Composition and Properties of Platinum–Rhodium Alloy Surfaces

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The use of Pt–Rh based three-way catalysts for automotive exhaust gas control stimulated us to study the surface composition and surface properties of various Pt–Rh alloy samples. In this paper we shall review our results concerning the relation of the surface structure and surface composition with the physical and chemical properties.

The surface composition was studied under various experimental conditions, both in vacuum and in the presence of an atmosphere of NO, O₂, CO and H₂. The effect of the temperature on the surface composition will be described and discussed on the basis of thermodynamics. We shall discuss the relation of surface composition with the physical properties (Debye Temperature) and with the chemical properties of Pt–Rh alloys, in particular towards NO, CO, O₂ and H₂ and their reactions.

Another part of the paper deals with the effect of the surface structure on the chemical properties of Pt–Rh alloys. NO dissociation, the first step in the NO reduction with CO or H₂, is extremely sensitive to both the structure and the composition of the surface.

KEY WORDS: platinum; rhodium; alloys; surfaces; nitric oxide; catalysts.

1. Introduction

In this introductory chapter a brief review is presented concerning the interest in the surface properties of Pt–Rh alloys. In addition, an outline of the present paper is presented.

The first interest in the understanding of the surface properties of Pt–Rh alloys was related to the industrial application: Pt–Rh gauze is used already for many years in two important industrial processes, *viz.* the production of nitric acid *via* the catalytic oxidation of ammonia and the HCN synthesis. Most of the nitric acid produced is used for the manufacture of nitrate fertilizers. A major problem in the production of nitric oxide is the loss of the noble metal during commercial use. This loss is related to the formation of volatile Pt oxides. It is known already for more than half a century that the addition of rhodium to the platinum catalyst results in a drastic reduction of the Pt loss combined with an improvement of the reaction selectivity and activity.¹⁾ However, even for the Pt–Rh catalysts direct noble metal loss accounted for about 85 % of the operating costs.²⁾ Another problem was related to the long initial activation period of the catalyst during commercial use.³⁾ Much fundamental research has been devoted to these problems and to the characterization of these Pt–Rh catalysts in general.^{1–9)} A short section will deal with these studies.

Pt–Rh gauze for nitric acid production is still the major demand for both Pt and Rh in the chemical sector, including the petroleum industry (about 50 %).¹⁰⁾ However, the over-capacity in the world fertilizer industry has led to a downturn in the pro-

duction of nitric acid for nitrates thereby decreasing the demand for the Pt–Rh gauzes.

By far the dominant and still growing usage of both Pt and Rh is the consumption of the automotive catalyst utilized for the control of air pollution by exhaust emission. In 1987 the automotive catalyst accounted already for more than 35 % of the total Pt consumption and for 73 % of the Rh consumption¹⁰⁾. A further increase in the demand can be expected in view of the growth in the proportion of gasoline-engined cars fitted with catalytic converters. The present generation converters are based on bimetallic Pt–Rh catalysts which are called three-way catalysts since the harmful carbon monoxide, nitrogen oxides and hydrocarbons are simultaneously converted into carbon dioxide, nitrogen and water.^{11,12)}

The major purpose of this paper is to review the present knowledge concerning Pt–Rh alloy surfaces in relation to the processes taking place on the three-way catalyst. One part of the paper deals with the chemical composition of well defined Pt–Rh alloy surfaces, under ultrahigh vacuum conditions and in the presence of O₂, CO, NO and H₂.^{13–17)} Another part of the paper deals with the chemical properties of well defined Pt–Rh alloy surfaces, in particular with respect to the adsorption of O₂, CO, NO and H₂, the reduction of NO and the oxidation of CO.^{15–18)} For our studies several Pt–Rh alloy surfaces have been used: polycrystalline foils, field emitters and various single crystal surfaces cut from a Pt_{0.25}–Rh_{0.75} single crystal. Up to now most detailed studies have been performed on the polycrystalline foils and the (100) and (410) single crystal surfaces. Some of the results are reviewed here.

2. NH₃ Oxidation

Already in 1908 Ostwald and Brauer operated the Pt catalyzed process on a commercial scale. Since that time it has grown to become one of the largest tonnage output processes in the world.⁹⁾ About 70 % of the nitric acid produced is used in the manufacture of nitrate fertilizers, the remainder being utilized in the production of nitrogen containing products such as plastics, explosives and dyestuffs.⁹⁾

Ammonia is oxidized according to the reaction with stoichiometry:

Undesired nitrogen is produced according to the following stoichiometric equation:

The catalyst requirement for the production of nitric acid is a high selectivity for reaction (1) under reaction conditions. The reaction must be carried out at a temperature above 900 K under oxidizing conditions. Only a few catalysts can withstand these conditions and Pt was the obvious choice. Alternative catalysts that have been used, are composed of various oxides such as iron oxides promoted with bismuth oxide. These catalysts are inferior to platinum and have only been used in countries where platinum was not available.¹⁾

The catalyst is usually made up in the form of woven wire gauzes. The use of Pt-Rh alloys instead of pure Pt results in much better mechanical properties of the gauze and a significant reduction of Pt loss during the process.^{4,8)} Handforth and Tilley examined the effect of increasing Rh content on the catalytic performance.¹⁾ They found that the Pt loss decreases with increasing Rh content and that the conversion efficiency is much improved by the addition of Rh.

The commercial synthesis of HCN is carried out with mixtures of NH₃, CH₄ and air on the same catalyst as that used for the nitric acid production (90 wt% Pt, 10 wt% Rh). The reaction is carried out at a temperature of about 1400 K, which is more than 200 degrees higher than that used for the ammonia oxidation (about 1200 K).

Filters have been used to recover platinum lost during the ammonia oxidation. Most of the nitric acid manufacture plants in Europe use now gold-palladium catchment gauzes to recover Pt lost from the catalysts.¹⁹⁾ In this way recoveries of about 50 % of the gross losses are achieved.¹⁹⁾

Changes in surface structure and composition of the Pt-Rh alloy catalysts during heating in ammonia-air mixtures have been studied with a range of techniques including SEM, EPMA, XPS, AES, FIM and atom-probe FIM.²⁻⁸⁾ After oxidation a stable Rh-rich oxide layer is formed.²⁻⁸⁾ However, McCabe and Smith found under some conditions that the outer layers of the oxide may become enriched in Pt.⁶⁾ This effect was ascribed to the redeposition of vapor-phase platinum oxide on the surface. The

wires of a new catalyst gauze are essentially smooth. During their use in the plant etching occurs along grain boundaries. The etching process spreads into the interior of the grains and well-developed facets appear. Deep etch-pits often with very regular shape are formed and after some time cauliflower-like growth appears.²⁻⁸⁾ It has been shown that the reconstructions are related to vapor transport of Pt (as PtO₂). Pielaszek found that a Pt-10%Rh single crystal is much more resistant to etching than a pure Pt crystal.⁸⁾

3. Automotive Catalysts

The current generation automotive catalysts are three-way catalysts designed for the simultaneous conversion of three automotive pollutants: CO, hydrocarbons ("HC") and NO_x.^{11,12)} The most essential components of the three-way catalysts are platinum and rhodium. The catalyst consists of a monolithic support in the form of a honeycomb composed of a high melting ceramic material. The walls are coated with a high surface "washcoat" consisting of alumina with a number of stabilizers and promoters added. The precious metals Pt and Rh are incorporated into the washcoat.

The exhaust emissions of CO, "HC" and NO vary strongly with the air-fuel ratio. Because the catalyst performance is at its best close to the stoichiometric air-fuel ratio (around 14.6), the catalyst system is equipped with a closed-loop emission control system with an oxygen sensor that tunes the carburetter. The overall catalytic reactions which are important for control of the exhaust emission are given by the following stoichiometric equations:

The desired products are N₂, CO₂ and H₂O. These reaction products are thermodynamically favored at typical exhaust temperatures (around 800 K).

Platinum is an effective oxidation catalyst for the oxidation of CO and "HC". However, for the reduction of nitric oxide this metal is less effective.^{11,12)} One undesired reaction product is ammonia formed according to the stoichiometric equation.

Unfortunately, the selectivity of Pt to promote the NO reduction to N₂ rather than to NH₃ is poor. Rhodium is the essential ingredient in the catalyst for the conversion of NO to N₂.

Three-way catalysts used in the USA contain 1 to 2 g of noble metal in the weight ratio Pt/Rh of 10/1, if not lower Pt. This ratio differs significantly from the mine ratio for these metals (Pt/Rh is 16.5/1). It has been established that Pt and Rh can form alloys in the three-way catalyst. The present paper describes some of the properties of well defined Pt-Rh

alloy surfaces.

4. Surface Composition

4.1. In Vacuum

Pt and Rh are completely miscible at all concentrations with a slightly negative (exothermic) enthalpy of mixing. Ordered phases have not been reported, although some studies may indicate the presence of some short range order.²⁰⁾ Let us first summarize what we may expect from the theories of surface segregation.

The approach used in many surface composition calculations is the application of the so-called broken-bond approximation.²¹⁻²⁴⁾ According to this model the surface is considered as a termination of the bulk with broken bonds with the missing neighbor atoms. The energy gain due to surface segregation is calculated assuming additivity of bond energies per pair of atoms. The binding energies of pairs of atoms E_{AA} and E_{BB} can be derived from the enthalpies of sublimation of the alloy components A and B. The binding energy of a pair of A and B atoms can be calculated from E_{AA} , E_{BB} , the enthalpy of mixing ΔH_{mix} and the molar bulk fraction of A and B. In the simplest model the *ideal solution* model, only the enthalpies of sublimation of both components are considered. It predicts surface enrichment of the component with the smaller enthalpy of sublimation. In the *regular solution model* corrections are made for $\Delta H_{mix} \neq 0$. If the bulk mixing enthalpy is large and negative (exothermic) as for intermetallic compounds, the atoms A in the bulk favor an intimate contact with B atoms and *vice versa*. As a result, the system tends to attain a bulk composition with a maximum number of A-B bonds (AB_3 and A_3B for the fcc and AB for the bcc structure) and, hence, the component present in excess segregates to the surface. However, if the bulk mixing enthalpy is large and positive (endothermic), large clusters of A and large clusters of B are formed and the component with the smaller enthalpy of sublimation segregates to the surface. A third effect that can influence the surface composition is that of the difference in atomic size of A and B. The lattice strain energy due to the difference in the size of atoms is lowered when the minority component is interchanged with the "solvent" component on the surface. Hence, these strain effects favor surface segregation of the minority component.

In all these models the principle factors affecting surface segregation are differences in bond strengths (A-A, A-B and B-B) and atomic size. In addition, microscopic electronic theories have been proposed. An example is a recent paper of Mukherjee and Morán-López who presented a tight-binding electronic model using the *d*-band density of states of the constituent metals with bandwidth, band center and band filling as the input parameters.²⁵⁾

Table 1 shows some relevant parameters for Pt-Rh. It shows that the differences in heats of sublimations are very small (1 to 2 % difference), Pt and Rh are nearly of the same size (Rh is about 3 % smaller

than Pt) and that the enthalpy of mixing is only slightly negative.

Fig. 1 shows the results of our calculations based on a Monte Carlo method.³⁰⁾ The computed surface composition is almost equal to the bulk composition due to the almost equal values of the sublimation enthalpies and the atomic sizes of Pt and Rh in combination with the almost zero enthalpy of mixing.

Contrary to the predictions based on model calculations most of the experimental data point to a large Pt surface enrichment. Using LEISS, Williams and Nelson³¹⁾ found that Pt segregates to the surface of polycrystalline Pt-Rh alloys with a heat of segregation of 14 kJ/mol in the temperature range 800-1400 K. That result is consistent with the interpretation of the AES analysis of Holloways and Williams³²⁾ for the (111) surface of a $Pt_{0.1}-Rh_{0.9}$ alloy equilibrated at 1100 K and of our own data obtained for the (100) and (410) surfaces of a $Pt_{0.25}-Rh_{0.75}$ single crystal. The temperature dependence of the surface composition is shown in Fig. 2. Van Langeveld and Niemantsverdriet^{34,35)} found for a polycrys-

Table 1. Relevant data of Pt, Rh and Pt-Rh.

	Pt	Rh	Pt-Rh	Ref.
ΔH° subl. 298 (kJ/mol)	565	557	—	26)
r (Å)	1.39	1.34	—	—
$\theta_D(b)$ (K)	234	350	—	27)
$\theta_D(s)$ (K)	80*	160*	—	28)
ΔH_{mix} (kJ/mol)	—	—	<0	29)

* (111) surface

Fig. 1. Variation of the computed surface composition with bulk composition for (a) Pt-Rh(111) and (b) Pt-Rh(100) at 1100 K. (from Ref. 30))

Fig. 2. Temperature dependence of the surface composition of $Pt_{0.25}-Rh_{0.75}$ (100) and (410) faces.

talline $\text{Pt}_{0.6}\text{-Rh}_{0.4}$ sample that has been equilibrated at 1000 K a Pt surface concentration of about 80 %. Using atom-probe FIM, Ahmad and Tsong³⁶⁾ found for the (100) surface of a Pt-Rh tip that Rh segregates to the top layer after annealing at 1000 K. Later research of the same group showed that the Rh segregation was an effect of sulfur.³⁷⁾ Although the bulk S content was less than 100 ppm, a S surface coverage of more than 20 % of a monolayer was obtained.

In Fig. 3 composition depth profiles of two $\text{Pt}_{0.55}\text{-Rh}_{0.45}$ alloys both having the same bulk composition, but one with 50 ppm S, are shown. Obviously, Pt segregates to the top layer whereas the 2nd layer is depleted of Pt. However, this segregation behavior is reversed when the crystal contains small amounts of S.

Pt surface segregation is not confined to the close-packed surfaces since FEM observations of Pt-Rh alloys suggest a Pt like behavior towards gases like nitrogen and carbon monoxide of the rough surfaces of a $\text{Pt}_{0.5}\text{-Rh}_{0.5}$ alloy and a strong Pt surface enrichment for $\text{Pt}_{0.12}\text{-Rh}_{0.88}$ above 1500 K.¹⁶⁾ Some results are shown in Fig. 4.

Fig. 4(a) illustrates that the apparent work function of the clean $\text{Pt}_{0.12}\text{-Rh}_{0.88}$ tip increases with increasing annealing temperature. This observation suggests again that the amount of surface Pt increases with increasing annealing temperature since the work function of Pt is about 0.5 eV higher than that of a Rh field emitter. This effect is even better illustrated by the adsorption of nitrogen, as shown in Fig. 4(b). The work function change produced by nitrogen was measured as a function of the annealing temperature. Following annealing above 1200 K the work function change is equal to that found on pure Pt. The work function change found after annealing at 600–700 K is between the values found on pure Rh and pure Pt. It suggests that the Pt surface concentration of atomically rough surfaces, as found on field emitters, increases with increasing annealing temperature. The

Fig. 3. Composition depth profile for the (100) surface of a high purity $\text{Pt}_{0.55}\text{-Rh}_{0.45}$ alloy equilibrated at 1000 K and a same alloy but containing about 50 ppm of impurity sulfur. (from Ref. 37), with permission)

largest change in surface composition occurs upon annealing around 1000 K.

Summarizing we can conclude that the experimental data suggest that clean Pt-Rh alloy surfaces, both atomically rough and smooth surfaces, show a pronounced Pt surface enrichment that increases with increasing equilibration temperature. This temperature dependence is illustrated in Fig. 5. As we have discussed before, the Pt surface segregation can not be understood with the conventional surface segregation models. The small negative (exothermic) enthalpy of mixing can not be responsible for the Pt surface enrichment because Pt surface segregation is found both for Pt rich and Rh rich bulk compositions.

Fig. 4(a). Work function of a clean Pt-Rh tip at varying annealing temperatures, relative to the work function of the tip annealed at 1450 K.

(b). Work function change as a result of nitrogen-adsorption at 80 K at varying annealing temperatures. (from Ref. 16))

Fig. 5. The temperature dependence of the surface composition of (a) polycrystalline $\text{Pt}_{0.62}\text{-Rh}_{0.38}$ (▲) and (b) $\text{Pt}_{0.25}\text{-Rh}_{0.75}(100)$ (●).

A possible model that can explain the Pt surface segregation has been put forward by Van Langeveld and Niemantsverdriet.^{34,35)} They noticed that the surface Debye temperature of Pt is extremely low compared to that of Rh and compared to the bulk Debye temperatures. The surface and bulk Debye temperatures represent the vibrational properties of the atoms on the surface and in the bulk, respectively. The values have been included in Table 1. In the surface segregation models discussed so far the effect of lattice vibrations on the surface composition was neglected. Hoshino³⁸⁾ showed that the surface phonon softening (*i.e.*, the Debye temperature is lower for the surface than for the bulk) may affect the surface composition of alloys. The reason is that surface segregation of the component with low surface Debye temperature leads to a larger entropy corresponding to the surface phonon. It should be noted that reliable values of the surface Debye temperature of Pt and Rh surfaces are not available and that the conventionally used method for determination of the surface Debye temperature is essentially not correct.²⁸⁾ However, qualitatively the Pt surface segregation can be correctly predicted by the surface phonon softening model as is shown in Fig. 5.^{14,33)}

It should be pointed out that the pronounced Pt surface segregation is not a definite proof that the surface phonon softening is the decisive factor. An interesting, alternative model that may explain the Pt surface segregation has been put forward for the explanation of Pt surface segregation observed for Pt-Ni alloys. This alloy is another example of the few alloy systems, whose surface segregation behavior can not be understood with the conventional surface segregation models. The models predict a Ni surface enrichment whereas several studies confirmed a pronounced Pt surface enrichment for the (111) surfaces of Pt-Ni alloys. For example, Massadier *et al.*^{39,40)} reported a surface composition of 35 ± 5 % Pt for Pt_{0.10}-Ni_{0.90} (111) and a quasi complete Pt surface layer with less than 2-4 % Ni for Pt_{0.78}-Ni_{0.22} (111) and Pt_{0.50}-Ni_{0.50} (111). Spencer⁴¹⁾ suggested that the discrepancy between the calculated and the experimentally determined surface composition may be due to neglect of changes of bond energies due to surface relaxation. According to De Temmerman *et al.*⁴²⁾ the Pt surface enrichment is driven by a strengthening of the Pt-Pt bonds in the surface region. This model is consistent with the adsorption behavior of the Pt-Ni (111) surfaces. It has been found that the heat of adsorption of several gases is significantly lower on the Pt-Ni (111) surfaces than on the (111) surfaces of pure Ni and Pt.^{39,40)} As we shall see such a weakening of the adsorption bond does not occur on Pt-Rh surfaces. Moreover, the temperature dependence of the surface composition of Pt-Rh alloys is completely in line with the earlier mentioned model based on surface phonon softening. Evidently, the surface phonon softening model predicts that the Pt surface concentration becomes larger with rising temperature because of the increasing importance of the entropy contributions to the free energy at higher tempera-

ture. At lower temperatures the increasing importance of the enthalpy contributions results in a lowering of the Pt surface concentration as has indeed been observed. If the driving force for Pt surface segregation would be dominated by enthalpy contributions the surface excess of Pt must decrease with increasing temperature, whereas the opposite effect is observed. The peculiar surface segregation behavior of Pt-Rh alloys is due to the very small differences in the binding energy parameters ($E_{\text{Pt-Pt}}$, $E_{\text{Rh-Rh}}$ and $E_{\text{Pt-Rh}}$). In consequence, the surface composition is extremely sensitive to the presence of adsorbate atoms. Any contaminant that has a slight preference for either Pt or Rh may induce surface segregation.

4.2. In an Atmosphere of Reactive Gases

It is known that the presence of a gaseous environment can modify the intrinsic surface segregation tendency of alloys.^{21,22,24)} As we have discussed before, Pt-Rh alloys exposed to oxygen at elevated temperatures show Rh surface segregation.^{5,6)} In order to investigate the gas induced surface segregation in more detail several Pt-Rh alloy single crystal surfaces were exposed to flows of several gases while the temperature was varied.¹⁷⁾ The surface analytical technique used was AES. First the temperature was increased in steps from 300 to 1200 K and then the temperature was decreased, again stepwise. For the interpretation of the AES results it is convenient to define the parameter δ :

$$\delta = \frac{I(\text{Pt } 64 \text{ eV})}{I(\text{Rh } 302 \text{ eV})} [\text{in vacuum}] - \frac{I(\text{Pt } 64 \text{ eV})}{I(\text{Rh } 302 \text{ eV})} [\text{in gaseous environment}],$$

where, I : the intensity of the relevant surface sensitive Auger signal.

Several processes may contribute to changes in δ . For Pt-Rh the major contributions are

gas induced Rh surface segregation:	$\delta > 0$
selective adsorption on Pt:	$\delta > 0$
gas induced Pt surface segregation:	$\delta < 0$
selective adsorption on Rh:	$\delta < 0$.

Some of the results are shown in Fig. 6 for Pt-Rh(410) in an oxygen atmosphere of 5.10^{-7} mbar. It can be concluded from the figure that at low temperature oxygen is selectively adsorbed on the Rh sites while heating in the oxygen atmosphere results in oxygen induced Rh surface segregation. This process is observed in the temperature range 600 to about 1000 K. The oxygen induced Rh segregation is responsible for the fact that the maximum temperature at which oxygen is present on the surface does not depend on the equilibration temperature. The maximum in δ is related to the decrease in oxygen coverage above 800 K. Oxygen desorbs from the surface above 800 K, first from the Pt sites and as a result δ decreases above 800 K.

Similar measurements have been performed in the presence of a flow of 5.10^{-7} mbar of NO, CO and

Fig. 6. AES results obtained for Pt-Rh(410) in a flow of 5.10^{-7} mbar O_2 . δ as a function of the temperature for (a) Rh rich surface and (b) Pt rich surface. Auger O signal intensity as a function of the temperature for (c) Rh rich surface and (d) Pt rich surface. (from Ref. 17))

H_2 .¹⁷⁾ For CO and H_2 the change in δ with increasing temperature was very small and, hence, these gases do not exert a significant influence on the surface composition. For NO a similar effect as for oxygen was observed but the induced surface segregation is much less pronounced than for O_2 . These results suggest that NO dissociates both on Pt rich and Rh rich alloy surfaces and the O formed can induce some oxygen induced surface segregation.

5. Adsorption Properties

The adsorption properties of several polycrystalline Pt-Rh foils, pure Pt, pure Rh and of various single crystal surfaces cut from a $Pt_{0.25}-Rh_{0.75}$ single crystal have been investigated.^{15,17,18)} The comparison of the behavior of the various single crystal surfaces allows to examine the effect of the surface structure. The surface composition of the single crystal surfaces was varied from Rh rich to Pt rich simply by variation of the equilibration temperature. In this review paper only some of our results are presented. The techniques used were TDS, AES, XPS and LEED.

The adsorption of hydrogen and carbon monoxide is rather similar on all the Pt-Rh alloy surfaces, as well as on the pure Pt and Rh surfaces. Both the surface structure and the surface composition exert some influence on the TD spectra and hence, on the heat of adsorption. These relatively small effects are, however, not relevant for the present discussion. No indication of CO dissociation was found.

Striking differences have been observed in the behavior of Pt rich and Rh rich alloys towards oxygen. As a first example Fig. 7 shows some AES results obtained for polycrystalline foils. After an exposure of 100 L the oxygen was pumped out the vacuum chamber and the O (510 eV) signal intensity was monitored during a stepwise increase of the temperature. In the figure the intensities normalized to their

Fig. 7. Normalized O signal intensity as a function of the temperature for 100 L O_2 exposure on: (a) Pt and $Pt_{0.55}-Rh_{0.45}$ and (b) $Pt_{0.12}-Rh_{0.88}$. (from Ref. 18))

initial values at 300 K are shown. The initial amount of oxygen on Pt rich alloys is much smaller than on Rh rich alloys. On Pt rich alloys the small oxygen signal disappears already at about 400 K, probably by reaction with residual hydrogen and CO (Base pressure in the ultrahigh vacuum system was 1.10^{-9} Torr consisting of 90 % H_2 and 10 % CO). On Rh rich alloys the amount of surface oxygen decreases upon heating in the temperature range up to 500 K, probably by reaction with the residual gas. However, above 500 K the oxygen surface concentration increases before it desorbs in the temperature range 800–1200 K. Apparently, subsurface oxygen is present in large amounts and it diffuses to the surface above 500 K. Since the oxygen signal intensity becomes larger than the signal intensity at 300 K, the subsurface oxygen must have been formed already at the exposure temperature of 300 K. The $Pt_{0.55}-Rh_{0.45}$ sample shows a Pt like behavior. For the $Pt_{0.12}-Rh_{0.88}$ alloy either the Pt like or the Rh like behavior was observed depending on the experimental conditions. A similar ambivalent behavior has been found for the $Pt_{0.25}-Rh_{0.75}(100)$ surface. It appeared that subsurface oxygen is formed after low temperature annealing (975 K, Rh rich surface) whereas high temperature equilibration (1425 K, Pt rich surface) results in the Pt like behavior.

The effect of an exposure of 100L NO on the various samples was studied in the same way as described for oxygen. The behavior of the oxygen signal was identical to that found after exposure to oxygen for all samples. This indicates that NO dissociates on all surfaces leaving oxygen adatoms. The NO dissociation is partly due to the intrinsic chemical activity of the surface and, most probably, partly induced by the primary electron beam.

According to several studies, NO dissociation is very sensitive to the surface structure of Rh⁴³⁾ and, in particular, of Pt.^{44–46)} For example, it has been reported that the Pt(111) surface can not break the NO bond whereas the Pt(410) surface is very active in NO bond breaking.⁴⁵⁾ In general, Rh is a better catalyst for NO dissociation than Pt.⁴³⁾ XPS has been used to investigate the NO dissociation on Pt-Rh single crystal surfaces.¹⁵⁾ The results are sum-

Fig. 8. The NO dissociation percentage as a function of the temperature for various Pt-Rh surfaces.

marized in the Figs. 8 and 9. The figures show:

(1) The dissociation activity is sensitive to the surface structure. The (410) and (210) surfaces are more active in NO bond breaking than the (321) surface whose activity is larger than that of the (111) surface. The effect of the surface structure is larger for the Pt rich than for the Rh rich surfaces.

(2) The dissociation activity is higher for the Rh rich (equilibration at 800 K) than for the Pt rich surfaces (equilibration at 1100 K).

6. CO Oxidation and NO Reduction

In order to investigate the influence of the initial surface composition and of the gas induced surface segregation on the reactivity TPRMS and AES measurements have been performed in various gas mixtures of CO+O₂ and CO+NO using the Pt-Rh(410) surface.

Fig. 10 shows the CO₂ production for the reaction of CO with O₂ and for CO with NO starting with a Pt rich and with a Rh rich surface as observed during a stepwise increase of the temperature using stoichiometric gas compositions (CO/O₂=2/1 and CO/NO=1). For comparison the Auger N (380 eV) and O (510 eV) signal intensities as observed in a flow of 5.10⁻⁷ mbar NO are also shown in the figure. In the relevant temperature range (500–800 K) NO dissociation is very fast. The temperature of maximum CO₂ production (T_m) is the same for both reactions. Hence, it can be concluded that NO dissociation is not the rate determining step in the reaction CO+NO under our experimental conditions. This conclusion is consistent with the results described in Chap. 5.

The Rh rich surface shows a maximum rate of CO₂ production around 665 K. However, on the Pt rich surfaces the maximum occurs at the significantly lower temperature of 615 K. Apparently, the surface composition has a significant influence on T_m . This can

Fig. 9. The temperature at which a dissociation percentage of 25 % is obtained for Pt rich Pt-Rh alloy surfaces vs. the same parameter for Rh rich Pt-Rh alloy surfaces. (from Ref. 15))

Fig. 10. TPRMS results for a stoichiometric flow of CO and O₂.

(a) Rh rich Pt-Rh(410); (b) Pt rich Pt-Rh(410) and for a stoichiometric flow of CO and NO; (c) Rh rich Pt-Rh(410) and (d) Pt rich Pt-Rh(410). Auger nitrogen and oxygen signal intensities in a flow of 5.10⁻⁷ mbar NO for (e) Rh rich Pt-Rh(410) and (f) Pt rich Pt-Rh(410). (from Ref. 17))

be explained on the basis of the metal oxygen bond strength,⁴⁷⁾ which is weaker for Pt than for Rh, as is also confirmed by the Figs. 10(e) and 10(f).

Fig. 11 shows the results of similar measurements for increasing, decreasing and again increasing tem-

perature (1st, 2nd and 3rd branch, respectively). In the 1st branch T_m is higher for the Rh rich surface, as has been discussed. The 2nd branch shows a higher CO_2 production, with T_m almost similar for the two surfaces. The 3rd branch shows a higher CO_2 production than the 1st branch, but lower than the 2nd. T_m is now equal for the initially Rh rich and Pt rich surfaces, and it is slightly higher than in the 2nd branch and in between the values of the 1st branch. Apparently, the surface composition alters during the reaction and is not dependent anymore on the initial equilibration temperature. AES measurements, not shown in this paper, support this conclusion. The largest changes occur on the initially Rh rich surface.

In the Figs. 11(c) and 11(d) the C (272 eV) and O (510 eV) signal intensities are shown as a function of the temperature program. The product of the carbon and oxygen signal intensities is at a maximum in the same temperature region where the CO_2 production is at a maximum, confirming the essential reaction step between CO(ads) and O(ads) .⁴⁷⁾ The higher CO_2 production in the 2nd branch might be expected if, starting at high temperatures, O_2 is the 1st gas that will adsorb, whereas at low temperatures the surface is inhibited by excess CO (high sticking probability). However, the AES results in the Figs. 11(c) and 11(d) do not support this model; here the carbon signal intensity is higher in the 2nd branch, especially for the initially Rh rich surface, whereas the oxygen signal intensity is smaller.

Apparently the enlarged CO_2 production for the 2nd branch is due to a more favorable surface composition. Pt surface segregation can only take place

Fig. 11. TPRMS results for a stoichiometric flow of CO and O_2 . (a) Rh rich Pt-Rh(410); (b) Pt rich Pt-Rh(410) with increasing (1), decreasing (2) and again increasing (3) temperature. AES carbon and oxygen signal intensities in the same flow for (c) Rh rich Pt-Rh(410) and (d) Pt rich Pt-Rh(410). (from Ref. 17))

at high temperatures for low adsorbate coverages, if the Pt surface segregation is due to a vibrational entropy effect. Adsorbates may dim the vibrations and, hence, influence the segregation. Moreover, the enthalpy terms involved in the surface segregation process are rather small and, consequently a slight preference of an adsorbate for one of the components can seriously influence the surface composition. Another effect that should be considered for explanation of the enlarged CO_2 production in the 2nd branch is a difference in surface structure for rising and falling temperature in the gas mixture. Anyhow, the results presented in Fig. 11 suggest that the initial surface composition is altered by chemisorption induced segregation and/or thermal segregation effects.

In Fig. 12 the maximum CO_2 production is shown as a function of the equilibration temperature, for the increasing and decreasing temperature branches in the various gas mixtures studied. In general, with decreasing temperature the maximum CO_2 production is higher than with increasing temperature. As discussed above, different adsorbate coverages can not be used to explain this difference for a stoichiometric $\text{CO} + \text{O}_2$ mixture. An adapted surface composition and, possibly, structural changes in the surface are responsible for this effect. The curves for decreasing temperature are slightly less pronounced than those for increasing temperature, indicating that the surfaces tend to attain the same final composition. The optimum initial and induced final surface composition appears to be Pt-rich for stoichiometric and reducing gas mixtures and moderately Pt rich for slightly oxidizing gas mixtures. The curves in Fig. 12 show clear maxima for the alloy surfaces confirming the syn-

Fig. 12. The maximum CO_2 production as a function of the equilibration temperature for increasing (—) and decreasing temperature branches (---) (from Ref. 17)).

ergism as observed by Oh and Carpenter⁴⁸⁾ for supported Pt/Rh compared to pure Pt and pure Rh. Dual selective chemisorption (oxygen on Rh sites and CO on Pt sites simultaneously), resulting in an optimum mixing of the reacting adsorbates on the surface might form a basic line of thought for understanding the reported synergism of alloying for the CO oxidation reaction.

7. Concluding Remarks

Bimetallic Pt-Rh catalysts are used for two important processes: the purification of the exhaust gases from automobiles and the oxidation of ammonia for the production of nitric acid. This paper describes the composition and the chemical properties of Pt-Rh alloy surfaces in relation to these applications of Pt-Rh catalysts.

The alloy Pt-Rh is unique in the sense that the binding energy parameters, $E_{\text{Pt-Pt}}$, $E_{\text{Rh-Rh}}$ and $E_{\text{Pt-Rh}}$ are virtually equal. Moreover, the vibrational entropy difference for surface segregation is relatively large. As a result, the surface composition of Pt-Rh alloys is rather unique, and also flexible: it varies easily with changing experimental conditions (Temperature, gas phase composition). This has important consequences for the chemical behavior of Pt-Rh catalysts. Strong Pt surface segregation is observed for clean Pt-Rh alloys, especially after high temperature annealing ($T > 1000$ K). However, for Rh rich Pt-Rh alloys the surface composition is almost bulk like following low temperature equilibration ($T \sim 800$ K). Adsorbates can easily induce segregation of Rh or Pt to the surface and the chemical properties of the surface are changed accordingly.

It is tempting to speculate about the possible relevance of these results for automotive pollution control. It has been reported that bimetallic Pt-Rh catalysts exhibit a synergetic effect towards CO oxidation.⁴⁸⁾ Our results also indicate a beneficial effect of alloying Pt with Rh on the CO oxidation activity (Chap. 6). Moreover, alloying of Rh with Pt results in a higher stability in an oxidative atmosphere.⁴⁹⁾ Pt and Rh are most probably present in the form of Pt rich alloy particles in the three-way catalyst. The surface composition of the alloy particles will depend on the particle size, the temperature, the ambient composition and the presence of impurities. Under conditions of lean fuel-air mixtures (oxidizing mixture) a severe Rh surface enrichment must be expected, eventually leading to the formation of a less active Rh oxide on the surface of the catalyst particle. In this case the particle will show a catalytic behavior comparable with that of pure Rh although it will be more resistant to oxidation due to the presence of Pt. However, under rich conditions (reducing mixtures) a Pt rich surface is expected because of the Pt rich bulk. Hydrocarbon fragments and traces of impurities (P, S, Si, B) from the gasoline and from the lubricant may severely alter the surface composition and, consequently, modify the catalytic behavior of the alloy particles. Excursions to high tempera-

ture (above 1000 K) may result in a pronounced Pt surface segregation provided that the temperature is sufficiently high to obtain an uncovered surface. These considerations show that the surface composition of the catalyst particles in the three-way catalyst and, hence, the catalytic behavior of these particles may be very variable.

Nomenclature

AES:	Auger Electron Spectroscopy
EPMA:	Electron Probe Micro-Analysis
FEM:	Field Electron Microscopy
FIM:	Field Ion Microscopy
LEED:	Low Energy Electron Diffraction
LEISS:	Low Energy Ion Scattering Spectroscopy
SEM:	Scanning Electron Microscopy
TDS:	Thermal Desorption Spectroscopy
TPRMS:	Temperature Programmed Reaction Mass Spectroscopy
XPS:	X-ray Photoelectron Spectroscopy

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REFERENCES

- 1) S. L. Handforth and J. N. Tilley: *Ind. Eng. Chem.*, **26** (1934), 1287.
- 2) L. D. Schmidt and D. Luss: *J. Catal.*, **22** (1971), 269 and refs. therein.
- 3) J. A. Busby and D. L. Trimm: *J. Catal.*, **60** (1979), 430.
- 4) R. W. McCabe, T. Pignet and L. D. Schmidt: *J. Catal.*, **32** (1974), 114.
- 5) T. Wang and L. D. Schmidt: *J. Catal.*, **71** (1981), 411; **70** (1981), 187.
- 6) A. R. McCabe and G. D. W. Smith: *Proc. 8th Int. Congr. Catal.*, Berlin, DEHEMA, Frankfurt, (1984), IV-73.
- 7) A. R. McCabe and G. D. W. Smith: *Plat. Met. Rev.*, **32** (1988), 11.
- 8) J. Pielaszek: *Plat. Met. Rev.*, **28** (1984), 109.
- 9) K. G. Gough and B. L. Wibberley: *Plat. Met. Rev.*, **30** (1986), 168.
- 10) Platinum 1988, Johnson Matthey Public Ltd. Co., London, (1988), 29, 59.
- 11) K. C. Taylor: *Catal. Sci. Technol.*, J. R. Anderson and M. Boudart, ed., Springer, Berlin, **5** (1984), 119.
- 12) K. C. Taylor: "Catal. and Automotive Pollution Control", *Stud. Surf. Sci. & Catal.*, Vol. 30, A. Crucq and A. Frennet, ed., Elsevier, Amsterdam, (1987), 97.
- 13) F. C. M. J. M. van Delft and B. E. Nieuwenhuys: *Surf. Sci.*, **162** (1985), 538.
- 14) F. C. M. J. M. van Delft, A. D. van Langeveld and B. E. Nieuwenhuys: *Surf. Sci.*, **189/190** (1987), 1129.
- 15) F. C. M. J. M. van Delft, J. Siera, R. J. Vreeburg, M. J. Koster van Groos, A. D. van Langeveld and B. E. Nieuwenhuys: *Proc. 9th Int. Congr. Catal.*, Calgary, Chem. Inst. Canada, Ottawa, (1988), 1114.
- 16) R. M. Wolf, M. J. Dees and B. E. Nieuwenhuys: *J. Phys. Paris*, **47 (C-7)** (1986), 419/11.
- 17) F. C. M. J. M. van Delft, J. Siera and B. E. Nieuwenhuys: *Surf. Sci.*, **208** (1989), 365.

- 18) F.C.M.J.M. van Delft, G. H. Vurens, M. C. Angevaere-Gruter and B. E. Nieuwenhuys: "Catal. Automotive Pollution Control", Stud. Surf. Sci. & Catal., Vol. 30, A. Crucq and A. Frennet, ed., Elsevier, Amsterdam, (1987), 229.
- 19) A. E. Heywood: *Plat. Met. Rev.*, **26** (1982), 28.
- 20) H. J. Goldschmidt and T. Land: *J. Iron Inst.*, **155** (1947), 221 and refs. therein.
- 21) H. J. Kelley and V. Poncet: *Progr. Surf. Sci.*, **11** (1981), 139.
- 22) W.M.H. Sachtler and R. A. van Santen: *Adv. Catal.*, **26** (1977), 69.
- 23) A. D. van Langeveld: *Thin Solid Films*, **129** (1985), 161.
- 24) B. E. Nieuwenhuys: "Chemisorption of Gases on Metal Films", Stud. Surf. Sci. & Catal., Vol. 32, P. Wissmann, ed., Elsevier, Amsterdam, (1987), 476.
- 25) S. Mukherjee and J. L. Morán-López: *Surf. Sci.*, **189/190** (1987), 1135.
- 26) M. Kh. Karapetyants and M. K. Karapetyants: *Handbook of Thermodynamic Constants of Inorganic and Organic Compounds*, Ann-Harbor-Humphrey Sci., Ann Harbor, (1970).
- 27) G. A. Somorjai: *Chemisorption in Two Dimensions: Surfaces*, Cornell Univ. Press, Ithaca, (1981).
- 28) F.C.M.J.M. van Delft, M. J. Koster van Groos, R.A.G. de Graaff, A. D. van Langeveld and B. E. Nieuwenhuys: *Surf. Sci.*, **189/190** (1987), 695.
- 29) A. K. Niessen, F. R. de Boer, R. Boom, P. F. de Chatel, W.C.M. Matters and A. R. Miedema: *Calphad*, **7** (1983), 51.
- 30) G. H. Vurens, F.C.M.J.M. van Delft and B. E. Nieuwenhuys: *Surf. Sci.*, **192** (1987), 438.
- 31) F. L. Williams and G. C. Nelson: *Appl. Surf. Sci.*, **3** (1979), 409.
- 32) P. H. Holloway and F. L. Williams: *Appl. Surf. Sci.*, **10** (1982), 1.
- 33) F.C.M.J.M. van Delft: Ph.D. Thesis, Leiden Univ., Leiden, (1988), Chapter XII, 162.
- 34) A. D. van Langeveld and J. W. Niemantsverdriet: *Surf. Sci.*, **178** (1986), 880.
- 35) A. D. van Langeveld and J. W. Niemantsverdriet: *J. Vac. Sci. Technol.*, **A5** (1987), 558.
- 36) M. Ahmad and T. T. Tsong: *J. Chem. Phys.*, **83** (1985), 388.
- 37) T. T. Tsong: *Surf. Sci. Rep.*, **8** (1988), 127.
- 38) K. Hoshino: *J. Phys. Soc. Japan*, **50** (1981), 577.
- 39) J. Massardier, B. Tardy, P. Delichère, M. Abon and J. C. Bertolini: Proc. 8th Int. Congr. Catal., Berlin, DECHEMA, Frankfurt, (1984), IV-185.
- 40) J. C. Bertolini, B. Tardy, M. Abon, J. Billy, P. Delichère and J. Massardier: *Surf. Sci.*, **135** (1983), 117.
- 41) M. S. Spencer: *Surf. Sci.*, **145** (1984), 153.
- 42) L. De Temmerman, C. Creemers, H. van Hove and A. Neyens: *Surf. Sci.*, **183** (1987), 565.
- 43) H.A.C.M. Hendrickx and B. E. Nieuwenhuys: *Surf. Sci.*, **175** (1986), 185.
- 44) R. J. Gorte, L. D. Schmidt and J. L. Gland: *Surf. Sci.*, **109** (1981), 367.
- 45) R. I. Masel: *Catal. Rev.-Sci. Eng.*, **28** (1986), 335.
- 46) P. Leerkamp, R. M. Wolf and B. E. Nieuwenhuys: *J. Phys. Paris*, **49 (C-6)** (1988), 227.
- 47) B. E. Nieuwenhuys: *Surf. Sci.*, **126** (1983), 307.
- 48) S. H. Oh and J. E. Carpenter: *J. Catal.*, **98** (1986), 178.
- 49) A.J.S. Chowdhury, A. K. Cheetham and J. A. Cairns: *J. Catal.*, **95** (1985), 253.