JOURNAL OF CATALYSIS 38, 218-222 (1975)

Auger Spectroscopic Study of the Poisoning of a Commercial Palladium-Alumina Hydrogenation Catalyst

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Received December 10, 1974

A commercial palladium-alumina catalyst used for the selective hydrogenation of diolefins in an olefin-aromatic-paraffin stream had lost most of its hydrogenation activity. It was examined by Auger electron spectroscopy after other typical physical measurements on the spent catalyst had failed to clearly establish the cause or causes of catalyst deactivation. Surface areas and levels of S and Cl in the fresh and the spent catalysts were not significantly different. However, iron to the extent of 1.7% by weight was found on the spent catalyst. This level of iron on a ~200 m^2/g surface area support is not necessarily a poison. However, Auger surface analysis has now revealed that iron was coating a majority of the palladium catalyst surface thereby masking (and poisoning) the active Pd surface atoms as well as the atoms of the promoters like Cr and Mo. The iron deposited on the catalyst came from a bad batch of feedstock. The surface analysis by Auger electron spectroscopy also revealed substantial amounts of surface Ca and large gradients of Pd, Cr, and Mo, from the outside to the inside of the pellets. The spent catalyst also had much higher amounts of iron on the outside than the interior surface of the catalyst pellets.

INTRODUCTION

A commercial selective hydrogenation catalyst (in the form 3/16 in cylindrical pellets) lost most of its activity during normal operation. This catalyst consists of 0.5% Pd, with chromium and molybdenum added as promoters, supported on a γ-alumina support. It is used for the selective hydrogenation of diolefins in an olefin-aromatic-paraffin containing stream. The loss in catalyst activity appeared to be associated with a change in feedstock that occurred a few days before. The catalyst was unloaded, the loose dust screened, and analyzed by X-ray fluorescence spectroscopy (XRF). The XRF analysis showed the presence of 1.7% Fe, 0.16% S and 0.01% Cl. This level of iron is not necessarily a poison since iron oxide is a weak hydrogenation catalyst and moreover this amount of Fe is not very large for a ~200 m^2/g surface area support. As far as sulfur is concerned, about 0.1% is also present in the fresh, active catalyst. The sulfur is very likely in sulfide or sulfate form and is not deleterious to catalyst activity. The surface area of spent catalyst was also not changed significantly. Auger electron spectroscopic analysis was performed on the fresh and the spent catalyst to understand the cause or causes of catalyst deactivation. The very high sensitivity and the usefulness of Auger analysis in catalytic (*1*) and other surface studies (*2,3*) have been reported recently. This paper describes how the Auger analyses have helped in understanding the catalyst deactivation problem.

EXPERIMENTAL METHODS

No sample preparation was necessary for Auger analysis, however, precaution was taken not to touch samples by hand and to cleave the catalysts without

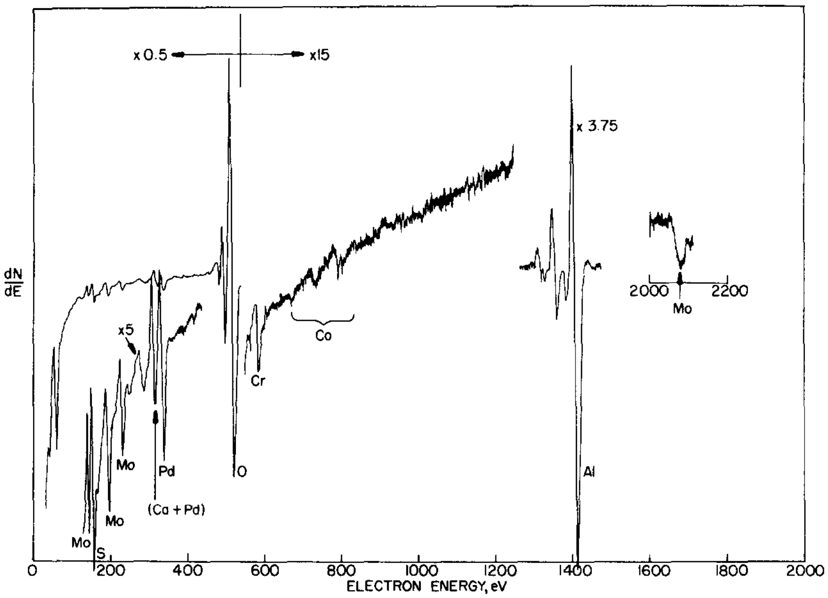

FIG. 1. Auger analysis of fresh catalyst (outer surface).

scraping so as not to introduce any iron to the specimen. The outside surface and the inside cleavage surface of both the fresh and the spent catalysts were analyzed. The Auger analysis of these samples is given in Figures 1–4. Physical Electronics Industries, Inc., Model 40–100 Auger spectrometer was used in this work. All work was done under 5 keV incident electron voltage using a cylindrical mirror analyzer. Typical beam currents of 15–30 μA were used in all Auger scans. Since the catalyst samples contained some adsorbed water, the pressure in the vacuum chamber increased from 10^{-8} to $\sim 10^{-6}$ mm when the electron beam hit the surface. However,

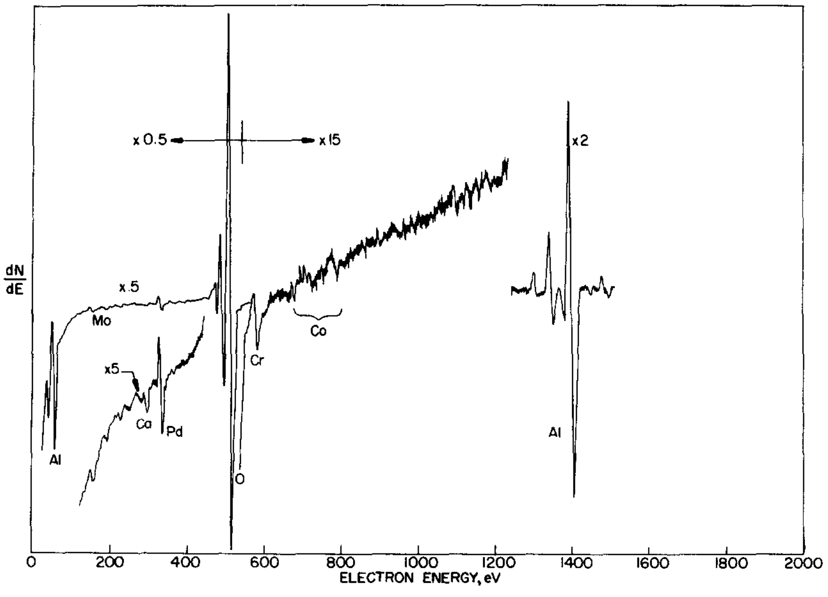

FIG. 2. Auger analysis of fresh catalyst (interior surface).

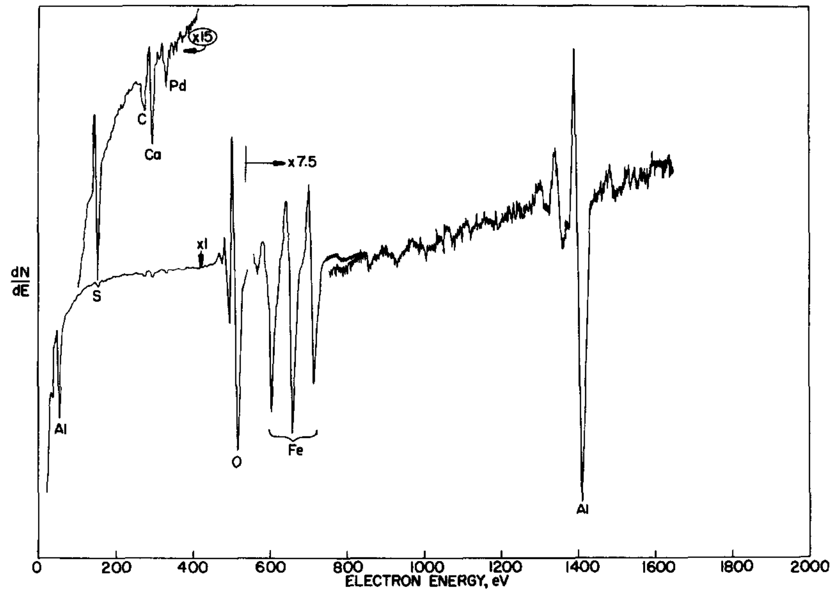

FIG. 3. Auger analysis of spent catalyst (outer surface).

this loss of vacuum did not present any problem in recording high sensitivity scans. The problem of water desorption was solved later by drying the samples at 150–400°C in dry nitrogen or air and then storing them under nitrogen in larger bottles containing silica gel. Minimal exposure to laboratory air during loading of such dried samples did not upset the high vacuum (10^{-8}–10^{-9} Torr) in the vacuum chamber during Auger measurements. The fresh and used catalysts consisted of dark outer ringed areas (where most of the catalytic components were concentrated in order to minimize diffusional resistance) and light inside areas. Both of these areas

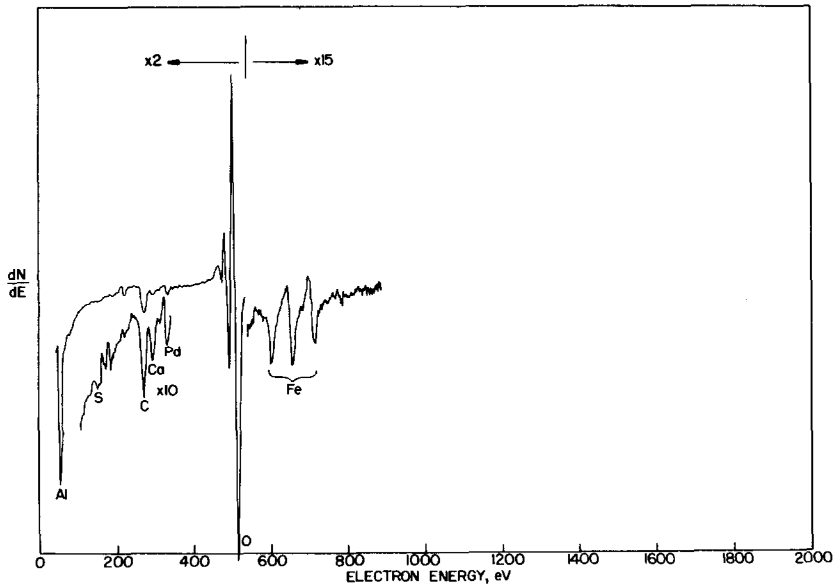

FIG. 4. Auger analysis of spent catalyst (interior surface).

were examined for elemental composition by Auger spectroscopy. Typically, the size of the circular spot analyzed was ~0.1 mm in diameter. Although only the analysis of one spot is given in the figures, several spots were scanned to gain better statistical confidence in the results.

Sensitivity factors for elements of interest were obtained from standard Auger spectra (at 3 keV) published in Ref. (*4*). These factors may not be very accurate in themselves at 5 keV, but the comparison of relative amounts from like samples is reasonably good.

RESULTS AND DISCUSSION

The Auger spectrum of the outer surface of fresh catalyst is shown in Fig. 1. This spectrum is shifted by ~10 eV and this energy should be subtracted from all peaks below 520 eV oxygen peak. The outer surface is rich in Pd, Cr and Mo, while Co is present in only small amounts. Some sulfur is also present on the fresh catalyst. The sulfur signal at 150 eV also contains one of the secondary peaks of Mo. The sulfur concentration is obtained by subtracting the proportional amount of Mo signal (relative to the 180 eV Mo major peak). The presence of Mo is further confirmed by the presence of high energy Mo peak at ~2080 eV. As is evident in Fig. 1, a substantial amount of Ca is also present. The relative surface atomic percent of these elements shown in Fig. 1 and Figs. 2, 3, and 4 (for other catalysts) are given in Table 1. In contrast to the richness of catalytically active components and the impurities (Ca and S) on outer dark surface, the interior surface (see Fig. 2 and Table 1) has only a trace of Mo and S and only a small amount of Pd while Cr and Co are present in about the same amount as the outer surface.

TABLE 1

SURFACE ATOMIC PERCENT[a]

Elements	Sensitivity factor[a]	Fresh catalyst		Spent catalyst	
		Dark area (outer surface)	Light area (interior surface)	Dark area (outer surface)	Light area (interior surface)
Mo	0.5[b]	3.26	0.16	0.0	Tr
S	1.5[b]	1.51	0.11	1.40	Tr
Ca	1.5	0.70	0.11	0.93	0.60
Pd	2.0	1.26	0.52	0.32	0.54
O	1.0	55.79	56.88	70.16	57.94
Cr	0.4[c]	0.75	0.48	0.00	0.00
Fe	0.5	Tr	0.00	13.68	2.53
Co	0.5	0.24	0.19	0.35	Tr
Al	0.25	36.49	41.55	13.16	38.38 (Est.)
		100.00	100.00	100.00	99.99

[a] Divide the peak heights of Auger peaks by their corresponding sensitivity factors to obtain relative atomic ratios, which on normalizing give the surface atomic percentages.

[b] Sulfur peak at 150 eV interferes with Mo secondary peak at 148 eV. Sulfur peak height is obtained by subtracting 0.17 times the Mo peak height at 186 eV.

[c] The sensitivity factor for Cr corresponds to full peak at 570 eV. Due to interference from the tail of large oxygen peak at 510 eV, sometimes only half of Cr-570 eV peak is observed. If so, a sensitivity factor of 0.2 should be used.

The outer surface of the spent catalyst (Fig. 3 and Table 1) contains so much Fe that it has just about completely (>75%) suppressed the Pd, Mo, Cr signals and even the Al signal arising from the support. Thus, iron is not only covering substantial (>80%) amount of the catalytically active components (Pd, Cr, Mo) but is covering the surface of the alumina support also. Furthermore, since the Auger signal is known to originate in the first 2–5 atomic layers for most of the elements (*5*), iron may very likely be masking greater than 80 or 90% of the surface exposed atoms if iron is present in the topmost layer only. Thus, even though the presence of iron per se, in small amounts is not a poison, the masking of the highly active Pd surface atoms and of the Cr/Mo promoter atoms makes iron almost as deadly a poison as sulfur, mercury, lead, etc. Although analysis of only one spot of 0.1 mm is shown in Figs. 1–4, several other spots were analyzed to gain statistical confidence. The amount of iron present on the interior surface (Fig. 4 and Table 1) was much less (a factor of 5 to 6) but the amount of Pd is much less also. The sharp gradient in iron from the outside to the interior of the pellet strongly suggests that iron came from an outside source. The feedstream to the catalyst was found to contain both powdered rust and dissolved iron. The powdered rust was localized towards the top of the catalyst bed but the dissolved iron was spread throughout the bed. Screening of the powdered rust did not increase catalyst activity significantly. The dissolved iron was the major source of poison for the active sites on the palladium surface as well as the sites on the promoters.

CONCLUSIONS

Auger spectroscopy has been shown to be a very powerful tool for studying the poisoning of a typical commercial catalyst, detecting the presence of and determining the amount of surface impurities which may have concentrated on the surface, and in establishing the concentration gradients of active components within the pellets. Moisture present in the γ-alumina supported catalyst did not present any serious problems in the high vacuum chamber of the Auger spectrometer.

ACKNOWLEDGMENTS

The author acknowledges the many helpful discussions he has had with Dr. P. W. Palmberg of Physical Electronics Industries and Dr. K. D. Williamson of Union Carbide Corp. Many thanks to Union Carbide Corp. for approval to publish this work.

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