Adsorption and reaction of CO on a ceria–Rh(111) “inverse model catalyst” surface

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Abstract

The adsorption of CO and the reaction of CO with preadsorbed oxygen at room temperature has been studied on the Rh(111)2 \times 1-O surface and on ceria–Rh(111) “inverse model catalyst” surfaces using C 1s and O 1s core level and valence band photoelectron spectroscopy with synchrotron radiation. The adsorption of CO on the oxygen-precovered (2 \times 1)-O surface was found to proceed slower than on the clean Rh(111) surface, because of a kinetic limitation which is introduced by the O + CO clean-off reaction. The latter removes adsorbed oxygen as CO\textsubscript{2} at 300–320 K, which desorbs into the gas phase. On the ceria–Rh(111) surfaces the O + CO oxidation reaction is much faster than on the Rh(111)2 \times 1-O surface suggesting a catalytically active role of the ceria–Rh interface. The XPS spectra indicate a preferential occupation of hollow-type CO adsorption sites on the ceria–Rh(111) surface, which might be located at the oxide–metal interface. No CO dissociation has been detected on the Rh(111) supported ceria inverse catalyst surfaces. On a CeRh\textsubscript{3} alloy surface, prepared by thermal decomposition of the ceria in ultrahigh vacuum, the hollow-type CO adsorption sites are energetically favoured suppressing the on-top sites almost completely, but the global adsorption energy is lower than on Rh(111) as indicated by the reduced CO saturation coverage.

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1. Introduction

Rhodium and cerium oxide (ceria) constitute important components of the commercial three-way catalyst for automotive emission control. The addition of ceria to this multi-component sup-
port metal catalyst improves the performance of the different group VIII metals and several mechanisms have been proposed to explain the promoting role of ceria [1]: amongst others, a stabilising role against sintering of the metal particles and an enhancement of the activity for the water gas shift reaction has been discussed. The strong interaction of noble metal atoms with ceria surfaces in general and the ability of oxygen to migrate from CeO\textsubscript{2} to Rh has been invoked to rationalise the increase of the CO oxidation
activity of the metal. Several papers in the literature have shown that ceria promoted Rh surfaces can exhibit enhanced reaction rates for CO oxidation, along with very different kinetic rate expressions when compared to Rh or ceria individually [2–5]. Also, the dissociative adsorption of CO on Rh particles deposited on ceria surfaces has been reported [6], while intact molecular adsorption is generally found on Rh low-index single crystal surfaces [7,8]. Mullins and Overbury [6] have associated the degree of CO dissociation on ceria supported Rh with the degree of reduction of the ceria, but have suggested that the morphology of the Rh particles does not affect the dissociation activity, although this latter proposition was based on indirect evidence.

In the present work we have adopted the concept of an “inverse model catalyst”, i.e. a well-defined metal single crystal surface that has been decorated with oxide nano-particles, to study the influence of the metal–oxide interface on the adsorption properties of CO at room temperature and the reaction of CO with preadsorbed oxygen on ceria promoted Rh(111) surfaces. The growth and morphology of ceria overlayers on Rh(111) have been characterised by scanning tunneling microscopy and photoelectron spectroscopy as reported in a previous publication [9]. Here, we present resonance valence band spectra and X-ray photoemission spectra (XPS) of C and O 1s core levels, recorded with synchrotron radiation, to follow the CO uptake and the distribution of adsorption sites on ceria decorated Rh(111) surfaces. The clean-off reaction of CO with oxygen preadsorbed on Rh(111) surfaces has been recorded with a photon energy of 400 eV and a combined energy resolution (SX 700-type monochromator plus spectrometer) of 0.3–0.4 eV, whereas the valence band spectra have been taken with a photon energy of 125 eV, i.e. at the Ce 4d–4f giant resonance, with a total energy resolution of ~0.1 eV. The O 1s and Ce 3d core level spectra have been excited with a conventional laboratory Mg Kα X-ray source because of monochromator limitations at higher photon energies. The laboratory X-ray source was attached in a symmetric position to the inlet of the synchrotron radiation, with photons incident at 47° in normal emission geometry.

We find as an important result that ceria decorated Rh(111) surfaces do not dissociate CO, this suggests that low-coordinated Rh atoms as present abundantly on small metal particles are likely to be the active centres for CO dissociation. However, a small amount of CO dissociation is identified on the Ce–Rh surface alloy. The effect of the ceria observed is a different balance of CO adsorption sites on the ceria promoted Rh(1 1 1) surfaces and an enhanced rate of the O + CO clean-off reaction, as compared on pure Rh(1 1 1).

2. Experimental

The experiments have been performed in a multi-chamber custom-designed high-resolution electron spectrometer, equipped with a Scienta SES 200 analyser and a preparation chamber containing sample cleaning, evaporation, and LEED facilities as reported elsewhere [10]. The system is pumped by turbomolecular and ion pumps and, in addition, contains a NEG pump (SAES Getters SpA) to minimise the partial pressure of hydrogen in the background gas; the base pressure in this system was \( \leq 1 \times 10^{-10} \) mbar. The spectrometer was attached to the Materials Science beamline (MSB) at the synchrotron radiation facility ELETTRA in Trieste, Italy; MSB is operated by the Czech Academy of Sciences in cooperation with Sincrotrone Trieste. The C 1s core level spectra have been recorded with a photon energy of 400 eV and a combined energy resolution (SX 700-type monochromator plus spectrometer) of 0.3–0.4 eV, whereas the valence band spectra have been taken with a photon energy of 125 eV, i.e. at the Ce 4d–4f giant resonance, with a total energy resolution of ~0.1 eV. The O 1s and Ce 3d core level spectra have been excited with a conventional laboratory Mg Kα X-ray source because of monochromator limitations at higher photon energies. The laboratory X-ray source was attached in a symmetric position to the inlet of the synchrotron radiation, with photons incident at 47° in normal emission geometry.

The Rh crystal was mounted on a Mo sample plate, could be cooled to ~100 K, and heated indirectly to 1400 K by electron bombardment from the back side. The crystal temperature was measured with a chromel–alumel thermocouple spot-welded to the edge of the crystal. Clean Rh(1 1 1) surfaces were prepared by Ar⁺ ion bombardment and annealing at 1300 K, and by heating cycles in
O\textsubscript{2} followed by a final anneal at 1400 K. The cleanliness of the Rh(1 1 1) surface was checked by XPS and LEED. Cerium oxide overlayers were deposited by reactive evaporation of cerium metal in $2 \times 10^{-7}$ mbar O\textsubscript{2} onto the Rh substrate at a temperature of 520 K. The evaporation rate was monitored by a quartz crystal microbalance and a typical evaporation rate was 0.5 monolayer min$^{-1}$. The CO and O\textsubscript{2} gases were dosed from the system ambient via leak valves.

Fig. 1 illustrates a typical ceria–Rh(1 1 1) inverse catalyst surface, as obtained after deposition of ~0.5 monolayers (ML) of ceria at 520 K and cooled down to room temperature in an oxygen atmosphere. The large scale constant-current topographic STM image reveals irregularly shaped cerium oxide nano-particles, which are randomly distributed over the Rh surface. The majority of the oxide particles consists of a double layer of (1 1 1) oriented fluorite-type CeO\textsubscript{2}, as indicated by LEED and XPS and established previously [9]. In between the oxide islands the Rh(1 1 1) metal areas are covered by a chemisorbed (2 $\times$ 1) oxygen adlayer, as a result of the oxygen ambient during the cerium oxide preparation.

**3. Results**

**3.1. Adsorption of CO on oxygen-precovered Rh(1 1 1)\textsubscript{2 $\times$ 1}-O**

Since the bare Rh areas of our inverse catalyst surfaces are covered by chemisorbed oxygen after preparation, it is necessary to establish the adsorption properties of CO on a corresponding Rh(1 1 1)\textsubscript{2 $\times$ 1}-O surface. The (2 $\times$ 1) oxygen surface was created by exposing the clean Rh(1 1 1) surface to 60 L O\textsubscript{2} (1 Langmuir (L) = 1 $\times$ 10$^{-6}$ Torr s) at 520 K and to an additional 60 L O\textsubscript{2} during cooling down to room temperature. This corresponds closely to the conditions during preparation of the ceria decorated Rh(1 1 1) surfaces. In accordance with Jaworowski et al. [11] the (2 $\times$ 2) LEED pattern observed from this surface is associated with the three equivalent domains of a (2 $\times$ 1)-O overlayer with an oxygen coverage of 0.5 ML.

The adsorption of CO on the ceria decorated Rh surfaces has been studied here at room temperature, in order to restrict the adsorption to the metal sites of the inverse catalyst. Note that “room temperature” is meant to correspond to a temperature of ~300–320 K. Since the saturation coverage of CO on clean Rh(1 1 1) at room temperature is a sensitive function of the exact adsorption temperature [8], we have used the (2 $\times$ 2)-3CO structure obtained at 120K with a coverage of 0.75 ML [12] as calibration point for our oxygen coverage evaluation.

Fig. 2(a) shows a series of C 1s XPS spectra of CO adsorbed on Rh(1 1 1)\textsubscript{2 $\times$ 1}-O at room temperature as a function of CO exposure. For low exposures a single peak at a binding energy of 286.2 eV is observed, whereas a second structure grows in at 285.7 eV at higher exposures. These C 1s binding energy values, derived from a decomposition of the spectra into the individual components using Donjic–Sunjic convoluted with Gaussian lineshapes as model functions, are associated, in agreement with Jaworowski et al. [11], with CO adsorbed in on-top and threefold hollow sites, respectively. Clearly, the on-top adsorption sites are populated first and then the hollow sites become occupied, as also observed on the clean
Rh(111) surface [12]. Fig. 2(b) gives the CO coverage on Rh(111)2 × 1-O as a function of CO exposure, i.e. the uptake curves for the total CO coverage and for the CO coverage in on-top and hollow adsorption positions, as derived from the areas of the respective C 1s peak components. As seen, the saturation of the surface with CO is only slowly established: after 350 L the total CO coverage amounts to ~0.47 ML, which is divided into 0.31 ML in on-top and 0.16 ML in hollow sites, i.e. \( \text{CO}_{\text{ON-TOP}}/\text{CO}_{\text{HOLLOW}} \approx 2 \). Fig. 2(c) shows a comparison of the uptake curves for the total CO coverage on clean Rh(111) and on Rh(111)2 × 1-O. The slower CO uptake on the O-precovered surface is clearly indicated and can also be quantified by calculating the initial sticking coefficient \( \delta_0 \) from the initial slope of the curves. Accordingly, \( \delta_0 \) on clean Rh(111) is close to 1, whereas it is reduced to 0.25 on the (2 × 1)-O surface.

The slower CO uptake on the O-precovered surface, as compared to the clean Rh surface, can be associated with a site blocking effect of the preadsorbed oxygen or with a reaction induced kinetic effect. Fig. 3 reveals that the latter is the case. In Fig. 3(a) O 1s XPS spectra of the Rh(111)2 × 1-O surface (bottom curve), of a Rh(111) surface saturated with a room temperature CO adlayer (middle curve), and of the

![C 1s core level spectra of CO adsorbed on the Rh(111)2 × 1-O surface at room temperature for various exposures. The spectra have been normalised to the background intensity at 283 eV. The curves below the data points are the result of the decomposition analysis, the lines through the data points are the resulting fits. The sketches at the top of the figure indicate the CO components in on-top and threefold hollow adsorption sites. (b) CO uptake curves in the form of coverage versus dose for the total CO coverage and for the CO coverage in on-top and hollow adsorption positions, as derived from the areas of the respective C 1s components. (c) Comparison of the total CO uptake curves on the clean Rh(111) and the Rh(111)2 × 1-O surfaces.](image-url)
Rh(111)2 × 1-O surface exposed to 350 L CO at room temperature (top curve) are displayed. The chemisorbed oxygen occurs with a O 1s binding energy of 529.4 eV, while the COON-TOP and COHOLLOW are characterised by O 1s binding energies of 531.9 and 530.6 eV, respectively. Most importantly, however, the top spectrum of Fig. 3(a) shows that the oxygen precoverage has been reduced from 0.5 to 0.08 ML by the clean-off reaction with CO, OADS + CO = CO2, which desorbs into the gas phase. The initial, relatively fast uptake of the on-top CO on the (2 × 1)-O surface (see Fig. 2(b)) may be the result of the incorporation of COON-TOP into the (2 × 2)-2O + CO structure, which has been proposed by Jaworowski et al. [11]. This latter structure, with θO = 0.5 ML and θCO = 0.25 ML, is obtained from the (2 × 1)-O structure by shifting every other oxygen into an adjacent hollow site and adsorbing CO at the resulting free on-top Rh site [11]. We suggest that this structure may be a precursor phase for the CO oxidation reaction at ≳ 300–320 K, as observed here.

The O + CO clean-off reaction is confirmed by the valence band spectra of Fig. 3(b). These spectra have been recorded with a photon energy hν = 125 eV, which is at the Cooper minimum of the Rh 4d photoionisation cross section, to emphasise the adsorbate features. The lower spectrum of Fig. 3(b) has been recorded from the Rh(1 1 1)2 × 1-O surface: the O 2p structure of the chemisorbed oxygen at ∼ 6 eV is the prominent
feature in the valence band, and the O 2s emission is seen at \( \sim 21 \) eV. After exposure to 350 L CO at room temperature (upper spectrum) both O 2p and O 2s emissions are strongly reduced in intensity and the well-known CO derived 5σ/1π (\( \sim 7.5 \) eV) and 4σ (\( \sim 11 \) eV) valence orbital emissions dominate the spectrum. Most of the chemisorbed O has thus been removed by the clean-off reaction.

### 3.2. Adsorption of CO on ceria–Rh(111) surfaces

The adsorption of CO on ceria–Rh(111) inverse catalyst surfaces is illustrated in Fig. 4. Fig. 4(a) shows a set of C 1s XPS spectra of CO adsorbed at room temperature on a \( \sim 0.5 \) ML ceria–Rh(111) surface as a function of exposure. For low CO doses the single C 1s peak at 286.2 eV binding energy indicates that the on-top Rh adsorption sites are populated first as on bare Rh(111), but the appearance of the second peak at 285.5 eV for higher exposures (\( \geq 10 \) L) shows that the threefold hollow Rh sites become populated as well, albeit delayed. There are no indications of CO adsorption on the oxide surface at room temperature, with an expected C 1s binding energy of 290–291 eV [6] (these spectra are not shown in Fig. 4(a)). The weak emission intensity at around 284 eV in the low-exposure spectrum is due to...
to adventitious carbon contamination of the initial surface. The fact that the intensity in this region does not grow and remains constant during CO dosing indicates that CO does not dissociate on the ceria–Rh(1 1 1) inverse catalyst surface.

A qualitative inspection of Figs. 4(a) and 2(a) reveals that the balance of adsorption sites is different on the ceria–Rh(1 1 1) as compared to the O-precovered Rh(1 1 1) surface, with a relative preference for the hollow sites in the former case. Fig. 4(b) gives a quantitative measure of this behaviour on ceria–Rh(1 1 1) in the form of the uptake curves of the total CO coverage versus exposure and of the CO coverage in on-top and hollow sites. We notice that the occupation of hollow sites is delayed until the on-top sites are nearly saturated (≈10 L), but that the ratio \( \frac{\text{CO}_{\text{ON-TOP}}}{\text{CO}_{\text{HOLLOW}}} \) becomes ≈1 at saturation (we recall that this ratio is 2 on the O-precovered Rh surface—see Section 3.1). The total CO saturation coverage on this particular ceria–Rh(1 1 1) surface is 0.32 ML, which agrees well with the corresponding ceria-free surface suggested from the ceria coverage estimated from the evaporation rate during preparation. Fig. 4(c) compares the total CO uptake curves on the ceria–Rh(1 1 1) and Rh(1 1 1)\( ^{2} \times 1 \)-O surfaces. The ceria–Rh(1 1 1) surface reaches CO saturation after a dose of ≈35 L, whereas the \((2 \times 1)\)-O surface is still not saturated with CO after offering 10 times more CO (350 L). The initial sticking coefficient of CO on the ceria–Rh(1 1 1) surface is \( S_{0} \approx 0.5 \) as referenced to the available Rh sites, which is about twice the value on the Rh(1 1 1)\( ^{2} \times 1 \)-O surface. These results clearly indicate that the O + CO clean-off reaction is significantly promoted on the ceria–Rh(1 1 1) surface.

The exposure of the ceria–Rh(1 1 1) surface to CO results in a partial reduction of the CeO\(_{2}\) layer. Fig. 5 displays valence band spectra of the pristine 0.5 ML ceria–Rh(1 1 1) surface and after exposure to 50 L CO at room temperature. The valence band spectrum of the pristine ceria–Rh surface (bottom curve) shows the emission of the Rh 4d states from the Fermi level to 2.5 eV below \( E_{F} \) and the characteristic O 2p double-peak structure of CeO\(_{2}\) in the range 2.5–8 eV [9]. The Ce 5p and O 2s emissions occur in the region 15–25 eV. After CO exposure (top curve) a feature at ≈1.5 eV below \( E_{F} \) has appeared which is associated with the emission from the Ce 4f\(^{1}\) states of Ce\(^{3+}\) species, indicating the partial reduction of the ceria. The spectra of Fig. 5 have been recorded with a photon energy of 125 eV, i.e. at the giant 4d–4f resonance of Ce.
atoms [13]: the emission from the Ce 4f states is thus resonantly enhanced and a low degree of reduction becomes detectable. The partial reduction of the oxide is also apparent in some changes in the region of the O 2p structure.

3.3. Adsorption of CO on (partially) reduced ceria–Rh(1 1 1) surfaces

Annealing of ceria–Rh(111) inverse catalyst surfaces in ultrahigh vacuum leads to a partial reduction of the ceria overlayer and eventually to the decomposition of the oxide; the latter is accompanied by the formation of a Ce–Rh surface alloy phase [9,14]. The degree of reduction depends on the annealing temperature [9]. Fig. 6 shows C 1s spectra of CO adsorbed to saturation on a 0.45 ML ceria–Rh(1 1 1) surface as prepared (bottom curve), on the reduced surface after annealing to 950 K (5 min) (middle curve), and on the alloy surface after annealing to 1200 K (5 min) (top curve). The CO coverage on the 950 K annealed surface increases somewhat as compared to the as-prepared surface, because the Rh area

![Fig. 6. C 1s core level spectra of CO (50 L room temperature exposure) on 0.45 ML ceria–Rh(1 1 1) in the as-prepared state (bottom spectrum), on the reduced ceria–Rh surface obtained after annealing to 950 K (middle spectrum), and on the ceria–Rh alloy surface after annealing to 1200 K. The curves below the data points show the spectral components after the fitting analysis. The insert shows CO coverages on the as-prepared and annealed surfaces and the percentage of Ce$^{3+}$ species at the surface, as derived from Ce 3d XPS spectra.](image-url)
covered by oxide particles decreases due to ripening and coalescing of the ceria islands [9], but the balance of CO adsorption sites (on-top vs. hollow) is only slightly modified. On the Ce–Rh alloy surface, however, formed after annealing to >1100 K, CO adsorption occurs almost exclusively in the hollow adsorption sites and the saturation coverage is reduced as compared to the clean Rh(111) surface. We notice a small C 1s emission peak at ~284 eV on the alloy surface (top curve of Fig. 6), which is due to surface carbide and could indicate a small amount of CO dissociation (see below). The insert of Fig. 6 summarises the analysis of the C 1s spectra in terms of CO coverages and also includes the percentage of Ce³⁺, i.e. the degree of ceria reduction, on the respective surfaces as deduced from Ce 3d XPS spectra [9]. On as-prepared ceria–Rh surfaces some Ce³⁺ species have always been detected in the Ce 3d XPS spectra for coverages less than several monolayers, and it has been argued that these are located at the Ce–Rh interface [9,15]. On the 950 K annealed surface the Ce³⁺ content of the oxide layer has increased to ~50%, and this is associated with the formation of oxygen vacancies at the oxide surface [16]. The ratio CO_{TOP}/CO_{HOLLOW} is still close to one, but significantly there are no indications of CO dissociation on this reduced ceria–Rh(111) surface (no C 1s signal of surface carbide). This is in contrast to what has been reported by Mullins and Overbury on Rh particles supported on reduced ceria surfaces [6], where the observed dissociation of CO has been ascribed to the reduced state of the ceria. After annealing to >1000 K progressive oxide decomposition and alloy formation characterise the surfaces, and the CO adsorption occurs with reduced saturation coverage but predominantly in the hollow sites. Most of the Ce⁴⁺ species of the oxide have been replaced by the Ce³⁺ of the alloy on this surface.

Annealing of 1 ML ceria on Rh(111) at 1200 K produces an ordered CeRh₃ alloy surface with a (2 x 2) LEED structure [17]. The adsorption of CO on this surface is illustrated in Fig. 7. The insert shows a set of C 1s spectra as a function of CO exposure and the main panel gives the corresponding total CO uptake curve. The C 1s peak is observed at 285.3 eV binding energy for low coverage and shifts slightly to 285.5 eV upon saturation, which is typical within the range of density effects in

Fig. 7. Total CO uptake curve on a (2 x 2) CeRh₃ alloy surface. The insert shows the normalised C 1s spectra as a function of CO exposure at room temperature.
adsorbate layers. This major C 1s peak is associated with CO in hollow adsorption sites on the alloy surface, with a somewhat modified binding energy with respect to the corresponding sites on the Rh(111) surface as a result of the different alloy surface potential. A minor spectral component at 285.9 eV is necessary for a good fit of the saturation C 1s spectrum (see also Fig. 6, top curve), and it is ascribed to CO minority species in on-top sites. The C 1s emission intensity at 283.9 eV is due to the presence of surface carbon and suggests a small amount of CO dissociation on the alloy surface. The coverage of this surface carbon in the saturation C 1s spectrum (top curve of insert) is estimated to 0.03 ML. The adsorption of CO on the alloy surface is fast, with an initial sticking coefficient $S_0 \approx 0.7$, but the saturation adsorption coverage of $\sim 0.37$ ML at room temperature is smaller than on the clean Rh(111) surface (0.55 ML). This is similar to what has been observed on other alloy surfaces, e.g. on V–Pd [18].

4. Discussion

The adsorption of CO on the Rh(111)2 x 1-O surface is followed by the O + CO oxidation reaction at room temperature or slightly above, which removes the preadsorbed oxygen from the surface. The initial fast uptake of CO into on-top adsorption sites suggests that the (2 x 2)O + CO structure, in which CO adsorption can take place in on-top positions after a rearrangement of the chemisorbed oxygen atoms [11], may be a precursor phase for the oxidation reaction. After removal of $\sim 0.25$ ML oxygen the threefold hollow sites become also available for CO chemisorption, as observed in Fig. 2. On the ceria–Rh(111) surface a similar mechanism is possible in principle, however the CO uptake is much faster on this surface. The initial abundance of CO$_{ON\_TOP}$ may also be understood by the incorporation into the (2 x 2)O structure, but the faster uptake indicates that the clean-off reaction, i.e. the CO oxidation, is enhanced. It is most natural to associate the promotion of the CO oxidation reaction with adsorption sites close to the ceria–Rh interface, i.e. with sites at the boundaries of the ceria island structures. A different balance of CO adsorption sites on the Rh(111) areas in the presence of the ceria nano-structures has indeed been established (see Fig. 4(b)), with a coverage ratio CO$_{TOP}$/CO$_{HOLLOW}$ $\approx$ 1. However, the experimental XPS spectra indicate only that CO species with a binding energy similar to CO in hollow sites are preferentially present on the ceria–Rh(111) surface. It is reasonable to associate at least part of these CO species with particular sites at the metal–oxide phase boundaries (they need not necessarily be hollow sites), but the present XPS results do not allow us to specify their exact coordination. The delayed detection of these CO species at the surface may then also be due to the fact that they are more efficiently removed as CO$_2$ in the vicinity of the oxide–metal interface during the initial stages of the adsorption/reaction process. Some participation of oxygen from the periphery of the ceria islands in the CO oxidation reaction may also be indicated by the partial reduction of the ceria overlayer, but this reaction path appears to be less important at the relatively low temperatures of the present experiments than reported at higher temperatures [4].

Dissociative adsorption of CO has been reported in the literature on ceria supported Rh model catalyst surfaces [6]. On the Rh(111) supported ceria inverse catalyst surfaces no dissociation of CO has been detected here after room temperature exposure, and even after significant reduction of the ceria island surfaces only molecular CO adsorption has been identified. This is significant since the reduction of the ceria has been invoked as an important factor for the dissociation of CO on the Rh particles [6]. The present results demonstrate that the morphology of the Rh particles, with their low-coordinated Rh sites, are most likely to play a decisive role in the dissociation process.

The energy balance of CO adsorption sites on Ce–Rh alloy surfaces is different from that on the Rh(111) surface. The hollow sites constitute clearly the lowest energy sites for CO adsorption, they are almost exclusively populated at room temperature, but the lower saturation coverage of CO indicates that the global adsorption energy is
smaller on the alloy than on Rh(111). Recently, a similar preference for the population of hollow CO adsorption sites has been found experimentally on a V–Pd alloy surface [18], where the relative stability of the hollow adsorption sites has also been predicted theoretically by density functional theory calculations [19]. A reduction of the CO adsorption energy on the V–Pd alloy surface as compared to Pd(111) has also been calculated in this latter work, in close agreement with the experimental findings. The results obtained here are in line with these observations and suggest that this trend is more general for the adsorption of CO on alloy surfaces. The weak dissociation activity observed on the Ce–Rh alloy surface is probably a defect induced effect.

5. Summary

The adsorption of CO and the reaction of CO with preadsorbed oxygen has been investigated by comparing the Rh(111)2 × 1-O surface and ceria decorated Rh(111) inverse model catalyst surfaces using C 1s and O 1s core level and valence band photoelectron spectroscopy with synchrotron radiation. The ceria–Rh(111) surfaces have been prepared by reactive evaporation of cerium metal in an oxygen atmosphere and have been characterised by XPS, LEED and STM [9]. The CO exposures in this work have been performed at 300–320 K to restrict the adsorption of CO to the Rh sites of the catalyst surface. The adsorption of CO on the oxygen-precovered Rh(111)2 × 1-O surface was found to proceed slower than on the clean Rh(111) surface, as a result of the kinetic constraints imposed by the O + CO oxidation reaction, which removes the adsorbed oxygen as CO2 in a clean-off reaction at 300–320 K. On the ceria–Rh(111) surfaces the O + CO oxidation reaction is much faster than on the Rh(111)2 × 1-O surface and a catalytically active role of the ceria–Rh interface is suggested; the latter may be promoted by CO adsorption sites near the metal–ceria island phase boundaries. The XPS results support the notion that these CO sites close to the periphery of ceria islands are of the threefold hollow type. No dissociation of CO has been detected on the Rh(111) supported ceria inverse catalyst surfaces, but a small amount of CO dissociation is seen on CeRh3 alloy surfaces; the latter have been prepared by thermal decomposition of the ceria in UHV at high temperature. On the CeRh3 alloy surface the hollow-type CO adsorption sites are energetically favoured, but the global adsorption energy is lower than on Rh(111), as indicated by the reduced CO saturation coverage.

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