Unexpected Behavior of the Surface Composition of PtRh Alloys during Chemical Reaction

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Abstract: The changes in the surface composition of a $Pt_{50}Rh_{50}(100)$ alloy due to an ongoing $2H_2 + O_2 \rightarrow 2H_2O$ chemical reaction have been studied in situ. Exploiting the high-energy resolution and surface sensitivity of synchrotron radiation core-level spectroscopy it was possible to monitor the population of the two transitions metals atoms at the gas−surface interface. Sequences of fast high-resolution core-level spectra of the $Rh3d_{5/2}$, $Pt4f_{7/2}$, and $O1s$ core levels showed a continuous exchange of atoms between the first and subsurface layers. An unexpected Pt surface enrichment was found under slightly oxidizing conditions, opposite to what found in a highly oxidizing atmosphere.

It is well-known that alloying may lead to materials with properties significantly different from those of the monometallic materials.[1] This fact is used for the fabrication of bimetallic catalysts with higher performance in terms of selectivity and reactivity.[2,3] From the experimental point of view, the investigation of the alloying-induced modification of the catalytic properties is not an easy task, as the composition and the structure of the alloy surface and near-surface layers strongly depend on the gas environment and sample temperature. One of the main problems is that the local organization of the two metals at the surface is a dynamic process.[3−6] In the last 10 years remarkable progress has been made toward a detailed understanding of these processes, driven also by the advances in the experimental techniques that now provide greatly improved in situ experimental information. For example, scanning tunneling microscopy (STM) studies showed that the temporal evolution of the surface composition is governed by migration of single atoms or two-dimensional islands.[7−9]

However, STM still shows a limited capability of distinguishing the chemically different adsorbate−alloy configurations during a reaction, especially for highly mobile adsorbates,[10] and does not provide any information on the subsurface layers' composition, which plays an important role in the adsorbate-induced surface segregation processes.

Here we show that for a bimetallic PtRh alloy the exact composition of the first and subsurface layers and the different adsorbate−substrate chemical configurations can be continuously probed during a chemical reaction using high-resolution core-level spectroscopy, yielding information not previously accessible. In particular we studied the response of the Pt_{50}-$Rh_{50}(100)$ surface composition to the $2H_2 + O_2 \rightarrow 2H_2O$ reaction/reduction cycling: this provides basic knowledge for predicting the surface segregation behavior of this alloy, which is used as "three-way" automotive exhaust gas catalysts.[11−14] By analyzing the line shape and intensity variations of the $Pt4f_{7/2}$, $Rh3d_{5/2}$, and $O1s$ core levels measured at high-energy resolution and surface sensitivity, it is possible to describe both the population and the chemical configuration of the alloys first-layer surface atoms, along with the corresponding variations in the subsurface

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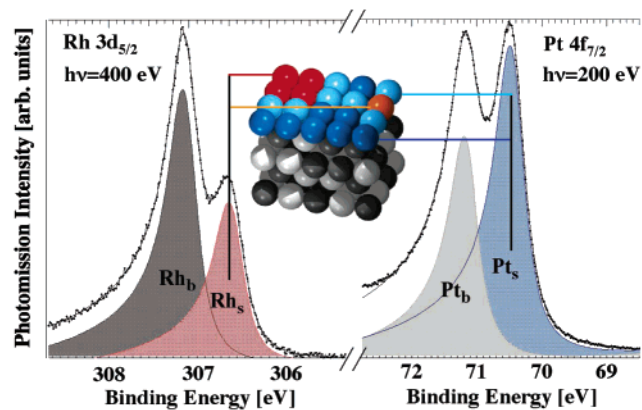(14) Tamura, H.; Sasahara, A.; Tanaka, K. *Surf. Sci.* **1994**, *303*, L379.

Figure 1. $Pt4f_{7/2}$ and $Rh3d_{5/2}$ core-level spectra of the clean PtRh(100) surface. The higher binding energy components correspond to bulk atoms, while the lower binding energy peaks originate from first-layer atoms.

composition. This is a key factor for understanding the reactivity properties of bimetallic surfaces. Our results provide direct evidence that the population of the two metallic species is governed not only by the adsorbed atoms but by their interactions and intermediate reactions products.

The reactivity experiments were performed at the SuperESCA beamline of ELETTRA, where fast photoelectron spectra can be collected ($\sim$15 s/spectrum) with an overall energy resolution better than 100 meV.[15] The reaction cycles were made by exposing the sample to a constant H_2 ambient pressure, while modulating the O_2 exposure with the shutter of a supersonic molecular beam.[17] The oxygen exposure was reproduced with high precision and with a rising constant below 100 ms. A well-ordered clean $Pt_{50}Rh_{50}$(100) surface was prepared by cycles of Ar^+ sputtering, oxygen treatments, and reduction in hydrogen to remove the residual oxygen.

Figure 1 shows the $Pt4f_{7/2}$ and $Rh3d_{5/2}$ spectra of the clean PtRh surface. The core-level spectra are fitted by using a sum of two Doniach–Sunjic[18] functions, which combine a Lorentzian width (Γ) with the singularity index (α), convoluted with a Gaussian function that describes the phonon, instrumental, and inhomogeneous broadening. A linear background is included in the fitting procedure. In both cases, one component (Rh_b and Pt_b) originates from the bulk atoms and the other (Rh_s and Pt_s) from the surface ones. Since the probing depth in our experimental setup corresponds to very few layers, the Rh_b and Pt_b components are dominated by emission from the second and third layer atoms. For the clean surface, the $Pt4f_{7/2}$ and $Rh3d_{5/2}$ surface core level (SCL) components are shifted by -705 (Pt_s) and -575 meV (Rh_s) with respect to the bulk peaks. It should be noted that the SCL components originate from Pt and Rh surface atoms, which can have several different local coordination, as shown in Figure 1. The relatively narrow widths of the SCL components for the clean surface indicate that the existing different local configurations of the Pt and Rh surface atoms[19]

do not affect appreciably the SCL energies, which are mainly caused by an electronic effect of transition metal surfaces, i.e., the narrowing in energy of the local density of d states at the surface due to the reduced atomic coordination.

An important feature of the SCL spectroscopy is that the spectral intensities (I_{Pt}, I_{Rh}) can be used as a measure of the Pt and Rh surface concentration, after appropriate normalization. The latter is obtained by two constants, c_1 and c_2, which better satisfy the conservation law $c_1 I_{Pt_s} + c_2 I_{Rh_s} = 1$ ML (one monolayer equals the number of surface atoms) for several spectra corresponding to different experimental conditions. The c_1/c_2 ratio depends on the photoelectron kinetic energies and emission angles and can be used to evaluate the first-layer composition at different surface temperature, coverage, and chemical composition. Following this procedure, we found that at the highest reaction temperature of the present study, 520 K, the clean surface is strongly Pt-enriched (86 $\pm$ 3%), in agreement with previous reports.[19−24]

During the $H_2 + O_2$ reaction at constant temperature, the spectral fingerprints of the PtRh surface undergo the following changes: (i) growth of new SCL peaks induced by the O and H adsorption, accompanied by gradual extinction of the clean surface components (Rh_{surf} and Pt_{surf}), and (ii) intensity variations of the components due to adsorbate induced segregation, which affects the Pt/Rh ratio at the first-layer and subsurface regions.

The O- and H-induced shifts of the $Pt4f_{7/2}$ and $Rh3d_{5/2}$ core levels were obtained by measuring the corresponding uptakes on the clean surfaces. On the basis of previous results on oxygen adsorption on Rh(100), the Rh_{iO} components can be attributed to Rh atoms bonded to i oxygen atoms,[25] assuming that the presence of Pt atoms does not affect the value of the O-induced Rh SCLs. For the Pt and the H-induced core-level shifts, the situation appears to be more complicated and a straigthforward assignment cannot be performed on the basis of previous results.[26]

Figure 2 illustrates the intensity changes of (a) Rh_s and Rh_{iO} components, (b) the sum of all Rh (Rh_{surf}) and Pt (Pt_{surf}) surface components, and (c) Rh_b as a function of oxygen coverage at 520 K. Calibration of the oxygen coverage was obtained by measuring the O1s core-level signal at a binding energy of 530.7 eV and assuming that the p(3×1) structure at saturation corresponds to a coverage of 0.33 ML. The almost symmetrically inverse Rh_{surf} and Rh_b plots indicate that the previously reported[2] oxygen-induced Rh segregation takes place only at near-saturation oxygen coverage, when the p(3×1) structure is forming, whereas at low oxygen coverage depletion of Rh occurs. This *unexpected* result is confirmed by the intensity of the Pt surface component (Pt_{surf}). Apparently the significant Rh segregation previously reported[2] occurs only under heavy oxygen doses, which do not occur under the

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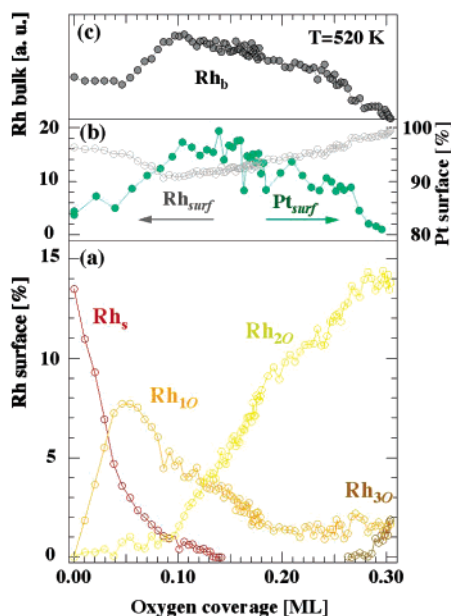
Figure 2. Coverage dependence of the oxygen-induced $Rh3d_{5/2}$ SCL shifted components; (b) sum of the all Rh (Rh_{surf}) and Pt (P_{surf}) surface components; (c) bulk concentration (Rh_b). O-induced $Rh3d_{5/2}$ SCLSs are $Rh_{1O} = -200$ meV, $Rh_{2O} = +260$ meV, and $Rh_{3O} = +510$ meV.

reaction conditions discussed here, where the oxygen coverage does not exceed 0.2 ML.

Close inspection of the plots in Figure 2 shows that the onset of the Pt segregation is at an oxygen coverage when most of the Rh surface atoms have been bonded to one oxygen atom. The factors favoring the segregation process are the reduction of the surface energy and the relative strength of the O–Pt and O–Rh adsorption bond, the latter being a function of the O coordination number. Thus, in single coordination configuration, the O-induced Pt segregation within a rather narrow oxygen coverage range below ~0.15 ML can be rationalized by assuming that the reduction of the surface energy per segregated Pt yields an energy gain compensating for the smaller O–Pt adsorption energy. The composition of the second layer, Rh enriched,[6] may also contribute to the energy balance.[27] With increasing O coverage, when the Rh coordination number with O becomes 2, the segregation process is reversed, because apparently in such configuration the contribution of the O bond strength to the energy balance dominates.

To understand the variations in the PtRh(100) surface composition during the $2H_2+O_2 \rightarrow 2H_2O$ reaction, we monitored the temporal evolution of the $Pt4f_{7/2}$ and $Rh3d_{5/2}$ SCLs and O1s intensity, at different O_2/H_2 partial pressures and temperatures ranging from 330 to 520 K. Figure 3 shows representative sets of plots obtained at 520 K, which provide detailed information concerning the changes in the surface composition during the reaction cycles. In a H_2 low-pressure ambient, only the Pt_s and Rh_s peaks are present, because above 400 K the lifetime of adsorbed H is negligible. Once the oxygen beam is open and the exposure increases, a single O1s component at the same binding energy of the adsorbed atomic oxygen grows, thus indicating that at this temperature water and OH species have a very short surface lifetime. In parallel, the Pt_s and Rh_s SCLs are replaced rapidly by the Rh_{iO} and Pt_O
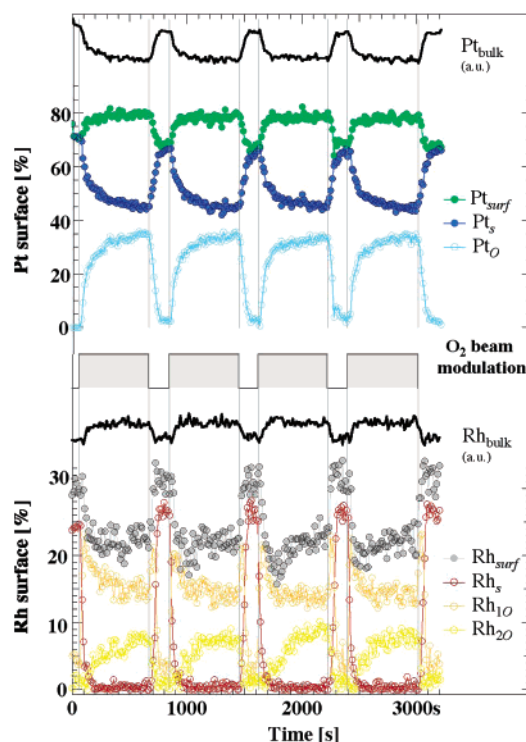
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Figure 3. Temporal behavior of the clean and O-induced $Pt4f_{7/2}$ and $Rh3d_{5/2}$ SCL component during the reaction at $T = 520$ K. $p_{H_2} = 6.6 \times 10^{-8}$ mbar, $p_{O_2} = 2.5 \times 10^{-7}$ mbar.

components. The steady-state is achieved ~400 s after opening the shutter. The starting surface is recovered after closing the oxygen beam. At $T \leq 400$ K (e.g. 330 K), the initial surface is partially covered by hydrogen (Rh_s and Pt_s coexist with the H-induced Rh and Pt surface core-level components), while under reaction conditions only the O-related SCLs are present in the steady-state, similarly to what is shown in Figure 3. The only difference is that the steady-state O coverage at 330 K is ~0.2 ML (compared to ~0.16 ML at T above 400 K), indicating that at 330 K the reaction rate is slower. The variations of the Rh_s, Rh_{iO}, Pt_s, and Pt_O intensities, which correspond to the time evolution of the surface composition, confirm the Rh depletion observed in the oxygen adsorption measurements (Figure 3). This effect is significantly weaker at 330 K, as shown in Figure 4, where we report the surface segregation behavior at three different temperatures. Careful investigation of the RhPt surface composition evolving during the reaction cycles unexpectedly revealed that only when the reaction was carried out at 330 K, the working catalyst preserved the surface composition of the fresh sample in reduction ambient. As shown in Figure 4, upon increasing the reaction temperature from 330 to 520 K, the Rh concentration of the working catalyst in reduction ambient increases from 14 to 31%, an enrichment which was not obtained in H_2 ambient alone. This is a clear demonstration of the complexity of processes occurring under reaction conditions, when not only O and H but also other intermediate species (OH in the present case) undoubtedly affect the energetics, which in turn determines the surface composition. The behavior of the Pt and Rh bulk components, clearly in antiphase with respect to the surface populations, is a fingerprint of the process of atomic exchange between the first layer and subsurface layers. It is important to note that bulk intensities, reported in Figure 3, are given in arbitrary units because of the presence of the
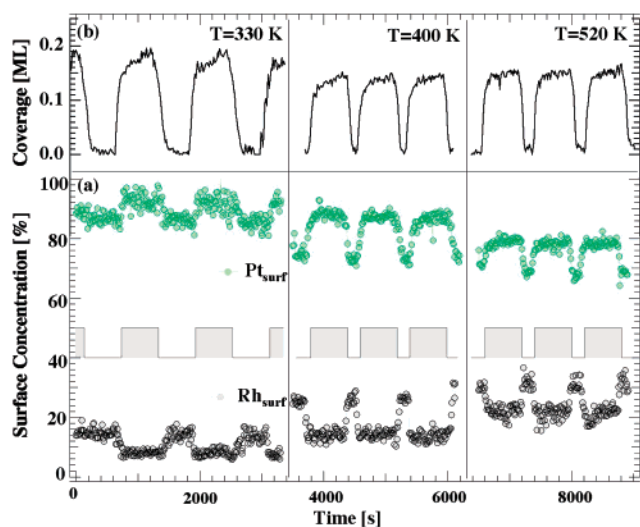
Figure 4. (a) Temporal behavior of the Pt_{surf} and Rh_{surf} components at 330, 400, and 520 K. (b) Oxygen coverage is shown as a black line. $p_{H_2} = 6.6 \times 10^{-8}$ mbar, $p_{O_2} = 2.0 \times 10^{-7}$ mbar.

same concentration of Rh, but in different subsurface layers, different core-level intensities would result.

At variance with the previously reported Rh enrichment under heavy oxygen doses, we find that the reacting surface of the PtRh alloy for steady-state oxygen coverage far from saturation tends to be Pt enriched. In fact, under heavy oxygen doses, when the surface becomes Rh-rich, the formation of oxide-like phases should deactivate the catalyst,[28] because of their high thermal stability (up to ~750 K).

In conclusion, we demonstrated the potential of high-resolution core-level spectroscopy in monitoring the dynamics of surface composition for alloy catalysts under reaction conditions. The response of the PtRh(100) catalysts to the presence of different surface species during the $2H_2 + O_2 \rightarrow 2H_2O$ reaction has been directly illustrated. We demonstrated that the evolution of surface composition during the reaction cycles cannot be assigned to single adsorbate-induced segregation processes. Instead we observe a strong coupling between different effects, such as the interactions between adsorbates and the presence of short-living reaction intermediate species. Our results indicate that the difficulties in quantitatively understanding the reaction kinetics in bimetallic catalysts can be originated by the complex balance between energetic terms due to different simultaneous effects.

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