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# Physical and Chemical Characterization of Platinum–Rhodium Gauze Catalysts*

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Scanning electron microscopy, Auger spectroscopy, and sputtering techniques are used to examine platinum–10% rhodium gauze catalysts which had been employed in commercial oxidation of $NH_3$ and in production of HCN from $NH_3$, $CH_4$, and air.

It is shown by electron microscopy that the normal activation of these catalysts produced an increase in surface area and formation of randomly oriented facets. An HCN catalyst which was observed to have a high selectivity due to unknown causes was found to possess hollow crystalline structures built up from the original wire.

Catalyst samples which had been treated with ~100 ppm of $H_2S$ for higher activity showed entirely different morphology. In this case, the surface was again perfectly crystalline but consisted predominantly of (100) planes or another plane with two- or fourfold symmetry. Also the wires of the gauze were permeated by rectangularly shaped channels of $\sim 3\ \mu$ width which produced an expansion of the wires.

Chemical analysis by Auger spectroscopy combined with ion bombardment sputtering showed that the $H_2S$-activated catalyst contained negligible sulfur except at the original surface. Carbon was present to a considerable depth, and some silver was observed near the surface. Aside from these elements, the catalyst surface consisted of fairly pure platinum and rhodium.

## INTRODUCTION

Catalytic platinum gauzes are used in several important industrial processes such as the catalytic oxidation of ammonia and HCN synthesis. It is well-known that, while the catalytic surface affects the reaction between the reactants, the gases in turn cause changes in the structure of the surface. These changes are responsible for an initial activation period during commercial use.

Platinum loss is a major problem in the production of nitric acid from ammonia, and the direct catalyst loss accounts for about 85% of the operating cost of the conventional process (*1*). Parsons (*2*) has published several pictures showing the surface changes and Handforth and Tilley (*3*) published an extensive set of data on catalyst losses.

Bartlett (*4*) and Nowak (*5*) proposed a theory explaining platinum losses during ammonia oxidation as due to oxidation of the platinum. However, the correlation derived by Nowak (*5*) differs from the observed loss rate by a factor of about four.

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It was shown by Garton and Turkevich (*6*) that heating platinum ribbons to 1000°C for 10–24 hr in vacuum or in oxygen, pure ammonia, nitric oxide, or nitrogen pentoxide failed to produce structural changes equivalent to those obtained during ammonia oxidation.

The commercial synthesis of HCN is carried out on the same catalyst as that used for ammonia oxidation. Here also, changes in surface structure and roughness as well as an initial activation period have been reported in the literature (*7–10*). This reaction is carried out at a temperature of about 1125°C which is about 200° higher than that used in the ammonia oxidation. However the catalyst losses in this reaction are negligible (*7*) and certainly much smaller than those during ammonia oxidation, even though both incoming mixtures contain similar amounts of oxygen. However, it should be noted that the partial pressure of $O_2$ leaving the catalyst is much lower in the HCN process due to its consumption by reaction with $CH_4$. In the case of $NH_3$ oxidation the platinum loss can be reduced by reducing the $NH_3$ concentration in the feed.

It was found by Pan (*9*) that the crystalline structure of the gauze had an important effect on the selectivity of the reaction and that the fct structure had a better catalyst performance (a higher HCN yield) than that of the fco. Thus, surface rearrangements occurring during the activation period strongly influences the selec-

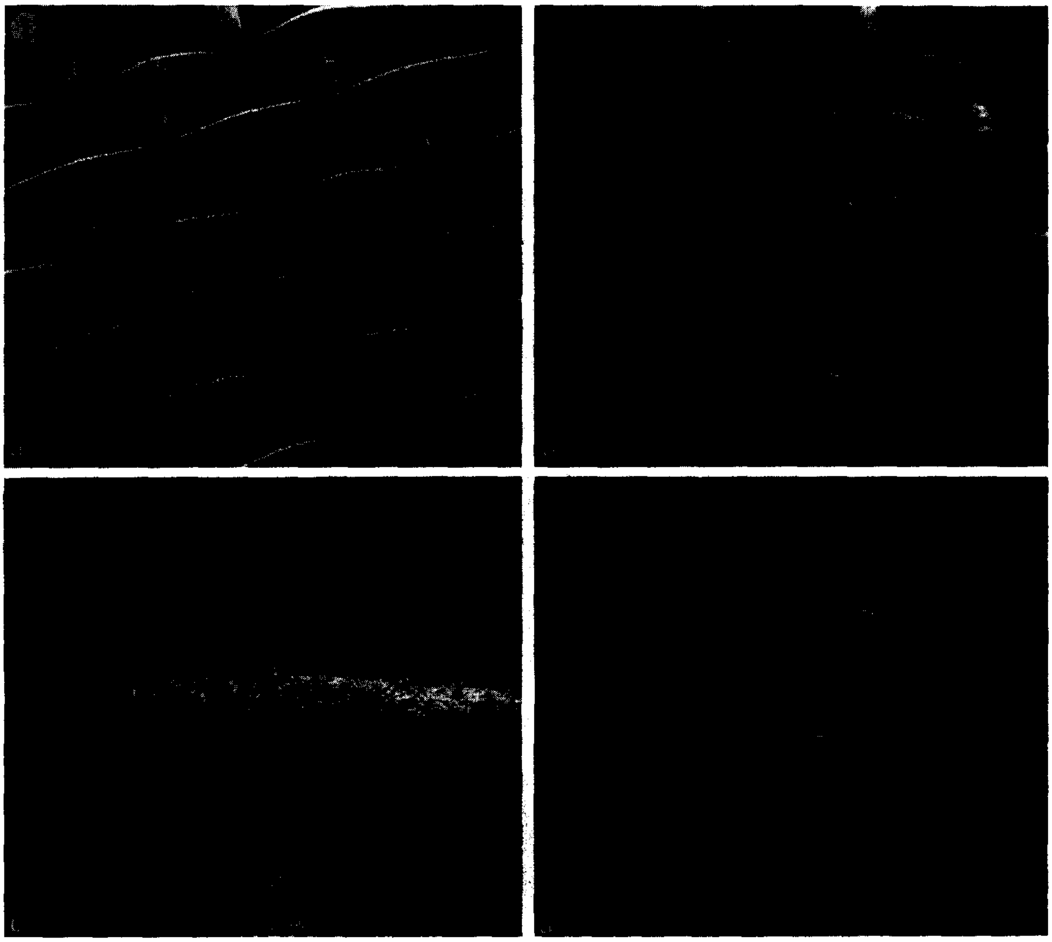

FIG. 1. Scanning electron micrographs of platinum–rhodium gauzes after use in ammonia oxidation. The original gauze is shown in (a), and photographs (b), (c), and (d) show a similar gauze after use for ∼4000 hr.

tivity of the reaction. These surface changes are often very sensitive to small changes in the gas composition. For example, it is reported (*11*) that addition of a small amount of sulfur containing compounds (2–200 mg S/m$^3$) during the first hours of HCN synthesis decreases substantially the activation period and increases selectivity.

In this work, we present a comparison of the structural changes occurring on platinum–rhodium gauzes in commercial convertors for these two reactions. The differences are most striking, and an understanding of their causes should be of much academic significance and industrial importance.

Samples were taken from commercial convertors used for ammonia oxidation and HCN synthesis. These two processes were chosen because of their industrial importance and since both use the same catalytic gauze (90% Pt, 10% Rh).

## AMMONIA OXIDATION CATALYST

An electron micrograph of the original Pt–10% Rh wire gauze before use in the reactor is shown in Fig. 1a. Figures 1b, 1c, and 1d show an identical gauze which had been in an ammonia converter for ~4000 hr at a temperature of 940°C and a pressure of 110 psig. The reaction mixture contained ~9% $NH_3$ in air and the gas velocity was ~30 ft sec$^{-1}$ (based on the reaction temperature).

It is evident that the wires have become roughened during use and that extensive facetting has occurred. These facets have a size range of 1 to 10 $\mu$ and consist almost entirely of flat crystal planes. The radius of curvature of the plane edges is $\leq 0.1\ \mu$.

The facets appear to be randomly oriented planes. One can observe many regions with sixfold symmetry characteristic of (111) planes (presumably the plane of minimum surface free energy) and also some regions with twofold and fourfold symmetry. There are also many facets at large angles to each other implying the existence of high index planes. The crystal structure of the alloy is assumed to be fcc, the structure of both constituent metals. While some distortion into tetragonal and orthorhombic structures has been reported by X-ray diffraction, it is regarded as unlikely that any structures except cubic could exist at the operating temperatures of 900 to 1200°C.

It is evident from Fig. 1d that many of the crystallites protrude considerably from the wire surface, some of these protrusions appearing to form bridged structures. There are also a small number of noncrystalline regions. On the other catalysts examined few of these noncrystalline particles were observed. It is suggested that these may be either oxides, particles which impinged during reaction, or dust particles introduced after the catalyst was removed from the reactor.

## HCN CATALYSTS

### *Normal Catalysts*

Figure 2 shows gauzes after use in HCN production. These catalysts had been in use for 2600 hr (Fig. 2a) and 1125 hr (Figs. 2b and 2c) at 1125°C with a reaction mixture of 12% $NH_3$ and 13% $CH_4$ in air at 1 atm. The velocity of the reactants was 15 ft sec$^{-1}$ and the HCN yield from this catalyst was ~65%.

The original wires are evident in Fig. 2a, but even more extensive facetting is evident than was observed in ammonia oxidation. Several layers of gauze are present in this and succeeding micrographs because the layers were fused together in use. Except for the more extensive rearrangement, the crystallites are generally similar to those observed before: perfect facets of a somewhat larger size are exposed.

### *High Conversion Catalyst*

Electron micrographs of a catalyst which for unknown reasons had been observed to produce an unusually high conversion as an HCN catalyst are shown in Fig. 3. This catalyst had been in service for ~1770 hr under conditions nominally identical to those above but gave a 5% higher yield of HCN. In Fig. 3a the individual wires are clearly evident as before. However in addi-

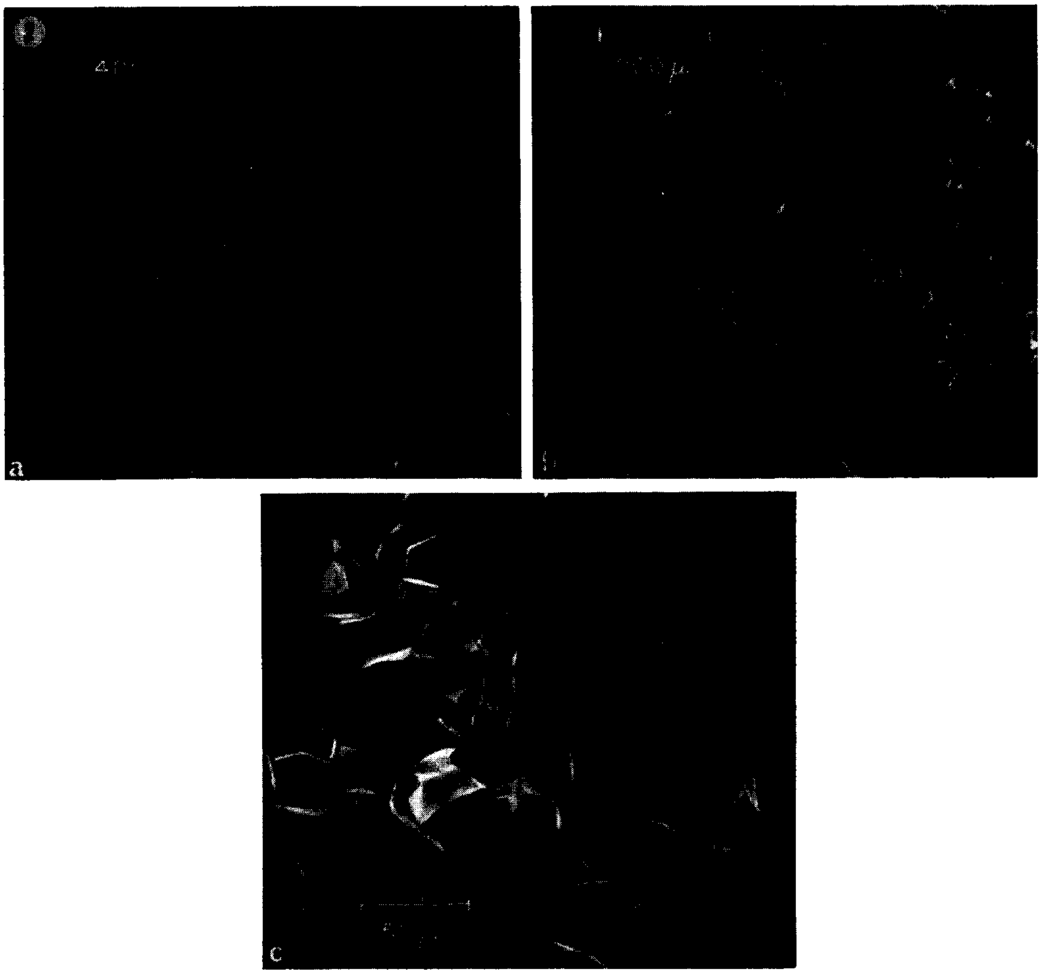

FIG. 2. Scanning electron micrographs of gauze after use in HCN production. The individual wires are evident but even more extensive facetting has occurred than in $NH_3$ oxidation.

tion to the facetting observed on the "normal" catalyst, there are now evident large hollow structures built up from the wires. Figure 3b shows an enlargement of the region indicated by dashed lines in Fig. 3a. This shows a single wire of the gauze. Figures 3c and 3d show this wire at even higher magnification. In Fig. 3c, a single structure is shown; in addition the normal facetting is evident on the wire itself. The angles between planes again indicates that randomly oriented facets are formed.

### *Sulfur Treated Catalysts*

In Fig. 4 are shown electron micrographs of two catalysts which after ~1000 hr in normal HCN production had been treated with ~100 ppm of $H_2S$ for 110 hr during continued HCN production. Upon addition of $H_2S$ a 4% increase in HCN production and a 20° increase in temperature were observed. In Figs. 4a and 4b the individual wires are again evident, and again considerable facetting has occurred. However in this case the structure is quite different: the wires are permeated by many channels which are *all rectangular* with outside dimensions of 2–4 μ.

The crystal planes exposed on this surface are also completely altered: instead of random planes the surface now exposes predominantly either (100) planes or another plane for which the edges would form right angles. Figure 4d shows an example where

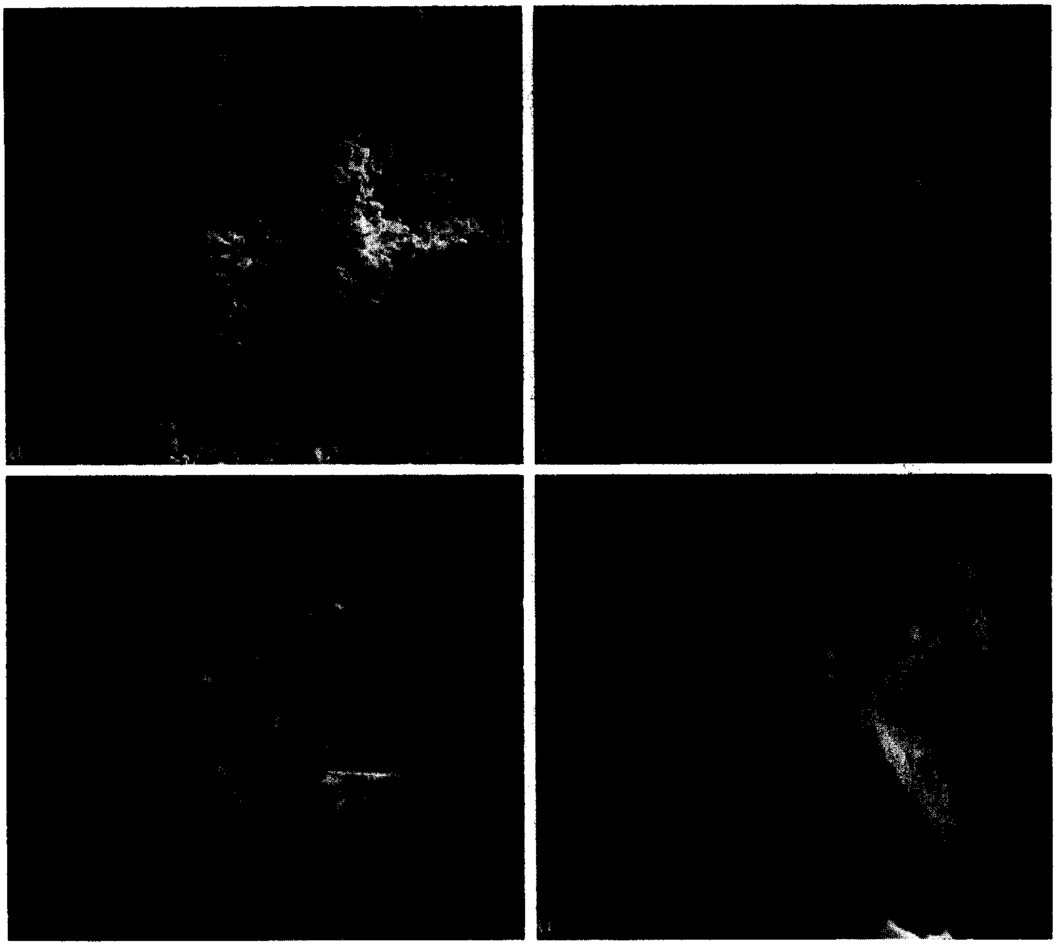

FIG. 3. Scanning electron micrographs of gauze which gave higher yields in HCN production. The dashed regions in (a) are shown at higher magnification in the succeeding photographs. Large built-up crystallites on the wires are evident.

(100) planes probably exist. The structures here are triangular pyramids which point in the [111] direction; however, the walls of these pyramids appear to be (100) planes. Also note that the holes in these walls are all rectangular or square.

It is also evident that the two $H_2S$-treated catalysts (Figs. 4b and 4c) have a slightly different morphology. Also on both surfaces there are some convex and concave facets, in contrast to the previous catalysts where only planar structures were noted.

A final difference between the $H_2S$-treated catalysts and the normal ones is that accompanying the formation of the channnels the wires have evidently *expanded*. This provides an obvious explanation for the fact that a gradual increase in the pressure drop occurs with these catalysts.

## CHEMICAL COMPOSITION

At present one of the major complications in interpreting practical catalytic reactions on an atomic scale is the almost complete lack of information on the chemical composition of the surface layer in engineering situations. The active surfaces in the present reactions are probably not 90% platinum and 10% rhodium: The surface composition of these elements probably differs from the bulk composition and there may be many other species in or near the surface layer.

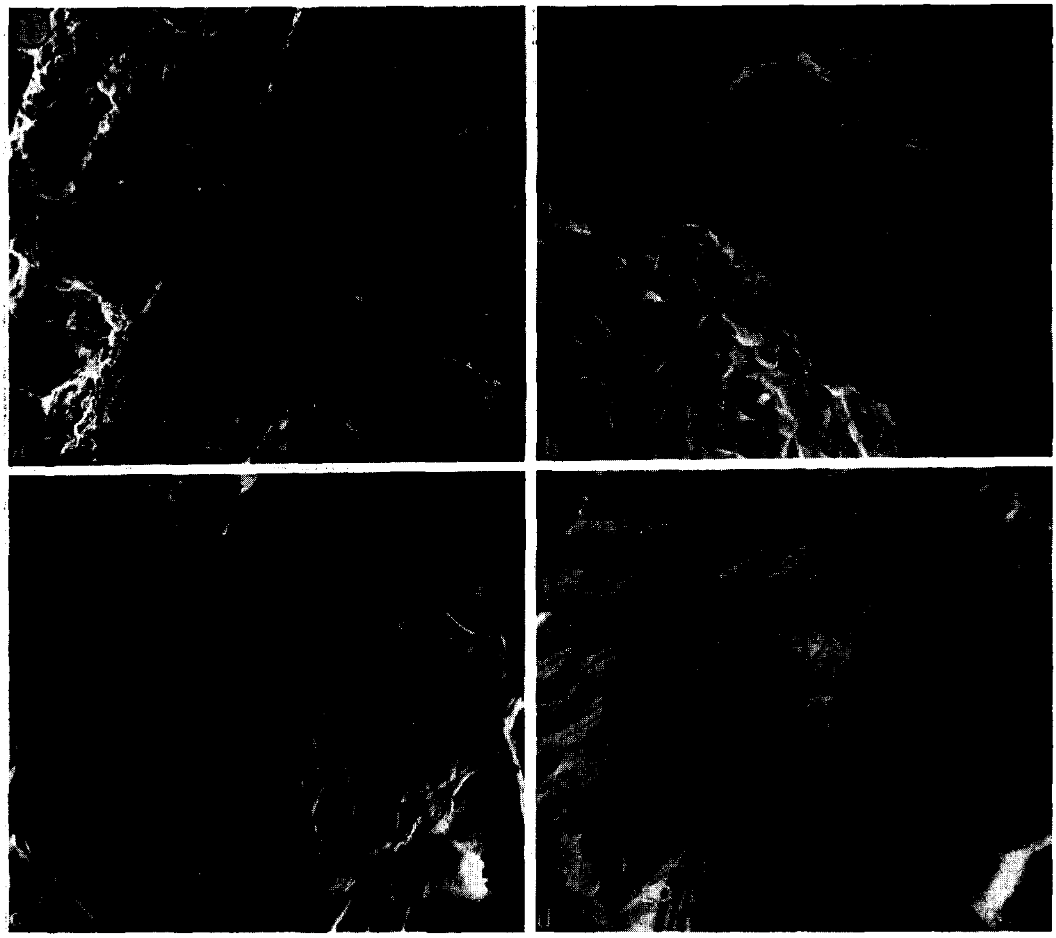

Fig. 4. Scanning electron micrographs of gauzes which had been treated with ~100 ppm of $H_2S$ during HCN production. Rectangular channels have been produced in the wires.

It is known that, upon exposure to air, polished or etched platinum surfaces consist almost entirely of carbon and sulfur to a depth of many atom layers (*12*); evidently the carbon and sulfur containing compounds in air decompose on the platinum surface rapidly enough that it would be impossible to eliminate them except by using ultrahigh-vacuum procedures throughout.

The above considerations imply that the surface layer will probably change in composition upon cooling from the reactor temperature and being transferred into the measuring apparatus. However by combining Auger chemical analysis and ion-bombardment sputtering to selectively remove known thicknesses of material from the surface, it should be possible to qualitatively determine compositions of the actual catalytic surface.

### *Auger Spectroscopy*

In Auger electron spectroscopy (*13, 14*), a solid is bombarded by high-energy electrons (typically 1000–3000 V) which cause core excitations of the constituent atoms. Some of these are de-excited by radiationless (Auger) processes whereby an electron from an upper level drops to the core level, and, to conserve total energy in the process, another electron is raised in energy. The energy of this electron is characteristic of the atom (approximately the X-ray energies). Thus by measuring the energies of the Auger electrons emitted from the solid, one can identify the atoms in which the process is occurring.

This technique is highly sensitive to surface composition because both the primary and Auger electrons have a mean free path of only a few atom diameters in solids; therefore, only atoms within the first few atom layers of the surface will emit detectable Auger electrons (*13*, *14*).

Other techniques for chemical analysis of surfaces, the electron microprobe and photoelectron spectroscopy, while capable of detecting elements at surfaces, sample a much thicker region because of the greater penetrating powers of X-rays and high-energy electrons.

The major problems in qualitative and quantitative analysis of surfaces by Auger spectroscopy are the possibility of overlapping peaks which may obscure certain elements and the uncertainty of the intensity calibration for most elements. While intensities appear to be proportional to concentration (in submonolayer amounts), there is no way to determine absolute concentrations except by independent calibration.

### *Ion Sputtering*

When high-energy ions (100–1000 V) strike a surface, they induce evaporation of atoms from the substrate (*15*). Since at high energies this process is primarily one of momentum transfer, it is fairly insensitive to the chemical nature of the atoms; therefore, by bombardment with inert gas ions, it is possible to more or less uniformly remove atoms from a substrate. Sputtering yields (atoms removed/incident ion) have been measured for most pure materials (*15*). From the flux (current) of bombarding ions one can therefore estimate the amount of material removed from the substrate by sputtering.

### *Apparatus and Procedure*

The sample was alternately chemically analyzed and xenon ion bombarded in a metal ultrahigh-vacuum system. The system was evacuated and baked at 180°C until a pressure of $\sim 10^{-9}$ Torr was attained. A manipulator permitted the sample to be positioned either for Auger spectroscopy or ion sputtering. The sample could be positioned in each configuration with sufficient reproducibility that the same region could be examined after each cycle.

The Auger electron spectrum was obtained in a hemispherical retarding analyzer (*14*). The signal was double differentiated with a lock-in amplifier to minimize electrical noise. The output signal, $d^2I/dV^2$, is proportional to the first derivative of the energy distribution. However, it has been found that the peak amplitude of this signal is proportional to the Auger electron intensity.

For sputtering, Xe was introduced into the system and $Xe^+$ ions of 500 V energy were allowed to impinge on the sample for known currents and times. Typical currents and times were 1 to 10 μamp and 1 to 2000 sec. The beam from the ion gun impinged more or less uniformly on a region of the sample ~3 mm in diameter, while the Auger electron beam impinged on a region ~1 mm in diameter.

### *Chemical Composition vs Depth*

The $H_2S$-treated catalyst shown in Fig. 4 was examined in this manner. Typical Auger spectra are shown in Fig. 5. The energies of several Auger peaks are indicated at the bottom of the figure. Spectra were obtained from the original surface, and after sputtering 4, 14, 70, 170, 1170, and 7200 layers of material. In Fig. 6, the intensities of the various peaks are plotted vs depth.

There are overlapping peaks for several elements which make some assignments uncertain. The major platinum peaks (*12*) at 170 and 240 V were proportional to each other at all depths giving an unambiguous assignment to platinum. Both sulfur and platinum give peaks at 150. However after 7200 layers had been removed, this peak is a doublet identical in shape to that reported for pure platinum (*12*). The sulfur content was, therefore, estimated by subtracting the platinum contribution to this peak from the total. On the original surface the 150-V

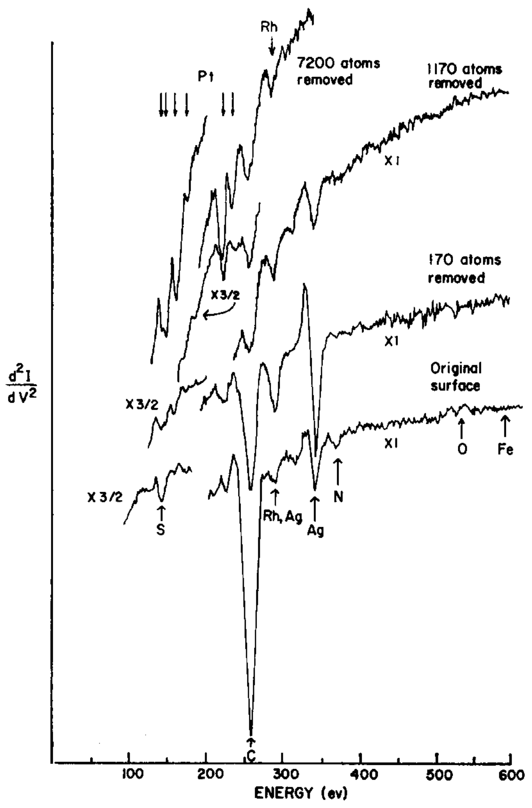

FIG. 5. Typical Auger electron spectra of the sulfur treated catalyst after various amounts of material had been removed by xenon ion sputtering. The positions of some of the elements are indicated.

peak must be due almost exclusively to sulfur because all of the other platinum peaks are very small.

There is a peak at ~350 V which is evident on the original surface, reaches a maximum at 170 layers, and disappears by 7200 layers. This is probably due to silver (*16*) which has a major peak at 349 V. Silver has a satellite peak at ~300 V, and therefore, quantitative assignment of rhodium (*17*) (major peak at 305 V) is not possible when the silver content is large.

The ordinate scale in Fig. 6 is arbitrary and has been chosen for each element to roughly correspond to *assumed* amounts. The original surface appears to consist predominantly of carbon (single peak at 270 V) and sulfur, but the Auger peaks from these elements are very strong, and other elements may be present in greater amounts than indicated. No iron (peaks at 600, 650, and 720 V) or oxygen (single peak at 520 V) were detected at any depth, and no sulfur or nitrogen (380 V) were detected beyond the first few layers.

The depth scale is also somewhat uncertain. This was estimated by assuming a sputtering yield of pure platinum metal. While this should be a good assumption for the bulk catalyst which contains 10% rho-

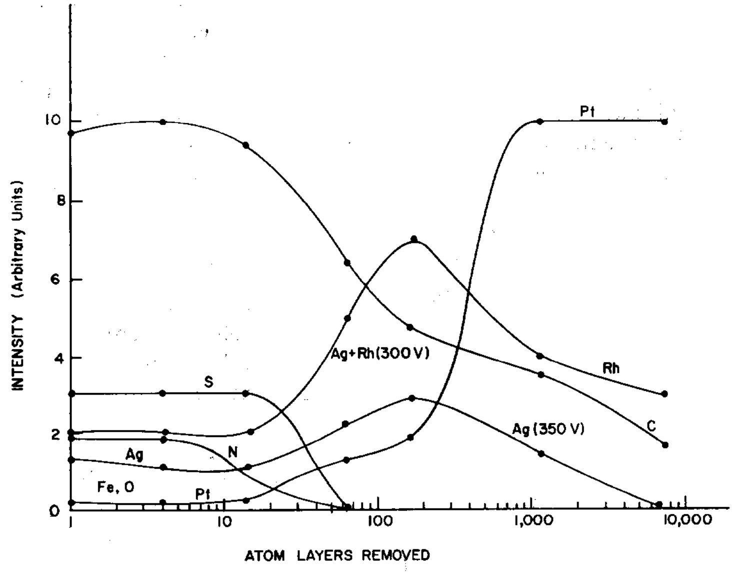

FIG. 6. Plot of intensity of several Auger peaks versus number of atom layers removed for a sulfur-treated HCN catalyst. Both axes are regarded as having only qualitative significance.

dium as the only impurity, near the surface one might expect the yield to differ markedly from this value. Therefore, the depth scale should be regarded as only qualitative until the platinum approaches its bulk concentration. Furthermore, the depth of the layer sputtered is probably not uniform. The sputtering yield depends sensitively on the angle of incidence, and, since the surface is highly facetted, different facets will be sputtered to different depths. The Auger electron beam samples an area large compared to facet dimensions, and therefore, the quantities measured should be an area weighted average.

Several interesting features are evident from these results. First, there is no detectable sulfur beyond the first few layers. This shows that treatment with $H_2S$ does not produce bulk contamination with sulfur. Second, there are no metal impurities in significant amounts except for traces of silver. The origin of the silver is not known, but it is not present in the bulk, and its concentration appeared to vary somewhat with position on the surface. Third, there may be an excess of rhodium near the surface compared to its bulk concentration; however, this conclusion is only tentative because of peak overlap. Fourth, while sulfur and nitrogen exist only near the original surface, carbon appears to be present at greater depths.

## DISCUSSION

The scanning electron micrographs indicate that marked surface rearrangements occur and that the surface atoms seem to possess mobility under reaction conditions. Both reactions occur at a very rapid rate. The commercial rate of ammonia oxidation is about $2.4 \times 10^{19}$ molecules/sec cm$^2$ while that of HCN is about $2 \times 10^{19}$ molecules/sec cm$^2$. Both these values are based on total conversion per original total surface area of the gauze. The reaction is often completed in the first layers of the gauze, and hence the actual rate might be even higher. These rates are rather close to the maximum possible mass transfer rate. However, the striking differences in the surfaces must be due to differences in surface chemistry and temperature.

These surface changes are of significant industrial importance. In the ammonia oxidation process the conversion is extremely high, and an important engineering goal is to change the surface structure such as to reduce the platinum loss without affecting the conversion. This might be accomplished by the addition of a trace component, and we believe that the economic advantages amply justify a thorough investigation of this possibility.

The HCN synthesis is a rather complex reaction in which the heat generated by the partial combustion of the cheaper reactant ($CH_4$) compensates for the endothermicity of the HCN production reaction. The change of the selectivity of this process by the addition of trace amounts of $H_2S$ should be investigated further. A continuous addition of $H_2S$ may increase the pressure drop through the gauze beyond practical values, and it should be of interest to explore the long-term effect of an initial activation with sulfur compounds on the catalyst structure and selectivity. The sensitivity of the selectivity to the surface structure raises the possibility that the method of gauze preparation strongly affects its performance in commercial convertors.

### *Facetting*

There appear to be no obvious explanations for the extreme facetting which accompanies reaction. While vapor transport of volatile platinum oxides provides a possible mechanism, the absence of metal loss in the higher temperature HCN process and the absence of facetting when the metal is heated in any of the reactants individually (*6*) implies that other processes may be operative. Other possible mechanisms associated with the exothermicity of the reactions are reaction-facilitated surface diffusion, production of energetic platinum atoms by reaction, and formation of hot regions locally on the surface. The relevant parameters are not known well enough to estimate the feasibility of these processes.

Surface tension provides a restoring force tending to minimize the surface area. This must be balanced by driving forces such as temperature gradients or flow patterns to give the observed behavior.

It is possible that both channeling and facetting could arise from preferential removal of material (perhaps as volatile oxides) around defects: removal of metal from a line defect (screw or line dislocations) could produce a channel, and removal from a grain boundary could lead to facetting. This removal may be caused by an increased rate of reaction at these defects with consequent local heating. To account for the fact that channels are only observed upon addition of $H_2S$ to the reaction mixture, sulfur is postulated to "catalyze" the reaction at line defects; otherwise reaction proceeds only at grain boundaries. Both channels and facets could be propagated by ignition of the reaction in the crevices thus formed.

One effect of addition of $H_2S$ is to cause (100) facets to develop. Presumably the surface energy of this plane is lower than the other planes in the presence of sulfur. Facetting of metal surfaces produced by gases is fairly common. For example the (111) planes of silver and nickel, also fcc metals, have by low energy electron diffraction been shown to facet into (100) planes upon exposure to sulfur (*19*, *20*).

### *Chemical Composition*

While the techniques employed here are very powerful ones for examining surface compositions, we regard the results presented here as having only qualitative significance and as indicating the directions which additional work should take. For example, the environment must be carefully controlled in the time between use of the sample as a catalyst and its chemical analysis. In the present situation it is impossible to determine whether the carbon, and sulfur and nitrogen on the surface were introduced during operation of the reactor or afterwards (their *absence* beyond the surface layer is assured, however). In addition, measurements must be made on catalysts whose composition and conditions of operation are more precisely defined. The surface composition of a fresh platinum–rhodium alloy has never been determined. While there appeared to be an excess of rhodium in the surface layer after use, the same could well be true of the original surface.

Finally, the Auger spectra and sputtering yields must be calibrated before they can be employed as quantitative tools. Sensitivities can easily be calibrated by depositing known amounts of the elements of interest on the substrate in the vacuum system and determining the resulting Auger spectra. Sputtering yields from complex materials can be determined in a similar fashion.

An obvious extension of the methods described here would incorporate scanning electron microscopy, Auger spectroscopy, and ion sputtering in the same ultrahigh-vacuum system. In this way, one could precisely determine the physical structure of the region being analyzed. Also the structures of the pits in the surface could be examined by sputtering away the original surface to large depths (1–10 $\mu$) to expose the interior of the voids. Capabilities for conducting such studies are currently being developed in this and other laboratories.

## ACKNOWLEDGMENTS

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