean Ru(0001) and Pd(111) surfaces. In contrast to the high reactivity shown by Ru(0001) at 100 K, the Pd/Ru(0001) system exhibits a monotonic decrease in the sticking probability of O₂ as a function of normal incident energy. At room temperature, the system was found to be inert. Thermal desorption measurements show that O₂ is adsorbed molecularly at 100 K. A completely different behaviour has been measured for the Pd_{0.95}Ru_{0.05}/Ru(0001) surface alloy. On this surface, the O₂ sticking probability increases with incident energy and resembles the one observed on the clean Ru(0001) surface, even at 300 K. Thermal desorption measurements point to dissociative adsorption of O₂ in this system. Both the charge transfer from the Pd to the Ru substrate and the compressive strain on the Pd monolayer contribute to decrease in the reactivity of the Pd/Ru(0001) system well below those of both Ru(0001) and Pd(111). *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983994>]

I. INTRODUCTION

Varying the catalytic activity of a surface in a controlled way can be generally achieved through different routes. A first approach consists in the modification of the lateral lattice constant of a given metal layer by growing pseudomorphic monolayers (MLs) of that metal on top of a substrate with a different lattice constant. This will introduce a tensile strain if the lattice parameter of the substrate is larger than that of the deposited metal [i.e., Cu on Ru(0001)] or a compressive strain if the lattice constant of the deposited metal is smaller than the one of the substrate [i.e., Pd on Ru(0001)]. Strain is known to strongly influence the surface reactivity,¹ with a tensile (compressive) strain inducing an upshift (downshift) of the d-band center and a corresponding enhancement (decrease) of the adsorption energy.^{2–6} This approach of growing metal layers epitaxially onto single-crystal metal substrates with different lattice constants has been demonstrated to result in very efficient selective catalysts in reactions involving H₂ molecules.⁷ A second route involves the formation of well controlled surface alloys, which often exhibit geometrical and electronic properties differing deeply from those of their constituent materials.^{8–14} As an example, recent studies have shown that small amounts of Pd atoms alloyed into the Cu(111) surface strongly reduce the dissociation barrier for H₂ on Cu(111) and can efficiently dissociate H₂ molecules, allowing them to spill over onto the host metal.^{15,16} A third route has been explored more recently and consists in controlling in an efficient way, using curved crystals and stepped surfaces, the type and density of steps present on a given surface.^{17–20}

The interaction of O₂ molecules with surfaces is a particularly interesting system, since the adsorption of oxygen is notoriously difficult to model because, in contrast to the case of H₂,²¹ it is generally believed that non-adiabatic transitions should be included in the calculations.²² Only recently, the experimental sticking coefficient of O₂ on the Al(111) surface²³ has been theoretically reproduced by including multiple Potential Energy Surfaces (PESs) associated with different spin configurations in the dynamics.^{24,25} To further test the validity of the calculated PESs, new experimental data on the dissociation dynamics of O₂ on a range of transition metal surfaces are badly needed.

In this respect, exploring the reactivity toward O₂ of the system formed by one monolayer (ML) of Pd grown epitaxially on Ru(0001) is quite interesting, since the first Pd layer grows pseudomorphically on Ru(0001)^{26,28–30} adopting the nearest neighbour distance of the substrate (2.65 Å), i.e., laterally compressed by 3.6% with respect to the Pd(111) surface. Hartmann *et al.*¹¹ have shown that deuterium molecules stick on this surface with a probability of 0.05, which is a factor of four smaller than the one measured on clean Ru(0001). Also the adsorption of CO is weaker on the Pd/Ru(0001) system than that on Pd(111) or Ru(0001).^{26,27}

In the present work, we explore the first two routes mentioned above by reporting measurements of the O₂ dissociation probabilities on the pseudomorphic monolayer of Pd/Ru(0001) and the surface alloy Pd_{0.95}Ru_{0.05}/Ru(0001) as a function of the incident energy of the oxygen molecules and the surface temperature. The measurements have been performed using the King and Wells method,³¹ whereby the kinetic energy of the molecular beam has been varied between

40 and 450 meV. At 100 K and for all impinging energies, the monolayer Pd/Ru(0001) presents a much lower initial sticking probability for O_2 as compared to the one observed on both clean Ru(0001) and Pd(111). At 300 K, the Pd/Ru(0001) surface was found to be completely inert to O_2 , again in sharp contrast with both Ru(0001) and Pd(111). Thermal desorption spectroscopy (TDS) suggests that O_2 is adsorbed molecularly on the monolayer Pd/Ru(0001) system. A different behaviour has been observed on the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface alloy, which presents a high reactivity to O_2 , even at room temperature. No O_2 desorption peak was observed in TDS below 300 K, which suggests the dissociative adsorption of oxygen on the PdRu surface alloy.

II. EXPERIMENTAL DETAILS

Experiments have been carried out in a Helium Atom Scattering (HAS) apparatus described elsewhere.³² It consists of a three-stage differentially pumped beam system and an 18 in. diameter UHV scattering chamber. The free jet expansion is produced through a nozzle of $d = 10 \mu\text{m}$ diameter. The nozzle temperature T_n can be varied between 100 and 700 K. The angular distribution of the scattered atoms is measured with a quadrupole mass spectrometer mounted on a two-axis goniometer. The base pressure in the scattering chamber is typically 5×10^{-10} mbar. The sample holder allows heating the crystal to 1500 K and cooling to 100 K. The sample temperature was measured with a type C thermocouple spot-welded to the sample. Details on Ru(0001) surface preparation can be found elsewhere.³³ Surface cleanliness and order of the Ru(0001) surface were checked using low-energy electron diffraction (LEED) and helium diffraction.³⁴

O_2 incident kinetic energies have been varied between 40 and 450 meV. They were controlled by seeding oxygen in a carrier gas (either Ne or He) and varying the oxygen concentration and the nozzle temperature. Since this HAS apparatus is not equipped with a time-of-flight system, the mean translational energy of the incoming O_2 molecules has been estimated as follows:³⁵

$$E_T = \left[(1-x) \frac{m}{M} + x \right]^{-1} C_p T_n, \quad (1)$$

where m and M are the molecular weights of the light and heavy gas, respectively, x is the mole fraction of the heavy gas, C_p is the mean heat capacity averaged according to gas concentrations, and T_n is the nozzle temperature. The uncertainty on the incident beam energy is estimated to be 10% of its mean value.

The HAS apparatus used in the current study has recently been modified³⁶ to allow sticking measurements using the King and Wells method.³¹ These measurements have been performed at an angle of incidence $\Theta_i = 15^\circ$, which is the smallest angle, which allows the detection of specular diffraction, owing to its limitations in the mechanism used for rotating the detector. It is worth emphasizing that the quality of the He beam (concerning angular divergence and energy spread) employed in the sticking experiments is the same as that usually employed for He and H_2 diffraction measurements using the same apparatus.³⁷

Pd was deposited from a commercial evaporator equipped with a Pd rod. The Ru(0001) crystal was kept at 700 K during film growth in order to avoid surface alloying, which starts around 850 K.²⁸ The deposited coverage and the structural quality of the epitaxial Pd layer have been checked by monitoring the changes in the intensity of the specular He beam, taking advantage of its high sensitivity to surface defects^{34,38} and the oscillatory behaviour with monolayer periodicity characteristic of systems that grow layer by layer.³⁹ A typical deposition curve is shown in Fig. 1. The observation of a clear maximum corresponds to the completion of the first Pd epitaxial layer. As it can be seen from Fig. 1, the first maximum in the reflected He-intensity occurred after about 40 min, corresponding to an evaporation rate of ~ 0.03 ML/min. Therefore, the HAS technique allows the growth of Pd monolayers to be monitored with a daily precision of 1%. The Cu monolayer was grown by the same procedure, keeping the Ru(0001) crystal at 500 K during Cu evaporation.³⁶

The $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface alloy was prepared by depositing 0.95 ML Pd at 300 K (just before the HAS maximum) followed by annealing at 1150 K. We took advantage of the fact that Hartmann *et al.*¹¹ have shown that annealing a certain amount of Pd on Ru(0001) to 1150 K results in the formation of a surface alloy with a negligible loss of Pd atoms from the surface. Thus, significant desorption or diffusion into the bulk can be excluded. This preparation method has been checked in our HAS system by performing H_2 sticking measurements. The results (summarized in Ref. 40) show that the same step-like dependence of the initial reactive sticking probability as a function of Pd concentration is observed in both experiments, with a sharp increase in reactivity for a Ru concentration of 5%. Thus, we can conclude that the alloy composition is essentially the same as the one reported in Ref. 11. Furthermore, as established by Hartmann *et al.*¹¹,

FIG. 1. Evolution of the intensity of the specular He beam during Pd evaporation on Ru(0001) as a function of time at a surface temperature of 700 K. The evaporation rate is ~ 0.03 ML/min. The maximum indicates the completion of the first monolayer.

the system of interest is actually the one containing just 5% Ru; at higher Ru coverages, the system behaves as pure Ru from the viewpoint of H_2 and O_2 sticking. For this reason, all results reported for the alloy refer to the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface.

III. RESULTS

Figure 2 shows the initial sticking coefficient as a function of the normal energy of the oxygen molecules, $E_n = E_i \cos^2 \theta_i$, for the clean Ru(0001) surface, the pseudomorphic, compressed ML Pd/Ru(0001), and the pseudomorphic, expanded ML Cu/Ru(0001) measured at 100 K. For comparison, data for the clean Pd(111) surface from Ref. 41 are also shown. On the pristine Ru(0001) surface, at 100 K, the initial dissociative adsorption probability, S_0 , decreases sharply with increasing incident normal energies, passes through a minimum around 80 meV, and increases again with the incident energy, until it saturates at about 500 meV. This is in agreement with the previous results reported in Ref. 42. This behaviour is indicative of a trapping-mediated mechanism into a physisorbed precursor state quickly followed by a temperature dependent kinetic competition between desorption and thermal dissociation. However, EELS and TPD studies yielded no evidence, at low coverages, for a stable molecularly chemisorbed state of oxygen on clean Ru(0001) at surface temperatures as low as 30 K.⁴³ At higher normal energies, the adsorption probability increases with energy, which is consistent with a direct dissociation mechanism dominated by the charge transfer from the substrate. At room temperature, in the low normal energy regime, there is a strong decrease in the initial sticking coefficient (see Fig. 3). This dependence of S_0 with the surface temperature confirms the existence of a precursor-mediated

FIG. 2. Initial sticking probability of O_2 versus the normal energy of the incident beam for clean Ru(0001), 1 ML Pd/Ru(0001), 1 ML Cu/Ru(0001) surfaces and the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface alloy. The sample temperature is 100 K. The data for clean Pd(111) are from Ref. 41. The experimental error in sticking probabilities is estimated as ± 0.03 . Lines are a guide to the eye.

FIG. 3. Initial sticking probability of O_2 versus incident beam normal energy for clean Ru(0001), 1 ML Pd/Ru(0001), and the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface alloy. The sample temperature is 300 K. The data for clean Pd(111) from Ref. 41 are also shown. Lines are a guide to the eye.

mechanism which becomes active for molecules impinging on the surface at low kinetic energy. In the high kinetic energy regime, the authors of Ref. 42 observed that the dissociative chemisorption probability, S_0 , increases with the surface temperature. This tendency is consistent with, but not clearly visible in our results at 300 K.

The data corresponding to the expanded ML Cu/Ru(0001) reveal that the oxygen sticking probability at $T_s = 100$ K closely follows the one measured for clean Ru(0001) in the full energy range studied, a behaviour observed previously at 300 K.³⁶ Our current data prove that this similarity includes the low kinetic energy behaviour, indicating that the trapping-assisted adsorption is also operative in the ML Cu/Ru(0001). Whether this mechanism leads to a stable molecularly chemisorbed state of O_2 on this surface [in contrast to clean Ru(0001)] is something that cannot be answered based on our current experimental data. However, our results clearly show that the ML Cu under tensile strain on Ru(0001) is much more reactive than Cu(111). Contrary to the observations on Ru(0001), our previous study³⁶ has shown also that the expanded ML Cu/Ru(0001) surface is fully passivated toward H_2 , even at relatively high incident energies (175 meV). This further allows us to exclude the existence of uncovered Ru islands in our system as the possible source of the high reactivity toward O_2 observed in the current results for ML Cu/Ru(0001) (see below).

Also shown in Fig. 2 are the results for clean Pd(111) taken from Ref. 41. On Pd(111), the adsorption of O_2 shows an initial sticking coefficient that corresponds to a molecular precursor dissociation mechanism over the entire translational energy range. At low kinetic energies, S_0 decreases with increasing normal energy and the molecular precursor is populated either directly or via a trapped physisorbed state, while at high kinetic energies, direct adsorption into

a chemisorbed molecular precursor state takes place before dissociation.⁴¹

For the ML Pd/Ru(0001) at $T_s = 100$ K, a sharp decrease in the oxygen sticking probability with the incident energy is observed at energies below 130 meV. This behavior suggests the existence of trapping into a molecular physisorbed well. In the high kinetic energy regime, the adsorption probability drops continuously with increasing translational energy, and the measured sticking probabilities are substantially lower than the ones observed on the clean Ru(0001) surface and approximately half of those obtained on Pd(111).

Figure 3 shows the initial sticking coefficient results for the clean Ru(0001) surface and the ML Pd/Ru(0001), measured at $T_s = 300$ K. For Pd(111), the sticking curve shows the same quantitative features as at $T_s = 100$ K, except for a steeper increase at higher translational energies.⁴¹ A quite different behaviour has been observed for the ML Pd/Ru(0001), which was found to be completely inert at room temperature, the initial sticking coefficient being below the detection limit of the King and Wells technique (S_0 below 0.01). This is in agreement with the XPS measurements showing this surface to be inert to the background oxygen at room temperature.³⁰ The behaviour of the Pd(111) surface is a consequence of the dissociative chemisorption of O_2 .^{41,44} On the ML Pd/Ru(0001) surface, in contrast, our data suggest that this process is energetically forbidden at 300 K. It should be noted that the reactivity of the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface alloy increases drastically in comparison to the ML Pd/Ru(0001), both at 300 K and 100 K. At room temperature, in contrast to the inert ML Pd/Ru(0001) surface, the PdRu alloy presents reactivity to oxygen which resembles in trend with energy and absolute values the one measured on clean Ru(0001). These results show that the presence of a small percentage of Ru atoms on the surface completely changes the dynamics of the interaction between the oxygen molecules and the substrate.

FIG. 4. Thermal desorption spectra of O_2 from 1 ML Pd/Ru(0001) and the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface alloy. The desorption peak observed at 145 K suggests that the adsorption is non-dissociative on the ML Pd/Ru(0001) surface at 100 K. The curves are shifted vertically for clarity.

To get more insight into the oxygen adsorption mechanism, we have performed thermal desorption measurements after O_2 exposure. The results are presented in Fig. 4. For the ML Pd/Ru(0001), an O_2 desorption peak appears at about 145 K after heating a surface previously saturated with the oxygen beam at $E_i = 450$ meV and $T_s = 110$ K. On the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ alloy surface, in contrast, this peak is much smaller and shifted to 155 K after performing the same experiment. For the $O_2/Pd(111)$ system, molecular desorption occurs at 150 K and 200 K.⁴⁴ Thus, the peak at 145 K in our current study resembles the first molecular adsorption peak on Pd(111), whereas no evidence was observed for the second peak at 200 K. These data suggest that O_2 adsorbs molecularly on the ML Pd/Ru(0001), desorbing at 145 K, although dissociation might take place simultaneously to molecular desorption. This also explains the observation of zero initial sticking at 300 K on this system. On the $Pd_{0.95}Ru_{0.05}/Ru(0001)$ surface alloy, the quite small O_2 desorption peak observed after heating points to the occurrence of dissociative adsorption on this surface when exposed to O_2 even at 100 K. The small desorption feature at 155 K could be due to the desorption of molecularly adsorbed O_2 from large Pd areas on the alloyed surface.

IV. DISCUSSION

The current experimental results for the ML Pd/Ru(0001) and the ML Cu/Ru(0001) systems follow the predictions of the d-band model, which correlates the position of the d-band center with respect to the Fermi level to the chemical reactivity.⁴⁵ According to this model, the farther (closer) the center of the d bands is from the Fermi level, the smaller (larger) is the chemisorption energy.^{2,3,45,46} The d bands are narrow, and small changes in the environment (strain, interaction with the substrate, etc.) can modify significantly the energy location of the d states and their interaction with adsorbate states.

The Pd monolayer grows pseudomorphically on Ru(0001) and is, therefore, laterally compressed by 3.6% compared to Pd(111), whereas the Cu monolayer is expanded by 5.5% in comparison to clean Cu(111). In general, a laterally compressed metallic surface is predicted to be less reactive than the unstrained one.¹⁻⁶ Density functional theory (DFT) six-dimensional dynamics calculations showed that the dissociative adsorption of H_2 on the ML Pd/Ru(0001) is an activated process with a threshold of ~ 130 meV.⁴⁷ Moreover, in order to analyze separately the role of surface strain, the authors have carried out similar DFT calculations for the pure Pd(111) surface with lateral lattice constants identical to that of Ru(0001). For a 3% laterally compressed Pd(111) surface, the top site is the most reactive one and the barrier height is only 20 meV, which means that it is practically non-activated. This result shows that the reactivity to H_2 for the ML Pd/Ru(0001) cannot be completely explained in terms of strain only, but it is also due to the electronic coupling with the Ru(0001) substrate, specifically Pd donates charge to the Ru(0001) substrate and, then, becomes less reactive. For this system, both the Pd/Ru interface-induced electronic effects and the compressive surface strain produce a downshift of the d-band center which

makes the system less reactive than Pd(111). The reported sticking probability of 0.05 with the background hydrogen⁴⁰ is very much reduced compared to the one of the clean Pd(111) surface and is thus in very good agreement with the mentioned calculations. The H₂ sticking value is lower than the one on clean Ru(0001) by a factor of ~ 4 , which allows us to exclude the presence of clean Ru islands in the Pd monolayer.

For the expanded ML Cu/Ru(0001), the data measured at 100 K (Fig. 2) suggest a strong electronic coupling between the Cu overlayer and the Ru substrate, since the O₂ sticking probability follows the same trend, both in the low and high kinetic energy regimes as the corresponding curve for clean Ru(0001). A similar behaviour of the sticking probability has been reported for measurements performed at 300 K,³⁶ which suggests dissociative sticking of O₂ on the ML Cu/Ru(0001) surface.

In the case of the ML Pd/Ru(0001), the dynamics is completely different, since the O₂ sticking probability monotonically decreases with the incident energy at 100 K, whereas no sticking of O₂ is observed at 300 K. This behaviour is consistent with the molecularly adsorbed oxygen. This is supported by the thermal desorption measurements presented in Fig. 4, which show an O₂ desorption peak at ca. 145 K. After a mild annealing, the clean ML Pd/Ru(0001) surface is recovered. A previous study of O₂ adsorption on Pd(111) has shown that molecular desorption occurs at 150 K and 200 K.⁴⁴ Our present study shows that the first of these peaks is also present on the ML Pd/Ru(0001), whereas no evidence has been found for the existence of the second peak. This may be an indication of weaker O₂ bonding on the the ML Pd/Ru(0001) surface in comparison to clean Pd(111). A weaker adsorption strength on the 1 ML Pd film compared to Pd(111) has been also reported for the CO adsorption.²⁶ A similar behaviour has been observed on the Pt/Ru(0001) system, for which the molecular chemisorption of oxygen is completely suppressed for the Pt monolayer.⁶ For 2 MLs of Pt, oxygen chemisorbs molecularly, but no dissociation occurs. Thermal desorption measurements show that oxygen desorption sets in prior to dissociation. The dissociation of O₂ is only observed for 3 MLs of Pt, where annealing leads to dissociation, like on Pt(111).⁶

The high reactivity of PdRu/Ru(0001) surface alloys toward H₂ was already known.¹¹ Those authors showed that PdRu/Ru(0001) surface alloys can be prepared with different Pd coverages. The deuterium adsorption probability was found to be independent from Pd concentration in the surface alloy, and almost identical within the experimental error to the one measured on clean Ru(0001), even for such a high Pd concentration as in Pd_{0.95}Ru_{0.05}/Ru(0001).¹¹ The reactivity was substantially reduced when the Ru surface was fully covered by a complete ML of Pd. This suggests that only a small percentage of Ru atoms present on the surface are required to change the reactivity of the surface drastically and dissociate efficiently H₂ molecules. This might be due to the existence of a short-living, mobile molecular precursor state, in which the Ru impurities become scattering centers, leading to an enhanced probability for dissociative adsorption. For the PdRu/Ru(0001) surface alloy, DFT calculations have shown that its high reactivity is actually due to an environment-driven mechanism,

which makes Ru atoms surrounded by Pd atoms even more reactive than in pure Ru(0001).⁴⁰ Our current results show that a similar increase in reactivity occurs for O₂ molecules. Both at 100 K and 300 K, the reactivity is highly enhanced and resembles the one measured for clean Ru(0001). Especially remarkable is the effect observed at 300 K. Whereas the ML Pd/Ru(0001) system was found to be inert to O₂ adsorption, the Pd_{0.95}Ru_{0.05}/Ru(0001) surface alloy exhibits a very high reactivity. Moreover, thermal desorption measurements suggest that the adsorption dynamics is very different on the two systems. No O₂ desorption peak was observed below 200 K from the Pd_{0.95}Ru_{0.05}/Ru(0001) surface alloy, suggesting that the O₂ molecules dissociate onto this surface due to the presence of the few available Ru atoms, while the adsorption is molecular on the ML Pd/Ru(0001) system.

V. CONCLUSIONS

Initial sticking probabilities have been measured for O₂ molecules on the monolayer Pd/Ru(0001). The system shows very different properties compared to the clean Ru(0001) and Pd(111) surfaces. For the compressed Pd monolayer, a lower reactivity than on Pd(111) is observed for O₂ molecules, due to both the compressive strain and the electronic interaction with the Ru substrate producing a downshift of the d-band center, as predicted also for H₂ molecules.⁴⁷ No sticking of O₂ could be detected at 300 K. Thermal desorption data suggest that the sticking observed at 100 K is due to the molecular adsorption of O₂. Surprisingly, a very small amount of Ru atoms left on the Pd_{0.95}Ru_{0.05}/Ru(0001) surface efficiently dissociate O₂ molecules, with initial sticking probabilities very close to those observed on the clean Ru(0001) surface. Theoretical work is needed to clarify whether the high reactivity observed for O₂ on the PdRu surface alloy is also due to an environment-driven mechanism, as already reported for the case of H₂ adsorption on the same system,⁴⁰ or to a different effect.

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