Initial Activation of Platinum–Rhodium Gauzes for the Catalytic Oxidation of Ammonia

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Studies have been made of the activation of platinum–rhodium gauze catalysts for the oxidation of ammonia, using optical microscopy, electron probe microanalysis (EPMA), and electron spectroscopy to characterize the surfaces. The initial washing procedure is found to remove calcium and to reduce carbon residues on the surface, as a result of which the catalyst is active at lower temperatures. Subsequent activation in a hydrogen flame or in oxygen causes surface rearrangements and results in rhodium enrichment at the surface: this latter trend is partially reversed in the early stages of the oxidation of ammonia. Water vapor is found to deactivate the activated gauze.

INTRODUCTION

The oxidation of ammonia over platinum–rhodium gauzes is a catalytic reaction of considerable industrial importance (*1, 2*) and much attention has been paid to the system (*3–9*). The use of modern analytical techniques has proved to be rewarding in the context of characterization. Thus, Philpott (*8*) and Sperner and Hohmann (*10*) have used scanning electron microscopy to study surface rearrangements of the catalyst during reaction, and Schmidt and Luss (*9*) as well as Contour *et al.* (*6*) have established rhodium enrichment at the surface of the gauze as a result of the catalytic reaction.

One aspect of the industrial operation has received little attention, namely, the activation of the gauze. Gauzes are found to be efficient catalysts provided that they are first washed in an organic solvent and

then activated by heating, either in a hydrogen flame or in oxygen (*11*). The present studies were carried out in order to investigate the scientific basis of this procedure.

EXPERIMENTAL

Pretreatment and catalytic reactions were carried out in a flow system in which known amounts of gases were mixed and passed through a pack of three Pt/10% Rh gauzes, mounted in a constant-temperature reactor, to an off-line gas chromatograph sample point. The temperature before, in, and after the gauze pack could be measured by sheathed thermocouples. The pack itself was made from three gauzes of known weight (ca. 24 mg; equivalent to a projected area of 0.64 cm²) knitted from Pt/10% Rh wire of 0.003-in. diameter to 80 meshes per linear inch. On occasions, the gauze pack was replaced by Pt/10% Rh foil of 0.003-in. thickness.

Gases leaving the reactor were sampled for analysis. Nitrogen, oxygen, and nitric

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oxide were separated on a molecular sieve 13X column (3 m: 20°C) and nitrous oxide, nitrogen dioxide, and ammonia were separated on a Porapak Q column (2 m: 40°C). In the presence of excess oxygen, it is possible that the reaction

$$2NO + O_2 \rightleftharpoons 2NO_2$$
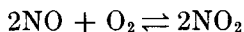
could occur in the chromatographic columns. Comparisons with wet analysis showed that an accuracy of ±4% could be obtained for the nitric oxide determination.

In general, gauzes were cut to size, washed, and mounted in the reactor. Any chosen pretreatment was carried out, and samples of the wire were taken. A flow of 14% NH₃/air (4300 cm³ min⁻¹) was then passed through the reactor and the furnace temperature was slowly raised until the gauze "lit off." This "light off" temperature is the temperature at which the catalytic activity is sufficient to raise the temperature of the gauze significantly above that of the furnace. The furnace temperature was then adjusted to operating conditions (280°C under standard conditions) to carry out the experiment. Samples of the gauze were taken for analysis after a given experiment.

Analysis involved several techniques. Optical microscopy was carried out using an Olympus metallurgical microscope (× 600 magnification) fitted with a camera. X-Ray and ultraviolet photoelectron spectroscopy (XPS and UPS) was carried out using a Vacuum Generators ESCA 3 machine. Samples could be pre- or post-treated in a chamber attached to the analyzer. Post-treatment usually consisted of argon ion bombardment to remove ca. 600 Å of surface from the sample. Electron probe microanalysis (EPMA) was carried out using a JEOL JXA-3A machine, the Pt and Rh Lα lines being used as a basis of analysis. No surface polishing was carried out, and an error of ±5% was possible.

No attempt was made to correlate

TABLE 1

Light Off Temperatures and Activity as a Function of Initial Activation

Treatment	Light off temperature (°C)	Activity after 2 h (% NO)
None	410	8
Solvent wash	310	11
Solvent wash plus activation with hydrogen flame	310	19
O₂:1000°C:2 h	310	19
H₂:1000°C:2 h	270	18
He:1000°C:2 h	380	16
No solvent wash O₂:1000°C:2 h	332	16

activity with concentrations of ammonia or oxygen, and the activity was expressed in terms of the percentage of free nitric oxide produced from ammonia. Activation has most effect on the initial activity and gauzes were only used to oxidize ammonia for a short time. As a result, conversions are not high. If an activated gauze was left on line for some time, the high conversions expected from industrial operation were always obtained.

RESULTS

Before use, all gauzes were washed twice in trichlorethylene, acetone, and water. This procedure was found to have a significant effect on light off temperature and on activity (Table 1). EPMA and XPS examination showed that unwashed gauzes had a high concentration of carbon on the surface, and that there was a substantial amount of calcium located in specks on the surface. Washing removed nearly all of this calcium and reduced the surface carbon concentration. The deliberate addition of calcium to a washed, activated gauze was found to increase the light off temperature by 165°C. The beneficial effect of washing would thus seem to result from removal of calcium,
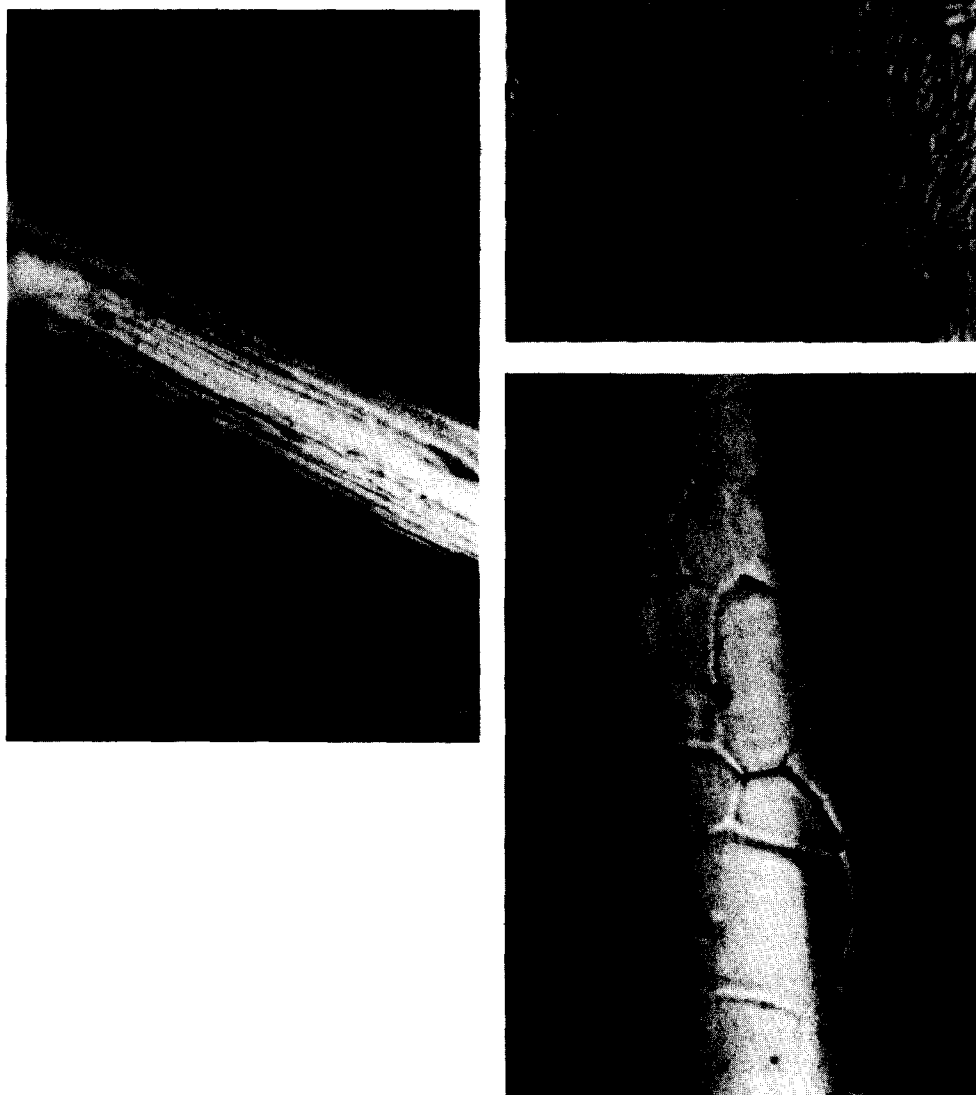
Fig. 1. Optical micrographs of Pt/10% Rh gauzes: (a) as supplied (× 350); (b) washed and activated for 10 s in a hydrogen flame (× 460); (c) as (b), and after 2-hr reaction under standard conditions (× 2000).

TABLE 2

Pt/10% Rh Catalysts: EPMA and XPS Analyses[a]

Treatment	EPMA (gauze)			XPS intensity ratios ($Pt_{N VII}$:$Rh_{M III}$)			
	Pt (wt%)	Rh (wt%)	Pt/Rh	Gauze		Foil	
				A	B	A	B
Washed	91.3	8.7	10.5	7:1	11:1	15:1	16:1
Washed and activated (H₂ flame)				5:1	14:1	6:1	14:1
Washed, activated (H₂ flame), and reacted						10:1	15:1
Washed and activated (oxygen, 800°C)	78.1	21.9	3.5			4:1	9:1
Washed, activated (oxygen), and reacted	89.7	10.3	6.9	18:1		7:1	14:1
Washed: no activation: reaction	91.5	8.5	10.7				

[a] A = Initial; B = argon ion bombarded to remove ca. 600 Å of surface.

possibly introduced as a lubricant during the preparation of the gauzes. We are not aware of any previous reports of calcium contamination on Pt–Rh gauzes.

Under industrial conditions, the next stage of activation involves treatment of the gauzes in a hydrogen flame (12), although activation in oxygen is also used (11). Preliminary experiments showed that hydrogen flame activation was very irreproducible, resulting in extensive surface reorganization centered about grain bound-

TABLE 3

Pt/10% Foil: XPS Spectra[a]

Treatment	Platinum				Rhodium ($Rh_{M III}$)	
	I (cm)	P (eV)	$Pt_{N VII}$		I (cm)	P (eV)
			C_{1s}	O_{1s}		
1. Solvent washed	(a) 22.2	71.8	3.13	3.13	1.45	497
	(b) 20.0	71.6	3.75	10.0	1.25	497
2. Washed and activated (H₂ flame)	(a) 21.2	71.8	3.42	2.74	3.5	498.5
	(b) 27.2	72.1	6.1	1.4	1.9	497.3
3. Washed, activated (H₂ flame), and reacted	(a) 15.4	71.6	4.0	3.64	1.55	497.5
	(b) 24.8	71.6	9.5	2.85	1.65	496.9
4. Washed and activated (oxygen)	(a) 11.6	71.6	2.79	1.3	3.05	498.2
	(b) 24.0	72.2	6.4	6.4	2.7	497.3
5. Washed, activated (oxygen), and reacted	(a) 15.6	71.9	5.1	2.18	2.15	498.2
	(b) 18.4	71.9	5.5	8.34	1.35	497.0
6. Washed: oxidation for 7 days at 750°C						498.5

[a] (a) Initial value; (b) after argon ion bombardment to remove ca. 600 Å of surface; I = intensity; P = position with respect to the Fermi level at 1490 eV.
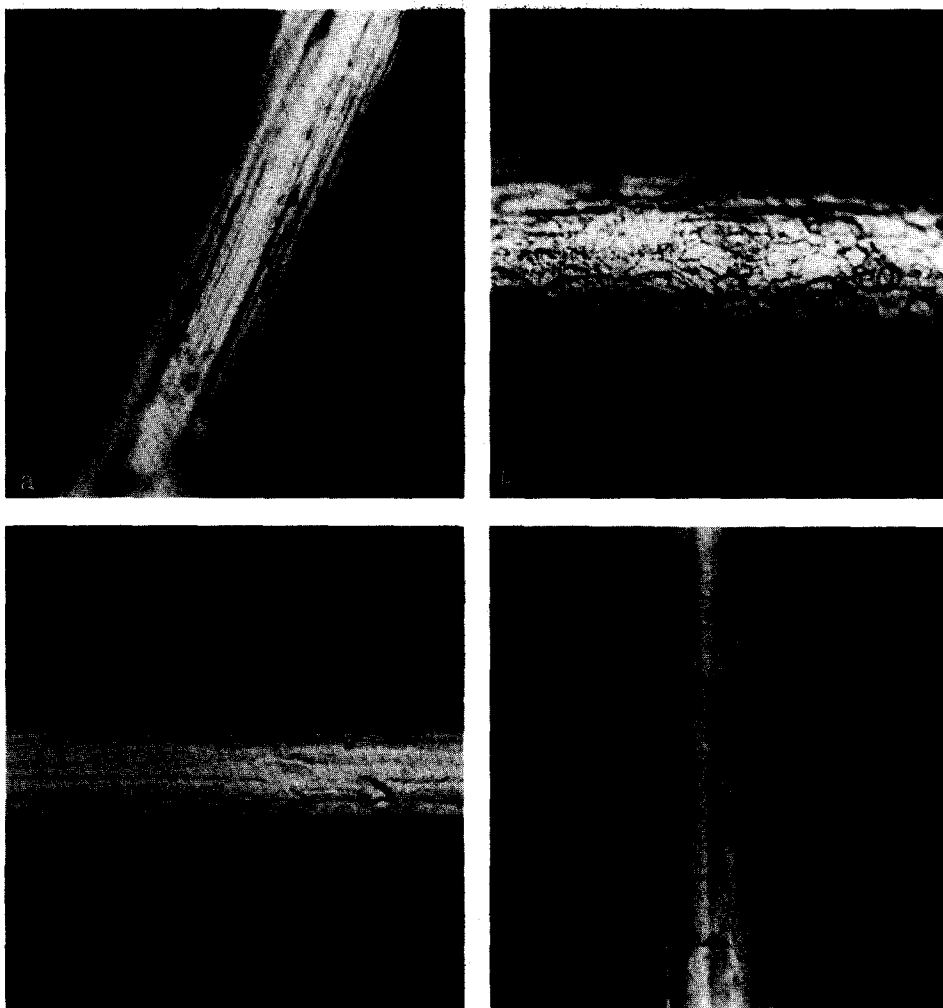
FIG. 2. Optical micrographs of activated Pt/10% Rh gauzes. Activation at 1000°C for 2 h: (a) as supplied ($\times$ 350); (b) in oxygen (200 cm^3 min^{-1}) ($\times$ 500); (c) in nitrogen (200 cm^3 min^{-1}) ($\times$ 500); (d) in helium (200 cm^3 min^{-1}) ($\times$ 350); (e) in hydrogen (200 cm^3 min^{-1}) ($\times$ 350); (f) in ammonia (200 cm^3 min^{-1}) ($\times$ 500).

aries in the wire (Fig. 1). As a result, attention was focused on gauze activation in different atmospheres. Light off temperatures and gauze activities are recorded in Table 1. Samples of gauze were examined before and after activation and after reaction. This involved optical microscopy (Figs. 1 and 2), EPMA (Table 2), and XPS examination (Fig. 3). In this latter case, gauzes from the reactor were too small to insert in the machine, and separate samples were mounted and treated in the preparation chamber attached to the spec-

trometer. Corresponding experiments were also carried out with Pt/10% Rh foil. Results are summarized and compared with the EPMA analyses in Table 2.

Difficulties were experienced in obtaining XPS spectra from gauze catalysts, and studies of the relative intensities of platinum, carbon, oxygen, and rhodium were carried out using Pt/10% Rh foils. The results are summarized in Table 3.

The effect of temperature on activation by oxygen was studied over the range 100 to 1000°C in a static atmosphere of
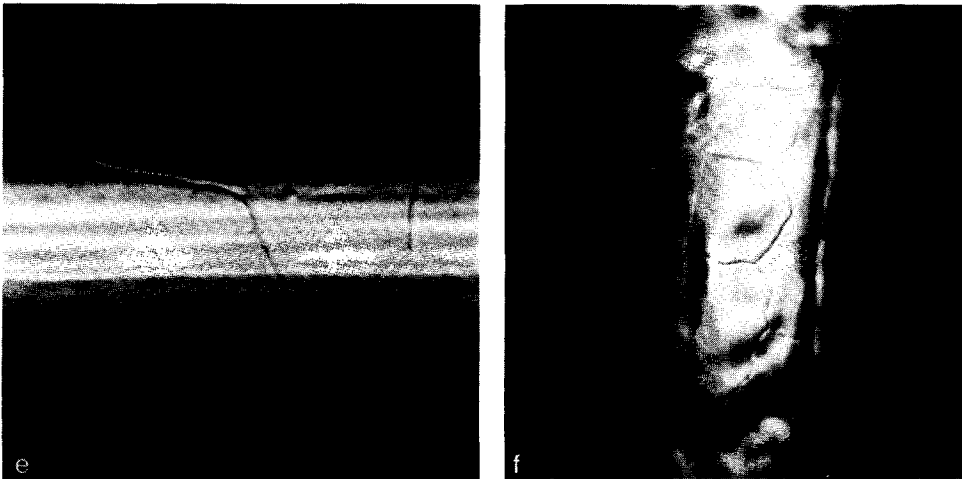
FIG. 2—*Continued.*

oxygen. The activated gauzes were examined by EPMA and the light off temperature and the temperature at which greatest activity could be observed for the oxidation of ammonia under the standard conditions were recorded (Fig. 4).

The development of activity during the ammonia oxidation reaction was studied for gauzes activated in different ways (Fig. 5). Optical micrographs of the surface rearrangement were also obtained (Fig. 6) for an oxygen-activated gauze.

If an activated gauze was left in the laboratory for any time, some deactivation was observed. Activated gauzes were stored in various atmospheres (Table 4) and water vapor was found to be the main deactivating gas. An activated gauze was soaked in distilled water for 2 h. XPS examination showed that the Pt/Rh intensity at the surface dropped from $4:1$ to $2:1$ during this process, while the bulk ratio remained unchanged at about $9:1$. The water was evaporated to dryness over a copper grid: XPS examination of the grid showed a small Pt_{NVII} peak and no trace of rhodium.

A sample of Pt/10% Rh foil was then cleaned and mounted in the ESCA 3 chamber. Exposure of the oxidized or reduced sample to ammonia at 900°C gave no indication of a UPS spectrum originating from any gas other than oxygen.

DISCUSSION

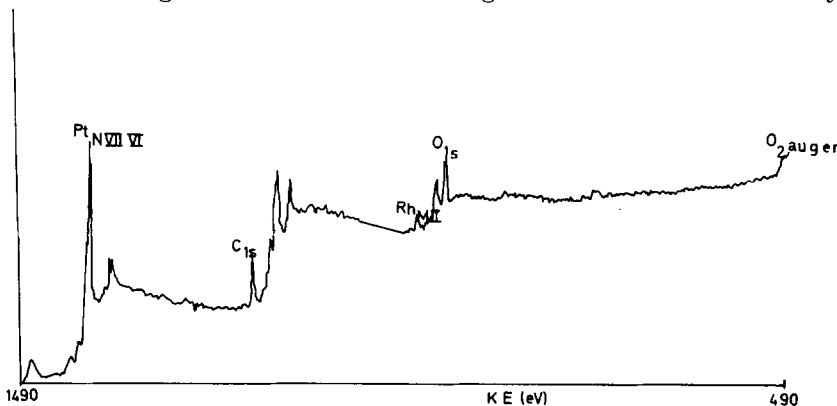The oxidation of ammonia over Pt/10% Rh gauzes is known to be a very efficient
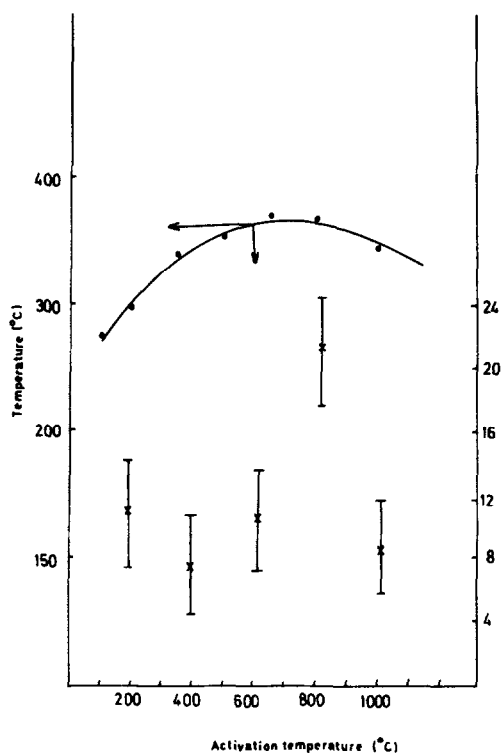

FIG. 3. XPS of a solvent washed Pt/10% Rh foil.

FIG. 4. The effect of activation in oxygen at different temperatures: O, light off temperatures; ✗, Rh concentration by EPMA.

activity of the gauze. The effects may be discussed individually before considering the overall activation process.

It is well known that the surface morphology of Pt/Rh wires changes during the activation and catalysis (7, 8, 10), and such effects are clearly seen in Figs. 1, 2, and 6. Both micro- and macro-geometric effects have been suggested to influence the reaction. On a microscale, for example, Fryberg and Petrus (14) have found that the oxidation of platinum leads to the development of (311) planes on the surface, and Somorjai (15) has established that oxygen is readily adsorbed on stepped surfaces. It is clearly seen from Figs. 1, 2, and 6 that different grains in the surface rearrange to different extents and, although it was not possible to assign crystal structures, the results agree with those reported by Flytzani-Stephanopoulos et al. (7). Whether this rearrangement affects activity is hard to judge, although, on a macroscale, surface rearrangements seem to play a less important role than has been suggested (8). Thus, for example, surface rearrangements are greatest for activation under oxygen (Fig. 2), while activation under hydrogen gives a reasonably smooth surface away from the grain boundaries. Comparisons with light off temperatures
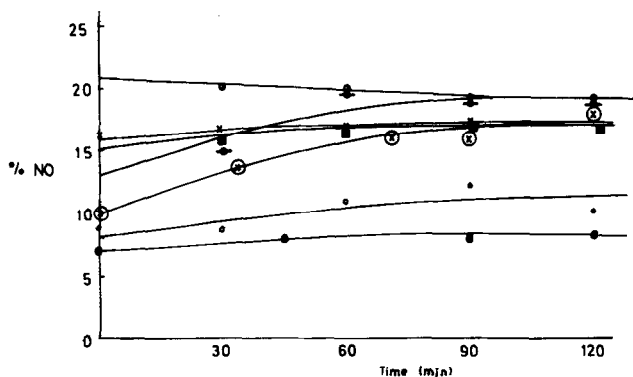
process once the gauzes have been activated and have been used for some time (13). The present results show that several processes occur during the initial activation and that nearly all of them affect the final

FIG. 5. The development of catalytic activity with time: ●, no pretreatment; O, solvent wash only; ◖●, solvent wash plus hydrogen flame activation; ◖, solvent wash plus oxygen activation (1000°C: 2 h); ■, solvent wash plus hydrogen activation (1000°C: 2 h); ✗, solvent wash plus helium activation (1000°C: 2 h) ⊗, no wash: oxygen activation (1000°C: 2 h).

and activities (Table 1) reveal no obvious correlation.

Another factor that is known to affect the activity of gauzes is the presence of sulfur or carbon on the surface, since this has the effect of reducing greatly the adsorption of oxygen on the surface (16). Activation is known to reduce the amounts of these surface poisons (5), and this trend is confirmed in the present studies (Table 3). Activation and reaction increase the Pt_{NVII}/C_{1s} ratio in all cases, and comparison of the surface and bulk compositions shows that carbon, originally present in the lattice, concentrates at the surface and is removed during activation. The small effect of activation in inert gas (Table 1) is almost certainly due to the absence of a carbon-removing reaction.

One other interesting feature emerges from the results summarized in Table 3 which throws light on the adsorption of oxygen on the gauze. Oxygen in the as-supplied gauze is seen to be concentrated at the surface, while activation results in diffusion of oxygen into the bulk catalyst. Somewhat surprisingly, the bulk concentration of oxygen is higher after hydrogen flame activation than after activation in oxygen (Table 3). This presumably results from the higher temperatures (ca. 2000 K) reached in the flame. The resolution of the electron spectrometer (±0.3 eV) is not good enough to identify the oxidation state of platinum, but oxidized rhodium is seen to be concentrated at the surface (Table 3).

It is believed that oxygen has a profound influence on changes in alloy composition that are observed during activation and reaction (Tables 2 and 3). Such changes have been observed both by XPS (depth of sample ca. 10 Å) and by EPMA (depth of sampling ca. 2000 Å). Attempts were made to quantify the peak intensities of the XPS spectra in terms of actual amounts, but this was found to be impossible, particularly on gauzes where the sample

TABLE 4

Deactivation of an Active Gauze

Treatment	Light off temperature (°C)	Activity after 2 h (% NO)
None	310	19
Flowing CO_2	320	19
Static CO_2	310	19
Static SO_2	295	18
Static cigar smoke	310	19
Water vapor	362	18
Immersion in water	400	18

geometry also affected the signal. The results from foils showed that although the ratio of intensities in the bulk was always about the same, initial activation always resulted in an increase of the rhodium concentration at the surface. Reaction, on the other hand, had the effect of partially reversing this trend (Table 2).

Confirmation of this trend was carried out using EPMA (Table 2), and these experiments were extended to investigate the effect of temperature on activation in oxygen (Fig. 4). Although the results are only accurate to $\pm5\%$, there is a clear correlation between activation temperature, light off temperature, and surface composition. Again, the trend of surface enrichment by rhodium was found to be partially reversed after reaction.

Enrichment of the surface by rhodium during initial activation could result from one or both of two phenomena. Bulk oxides of platinum decompose at about 700°C, while oxides of rhodium are stable to ca. 1140°C (17). The well-known phenomenon of surface enrichment by a minority component is known to be enhanced in oxygen atmospheres (18) and, as a result, bulk migration of rhodium oxides to the surface may be favored at temperatures such that platinum oxide decomposes. Alternatively, Darling (17) has reported that the vapor pressure of PtO_2 is greater than that of RhO_2 at
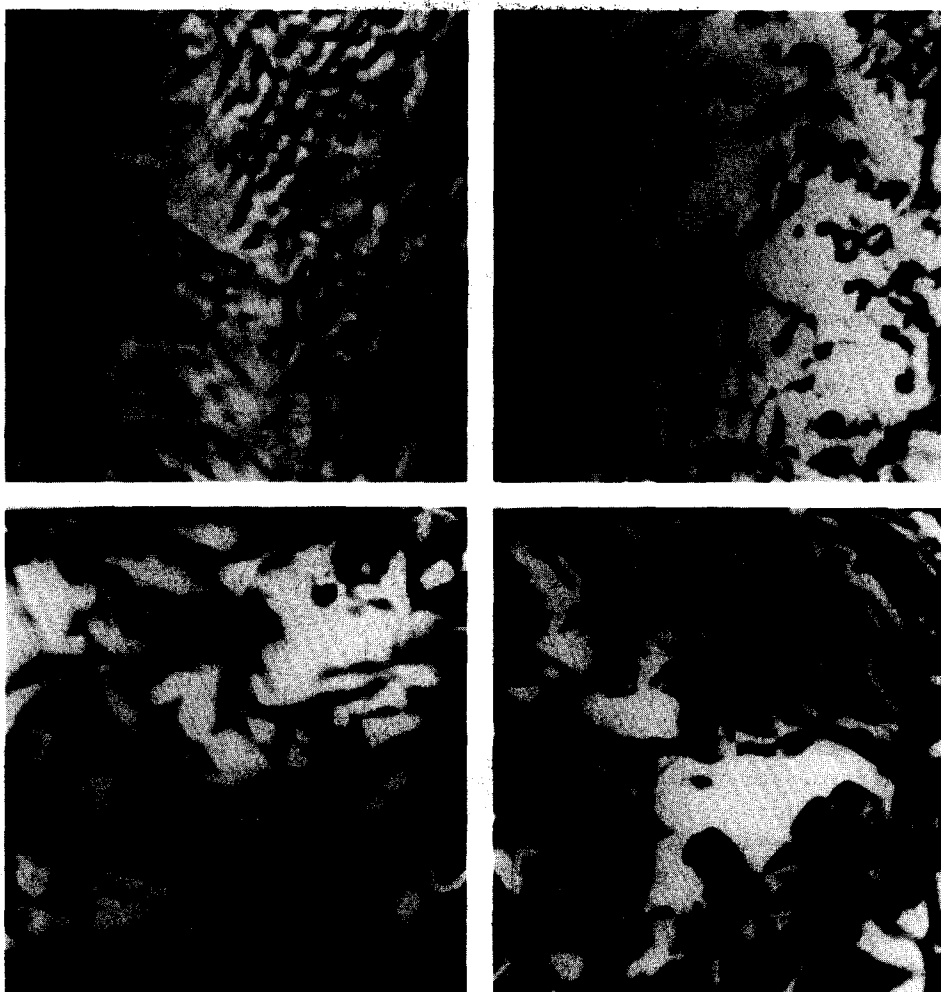
FIG. 6. Optical micrographs of used catalysts. Ammonia oxidation under standard conditions: activation in oxygen at 1000°C for 2 h: (a) after 50-s reaction (× 2000); (b) after 2-min 54-sec reaction (× 2000); (c) after 9-min reaction (× 2000); (d) after 41-min reaction (× 2000); (e) after 120-min reaction (× 850); (f) no activation: 120-min reaction (× 350).

temperatures less than ca. 1200°C, and another explanation of the observation could be that preferential evaporation of platinum oxide results in effective surface enrichment by rhodium. The observation that the more highly oxidized form on rhodium is formed near the surface (Table 3) is consistent with both explanations.

The partial reversal of this trend on using the alloy as a catalyst may result from the fact that the ambient gas is overall reducing (14% NH₃ in air). At the higher temperatures pertaining during

reaction, surface enrichment will depend upon the mobility of the two metals, and this could lead to some diminution of rhodium enrichment. It should be noted, however, that the surface is always more rhodium rich than the bulk (Table 3).

One other interesting observation was that gauzes which had been given the initial activation could be deactivated in the presence of gaseous or liquid water. As would be expected, no water adsorption could be identified by XPS or UPS against the background oxide spectra, but the fact
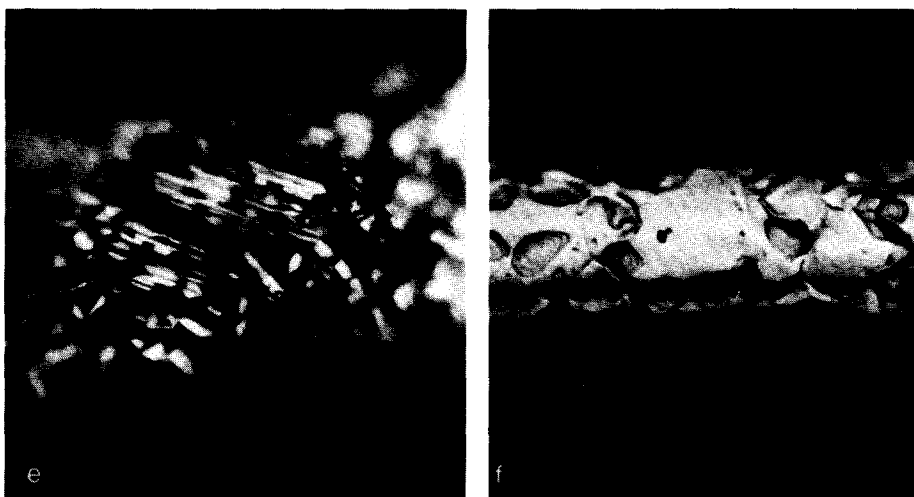
FIG. 6—*Continued*.

that platinum oxide could be dissolved from the gauze would indicate that interaction with water is feasible: such adsorption, either directly or indirectly (by causing surface rearrangements), increased the light off temperature of the gauzes by 50 to 100°C.

Finally, an attempt was made to see whether activation had any effect on gas adsorption on the gauze. Under near reaction conditions, no adsorption other than that due to oxygen could be identified.

As a result of these studies on initial activation effects, the overall process, is seen to be complex. Washing of the gauze removes calcium and reduces carbon on the surface. Subsequent activation induces geometric changes in the surface, reduces the amount of carbon on and in the catalyst, and causes rhodium enrichment of the surface. This latter trend is reversed, at least in part, on subsequent use of the catalyst for the oxidation of ammonia.

Studies of the activity of the gauzes after initial activation did show that some of the effects of activation could be obtained on reaction, provided that the catalyst was active enough to allow a conversion of ammonia greater than about 10% (Fig. 5). It must be stressed that these measurements were restricted to the very early

stages of reaction, so the activities did not approach those obtained after some 2 weeks of operation ($>90\%$ NO), but the trends are revealing. It would seem that if activation is sufficient to allow a minimal conversion, then the combination of high operating temperature (920–960°C) and oxidizing conditions led to activation *in situ*. In other words, if the gauze is activated initially, then it will proceed, in time, to the final activation. If the gauze is not activated initially, then it will not develop final activation on long use.

ACKNOWLEDGMENTS

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