Investigations on Platinum Gauze Surfaces Used in the Manufacture of Nitric Acid

THE DEPENDENCE OF THE ACTIVITY OF A PLATINUM CATALYST ON THE COMPOSITION OF SUB-SURFACE LAYERS

By P. A. Kozub, G. I. Gryn and I. I. Goncharov
Faculty of Inorganic Chemistry, Kharkiv State Polytechnic University, Kharkiv 61002, Ukraine

The oxidation of ammonia for the production of nitric acid is a well known process which has been in constant use since the 1890s for the manufacture of fertiliser. Ammonia is oxidised on the surface of a woven or knitted catalyst gauze made of noble metals. Fertiliser production throughout the world partly depends on this technology and research is continuously being undertaken aimed at optimising output and reducing the noble metal loss from the catalysts. Here, some investigations carried out in Ukraine on the surface composition of binary (platinum-palladium) and ternary (platinum-palladium-rhodium) alloys used for the ammonia oxidation process are described. Samples of catalyst received different pretreatments, and their activity was then measured in a laboratory reactor, paying particular attention to the composition of the first few nanometres below the surface. Analysis of the experimental data showed that the role of carbon is different to that of other elements and that the activity of the catalyst is a maximum for carbon concentrations in the range 6 to 10 atomic per cent. It seems most probable than the carbon is present as microcrystals embedded in the alloy and concentrated on the faces of the metal crystals.

Although many investigations into the industrial oxidation of ammonia have been carried out using base metal catalysts and base metal oxide catalysts, platinum, alloyed with additions of rhodium and palladium, is still the main catalyst material (1–3). However, the cost of the process has encouraged research into the amounts and causes of metal loss and how this may be prevented or reduced (4). Volatilisation and erosion of platinum are regarded as the most probable causes of platinum loss, and most published work describes the surface structure of the catalyst and its relationship to the operating conditions (1, 5). Such studies have shown that changes in the metal structure are the principal cause of platinum loss.

During the ammonia oxidation reaction:

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \]

the catalyst surface is transformed into “cauliflower-like” structures which have low mechanical strength and can be easily broken off and swept away in the gas stream (6). Palladium-gold or palladium-nickel alloy catchment gauzes, or oxide-catching mixtures of calcium and aluminum oxides, are generally used to trap the platinum oxide and platinum metal particles, and this, together with techniques to activate and regenerate the catalyst gauze, are generally considered to be the most promising ways of increasing the efficiency of using the platinum metals (7–10).

Surface morphology and composition have an effect on the activity of the catalyst (1). By changing the surface morphology (activation) before placing the catalyst in the reactor, it is possible to increase its activity, reduce the time of firing (time for the catalyst to achieve operating performance) and decrease the platinum lost by hardening the surface layer of the metal. However, there is no generally accepted explanation for the mechanisms of surface changes occurring during activation. In an attempt to clarify all aspects of the activation process, we carried out a series of experiments on the effects of different surface treatments under various operating conditions on the surface morphology of fresh...
platinum alloy gauzes, and gauzes after 100 hours of operation in the laboratory reactor.

Catalyst gauze samples were studied by Auger electron spectroscopy (AES) and Auger depth profiling, which are a way to establish the dependence of the composition of sub-surface layers (~ 60 monomolecular layers) on the method of treatment.

Experimental Technique

To optimise practical benefits from this work, samples of the two most used industrial catalyst gauzes, developed by GIAP (scientific research and project institute for the (Russian) nitrogen industry) (1, 2) were employed. The woven platinum-rhodium (Pt-Rh) and platinum-palladium-rhodium (Pt-Pd-Rh) gauzes had wire diameter 0.09 mm and 1024 mesh cm	extsuperscript{-2}, see Table I. The samples underwent various initial surface treatments, for example, etching in liquid, heating in gas, annealing using a hydrogen torch (to remove impurities), to enable all surface effects to be identified before the samples were used for ammonia oxidation for 8 and 100 hour periods, see Table I.

Profiles of the compositions of the surface and sub-surface layers were analysed by AES with a surface microanalyzer and a profiler LAS-3000 at a pressure of 10	extsuperscript{-7} to 10	extsuperscript{-4} Pa. Concentration profiles of the surface were obtained by an Ar	extsuperscript{+} ion gun, the angle between the surface and the argon ion beam being 30° with a 4 mm	extsuperscript{2} area of cut.

Auger depth profiling gave information about the variation in composition with depth below the surface. With this technique, material from the surface region is gradually removed by sputtering on exposure of the surface to the ion flux. Auger signals corresponding to the elements present in

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Treatment</th>
<th>Alloy</th>
<th>Carbon, at.%</th>
<th>Oxygen, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial/non-treated</td>
<td>Pt-Pd-Rh</td>
<td>45.8\textsuperscript{a}</td>
<td>17.2\textsuperscript{a}</td>
</tr>
<tr>
<td>2</td>
<td>Heating/burning in H	extsubscript{2} (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>4.9</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Heating/burning in H	extsubscript{2} (20 min)</td>
<td>Pt-Pd-Rh</td>
<td>10.2</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>HCOOH solution (15%, 60°C, 4 h)</td>
<td>Pt-Rh</td>
<td>35.0</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Electrolysis in 10% CH	extsubscript{3}COOH solution (20°C, 4 h)</td>
<td>Pt-Rh</td>
<td>90.1</td>
<td>8.7</td>
</tr>
<tr>
<td>6</td>
<td>CO treatment (240°C, 1 h)</td>
<td>Pt-Rh</td>
<td>18.7</td>
<td>8.2</td>
</tr>
<tr>
<td>7</td>
<td>CO	extsubscript{2} treatment (240°C, 1 h)</td>
<td>Pt-Rh</td>
<td>65.9</td>
<td>4.2</td>
</tr>
<tr>
<td>8</td>
<td>O	extsubscript{2} treatment (240°C 1 h)</td>
<td>Pt-Rh</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>9</td>
<td>CH	extsubscript{3}COOH vapour (over 40% solution, 100°C, 4 h)</td>
<td>Pt-Rh</td>
<td>16.2</td>
<td>5.9</td>
</tr>
<tr>
<td>10</td>
<td>H	extsubscript{2}O solution (33%, 20°C, 4 h)</td>
<td>Pt-Pd-Rh</td>
<td>34.6</td>
<td>12.8</td>
</tr>
<tr>
<td>11</td>
<td>H	extsubscript{2}O solution (24%, 20°C, 4 h) + burning in H	extsubscript{2} (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>13.3</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>H	extsubscript{2}O solution (33%, 20°C, 4 h) + burning in H	extsubscript{2} (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>48.2</td>
<td>9.2</td>
</tr>
<tr>
<td>13</td>
<td>H	extsubscript{2}O solution (16%, 20°C, 4 h) + burning in H	extsubscript{2} (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>6.3</td>
<td>6.8</td>
</tr>
<tr>
<td>14</td>
<td>H	extsubscript{2}O solution (4%, 20°C, 4 h) + burning in H	extsubscript{2} (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>5.2</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>H	extsubscript{2}O solution (33%, 20°C, 0.5 h) + burning in H	extsubscript{2} (10 s)</td>
<td>Pt-Pd-Rh</td>
<td>6.3</td>
<td>5.8</td>
</tr>
<tr>
<td>16</td>
<td>Sample 1 after 100 h on-stream</td>
<td>Pt-Pd-Rh</td>
<td>58.2</td>
<td>5.7</td>
</tr>
<tr>
<td>17</td>
<td>Sample 2 after 100 h on-stream</td>
<td>Pt-Pd-Rh</td>
<td>16.5</td>
<td>5.6</td>
</tr>
<tr>
<td>18</td>
<td>Sample 10 after 100 h on-stream</td>
<td>Pt-Pd-Rh</td>
<td>9.3</td>
<td>8.8</td>
</tr>
<tr>
<td>19</td>
<td>Sample 12 after 100 h on-stream</td>
<td>Pt-Pd-Rh</td>
<td>27.9</td>
<td>7.9</td>
</tr>
<tr>
<td>20</td>
<td>Sample 9 + burning in H	extsubscript{2} (10 s) after 100 h on-stream</td>
<td>Pt-Pd-Rh</td>
<td>28.9</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Alloy compositions are, at.% (wt. %): Pt86.9(92.5)-Pd6.9(4.0)-Rh6.2(3.5) and Pt87.5(93.0)-Rh12.5(7.0); solution concentrations in wt. %.

For Sample 5 the current density was 40 mA g	extsuperscript{-1} of gauze (-2 mA cm	extsuperscript{-2} for gauze with smooth surface).

\textsuperscript{a} The high surface concentration of carbon is assumed to come from the diamond wire dies used for wire drawing, the lubricating oil in the weave unit and oiled paper in which woven gauze is transported. Some oil remains on the surface after cleaning. The oxygen most probably comes from Na	extsubscript{2}O, reasons unknown, but other studies also indicate this. Na	extsubscript{2}O was also observed on the foil surface, so may come from the melting process or metal pretreatment.
each layer were measured as the ion beam etched away the surface material. By collecting Auger spectra during etching, information is obtained on the changes in composition below the surface.

AES spectra were measured for the surface and for three sub-layers. However, the high intensity ion beam can lead to upper layer atoms being pushed inwards (ion hammering). This can modify the composition of the next layer. Another negative effect of the high intensity ion beam is that it may cause mixing of surface atoms and sub-surface layers. To minimise these negative effects, the rate of sputtering was kept at around 0.20 to 0.25 nm µA⁻¹ min⁻¹, and the ion etching was performed in 3 cycles of 5 minutes each. The average thickness of each removed layer was 4 nm and the thickness of all the layers was 12 nm.

In order to determine the relative atomic composition of each etched surface, the range of the kinetic energy in the scanned spectra was 120 to 540 eV, which allowed the Pt, Pd, Rh, C and O Auger lines to be identified with a relative error of 5 to 7 per cent. However, for Samples 1, 2, 12 and 19 of the Pt-Pd-Rh alloy, the spectra were examined in the kinetic energy range 550 to 1900 eV, to look for other elements in the metal body which could be present from the reagents.

As Table II shows, the total amount of trace elements, chlorine (Cl), sodium (Na), magnesium (Mg), aluminium (Al) and sulphur (S), is less than 8 per cent and they are concentrated on the metal surface, most probably in an adsorbed form. The presence of Na in the sub-layers can be explained by the method of alloy manufacture (similar results were obtained by studying platinum foil). However, Na is absent in all treated samples because of its high reactivity. The source of adsorbed Cl, S and Al is the reagent mixture. Other elements, such as Ba, K, Ca and P, were not detected. Elements Pt, Pd, Rh, C and O were used for further data processing.

### Data Processing

Each sample was described by compositions measured at the surface and at sub-surface layers at depths of 4, 8 and 12 nm. The main aim was to establish if there were correlations between the concentrations of elements and the layers, and between the composition of the surface and the surface treatment. Correlations were verified for both alloys and relationships between the concentrations of elements in each layer were also verified.

Non-linear regression analysis was used to process the data and the coefficient of multiple correlation (coefficient of determination, $R^2$), widely used for estimating the closeness of calculated and experimental data, was used for the goodness-of-fit. A value for this parameter of more than 0.5 indicates a statistically significant correlation between estimated parameters.
Composition of the Catalyst Surface

The elements investigated can be grouped according to their concentration profile, surface pretreatment and the effects on catalyst activity:

- carbon and oxygen: the amounts depend on the depth of the layer and on the surface treatment
- palladium and rhodium: the concentrations depend on the times of catalyst operation
- platinum: which determines the catalyst activity.

Examples of typical depth profiles are shown in Figure 1. The most significant changes in composition are observed for the layer between the surface and 4 nm. Changes in composition are smoother for layers deeper than 4 nm. The best correlation with depth is found for carbon, but samples containing small amounts of carbon show little variation in their depth profile, see Figure 1(c).

Carbon Effects

On average, the amount of carbon moving into the metal bulk decreases according to:

\[ [C] = 29 - 7.3 (\text{Depth})^{2.39} \]

where \([C]\) is the atomic concentration of carbon, measured in at.%; \((\text{Depth})\) is the depth of ion beam etching, in nm.

This dependence is very stable and departures from the relationship only occur for samples with large amounts of carbon in the top 4 nm surface layer. Due to different sputtering coefficients for the metals and carbon, in a given time, different amounts will be removed from the surface. The high carbon concentration at the surface also changes the surface relief and leads to error in the measurement of carbon (11).

No obvious and reliable correlations were established between the carbon concentration and the surface treatment. For example, treating Sample 10 with \(\text{H}_2\text{O}_2\) solution gives the same surface concentration of carbon as treating Sample 4 with formic acid solution (34.6 and 35 at.% respectively). However, treatment with \(\text{H}_2\text{O}_2\) at different concentrations (Samples 12 and 14) leads to a different surface carbon content (48.2 and 5.2 at.%, respectively), see Table I.

The carbon concentration is also dependent on the total amount of palladium and rhodium. This relationship is observed for each layer, independent of its depth. As Figure 2 shows, an increase in the concentration of rhodium and palladium leads to a considerable reduction in the amount of carbon. This dependence holds true for all layers and all surface treatments. From this relationship...
we conclude that rhodium and palladium prevent the sedimentation of carbon and its compounds in the alloy. When chemical compounds are formed between carbon and the metals, the dependence between their concentrations has to be linear. In fact, the shape of the dependence (close to hyperbolic) indicates the physical nature of the interaction between carbon and rhodium and between carbon and palladium.

**Oxygen Effects**

The variation in the oxygen concentration profile is much smaller than for carbon. The maximum oxygen concentration was observed for Sample 1 of Pt-Pd-Rh (17.2 at.% on the surface and 6.4 at.% at 8 nm depth). Almost the same amount of oxygen was observed for Sample 5 which was treated electrolytically in acetic acid solution. Samples treated with the hydrogen torch do not have oxygen in their sub-surface layers, probably due to the high reactivity of hydrogen and its relatively high diffusion rate in the sub-surface layers.

The concentrations of carbon and oxygen appear to be independent of the surface treatment, but dependent on other parameters, such as the amount and type of the reagent (its carbon content), its reactivity (oxidising or reducing power), the phase state of the reagents (gas or liquid), and how long the surface treatment lasts. These factors all affect the determination of the O:(C + O) ratio, which can be interpreted either as the concentration of oxygen in the non-metal elements or as the relative concentration of oxygen.

The minimum relative concentrations of oxygen are shown in Figure 3 for samples treated by carbon-containing substances or by reducing agents. Treating samples with the hydrogen torch reduces the amount of oxygen to zero, while using hydrogen peroxide increases the O:(C + O) ratio to 60 per cent.

The effects on surface composition could be observed by comparing the surface composition at the start (after surface treatment but before the reaction mixture was admitted) and after 100 h exposure in the reactor, see Table III. Irrespective of the type of reagent, surface treatment or initial oxygen content in the layers, processing the catalyst for 100 h always resulted in an equilibrium oxygen concentration of ~ 3 to ~ 6 at.% for 4–12 nm layers, and an increase in the carbon concentration in all the layers. However, Samples 10 and 18 are exceptions; these were treated in H₂O₂ solution without annealing in the hydrogen torch, and are explained by special surface modification.

The increase of carbon concentration, regardless of initial treatment, during the ammonia-

![Fig. 2 Dependence of the carbon concentration on the total concentration of palladium and rhodium. Increasing concentrations of either of these metals leads to a reduction in the amount of carbon in all layers, irrespective of their depths](image-url)
oxygen reaction, can be explained by a hyperbolic dependence between the concentrations of palladium and rhodium, and carbon, see Figure 2.

Metal Concentration Effects

Palladium concentrations were found to be determined solely by the time on-stream. The relative concentration of palladium in the metal phase after 100 h of reaction dropped from 12–17 to 4–5 at.%. The decrease does not depend on the surface treatment of the initial samples, but leads to an increase in carbon concentrations in all layers.

The rhodium concentration, in contrast to palladium, does not depend on the processing time, but is closely related to the concentrations of palladium and oxygen. The effects of oxygen on the composition of the metal phase (Pt, Rh, Pd) is different for Pt-Pd-Rh and Pt-Rh alloys, see Figure 4.
In Pt-Pd-Rh alloy, the rhodium concentration is proportional to the total concentration of palladium and oxygen (proportionality factor is 0.3 to 0.5). As this alloy loses palladium from the metal phase during processing (in the ammonia-air mixture), it should also lose rhodium after samples are exposed to the reaction mixture.

The replacement of palladium by rhodium (to give Pt-Rh alloy) may promote the formation of platinum-oxygen composites (perhaps oxides) which displace platinum-rhodium compounds. As a result, when the oxygen concentration is 12 at.%, there is no rhodium present in the alloy (proportionality factor ~ 1). It should be noted that an increase in the oxygen concentration reduces the rhodium concentration, but the reverse is not true. This is because the oxygen concentration is determined by the surface treatment. Furthermore, most pretreatments were not at high temperature (except those where the hydrogen torch was used) or samples were prepared quite quickly in solution. This prevented the formation of volatile rhodium species and their rapid diffusion from the sub-surface layers.

Although there are no data on changes in the metal phase of Pt-Rh alloy after exposure to the ammonia-air mixture, our observations of the surface indicate that, as for the Pt-Pd-Rh alloy, the Rh:(Rh + Pt) ratio will fall.

These relationships allow predictions to be made about the compositions of the surface and sub-surface layers, depending on the surface preparation, the type of reagent used, the time of reaction with the ammonia-air mixture and the composition of the metal phase. We are then closer to finding the optimum surface treatment needed to produce a required catalyst surface. However, the relationship between the surface composition and catalyst activity still needs to be explained.

### Relationship between Surface Composition and Catalytic Activity

The relationship between the catalytic activity of the samples and the composition of the layers was studied after the ammonia oxidation reaction was performed for 8 and 100 hours in the laboratory reactor.

The reactor was a glass tube of diameter 1 cm with external electric heating. Reaction mixtures were fed at
Fig. 5 The calculated effects of the concentrations of carbon and oxygen, at a depth of 4 nm, on the catalytic activity:
1 effect of carbon for stable concentrations of Pd, Rh and O
2 effect of oxygen for stable concentrations of Pd, Rh and C
The optimum concentration for carbon is more than for oxygen. Only concentrations of more than 30 per cent significantly affect the yields of NO.

Atmospheric pressure onto the catalytic gauze. The temperature was held at ~780°C and the flow rate was kept constant giving a contact time of ~2 × 10⁻⁴ seconds. The ammonia concentration was 11 per cent, to be similar to that in an industrial reactor. To estimate the activity, a rate constant, \( k \), was used, assuming that the kinetics of the chemical process can be described by a first order equation (1).

One of the most important conclusions from these experiments is that the correlation of catalytic activity with the surface composition is smaller than the correlation with the composition of the sub-surface layers. The most reliable relationship is obtained between catalytic activity and the compositions of the 4 and 8 nm layers (coefficient of determination \( R² \) = 0.93 and 0.89, respectively). The corresponding relationship between catalytic activity and the surface is less reliable (\( R² \) = 0.63).

The empirical equation linking rate constant, \( k \), for the 4 and 8 nm layers (experimental conditions 780°C, ammonia concentration, \( C_{NH₃} \) = 11 per cent by volume, pressure = 0.1 MPa) can be written:

\[
k = -0.22 - \frac{1.0}{(C + O)} + 2.6 \times 10^{-4} \times [Pt]^2 \times (1 + 2[C])
\]

where \([C] \), \([O] \) and \([Pt] \) are concentrations, in at.%, of the respective elements, and \( k \) is the rate constant, measured in \( s^{-1} \times 10^6 \).

For carbon concentrations > 5 at.%, the effects of oxygen, rhodium and palladium on the alloy are all similar: they reduce the platinum concentration, thus decreasing catalytic activity.

The effects of carbon are more complicated. The shape of the rate constant/concentration curve, for constant concentrations of palladium, rhodium and oxygen (5 at.% of each), shows that there is an optimum carbon concentration (maximum NO yield and rate constant, \( k \)) in the range 6 to 10 at.%, see Figure 5. However, in contrast to earlier mentioned effects due to oxygen, rhodium and palladium, only increases in carbon concentrations > 30 to 35 at.% in the sub-surface layers affect catalytic activity.

Effects due to carbon can be explained by its modification of the platinum surface and an increase in platinum activity in spite of the reduction in total surface area. An increase in the carbon:platinum ratio of 1 per cent increases the alloy activity by 2 per cent. This compensates for the reduction (by up to 30 per cent) of the accessible surface area caused by the carbon. The probable mechanism for the effects due to carbon is the increase in the number of embedded micro-crystalline carbon particles which contribute to the formation of catalytically active platinum centres. This was confirmed by the effects of small concentrations of carbon and oxygen. Removing
non-metallic elements from the surface reduces the number of defects in the crystal structure, which decreases catalytic activity. This is noticeable for total carbon and oxygen concentrations < 5 at.%, both elements having a similar effect on activity.

The above mentioned results for $k$ were obtained at depths of 4 and 8 nm. Calculating the activity using only the surface layer composition underestimates the values of the rate constant, $k$. The more carbon on the surface, the larger the error in the calculated values. This is because there is an error in measuring the actual composition of the metal surface accessible for the reaction.

**Surface Structure**

Reviewing the depth profiling technique confirms that there is a measurement error and provides a way of obtaining new data about surface structure and its effects on catalytic activity and on the overestimated amount of carbon on the surface layer. The main cause of this error may be the presence of microcrystals of carbon on the alloy surface. When the surface is examined with the depth profiling technique, it produces a systematic error in measuring the composition, and the greater the concentration of microcrystals on the surface, the larger is the distortion, see Figure 6.

The sputtering coefficients, which indicate the number of etched ions caused by one atom of ion beam, are approximately equal for Pt, Pd and Rh, but about three times larger than that for carbon (11). After allowing for this, it was calculated that for crystallites of height $\sim 20$ nm and base width $\sim 10$ nm, the spectra of the surface would indicate that platinum was not present, although about 60 per cent of the surface would be accessible to the ammonia-air mixture.

After sputtering for 5 minutes, the surface profile becomes smoother. Most of the carbon crystallites are now smaller: 5 nm high and 7 nm base width. The reduced profile now only slightly distorts the measured concentration of elements on the active surface and the composition obtained most evidently determines catalyst activity. The next sputtering cycle removes both impurities from the surface and the top 4 nm of the catalytic layer. Thus, after sputtering for 10 min (8 nm) the measured concentrations correspond to a sub-layer approximately 6 to 8 nm from the surface but not to the active surface. The relationship between composition and activity becomes less evident.

After the final cycle of etching (15 min, 12 nm), the sub-layer lies further from the active surface.

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**Fig. 6** The depth profiling view of the microstructure of a catalyst surface of Pt-Pd-Rh alloy, showing the surface relief.
and the measured concentrations even less determine the activity of the catalyst.

The large quantities of carbon and oxygen present in the sub-surface layers — compared to other impurity elements found only on the surface — indicate either that they are forming chemical compounds with the metals or that they are embedded in the crystalline alloy lattice as microcrystals. Oxygen most probably forms chemical compounds or solutions in the metal. Increased oxygen reduces the rhodium concentration in the binary Pt-Rh alloy but increases the rhodium concentration in the ternary Pt-Pd-Rh alloy. After 100 h on-stream, all the catalyst samples have the same oxygen concentration (~ 3 to 6 at.%), independent of the depth and amount of carbon at that depth.

Carbon is most probably present as microcrystallites embedded in the alloy and concentrated on the crystal faces. Adding carbon can increase the specific surface area of the catalytically active sites and the total activity of the samples, so surface carbon is not the reason for the low catalytic activity. Only a large amount of carbon in the 4 to 8 nm sub-surface layer can radically decrease the active platinum surface and decrease the total activity of the catalyst.

Discussion

If the concentration of oxygen in the alloys is greater than 5 at.%, it behaves as an inert component, like palladium and rhodium, and only reduces platinum within the alloy; that is, enriching the surface with oxygen (during chemical treatment) reduces the catalyst activity.

Carbon additions (in amounts of 9 to 12 at.%) increase the number of metal lattice defects. An absence of carbon therefore has a detrimental effect on the catalytic activity. This contrasts with work where carbon is considered to have a negative effect on the reaction. However, carbon concentrations of > 30 at.% do adversely affect the catalytic activity of platinum alloys.

There are two ways in which the composition of the metal phase (surface and top few nm layers) could be changed. First, by the diffusion of palladium and rhodium deep into the metal bulk, by co-diffusion of the reagent flow. Second, by the diffusion of metals on the surface, their reaction with either solution or gas (during surface treatment or during the ammonia-oxygen reaction) and transfer into the bulk of the reagent. Our data do not indicate which process occurs, but as changes in the metal phase were observed both for different reagents and aggregative states, and as the low temperature surface treatment (the high temperature hydrogen torch was applied for only a short time) excludes the formation of volatile compounds (the usual explanation for metal phase changes), then the most probable means by which changes occur on the metal surface is by co-diffusion of palladium and rhodium deep into the metal bulk.

Conclusions

For the ammonia oxidation reaction, on Pt-Rh and Pt-Pd-Rh alloys, we have shown that:

- The amount of non-metallic elements in the alloy can be described by two parameters: first, the total concentration of carbon and oxygen depends on their depth in the alloy, and second, the choice of surface treatment determines the O:(C + O) ratio.

- Using oxidants increases the proportion of oxygen in the non-metallic elements, while using reducing agents (especially those containing carbon) increases the carbon concentration.

- The most important factor affecting the metal phase is the on-stream time in the ammonia-air mixture. The amount of palladium in the alloy after 100 h of exposure in the reactor drops to a third.

- The ammonia oxidation reaction occurs on the faces of the crystal lattice and carbon is one of the most important contributors to the lattice. The optimum concentration of carbon, in the 4 to 8 nm layer, is ~ 9 to 12 at.% (but high activity is observed from 5 to 20 at.%).

- Changes in surface structure on activation, before exposure in the reactor, can lead to unexpected changes in catalyst activity during ammonia oxidation (for example due to the decrease of carbon content in Sample 18 treated in hydrogen peroxide).

- The effect of solutions (organic acids and
hydrogen peroxide) on surface composition indicates that there could be a distortion in measurement during chemical analysis, and even when preparing samples for analysis. 

- The most exact measurements of reaction surfaces can be obtained, after surface preparation, by using an ion beam at a small angle of incidence and following AES measurements.
- Comparing the surface composition before and after ion etching provides information about structural particles of different elements.
- The composition of the preliminary etched surface best represents the composition of the active surface and gives the most accurate measure of catalyst activity for nitric oxide formation.

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Palladium-Based Catalysts for Nitrate Reduction

Nitrogen is essential for plant growth and, in the form of nitrates, is their primary source of nitrogen. Nitrates occur naturally in soil and water, but extensive farming can deplete the soil of its natural nitrogen, so nitrogen-containing fertilisers are often added. However, when more nitrogen is added to the soil than plants can use, excess nitrate can leach into groundwater supplies and could become a potential health risk.

Technologies for the removal of nitrate from drinking water and waste water are therefore of great importance. Palladium-based catalysts for the hydrogenation of nitrates to nitrogen represent one of the most promising approaches.

Now, an Italian research group has investigated palladium-copper and palladium-tin supported on zirconia and titania catalysts for the hydrogenation of nitrate in drinking water (G. Strukul, R. Gavagnin, F. Pinna, E. Modaferri, S. Perathoner, G. Centi, M. Marella and M. Tomasselli, Catal. Today, 2000, 55, (1–2), 139–149). Catalysts were prepared either as microspheres or in the form of membranes deposited on alumina tubes. The use of catalysts under diffusion control conditions reduced the amount of the byproduct ammonia formed while retaining a high catalytic activity.

Researchers in Germany, however, used palladium-tin and palladium-indium catalysts for the nitrate reduction (U. Prüse, M. Hähnlein, J. Daum and K.-D. Vorlop, Catal. Today, 2000, 55, (1–2), 79–90). In situ buffering with formic acid as a reductant instead of hydrogen and polyvinyl alcohol-encapsulated catalysts with superior diffusional properties have both been demonstrated. The above Pd-Sn and Pd-In catalysts are reported to be more efficient than prior palladium-copper regarding the nitrogen formation activity, the selectivity and the long-term stability.

As the removal of nitrates from drinking water and waste water is becoming more necessary, these concepts may lead to the establishment of a technical-scale nitrate reduction process.