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AES and SIMS of Carbonaceous Adsorbate Layers on Pt, Rh, and PtRh

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Carbonaceous adsorbate layers on polycrystalline Pt, Rh, and PtRh, formed from C_2H_4 at different temperatures, have been investigated by AES and SIMS. Information on the properties of the carbon has been derived from the fine structure of the carbon Auger peak. SIMS spectra of positive and negative ions in the 12–26 mass range exhibit great sensitivity for the nature of the carbonaceous deposits and reveal the influence of the substrate. Auger spectra indicate that Pt segregates to the surface of the clean PtRh alloy.

INTRODUCTION

Carbonaceous layers form an essential component of working catalysts in hydrocarbon reactions, since they affect catalytic activity, selectivity and stability. These layers are formed immediately when hydrocarbons are passed over the catalyst. The nature of the carbonaceous deposit depends on the substrate and the temperature at which it has been formed.

In the case of Pt, three temperature regimes can be distinguished.¹ At low temperatures, <340 K, hydrocarbons are reversibly adsorbed and can be removed by heating. At intermediate temperatures, 340 – 700 K, the Pt catalyst is readily covered by hydrocarbons which transform into a layer of reactive C_xH_y fragments. These species play an important role in determining the activity and the selectivity of the working Pt catalyst. At high temperatures, above 700 K, the hydrocarbons transform into inactive, graphitic layers which poison the catalyst. AES has successfully been applied to characterize gaseous hydrocarbons^{2,3} and carbonaceous adsorbate layers on several metals.^{4–8} Previous work on Pt and Rh revealed significant differences in the nature of the carbon species formed on these metals.⁸

SIMS has been applied to study the interaction of hydrocarbons with Ni and Ru.^{9–13} To the best of our knowledge, a comparative SIMS investigation of carbonaceous layers on Pt, Rh, and PtRh has not been described in the literature.

In this paper we report an investigation by means of AES and SIMS of carbonaceous layers formed by bringing polycrystalline foils of Pt, Rh, and PtRh in contact with C_2H_4 at three different temperatures, which represent the regimes of hydrocarbon interaction with Pt discussed above. The results show that SIMS spectra of hydrocarbon fragments are sensitive indicators of the state of the carbonaceous deposit.

EXPERIMENTAL

The experiments were carried out in an XPS/AES/SIMS spectrometer (Perkin-Elmer, PHI model 550), equipped with a double-pass cylindrical mirror analyzer and a PHI 2100 specimen introduction/reaction chamber. The base pressure of the UHV chamber is usually $2 \cdot 10^{-10}$ Torr. In the present experiments, however, pressures were typically in the low 10^{-9} Torr range, due to the frequent transfer of the sample between the UHV and the reaction chamber. The base pressure of the latter was $1 \cdot 10^{-7}$ Torr, obtained with a turbomolecular pump (Pfeiffer, TSU 110).

Auger spectra were measured in differential mode by using a $4.5 \mu A$ beam of 2 keV electrons, with a spot diameter of 0.5 mm. All spectra were measured in duplo at a scanning rate of 2 eVs^{-1} and a modulation amplitude of 2 eV. Each spectrum shown is the sum of two scans. Evidence for electronbeam-induced damage of the adsorbate layer has not been observed.

Static SIMS spectra were measured by using a 50 nA beam of 1 keV Ar^+ ions from a differentially pumped ion gun (PHI model 04-30) and a UTI 100C quadrupole mass spectrometer. Each sample was analyzed by measuring a positive SIMS spectrum for 60 s, followed by a negative spectrum also for 60 s. The total exposure of the sample during the SIMS experiments was $3.8 \cdot 10^{13} \text{ Ar}^+ \text{ ions cm}^{-2}$.

Data acquisition, storage, and instrument control were carried out with a Digital PDP 11/04 computer.

The samples consisted of a polycrystalline foil (specpure quality) of about $15 \times 5 \times 0.1 \text{ mm}$, spotwelded onto a tantalum hairpin. The temperature was monitored by a chromel–alumel thermocouple spotwelded onto the back of the foil. The cleaning procedure consisted of repeated cycles of sputtering with 5 keV Ar^+ ions and annealing at 1000 K, until no more contaminants could be detected by AES. Finally,

the samples were annealed at 1000 K for at least 5 min in order to remove damage caused by sputtering.

The metal foils were treated in the reaction chamber in 0.5 Torr C_2H_4 (Messer Griesheim, research grade purity) for 5 min, at 325, 525 or 775 K. The sample was cooled to room temperature, evacuated to about 10^{-6} Torr, and next transferred into the main chamber for AES and SIMS analysis. Hereafter, the sample was prepared for a subsequent experiment by applying one sputter and anneal cycle as described above.

RESULTS AND DISCUSSION

Surface composition of the PtRh alloy

Surface and bulk composition of the clean, equilibrated PtRh alloy were determined from the intensities of the Pt Auger transitions at 64, 168, and 1967 eV in the spectra of PtRh alloy and Pt metal, by using the Gallon model.^{14,15} Backscattering factors for the three Pt transitions in the alloy and in the metal have been calculated with the empirical relation proposed by Reuter,¹⁶ see Table 1.

Application of the Gallon model requires knowledge of the monolayer intensities, defined as the relative contribution of the surface layer to the Auger spectrum of the clean metal. The monolayer intensities (Table 1) were calculated from the empirical expression for the inelastic mean free path of electrons in solids proposed by Seah and Dench.¹⁷ As surfaces of polycrystalline specimens consist mainly of the most densely packed crystallographic planes, the interlayer spacing of Pt (111) planes has been used, the calculations resulted in a bulk content of 62 at % and a content of the uppermost atomic layer of 84 ± 5 at% Pt. Hence, the surface of our clean, equilibrated PtRh foil is enriched in Pt.

Surface segregation of Pt in PtRh has been reported by Holloway and Williams¹⁸ and Williams and Nelson¹⁹ for the (111) surfaces of various PtRh single crystals with different bulk compositions, and by van Delft and Nieuwenhuys²⁰ for the (100) surface of a Pt(0.25)Rh(0.75) single crystal. Ahmad and Tsong,²¹ on the other hand, reported surface enrichment of Rh in PtRh alloys, irrespective of the bulk composition. It should be noted, however, that the surface of the PtRh samples used by these authors was contaminated by a

fraction of a monolayer of sulphur. All results on the surface composition of PtRh alloys are summarized in Fig. 1.

Theory does not provide a clear answer about surface segregation in PtRh. As the thermodynamic data in Table 1 show, the heat of sublimation, ΔH^{sub} , of Rh is $2.3 \text{ kcal mole}^{-1}$ less than that of Pt in the temperature range of 298 K to 1000 K, and a slight enrichment of Rh at the surface might be expected. However, as the difference in ΔH^{sub} is small, and, moreover, the difference in atomic size between Rh and Pt is only 3% (Table 1), the driving force for surface segregation due to these effects is small. In such cases other effects, such as differences in surface entropy, or, perhaps, the presence of undetected impurities, may play a decisive role.

In conclusion, the surface of the clean, equilibrated PtRh alloy used in the present study consists of about 84% Pt and 16% Rh. Of course, this composition may be different when the surface is covered by an adsorbate layer.

AES of carbonaceous layers on Pt, Rh, and PtRh.

Auger spectra of the clean, equilibrated Rh, PtRh, and Pt foils, and of the foils after treatment in C_2H_4 at different temperatures are shown in Fig. 2, along with the carbon coverage, θ_c , of the sample. The amount of carbon on the foils has been calculated in the following way. For C_2H_4 on Rh metal, θ_c was estimated from the attenuation of the Rh 302 eV peak with respect to that of the clean metal. In this procedure, the exponential attenuation model, using the effective adsorbate layer thickness and the inelastic mean free path of electrons in the adsorbate layer, was applied. According to the empirical relation of Seah and Dench¹⁷, the inelastic mean free path of electrons in a carbon matrix can be calculated to be 0.65 nm. Previous time dependent experiments indicated the effective monolayer thickness of a carbonaceous adsorbate to be 0.11 nm.⁸

Figure 1. The composition of the uppermost atomic layer of PtRh alloys as a function of their bulk composition for various equilibration temperatures: $\circ$ = present results, 1000 K; $\triangle$ = Holloway and Williams, 1000 K (AES); $+$ = Williams and Nelson, 1300 K (ISS); $\square$ = Van Delft and Nieuwenhuys, 1200 K (AES/Selective chemisorption); $\bullet$ = Ahmad and Tsong, 1000 K (Atom probe).²¹

Table 1. Selected parameters of Pt and Rh

		Pt		Rh
(a) Auger transition (eV)	64	168	1967	302
Monolayer intensity (%)	47	43	8	28
Backscattering factor in Pt	2.32	2.28	1.88	
Backscattering factor in Pt	2.07	2.03	1.71	
		Pt		Rh
(b) Additional data				
Matrix density (mole ml ⁻¹)		0.110	0.121	
ΔH^{sub} (kcal mole ⁻¹ at 298 K)		135.3	133.0	
ΔH^{sub} (kcal mole ⁻¹ at 1000 K)		127.1	124.8	
Atomic radius (nm)		0.138	0.134

Figure 2. Differential Auger spectra of clean and ethylene-treated Pt, PtRh and Rh. All reactions were carried out in 0.5 Torr C_2H_4 for 5 min at the temperature indicated.

Taking into account the angle of acceptance of the analyzer (45°), and assuming a layer by layer growth of the adsorbate, the attenuation of the intensity of the Rh 302 eV Auger transition due to the presence of one and two monolayers of adsorbed carbon can be calculated; for uncompleted layers a linear interpolation between completed layers was used.

In the case of Pt, θ_c has been derived from the intensity ratios of the C 274 eV and the Pt 237 eV Auger peaks. It was assumed that an intensity ratio C 274/Pt 237 = 2.8 corresponds to monolayer coverage.¹ After corrections for differences in the backscattering factor of both substrates (according to Reuter¹⁶), the intensities of the various carbon Auger transitions on both pure metals could be compared. These corrected intensities were in good agreement with trends in the θ_c values, calculated. The method of the attenuation of the clean substrate signal and of the ratio of the adsorbate to substrate intensities cannot be used on the PtRh alloy, since the composition of the uppermost atomic layer of the latter may change as soon as hydrocarbons are adsorbed on the surface. Therefore, θ_c values on the alloys were calculated by comparing the corrected intensities of the C 274 eV peak. In these calculations effects due to the presence of different carbon species have been neglected. Of course, this is a serious simplification, and, hence, the θ_c values can only be considered as estimates.

The θ_c values shown in Fig. 2 indicate that for all samples the amount of carbon deposited from 0.5 Torr C_2H_4 increases with increasing temperature. Notice, that the amounts of carbon deposited at temperatures of 525 and 775 K are significantly higher for Pt than for Rh, whereas the PtRh alloy takes an intermediate position. On the assumption that the θ_c values of the carbonaceous deposit on PtRh formed at 525 and 775 K reflect the composition of the alloy surface, we find a Pt content of $63 \pm 10\text{at}\%$. This is much closer to the bulk composition than the surface composition of the clean alloy. Dynamic chemisorption experiments, which will be reported elsewhere, showed an unexpectedly rapid decrease of the Pt 64 eV Auger peak intensity as soon as the alloy was exposed to CH_4 . In contrast to this, the

decrease of the Rh 302 eV peak was less pronounced, also after appropriate corrections for the differences in escape depth of the Pt 64 and Rh 302 eV Auger electrons. These results suggest that surface enrichment of Pt in PtRh becomes less pronounced when the alloy is covered by a carbonaceous overlayer. The usual way to derive information on the nature of carbon from its Auger spectrum is to study the fine structure of the carbon spectrum between 240 and 260 eV. Unfortunately, this part of the spectrum is disturbed by the 256 eV transition of Rh and the 237 and 251 eV transitions of Pt. Spectrum subtraction techniques⁸ did not yield satisfactory results for the carbon-covered PtRh alloy, most likely due to differences in the surface composition between the clean and the carbon covered alloy, as discussed above.

However, the fine structure in the carbon spectra between 260 and 285 eV contains also information on the nature of the carbon. As Fig. 2 shows, three distinct features appear in the spectrum between 260 and 285 eV. Two of these are located at 268.8 ± 0.4 and 273.6 ± 0.4 eV on all samples. The relative intensity of the 268.8 eV peak decreases with increasing reaction temperature at which the carbonaceous layer was formed. In agreement with previous work⁸ we suggest that the 268.8 eV peak is characteristic of carbidic or molecular carbon species which are reactive toward hydrogen. The third feature is located at 277–280 eV. The exact position varies somewhat with the reaction temperature and with the substrate. This peak has been observed before in Auger spectra of graphitic overlayers on Ir,²² Pt,^{23,8} Rh,⁸ and Fe,²⁴ but it is absent in the spectrum of pure graphite. It is likely, therefore, that the 277–280 eV peak represents the interaction of graphitic carbon with the substrate, similarly as has been proposed for carbonaceous adsorbate layers on Fe(100).²⁴

In conclusion, the Auger spectra of Fig. 2 show that the carbonaceous layer formed on Rh, Pt, and PtRh at lower temperatures consists of carbidic and/or molecular carbon species, whereas at higher temperatures carbon of a more graphitic nature is formed. Pt is more sensitive to formation of graphitic carbon than Rh; the PtRh alloy behaves intermediate. The Auger results provide a useful background for the interpretation of the SIMS results which will be discussed hereafter.

SIMS of carbonaceous layers on Pt, Rh, and PtRh

As a representative example we show in Fig. 3 the positive and negative SIMS spectra of the PtRh foil which has been exposed to C_2H_4 at 325 K for 5 mins. Results of the other experiments are shown in a more condensed form in Fig. 4.

The positive SIMS spectrum in Fig. 3 shows peaks at atomic mass units (amu) 12, 13, 14, and 15, corresponding to C^+ , CH^+ , CH_2^+ , and CH_3^+ , and peaks in the range 24–29, corresponding to C_2^+ , $C_2H_2^+$, $C_2H_3^+$ or Al^+ , $C_2H_4^+$ or CO^+ , and $C_2H_5^+$. Unfortunately, not all peaks in the $C_2H_n^+$ ($n = 0, 1, \dots, 5$) can be assigned unambiguously to one species. Both Al^+ and $C_2H_3^+$ appear at 27 amu. As, for example, a chromel–alumel thermocouple has been used, the presence of Al^+ in

Figure 3. Positive and negative SIMS of PtRh treated in 0.5 Torr C_2H_4 at 325 K for 5 min.

the SIMS spectra cannot be excluded. The peak at 28 amu can be due to either $C_2H_4^+$ or CO^+ , the latter being a main constituent of residual gases in vacuum systems. In view of these considerations, we will only use the

SIMS peaks at masses 12–15 and 24–26, which are truly representative of hydrocarbon fragments.

The most intense peaks of the negative SIMS spectrum correspond to C_2^- , C_2H^- , and $C_2H_2^-$ ions at amu 24–26. The intensities in this range are typically 50 times larger than those of the CH_n^- ($n = 0–3$) ions. Note that the spectrum contains contributions due to O^- , OH^- , and F^- ions, at amu 16, 17, and 19, also. As the corresponding Auger peaks could not be detected, we believe that oxygen and fluorine are present in trace amounts which appear owing to their high sensitivity in SIMS.¹²

The SIMS patterns of the CH_n and C_2H_n ions are sensitive for the nature of the carbonaceous deposit formed from C_2H_4 at different temperatures. To illustrate this we show the distributions of intensities within the four ranges of the positive and negative CH_n and C_2H_n ions in Fig. 4. Note that the sum of the ion yields within each range has been set equal to 100%, and that, as a consequence, absolute comparisons between different ranges cannot be made.

In order to investigate if the Ar^+ ion current density used in the experiments, 50 nA cm^{-2} , gives rise to damage which may have influenced the results, the yields of selected ions were followed as a function of time during a SIMS measurement. It appeared that, although the yield of almost all ions decreased somewhat with time of exposure to the Ar^+ beam, correction for this result would not alter the picture as presented in Fig. 4 very much. Time-dependent experiments will be presented in a future publication.²⁵

The positive SIMS spectra in the 12–15 mass range of the adsorption at 525 K on all substrates indicate the presence of a surface species containing methylgroups,

Figure 4. Distribution of intensities of positive and negative ions in the mass ranges 12–15 and 24–26 of Pt, PtRh and Pt after treatment in 0.5 Torr C_2H_4 for 5 min at the temperatures indicated.

such as ethylidyne, in agreement with results of Creighton and White,²⁶ and Wang *et al.*²⁷

The SIMS results in Fig. 4 indicate that the properties of the carbonaceous deposit depends strongly on the temperature of formation and less on the substrate. The distribution of ions in each group of hydrocarbon fragments shows that the hydrogen content of the carbonaceous deposit decreases with increasing temperature of deposition. Comparison of absolute SIMS data showed that secondary ion yields from graphitic carbon are substantially lower than those of adsorbed hydrocarbons or reactive C_xH_y fragments formed at 325 and 525 K, respectively.²⁵ Hence, the actual hydrogen content of the graphitic carbon will be lower than suggested by the relative intensities of the CH_n and C_2H_n ions.

Since graphitization of carbon occurs through polymerization of smaller hydrocarbon fragments, the graphitic nature of the carbonaceous deposit will be reflected in the intensity ratio of the C_4^- and C_2^- ions (data not shown). In the case of Pt which, as is concluded from the Auger spectra in Fig. 2, is sensitive to formation of graphitic carbon, the C_4^-/C_2^- ratio increases from 0.01 for carbon deposited at 325 K to 0.05 for carbon deposited at 775 K. For Rh, the C_4^-/C_2^- ratio increases from 0.01 to less than 0.02, for carbon deposited at 325 and 775 K, respectively. This difference in graphitization between Pt and Rh is in agreement with a discussion of Beeck.²⁸ On PtRh the C_4^-/C_2^- ratio increases from 0.01 to 0.04 for C_2H_4 treatments at 325 and 775 K, respectively.

As Fig. 4 shows, the mass distribution of the $C_2H_n^-$ ions is the most sensitive indicator for the state of the carbonaceous layer, followed by CH_n^+ and CH_n^- ions, whereas the distribution of the $C_2H_n^+$ ions between 24

and 26 amu contains the least information. Unfortunately, potentially interesting fragments such as $C_2H_3^+$ and $C_2H_4^+$ cannot be used in the present case, because of possible interference with Al^+ and CO^+ , as discussed above.

Comparison of the SIMS patterns of carbonaceous layers formed at a certain temperature on Rh, Pt, and PtRh, reveals the influence of the substrate on the nature of the carbonaceous deposit. The SIMS data in Fig. 4 show that the hydrogen content of carbonaceous deposits formed on Rh at 525 and 775 K is lower than on Pt at these temperatures, suggesting that Rh is more active for C—H bond breaking than Pt, in agreement with catalytic experience.²⁹ It is also interesting to note that the SIMS patterns of carbon on PtRh differ from those on the constituent metals. The negative SIMS spectra of carbon on PtRh are more characteristic of carbon on Rh than on Pt, in spite of the fact that the alloy contains 62% Pt.

The present work shows that SIMS spectra can be used as fingerprints for the state of carbonaceous layers on metals such as Pt and Rh and their alloys, and that the spectra reveal differences in the properties of the carbonaceous deposits on the different substrates, in agreement with Auger line shape analysis described above. The relation between the SIMS pattern and the type of hydrocarbon species on the surface will be discussed in a future publication.²⁵

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