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The Modifying Effect of Added Metals on the Surface of Platinum Catalyst Used for Ammonia Oxidation[1]

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The surface of Pt-10%Rh catalyst has been coated by vacuum evaporation with Al, Mg, Zr, and Pd layers of a thickness of 1–25 nm, and long-term laboratory investigations have been carried out on its activity, catalytic etching, and mass losses during ammonia oxidation. The composition of the surface was examined by Auger electron spectroscopy and by an X-ray microprobe. It was found that contamination of the catalyst by the above metals decreases its catalytic properties, speeds up the etching of its surface, and increases platinum losses. The results obtained are in agreement with the oxide mechanism for the etching process and for the explanation of platinum losses.

INTRODUCTION

The surface of a platinum catalyst being used for ammonia oxidation undergoes rapid catalytic etching. The shape of crystalline grains being etched on the surface may to some extent be associated with its catalytic properties (*1*–*2*). The extent of etching is determined by operation conditions and is largely dependent on how the etching is initiated during the activation process (*2*–*4*).

The present paper describes the effect of modifying the surface of a Pt–10%Rh catalyst on its properties and on the etching process. The modification consisted of the vacuum evaporation of metals, forming high-melting oxides, and of palladium.

It should be noted that the samples whose surfaces were modified with Al, Mg, and Zr were certainly covered with these metals in the form of surface oxygen compounds, whereas palladium evaporated on Pt–10%Rh as well as platinum evaporated on palladium are soluble in the sample bulk.

EXPERIMENTAL METHODS

Experiments were carried out on punch-plate "screens" made of Pt–10%Rh foil 0.1 mm thick. Each screen had 52 holes of 0.3 mm in diameter on a surface of about 0.6 cm^2. The holes were made by means of an electron puncher. The gauzes commonly used in catalysis were replaced by screens for the present work since they can be covered uniformly with evaporated metal.

The surface of the screen was coated with a modifying metal by thermal evaporation under a pressure of 10^{-3} Pa using an Edwards Model 1GE7 pumping system. Before the evaporation process the screen was cleaned by being bombarded for 10 min under a pressure of 5 Pa with residual gas ions accelerated with 2.5–3 kV voltage. The thickness of the evaporated layer was determined by measuring, with the use of a calibrated photometer, the intensity of light reflected from a simultaneously evaporated glass plate. The estimated error for layers about 5 nm thick was about 50%, and for layers of a thickness of 25 nm was about 10%.

Long-term observations of the activity and selectivity of the tested samples were

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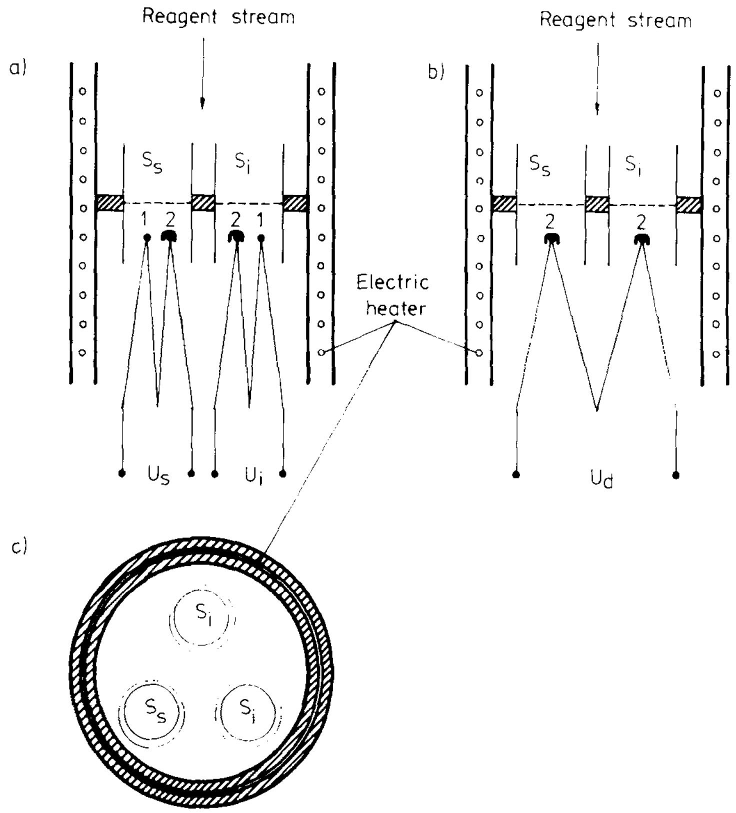

FIG. 1. Reactors for measurements of (a) catalytic activities and (b) catalytic selectivities of samples.

carried out in quartz reactors (Fig. 1) using an ammonia–air mixture containing 10 ± 0.5% of ammonia. This mixture was obtained by mixing an ammonia stream from a gas cylinder with an air stream from a compressor. The mixing and drying of the mixture was carried out by passing it through a drier filled with silica gel. In the reactor the gaseous mixture is heated and it forms three streams passing through three catalyst samples (Fig. 1c).

One sample was the standard catalyst S_s, and the remaining two (S_i) were the investigated samples (in general these were screens covered with thin and thick layers, respectively, of the same metal). Each sample was made up of three directly overlapping screens separated by quartz rings 0.5 mm thick. The loading of samples was similar. Gas flowing at a rate of 0.034 m^3 hr^{-1} (after correction to STP) passed through each sample. The reference point for all measurements was given by the standard samples which were Pt–10%Rh screens preactivated for 20 hr. The feed-furnace regulator was additionally controlled by a thermocouple placed under the standard catalyst, the gas temperature behind it being maintained at a temperature of 1123 K. Under these conditions ammonia on the standard catalyst underwent practically complete oxidation.

Evaporation of base metals onto the sample surface decreased the catalyst activity to an extent which made ammonia concentration behind these samples fairly high.

The activities of these samples were determined in the reactor shown in Fig. 1a by measuring the quantity of ammonia which had not undergone reaction. Ammonia concentration was determined by the thermocouple method described elsewhere (5).

The method consists of measuring the temperature difference between two Pt–10%Rh thermocouple junctions, one of which is shielded with a quartz tube. Ammonia in an air mixture oxidizes on the unshielded joint, which considerably increases its temperature. The temperature difference measured in this way is linearly dependent on ammonia concentration over a fairly wide range of concentrations.

The following quantity was accepted as a measure of the activity of the sample being measured:

$$A = \frac{a_i}{a_s} 100\%$$

where a_i and a_s denote the degrees of ammonia reaction on the sample being tested and on the standard one.

The platinum–rhodium catalyst coated with palladium and the palladium catalyst coated with platinum displayed activities similar to the activities of the standard. Virtually no ammonia was found in the gas stream after the catalyst. Thus only measurements of the relative selectivity of the oxidizing of ammonia to NO could be applied. As a measure of difference in selectivity between the tested sample and the standard one, the temperature difference after the standard catalyst and the tested one (ΔT) was used. This method of comparing the selectivity of catalysts is possible owing to a great difference in the thermal effects of oxidizing ammonia to NO and to N_2; they have the values 226.8 and 317.3 kJ/mole of ammonia, respectively. ΔT was measured by the differential thermocouple system shown in Fig. 1b.

Mass losses from the catalyst during the period of operation were determined by weighing the samples (three screens) before and after use.

Electron microscopic observations of new samples and of those after 100 hours of reaction, as well as investigation of the distribution of evaporated metals by means of an X-ray microprobe, were carried out on a Jeol JXA-50A scanning electron microscope. Measurements were made with an accelerating voltage of 25 kV and a beam current of 2×10^{-8} A. The distribution of aluminium and magnesium was measured by using the $K\alpha$ line, and that of zirconium by $L\alpha$. The photographs of samples after 300 hr of use were taken on a scanning electron microscope of Type JXA-5A with a voltage of 25 kV and a beam current of 1.510^{-9} A. Depending on the material, the excitation of X-ray radiation takes place in a layer 3–5 nm thick. The layers evaporated on a catalyst are many times thinner, so practically they do not undergo excitation. Observation of the evaporated metals with the use of a microprobe is possible only owing to secondary radiation induced by the initial X-ray radiation of the base (*6*). In many cases this makes it possible to investigate thin layers with the use of an X-ray microprobe.

The analysis of the surface composition of modified catalysts was made on an Auger mean resolution spectrometer. Measurements were carried out before using samples for ammonia oxidation catalysis and after 100 hr of carrying out this process. The Auger spectrum was recorded in a vacuum not lower than 10^{-7} Pa, with the use of an excitation electron beam energy of 1 keV. The spectrometer enabled the spectrum to be recorded in the range from 5 to over 500 eV. The spectra were recorded after creating a vacuum, and during this process the samples were annealed at a temperature of 673 K, and then after being annealed at 1173 K. The heating time was 5 to 15 min.

RESULTS

Figures 2–5 show the results of long-term measurements of the catalytic properties of catalyst samples on which different metals had been evaporated. They make it possible to compare the operation of these samples with that of Pt–10%Rh catalyst samples in laboratory reactors during several hundred hours. The results obtained should, however, be regarded as semi-quantitative.

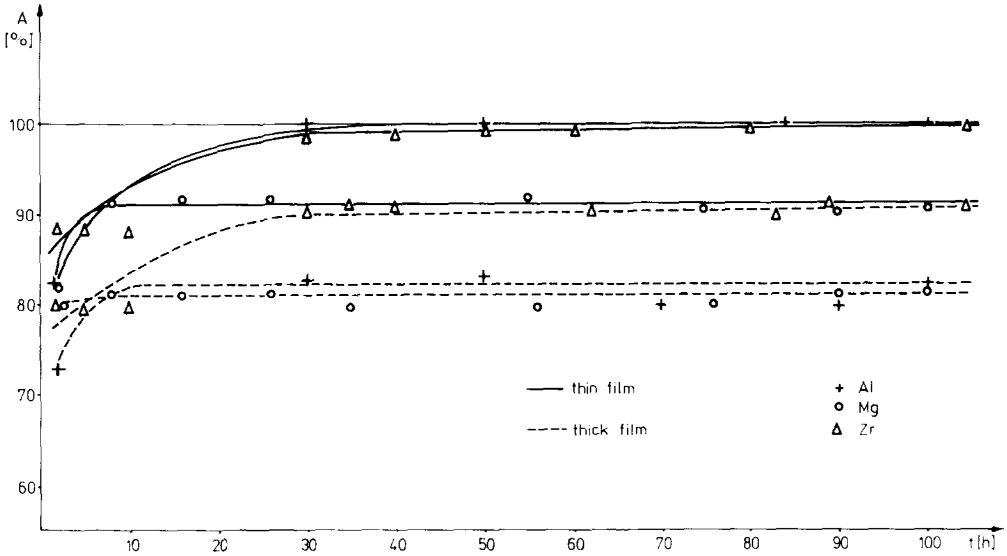

FIG. 2. Catalytic activities as a function of operating time of samples of Pt–10%Rh evaporated with common metals. Thickness of layers: 5 and 25 nm for Al and Mg; 1 and 5 nm for Zr.

This is due to several reasons. The methods of measuring activity and selectivity alone involve fairly high approximations. Also, it is not possible to obtain sufficient reproducibility of separating the streams of reaction gases. The small size of the reactor involves high-temperature gradients resulting in nonreproducibility of measurements of temperature differences by thermocouples made of thin wires. Long-term investigations are connected with difficulties in stabilizing all operation parameters. Moreover, the geometrical shape of samples as well as their surfaces undergo some changes. The nonrepeatability of measurements is also affected by methods of correcting the parameters and by considering the corrections determined in a reactor operating in a fixed state where the investigated samples are replaced by the samples of the standard catalyst. The low reproducibility of the mere evaporation of metals on to catalysts should also be considered. The quantitative differences between the results (Figs. 2 and 3) for the activity of samples evaporated with aluminium can be accounted for by the reasons mentioned above. An additional reason for differences between these parameters is that the measurements were carried out on different reactors of identical construction.

The layers of aluminium, magnesium, and zirconium evaporated on to the Pt–10%Rh catalyst decrease its activity and reduce complete over-reaction of ammonia. As is to be expected, its activity is not decreased by evaporated palladium or by platinum evaporated on palladium. In these two cases it is only possible to observe a change of the selectivity of oxidation to NO.

The results presented in Figs. 2 and 3 show that after a long-term observation the activities of catalysts coated with base metals gradually increase. In the case of thin aluminium and zirconium layers the screens slowly reach the activities of the standard sample. A general conclusion can be drawn from these investigations that the effect of evaporation with base metals lasts for a long period of time (several hundred hours), and the reducing of the activity depends on the type of metal and its quantity.

On account of the experimental methods used, nothing can be inferred as to the selectivity of the deactivated catalyst. It

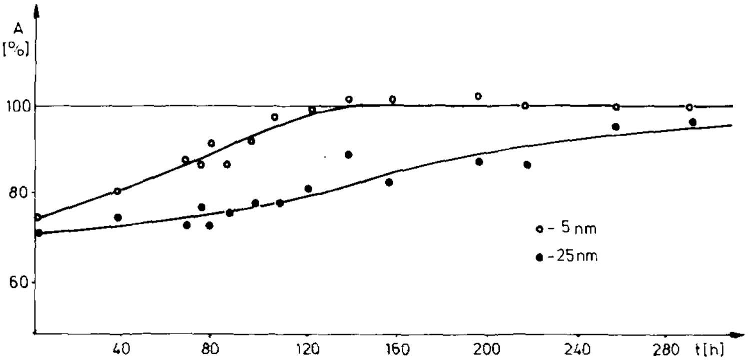

FIG. 3. Activity of the catalysts coated with Al (300 hr of operation).

would be possible to measure the selectivity of these samples only after they reach a fairly high total activity. Such measurements were not carried out since they would not provide any significant information. The data in Fig. 4 indicate that palladium evaporated on the catalyst causes a decrease in its selectivity. The ΔT dependence curves exhibit minima and they gradually approach the selectivity level of the standard catalyst. The curve minimum corresponding to the thick layer is significantly deeper and is reached after a considerably longer operation time.

The palladium catalyst, coated with a thin platinum layer, displays during the first few tens of hours, a selectivity equal to that of the standard (Fig. 5). After about 90 hr the ΔT curve shows a distinct maximum in which the catalyst selectivity is higher than that of the standard. With further reaction it decreases below the selectivity of the standard sample and continues to display a weak decreasing tendency. A similar behaviour is shown by the ΔT-dependence diagram of the palladium catalyst coated with a thick platinum layer. However, its initial selectivity is significantly lower, the maximum (after about 90 hr) is higher, and there is a slightly faster decrease during continued reaction. For the sake of comparison the same diagram shows the dependence of the selectivity of a pure palladium catalyst on the operation time, the dependence be-

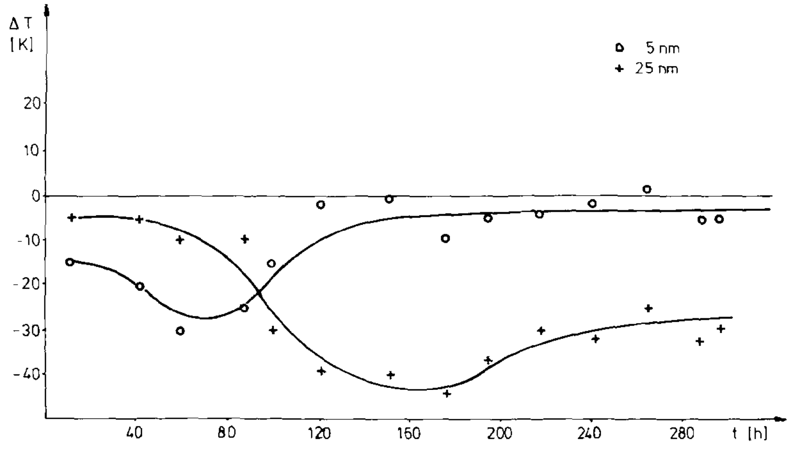

FIG. 4. Selectivities of catalysts coated with Pd (300 hr of operation). Zero taken as selectivity of the standard.

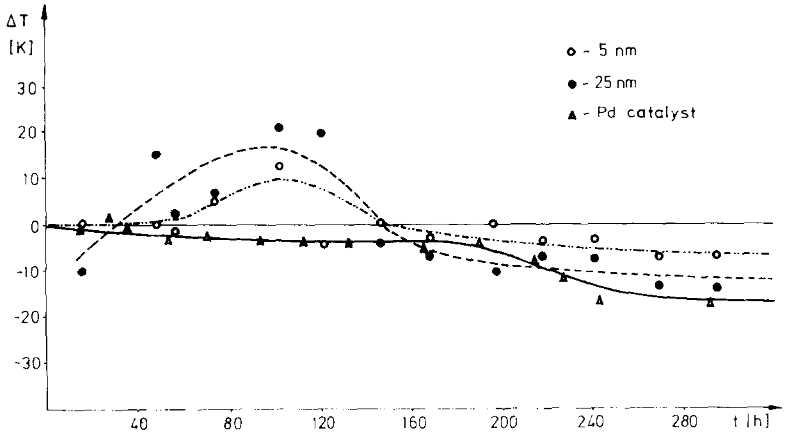

FIG. 5. Selectivities of palladium catalyst, and palladium catalysts coated with platinum (300 hr of operation). Zero—selectivity of the standard.

ing determined in the same reactor. As can be seen, the catalyst selectivity is initially only slightly lower than that of the Pt–10%Rh catalyst. However, after about 200 hr it decreases fairly rapidly.

The experimental results of the losses from the platinum catalyst during the ammonia oxidation process (Table 1) lead to the conclusion that their quantity increases with the presence of both aluminium and palladium on the surface. As a matter of fact the sample covered with a *thick* layer of aluminium displayed a lower mass loss than the standard sample; this, however, is caused by the low rate of the ammonia oxidation process in that case. Mass *gains* for the palladium catalyst result from the bonding of adsorbed oxygen on the rapidly developing palladium surface to form nonvolatile palladium oxide (*7*). Using a 100 × magnification with the X-ray probe no significant irregularities in Al and Mg distribution on the catalyst surface were observed. After 100 hr of operation the distribution of these metals did not undergo any significant changes. Electron microscope images of samples coated with metals do not differ from those of standard samples. They change rapidly in the course of ammonia oxidation catalysis. After 100 hr of action the surface is found to be covered with clearly cut crystallites showing differences in their direction (Fig. 6). The etched regions give an image of the structure of the catalyst alloy by providing a profile of its crystalline grains. Their dimensions are of the order of several hundred micrometers.

After being etched for 300 hr the standard samples are found to be covered with regular well-formed crystallites having flat faces (Fig. 7). Such surface morphology is characteristic of well-activated Pt–Rh catalysts of high selectivity (*1*, *2*). The samples on which aluminium, zirconium, and palladium have been evaporated have a similar post-etching morphology, although during the first 100 hr their etching is slightly quicker. This relates particularly to the catalyst evaporated with palladium.

TABLE 1

Catalyst Mass Loss During 300 hr of Operation

Catalyst	Mass loss during 300 hr (%)
Pt–10%Rh, standard	2.3 ± 0.2
Pt–10%Rh, 50 Å Al	3.3
Pt–10%Rh, 250 Å Al	1.4
Pt–10%Rh, 50 Å Pd	10.2
Pt–10%Rh, 250 Å Pd	4.8
Pd, 50 Å Pt	−2.4
Pd, 250 Å Pt	−2.6

FIG. 6. Scanning electron micrograph of the standard sample after 100 hr of operation × 1000.

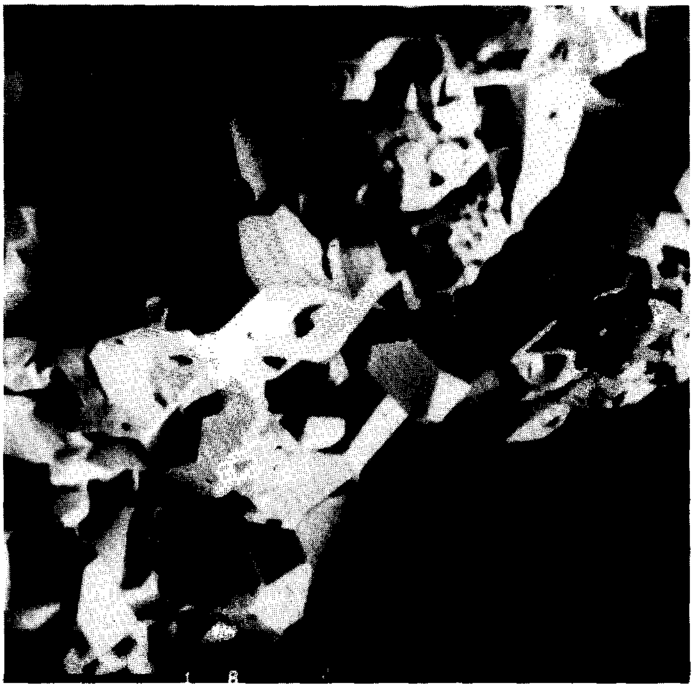

FIG. 7. Scanning electron micrograph of the standard sample after 300 hr of operation × 1000.

FIG. 8. Scanning electron micrograph of the sample coated with a thin layer of Mg after 100 hr of operation × 1000.

A sample coated with a thin magnesium layer also has a deeply etched surface. Its morphology, however, is characterized by rounded forms having neither smooth faces nor straight edges (Fig. 8). Similar forms were observed by McCabe *et al.* (*2*) on platinum wires after the catalysis of ammonia oxidation with ammonia in excess in relation to oxygen.

Thick layers of the common metals decrease to some extent the etching rate. This can be accounted for by a decrease in the rate of the catalyzed reaction, the more so that this effect is not noticed in the case of the catalyst covered with a thick layer of Pd.

The post-etched morphology of palladium coated with platinum is characteristic of the latter metal. The strongly developed surface takes the shape of a sponge, and a lack of smooth surfaces and separated crystallites can be observed. In addition, the thicker platinum layer slightly increases the etching rate (Fig. 9).

Analysis of the surface composition of the Al- and Pd-modified catalysts was carried out by Auger electron spectroscopy in the wide energy range of 5 to 510 eV. The spectrum of each sample was recorded before being heated and after different heating times at a temperature of 1173 K. The sulfur peak at 150 eV in all spectra was high and, in general, did not undergo any significant changes after annealing the sample. The heating did not cause a decrease in the oxygen peak at 506 eV in the sample coated with an aluminium layer of a thickness of 25 nm. The high carbon peaks at 268 eV in fresh samples modified with aluminium were decreasing at a low rate.

During the first few minutes of heating the samples, the peaks of platinum and rhodium grew rapidly. They were low only in the fresh sample covered with 25 nm platinum. A relatively low rhodium peak was displayed by a sample covered with 25 nm palladium. As could be expected, while cleaning the surfaces of samples, low-en-

FIG. 9. Scanning electron micrograph of a palladium sample coated with a thick layer of platinum after 300 hr of operation × 1000.

ergy platinum peaks (11.5, 62 eV) were growing much more rapidly than high-energy peaks (167, 232, and 253 eV). Low-energy peaks are mainly produced by the first (upper) monolayers of the sample, whereas the higher-energy peaks are coming from an alloy layer of a much greater thickness (*8*). A comparison made between the heights of rhodium and platinum peaks makes it possible to draw the conclusion that at 1173 K the rhodium content is increasing on the surface of Pt–10%Rh alloy. In samples modified with palladium this growth is significantly quicker.

The presence of palladium on the catalyst surface can be inferred from the peak at 75 eV. It is found in samples which did not act as catalyst beforehand. After heating the samples to 1173 K the peak disappears quickly, which indicates that at this temperature palladium diffuses to an alloy mass at an increased rate. A trace of this peak can be observed in samples after catalysis only before heating them.

Tables 2 and 3 show the heights of the more interesting Auger peaks of Pt–10%Rh catalyst samples modified with both thin and thick aluminium (Al-I and Al-II) as well as palladium (Pd-I and Pd-II) layers after heating them at a temperature of 1173 K. The indices f and w denote a fresh sample

TABLE 2

The Main Auger Peaks of the Samples Modified with Al

Elements	Peak eV	Peak intensity (peak-to-peak), arbitrary units			
		Al-If	Al-Iw	Al-IIf	Al-IIw
O	506	0	0	17	5
Rh	300	29	54	5	20
Pt	253	17	30	0	13
	232	27	15	0	0
	167	21	19	4	7
	62	66	56	24	62
	11	67	84	4	77
Pt + Rh	40	39	62	0	63
Al–O	52	Trace	0	86	0

TABLE 3

The Main Auger Peaks of the Samples Modified with Pd

Elements	Peak eV	Peak intensity (peak-to-peak), arbitrary units			
		Pd-If	Pd-Iw	Pd-IIf	Pd-IIw
Rh	297	56	28	4	40
Pt	251	20	0	Trace	22
	232	22	—	4	3
	166	7	Trace	5	4
	60	60	188	70	48
	11,5	80	60	66	48
Pt + Rh	39	46	23	35	40
Pd	75	Trace	0	2	0

and one after reaction, respectively. The heights of peaks were given in millimeters since their spectra had no peak with a constant height to which the heights of the other peaks could be referred.

It follows from the tables that in the course of operation the components of the catalyst (Pt, Rh) are uncovered. This can be observed particularly in the case of catalysts covered with thick layers of metals. The enrichment of the sample surfaces in rhodium can also be seen.

Oxygen permanently bound to the sample can be found only on samples covered with a thick aluminium layer, and above all, in a non-working sample. Also in this sample a high peak of aluminium bound to oxygen (52 eV) can be observed. Lack of oxygen on the surface of the working samples (except for Al-IIw) proves that rhodium in an oxidized form does not occur. This certainly arises from the operation conditions of the investigated screens. An analysis was made of the surfaces of the first (from gas inlet) screens which worked at the highest ammonia concentration. It is well known that high ammonia concentration does not favour the formation of oxides.

DISCUSSION

The base metals on the catalyst surface in the form of surface oxides decrease the catalytic activity first of all by screening the catalyst surface. It is possible for certain metals to decrease the catalyst activity also by initiating an unfavourable manner of etching. A practical conclusion can thus be drawn that it is necessary to protect the surface from inorganic impurities such as, for example, SiO_2, Al_2O_3, Fe_2O_3, especially during about 20 hr of activation. Evaporated palladium does not decrease the catalyst activity but only changes its selectivity.

Investigations of Auger spectra indicate that at a high temperature even a layer of a thickness of 100 atomic monolayers rapidly diffuses to give an alloy bulk. Thus palladium on the catalyst surface is found in metallic form. Even if it settles in the form of oxide in the course of deposition, it undergoes reduction on the Pt–Rh alloy surface.

The mechanisms of the catalytic etching of platinum and the origin of its mass loss were initially not treated separately. The oxygen mechanism of loss, in which volatile PtO_2 plays the major role, was presented by Bartlett (*9*) and Nowak (*10*). Schmidt and Luss (*3*), however, attributed the high rate of catalytic etching to the excitation of surface platinum diffusion by catalytic reaction. A more convincing etching mechanism was presented by McCabe *et al.* (*2*) according to which platinum transport at the surface takes place in a gaseous phase through the diffusion of volatile PtO_2.

Oxide diffuses from regions of lower activity, over which the pressures of oxygen and PtO_2 are higher, to regions of higher activity. The authors mentioned above were the first to treat the mechanisms of etching and loss separately. They have pointed out that the losses appear only when the PtO_2 pressure at the surface is high enough for its molecules to diffuse through the boundary layer to the gas stream. In other cases practically only the etching process takes place. they observed this effect while carrying out experiments on ammonia oxidation in which ammonia was in excess in relation to oxygen. In spite of the etching process taking place they did not find any losses to be occurring. This effect is also confirmed by platinum etching in hydrogen cyanide synthesis, i.e., in a *reduction* atmosphere where, at a high etching rate, the losses are smaller. The evaporated metals increase the etching rate of the catalyst.

The samples coated with palladium underwent the etching process the quickest. Their etching rates were identical although five different quantities of this metal were tested. This observation is in agreement with the etching mechanisms discussed above. For both mechanisms the diffusion transport of platinum may be accelerated as a result of the increase in the heterogeneity of its concentration on the surface, caused by the presence of evaporated metals. Common metals taking the form of oxides certainly undergo segregation along the catalyst surface to form islands or clusters on it. Palladium, which is soluble in platinum, can readily diffuse to form an alloy, but its presence will also cause concentration gradients on the surface. A significant accelerating factor is also a higher pressure of oxygen at the surface, which results from a decrease in the oxidation selectivity to NO. When one molecule of NH_3 is oxidized to NO, 2.5 O_2 molecules are consumed, as compared to 1.5 molecules for oxidation to N_2. In the case of coating with common metals the oxygen pressure increases owing to a decrease in selectivity. A higher oxygen pressure at the sample surface should be associated with the high losses of samples coated with palladium. It is interesting to find that a sample with a five times higher palladium quantity on its surface displayed, after 300 hr of use, a 50% lower loss of mass, but a twice higher one than the clean standard sample. A decrease in loss with a simultaneous increase in palladium quantity should be attributed to a decrease in the surface platinum concentration. This effect supports the theory that loss is caused by the diffusion of PtO_2 to the gas stream. This is also confirmed by the relatively high losses of samples evaporated with aluminium. The contribution of mechanical pulverization of platinum to the losses increases after a prolonged operation time when the catalyst surface is etched intensively enough.

To conclude it may be stated that any impurities on the surface of Pt–Rh catalyst increase its losses in the process of ammonia oxidation catalysis with an oxygen excess. Too close a covering of the catalyst surface with impurities may of course lead to a decrease in losses, but then the active surface will be reduced.

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