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LETTER TO THE EDITORS

Rhodium Oxide Formation on the Surface of Pt–Rh Gauzes Used in the Catalytic Oxidation of Ammonia

In their work on Pt–Rh gauzes used as catalysts for ammonia oxidation, Contour *et al.* (*1*) have shown that rhodium oxide forms at the surface. We have recently studied similar gauzes (*2*), and would like to add further information and contribute some comments.

Contour *et al.* (*1*) found at the surface of used catalyst a fine rhodium oxide layer 20 Å thick, accompanied by a rhodium-enriched layer extending to a depth of about 1 μm. These observations concern a relatively thin subsurface layer of 2–3 μm and suggest that the composition of the deeper layers is equal to the composition of the fresh catalyst.

We have studied (*2*) Pt-90%, Rh-10%-catalyst gauzes (wire diameter of 76 μm)

(a)

FIG. 1. Scanning electron micrographs of rhodium oxide sheaths separated from the wire core: (a) sheaths magnified 100×; (b) fragment of single sheath, magnified 1000×; (c) fragment of the sheath wall, magnified 10,000×.

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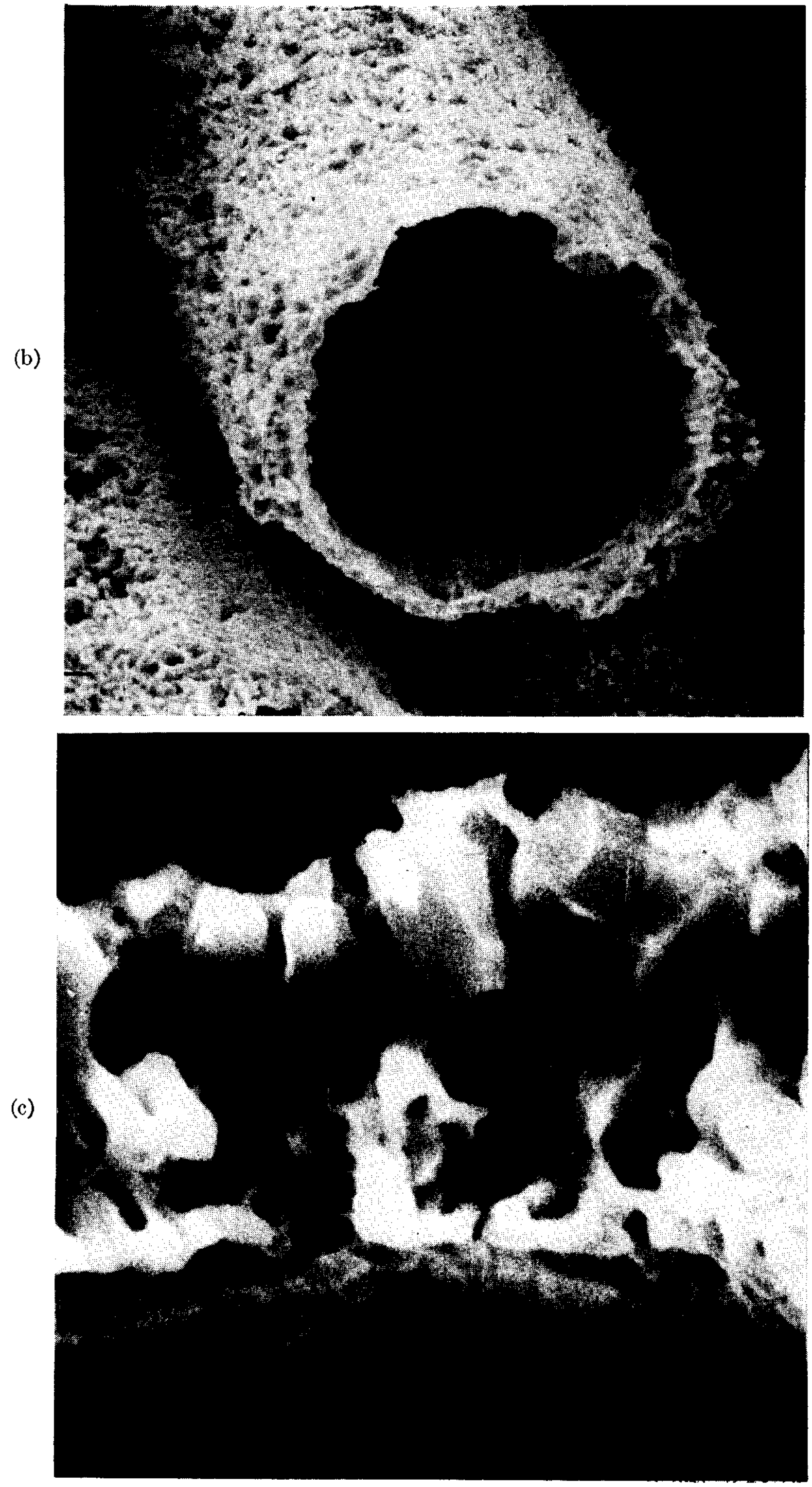

FIG. 1—*Continued.*

used for the ammonia oxidation process under the following technical conditions: pressure 4 atm., temperature 870°C, total working time of the catalyst ca. 4500 hr, four gauzes used in a burner. Using X-ray microanalysis to study a cross-section of gauze wire we have found that the spent catalyst wires are sheathed with a rhodium oxide envelope whose thickness attains 8 to 10 μm; i.e., it is some thousand times thicker than that found by Contour *et al.* (*1*). This oxide layer is compact and strong enough to be isolated by chemical dissolution of the wire core. As a result of this operation, cylindrical tubelike sheaths are obtained as shown in Fig. 1. Their shape was determined and their wall thickness was estimated by the scanning electron microscope.

The rhodium oxide layer grows gradually during catalyst use. After 10 hr of usage a few agglomerates of rhodium oxide appear; 100 hr later, the agglomerates become larger and many others are formed. After 1000 hr the cylindrical rhodium oxide sheath can be chemically isolated. It is very fine and fragile with many voids. After 2000 hr the sheath becomes visibly thicker and more compact. Microscopic examination and X-ray microanalysis show that in the lateral cross section of wires taken from spent catalyst gauzes, three zones differing in composition and structure can be distinguished as follows:

(1) an external layer composed of partially disintegrated Pt–Rh crystallites, loosely bound to the layer beneath, the crystallites containing numerous voids, cavities, and crevices;

(2) a rhodium oxide sheath in the form of a cylindrical envelope with a wall thickness of about 10 μm;

(3) a wire core (about 40 μm in diameter) with a platinum and rhodium content close to the composition of the fresh catalyst.

It appears that the differences between our results and the results obtained by Contour and co-workers (*1*) may be explained in the following ways: (a) a different type of technological burner and conditions of catalyst use result in a different modification of the catalyst wire during the same usage time, or (b) the observations of Contour *et al.* concern only the outer layer of crystallites under which the thick solid oxide layer is formed.

It seems that the three-layer model for the wire structure can explain the decrease of catalyst activity. The oxide layer gradually isolates the metal core from the reacting gases, and after total destruction of the Pt–Rh crystallites in the outer layer the activity goes down. Our current work suggests that the rhodium enrichment of the wire surface with the concomitant formation of the thick rhodium oxide envelope is due not only to sublimation of platinum oxide from the surface but most probably it is caused also by a simultaneous segregation of rhodium from the wire core toward the surface. Analysis of the transverse cross section of the gauze wires shows clearly that during use of the catalyst the rhodium concentration in the wire core decreases from about 10% in new gauzes to about 9.6% after 4000 hr. The determination was carried out by X-ray microanalysis (SE-MQ-A.R.L.) and was based on a large amount of statistical material (three different gauzes, with 40 analyses for every gauze). The above phenomenon is still the subject of investigation and the final results will be published later.

REFERENCES

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