JOURNAL OF MATERIALS SCIENCE 27 (1992) 685–691

Characterization of catalyst and catchment gauzes used in medium- and low-pressure ammonia oxidation plants

J. L. G. FIERRO*, J. M. PALACIOS
Instituto de Catálisis y Petroleoquímica, C.S.I.C., Serrano 119, 28006 Madrid, Spain
F. TOMAS
Escuela Universitaria Politécnica, Alfonso XIII 34, Cartagena, Spain

Morphological and chemical changes of the Pt–Rh catalyst and palladium-based catchment gauzes used in medium- and low-pressure ammonia oxidation plants have been studied by scanning electron microscopy, combined with energy dispersive X-ray analysis (SEM–EDX), and X-ray photoelectron spectroscopy (XPS). It has been observed that the noble metals are mostly in the metallic state, and catalyst deactivation is determined by rhodium enrichment in the alloy surface. In the cases of a strong "faceting" of the wires, which tends to homogenize the catalyst surface, a good agreement between the surface composition determined by EDX and XPS was found. The Pt/Pd and Rh/Pd ratios in the catchment gauzes decreased markedly from the top to the bottom gauzes of the pack, indicating the directional effect of metal condensation or deposition from the gas stream.

1. Introduction

Platinum–rhodium alloys find widespread use as industrial catalysts. A major application is in the manufacture of nitric acid, via ammonia oxidation, where the catalyst is used in the form of a woven gauze pack. As the reaction takes place under very severe reaction conditions, i.e. temperatures as high as 900 °C, pressures of 1–10 kg cm^{-2} and a strongly oxidant environment, the catalyst may undergo extensive changes during operation, which determine important activity losses. Consequently, the catalyst gauzes and the catchment systems, if any, must be changed [1] when the activity decay makes the process uneconomical.

Among the processes involved in the deactivation of the catalyst, both morphological changes, derived from the recrystallization and reconstruction of materials, and the surface chemical changes, usually consisting of rhodium enrichment with the subsequent change of its oxidation state, and impurities accumulation [2–4], are the most frequently encountered. Several mechanisms have been proposed to explain these morphological [4–6] and chemical [7] transformations. These changes are important requirements in the fresh catalyst gauzes because they increase or maintain a high activity level by keeping a fresh catalyst surface; however, they act negatively during long periods on-stream because the surface concentration of the active component (platinum) becomes strongly decreased [8–12].

Both morphological and chemical changes depend to a great extent on several parameters, such as the flow rate and composition of the gas stream, the overall pressure and reaction temperature, the presence of impurities, etc. [13–15], which not only change from plant to plant but also from gauze to gauze within the same pack. In order to ensure a better control of these parameters, most studies have been carried out with laboratory reactors, and only in a few instances in pilot plants. Considerably fewer studies, however, have been conducted in industrial plants, where the operation conditions are presumably quite different. As the preliminary studies carried out in our laboratory either on the catalyst gauzes [16] or on the catchment systems [17] used in high-pressure ammonia burners revealed a very strong deterioration of Pt–Rh gauzes, even for 2–3 month campaigns, in this work we focused on the changes of catalyst used in medium- and low-pressure nitric acid plants, in which minor transformations are expected to occur [18], however, for much longer periods on-stream.

2. Experimental procedure

The samples were collected from different nitric acid plants at the end of a given campaign, when the deactivated catalyst and catchment systems were replaced by new ones. The operation conditions of the plants are summarized in Table I. For comparative purposes, the operation conditions of a high-pressure plant whose catalyst gauzes were studied elsewhere [16, 17] are also included in this table. The operation conditions of a given plant determine to a great extent

---

* Author to whom all correspondence should be addressed.

0022–2461/92 $03.00 + .12 © *1992 Chapman & Hall*

TABLE I Average operation conditions in the plants

Plant	Type[a]	p[b] ($\mathrm{kg\,cm^{-2}}$)	T (°C)	NH_3/air (% vol/vol)	Camp. (day)	Conv. (%)	Catalysis losses (%)	Recovery (%)
A	HP	8.5	920	9.2	70	92	78	80
B	MP	4.2	870	10.2	90	96	13.7	–
C	MP	4.3	880	10.7	87	96	14.3	–
D	MP	4.9	795	10.8	120	96	27.3	55
E	MP	3.5	820	10.8	120	96	11.5	–
F	LP	atm	750	11.2	218	96.4	2.8	–
G	LP	atm	850	13.0	112	96.0	9.8	–

[a] HP = high pressure, MP = medium pressure, LP = low pressure.
[b] atm = atmospheric.

TABLE II Characteristics of the gauzes used in the plants

Plant	Type[a]	Catalytic pack				Recovering pack		
		No.	Wire diameter (mm)	Mesh	Alloy Pt/Rh	No.	Wire diameter (mm)	Alloy
A	HP	30	0.076	1000	90/10	7	0.120	Pd95/Cu5
B	MP	8	0.060	1024	90/10	3	–	–
C	MP	8	0.072	1024	90/10	2	0.120	Pd95/Ni5
						1	0.072	Pd95/Ni5
D	MP	3	0.076	1024	90/10	2	0.076	Pd95/Cu5
		2	0.060	1024	95/5	1	0.072	Pd95/Cu5
E	MP	3	0.060	1024	95/5		n.e.[b]	
F	LP	3	0.060	1024	95/5		n.e.	
G	LP	3	0.060	1024	95/5		n.e.	

[a] HP = high pressure, MP = medium pressure, LP = low pressure.
[b] n.e. = non existent.

the principal characteristics of the gauzes to be used. However, small design differences of the packs may exist (Table II) among plants of the same type. Another important requirement of the medium and especially of the high-pressure plants is the incorporation of a catchment pack just at the outlet of the reactor. This study includes the characterization of catalyst and recovering gauzes by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The gauzes will be referred to hereafter by a number, which indicates the number of the gauze with respect to the top one of the pack. Morphological studies were carried out in an ISI DS-130 scanning electron microscope equipped with an energy dispersive X-ray analyser (SEM–EDX), which allows analysis of depths of the order of 1 μm. Surface analyses were obtained with a Leybold LHS 10 X-ray photoelectron spectrometer (XPS), working in the ΔE = cnt. mode with a pass energy of 50 eV.

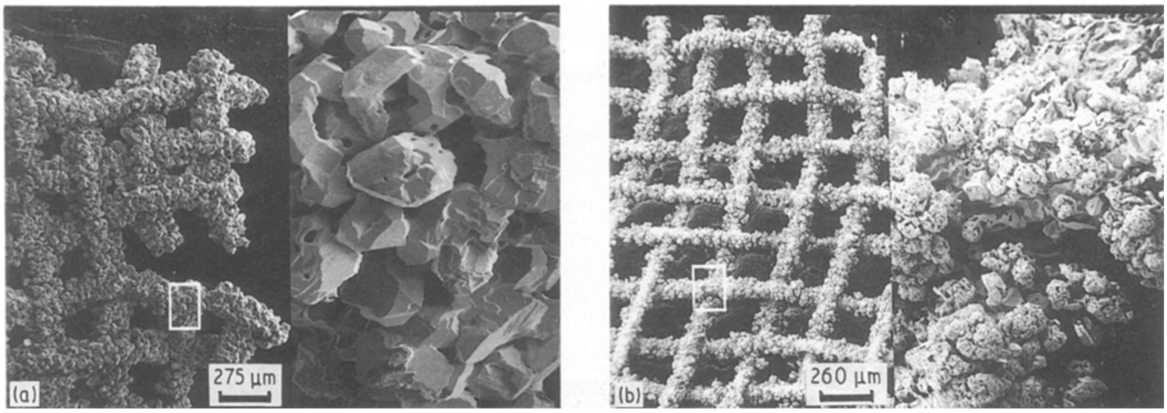
The spectrometer was provided with a magnesium X-ray source ($h\nu$ = 1253.6 eV) operating at 12 kV and 10 mA. The residual pressure in the analysis chamber was below 4×10^{-9} torr (1 torr = 133.322 Pa) during data acquisition. The 20 eV energy regions of the photoelectrons of interest were signal-averaged for a number of scans in order to obtain good signal-to-noise ratios. The binding energies (BE) were calculated by taking the energy of the C 1s photoelectrons as 284.6 eV relative to the Fermi level.

3. Results and discussion

3.1. Comparative study of gauzes from different plants

Fig. 1a–c show the morphological aspect of gauzes arising from high-, medium- and low-pressure ammonia oxidation plants, respectively. In all cases a strong deterioration of gauzes due to the well-known phenomenon of "faceting", can be seen. However, the extent of degradation decreases from the high- to the low-pressure plants. Similarly, the final state of the catchment gauzes (Fig. 2a and b) again show a stronger "faceting" in those arising from high-pressure plants than in the medium-pressure one. These results, which agree with those of McCabe *et al.* [13], indicate that surface reconstruction depends mainly on the reaction temperature and composition of the feed; both parameters being quite different from plant to plant.

In addition to the morphological changes, important composition changes are also operative. These are illustrated in Fig. 3, in which the Rh/Pt ratios for the catalyst gauzes and the Pt/Pd ratios for the catchment ratios are given. As expected, the oxygen partial pressure in a high-pressure plant is higher, which leads indeed to platinum losses, as volatile PtO_2, and parallel to rhodium enrichment at the catalyst surface. This behaviour contrasts with the low rhodium enrichment found in the surface of catalyst gauzes in the low-pressure plants. Similarly, the Pt/Pd ratio in the catch-



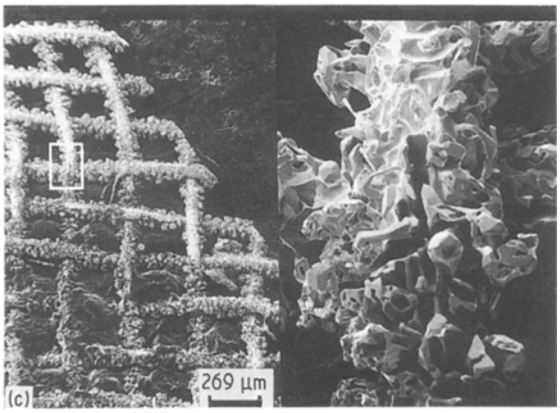


Figure 1 Scanning electron micrographs of the top gauzes of the catalyst pack: (a) high-pressure, (b) medium-pressure, (c) low-pressure plants.

ment gauzes follows the same trend as the Rh/Pt ratio in the catalyst gauzes, because most of the platinum released from the catalyst wires is trapped by the recovering palladium gauzes. The Rh/Pt ratios, averaged for all gauzes of the pack and corrected for the same time on-stream (100 days), are given in Fig. 4 as a function of the operation temperature of each plant. With the exception of Plant D, a good correlation is observed, which indicates that the reaction temperature is the principal factor that controls surface rhodium enrichment. Moreover, the Rh/Pt ratio increases abruptly in the temperature range 850–950 °C, consistent with the well-known phenomenon of platinum oxide formation and its subsequent volatilization.

3.2. Analysis of catalyst gauzes of medium- and low-pressure plants

In previous work on catalyst gauzes used in a high-pressure ammonia oxidation plant [16] it was found that platinum was essentially in the metallic state in the first gauzes of the catalyst pack, while rhodium was mostly oxidized to Rh_2O_3. As the gas stream becomes more oxidant and the reaction temperature decreases downstream, the Rh_2O_3 layer was observed to attain the maximum thickness in gauzes 5–8 of a pack of 30. Apart from this, no morphological differences were found among the catalyst gauzes because of the strong "faceting" of the wires. This behaviour is quite different in the gauzes of low and medium pressure ammonia oxidation plants.

The XPS spectra of Pt 4f and Rd 3d core levels are given in Figs 5 and 6, respectively, and the respective BEs are summarized in Table III. Judging from the BE data, it results that both platinum and rhodium are in the metallic state. The presence of minor proportions of oxidized species, such as PtO or PtO_2 and Rh_2O_3, cannot be excluded from the XPS spectra because the Pt 4f and Rh 3d peaks show a tail extending in the high BE side of the principal peaks. Notice that this finding contrasts with the dominant Rh_2O_3 species observed in the catalyst gauzes of a high pressure plant. Moreover, there is no agreement with the accepted idea for

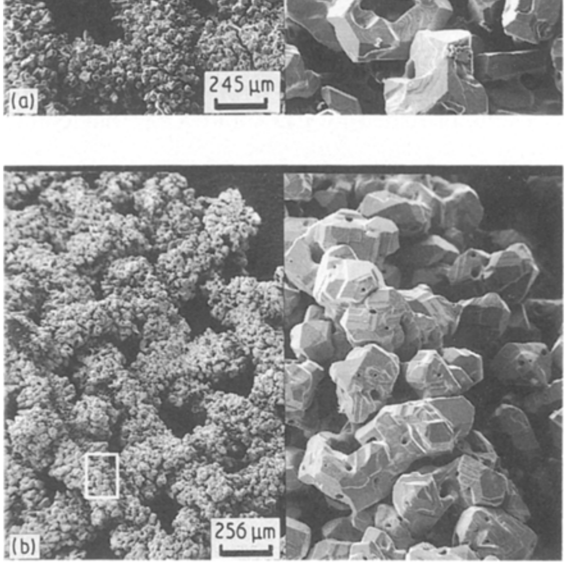


Figure 2 Scanning electron micrographs of the top gauzes of the catchment pack: (a) high-pressure, (b) medium-pressure plants.

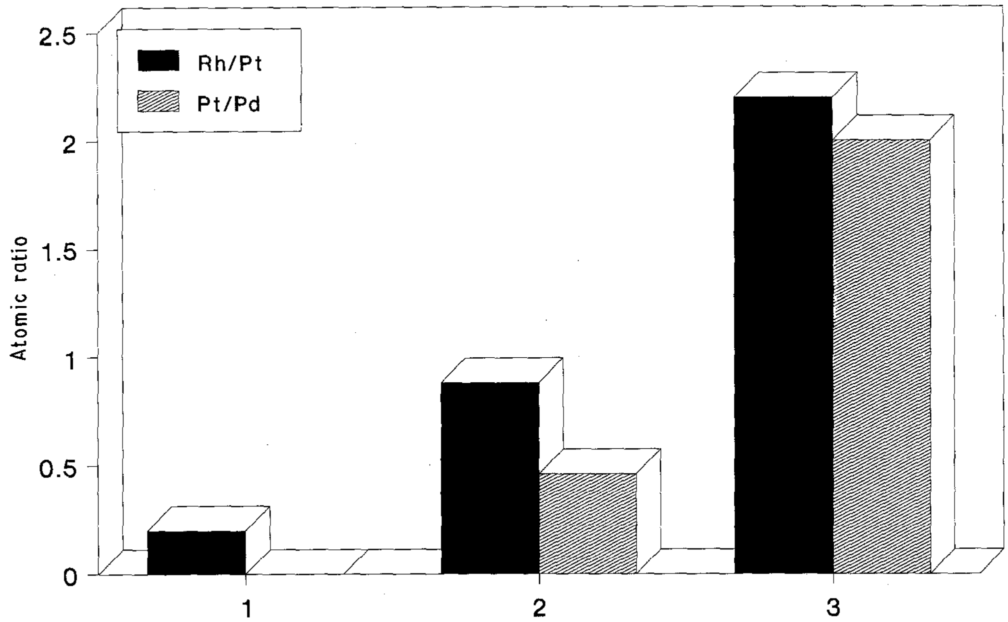


Figure 3 Comparison of the Rh/Pt ratio in catalyst gauzes and of Pt/Pd in catchment gauzes for (1) low-pressure, (2) medium-pressur
(3) high-pressure plants.

laboratory microreactors that the surface Rh_2O_3 is the source of catalyst deactivation. On the contrary, these results agree with the conclusions of McCabe and Schmidt [19], who emphasized the necessity of a clean metallic surface as the principal requirement for ammonia oxidation.

From the XPS peak intensity areas and published atomic sensitivity factors [20], the Rh/Pt ratios have been calculated for catalyst gauzes. The results, summarized in Table IV, show that the Rh/Pt ratio is higher in the medium-pressure than in the low-pressure plant, but in both cases the surface wires become less and less rhodium-enriched downstream. This observation may result, in principle, unexpected in the light of our previous findings in a high-pressure plant [16], and also of the EDX data.

The analysis of the catalyst wire surfaces by EDX, averaged in a depth of ~ 1 μm (typical of the technique), is given in Figs 7 and 8. These results indicate that the Rh/Pt ratio increases downstream, and also that this ratio is somewhat lower at the front face than at the back face. Although discrepancy exists among the results provided by EDX and XPS, they coincide

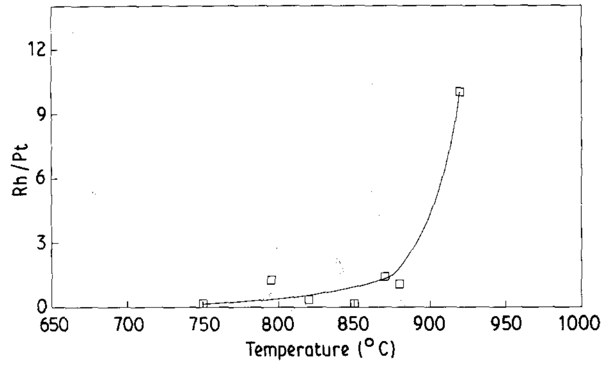


Figure 4 Dependence of the averaged Rh/Pt ratio within the pack on the reaction temperature in the different plants studied.

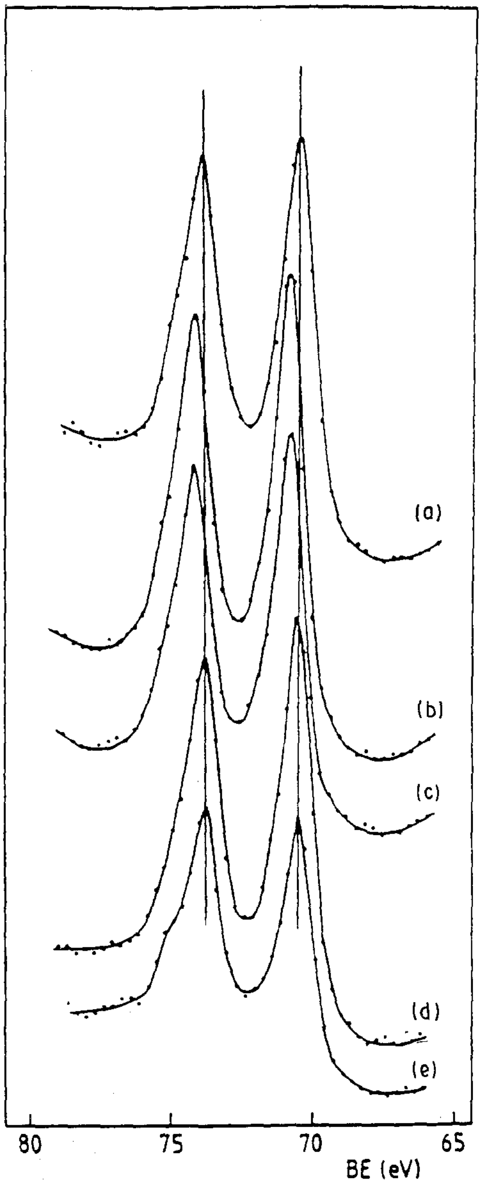


Figure 5 Pt 4f core level spectra of catalyst gauzes (a) 1, (b) 4 and (c) 8, and of catchment gauzes (d) 1, (e) 3, in the medium-pressure plant C.

TABLE III Binding energy (eV) of core levels in gauzes

Sample	O 1s	Rh 3d	Pt 4f	Pd 3d
C-1 (cat.)	532.6 (530.3)	313.1–308.0	73.9–70.4	–
C-4 (cat.)	532.2 (530.2)	313.4–308.2	74.1–70.8	–
C-8 (cat.)	532.2 (530.3)	313.6–308.2	74.3–70.9	–
C-1 (rec.)	531.6 (529.7)	313.2–308.0	73.4–70.4	339.7–334.4
C-3 (rec.)	531.1 (530.1)	313.3–308.2	73.6–70.5	339.9–334.5
F-1 (cat.)	532.3 (529.9)	314.0–308.1	74.4–70.9	–
F-3 (cat.)	531.5 (?)	313.6–308.0	74.1–70.7	–

in the first gauzes, and divergences are observed in the last gauzes of the pack. Depending on the location within the pack, the gauzes show clearly differentiated morphological changes, in contrast to the uniform aspect found in those of high-pressure plants. A detailed analysis of these aspects will allow us not only to understand the process better, but also to explain the discrepancies between the EDX and XPS results.

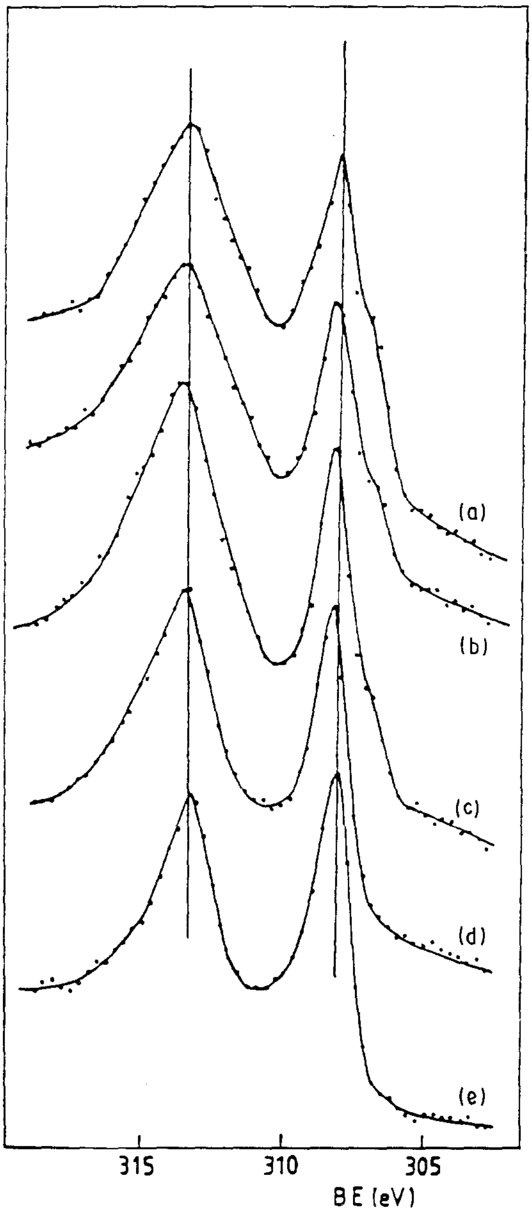


Figure 6 Rh 3d core level spectra of catalyst gauzes (a) 1, (b) 4 and (c) 8, and of catchment gauzes (d) 1 and (e) 3, in the medium-pressure plant C.

Fig. 9a and b show the morphology of catalyst wires used in a medium-pressure plant. From these pictures, it is clear that "faceting" and reconstruction of wires occur to a greater extent in the top gauzes (Fig. 9a) than in the bottom ones (Fig. 9b). An opposite trend is, however, observed with intergranular "etching", which becomes strong in the bottom gauzes and negligible in the top ones. The morphological changes in catalyst gauzes brought about by progressive

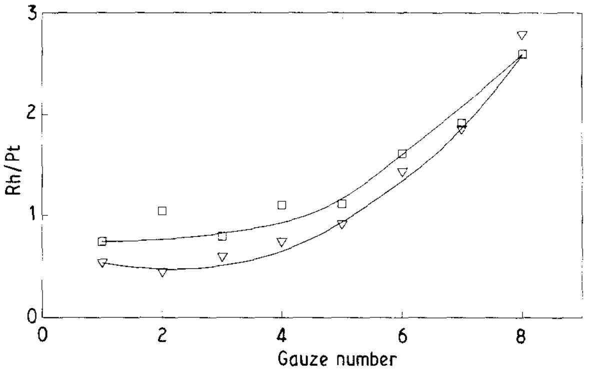


Figure 7 Dependence of the Rh/Pt ratio of catalyst gauzes from plant B on the location within the pack: (▽) front face; (□) back face.

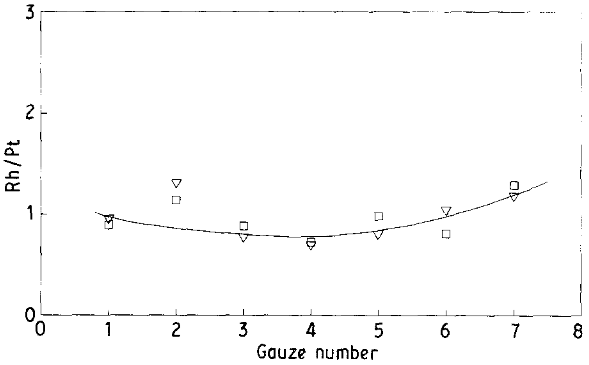


Figure 8 Dependence of the Rh/Pt ratio of catalyst gauzes in plant C on the location within the pack: (▽) front face; (□) back face.

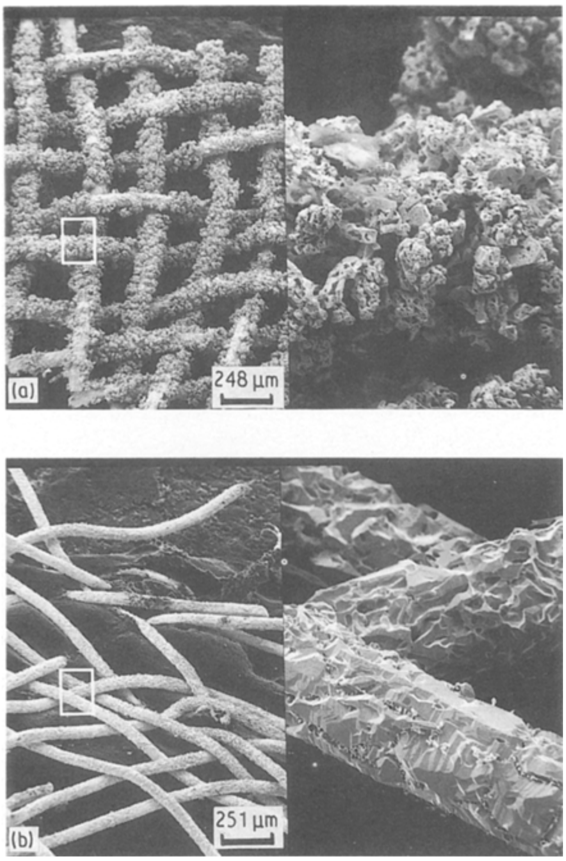


Figure 9 Scanning electron micrographs of the catalyst gauzes of a medium-pressure plant D: (a) 1; (b) 5.

“etching” and “faceting” are shown in Fig. 10a–c. The “etching” is intergranular and the “faceting” negligible in Fig. 10a, both intergranular “etching” and “faceting” are important in Fig. 10b, and the “etching” becomes intragranular and the “faceting” very strong in Fig. 10c. A strong intergranular attack, together with negligible “faceting”, as occurs in the bottom gauzes of packs of low- and medium-pressure plants, give rise to a very heterogeneous surface, because the Rh/Pt ratio is low within each grain but it attains very high values at grain boundaries. Under these circumstances, the contribution of grain boundaries to the overall analysis is overestimated by the non-surface sensitive EDX technique, while this contribution is underestimated by the surface-sensitive XPS technique. This is likely to be the origin of the discrepancies of quantitative EDX and XPS data for the bottom gauzes of the pack. In contrast, strong “faceting”, as occurs in the top gauzes, yields a much more homogeneous wire surface, which led to consistent analyses.

TABLE IV Surface composition of spent gauzes

Sample	Rh/Pt	Pt/Pd	Rh/Pd
C-1 (cat.)	0.82	–	–
C-4 (cat.)	0.46	–	–
C-8 (cat.)	0.40	–	–
C-1 (rec.)	0.46	0.47	0.22
C-3 (rec.)	0.28	0.15	0.04
F-1 (cat.)	0.50	–	–
F-3 (cat.)	0.22	–	–

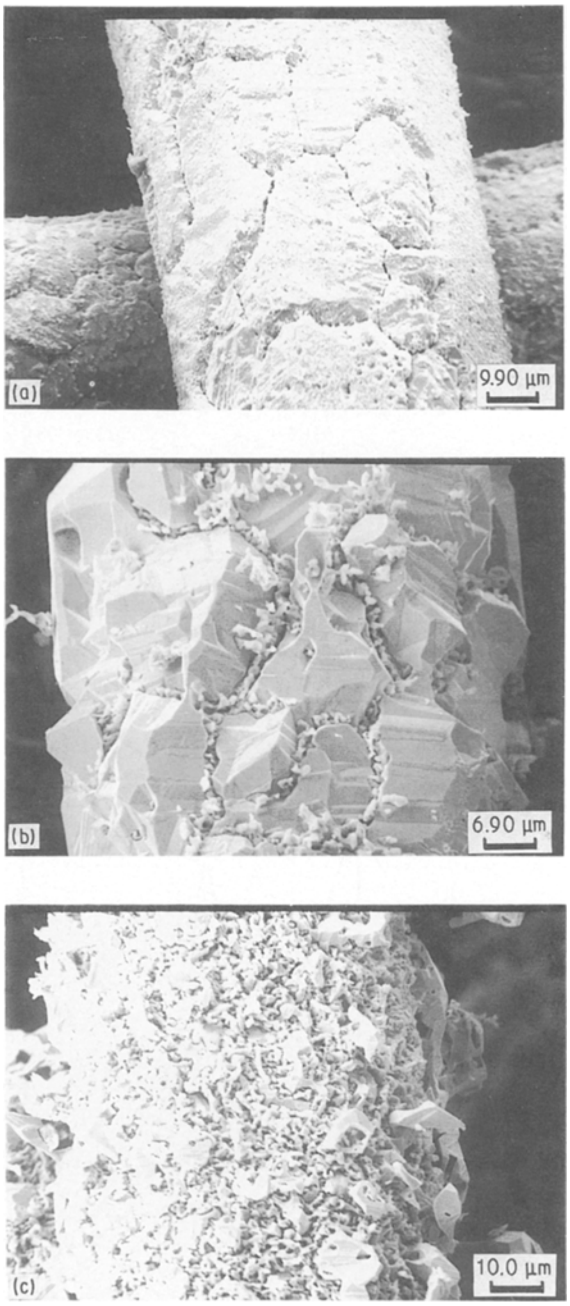


Figure 10 Scanning electron micrographs of catalyst gauzes with different degrees of “etching” and faceting.

3.3. Analysis of catchment gauzes

The characterization of the catchment gauzes used in a high-pressure plant, carried out elsewhere [17], is now extended to the medium-pressure plants. Fig. 11 shows the Pd 3d core level XPS spectra. The BEs of the most intense Pd 3d5/2 peak of samples C-1 and C-3 at 334.4 and 334.5 eV are characteristic of Pd°. However, this peak shows a small shoulder in Sample C-1 and a bigger one in Sample C-3 on the high BE side, whose BE closely corresponds to PdO. As occurs in catalyst gauzes, and judging from the BE of Pt 4f and Rh 3d levels (Table III), both platinum and rhodium are in the metallic state. This finding contrasts again with our earlier study on the catchment gauzes [17], used in a high-pressure plant, in which only metal oxides were detected.

The Pt/Pd and Rh/Pd atomic ratios have also been calculated for Samples C-1 and C-3, and are sum-

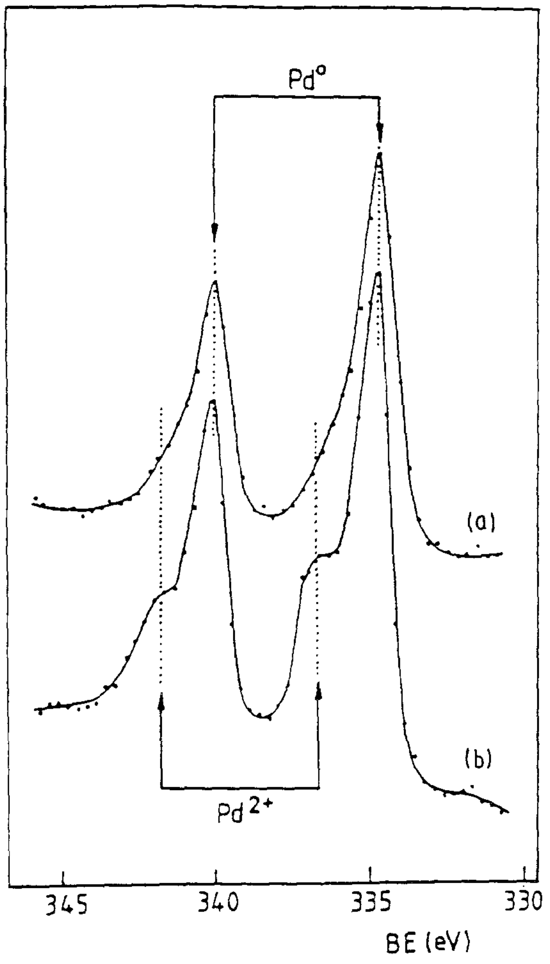


Figure 11 Pd 3d core level spectra of catchment gauzes in the medium-pressure plant C: (a) 1, (b) 3.

marized in Table IV. As can be seen, both ratios decrease from the top to the bottom of the gauze pack, which indicates the directional effect of metal recovery. It is also noted that platinum concentration in the catchment gauzes of the medium-pressure plant is lower than in those of a high-pressure one, as expected from the lower evaporation rate of PtO_2 from catalyst wires in the former case. In agreement with these results are also the Pt/Pd EDX ratios (Fig. 12), which show again the Pt/Pd ratio to decrease downstream, as well as the differences between the front and back face of the wires; both facts support the directional deposition of metals. Finally, the almost coincident EDX and XPS results are due to the strong "faceting" observed in this case, which makes the surface homogeneous.

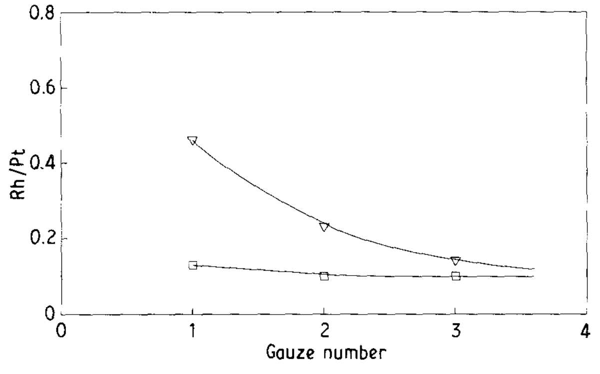


Figure 12 Dependence of the Pt/Pd ratio of catchment gauzes in plant C on the location within the pack: (▽) front face; (□) back face.

4. Conclusion

From the comparative study on the morphology and the chemical state of the catalyst and catchment gauzes used in medium- and low-pressure ammonia oxidation plants to that on a high-pressure plant, it results that the operation conditions of the reactor decisively influence not only the reconstruction of the wires but also rhodium-enrichment in the catalyst and platinum-enrichment in the recovering gauzes, as well as the oxidation state of noble metals. The lower oxygen partial pressure and lower reaction temperature in the medium- and low-pressure plants keep mainly noble metals in the metallic state. In this case, the activity loss observed at the end of the catalyst's life can be associated with Rh° enrichment in catalyst wires, instead of the Rh_2O_3 phase [16] found in a high-pressure plant.

Acknowledgements

The technical assistance of Mrs L. Bajón with SEM and of Mr E. Pardo with XPS is greatly appreciated.

References

1. J. A. BUSBY, A. G. KNOPTON and A. E. R. BUDD, *Proc. Fert. Soc.* **169** (1978).
2. J. E. PHILPOTT, *Plat. Met. Rev.* **15** (1971) 52.
3. M. PSZONICKA and T. DYMKOWSKI, *Pol. J. Chem.* **52** (1978) 121.
4. M. FLYTZANI-STEPHANOPOULOS and D. SCHMIDT, "Progress in Surface Science", Vol. 9 (Pergamon Press, Oxford, 1979) p. 83.
5. M. FLYTZANI-STEPHANOPOULOS, S. WONG and L. D. SCHMIDT, *J. Catal.* **49** (1977) 51.
6. A. R. McCABE, G. D. W. SCHMIDT and A. S. PRATT, *Plat. Met. Rev.* **30** (1986) 54.
7. J. ZABRZESKI and R. ZMYSLONY, *Appl. Catal.* **35** (1987) 13.
8. D. R. ANDERSON, *Stud. Surf. Sci. Catal.* **38** (1988) 445.
9. *Idem., J. Catal.* **113** (1988) 475.
10. A. R. McCABE and G. D. W. SCHMIDT, in "Proceedings of the 8th International Congress on Catalysis", Vol. 4, Berlin, 1984 (Verlag Chemie, Weimheim, 1984) p. 654.
11. L. D. SCHMIDT and D. LUSS, *J. Catal.* **22** (1971) 269.
12. M. PSZONICKA, *ibid.* **56** (1979) 472.
13. R. W. McCABE, T. PIQUET and L. D. SCHMIDT, *ibid.* **32** (1974) 114.
14. J. SCHROEDER, J. JARMAKOWICZ and J. ZBRZESKI, *J. Catal.* **82** (1983) 66.
15. J. A. BUSBY and D. L. TRIMM, *Chem. Engng J.* **13** (1977) 149.
16. J. L. G. FIERRO, J. M. PALACIOS and F. TOMAS, *Surf. Interface Anal.* **13** (1988) 25.
17. *Idem., ibid.* **14** (1989) 529.
18. J. K. BRADLEY and G. DRAKE, *Proc. Fert. Soc.* **200** (1981).
19. A. R. McCABE and G. D. W. SCHMIDT, in "Proceedings of the 11th International Precious Metals Institute Conference", Brussels, 1987, p. 607.
20. C. D. WAGNER, L. E. DAVIS, M. V. ZELLER, J. A. TAYLOR, R. H. RAYMOND and L. H. GALE, *Surf. Int. Anal.* **3** (1981) 211.

Received 4 October 1990
and accepted 20 March 1991