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An Auger Spectroscopic Study of Radial Concentration Profiles in Spent Co,Mo/γ-Al_2O_3 Hydrodesulfurization Catalysts

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Auger electron spectroscopy has been used to determine radial concentration profiles in pellets of spent Co,Mo/γ-Al_2O_3 hydrodesulfurization catalysts containing deposited carbon, sulfur, and vanadium. The data, which were semiquantitatively processed according to a specific catalyst model, indicate that vanadium and sulfur, possibly present as vanadium sulfide, are found at the interface between γ-Al_2O_3 and a carbon overlayer. The amount of carbon deposited is smallest in the center and increases toward the periphery of the catalyst pellets.

INTRODUCTION

Auger electron spectroscopy (AES) is now widely accepted as a technique for the analysis of solid surfaces (*1–4*). Up to the present, the application of AES has been almost exclusively restricted to surface studies of (semi) conductors, especially metals and alloys, where AES has amply demonstrated its usefulness for the determination of surface composition and the study of surface segregation.

The application of AES to insulators has proved much more difficult, especially in those cases where the samples have a rough surface. The occurrence of uncontrollable static charging and the possibility of sample destruction by the incident electron beam are the likely causes of the lack of studies reported in this field. Nevertheless, it would seem that in spite of some difficulties AES studies of insulators, even those having rough surfaces as encountered with catalysts, can be performed. Static charging can be prevented by a proper selection of instrumental conditions and/or by using sophisticated sample application methods. Destruction by the primary beam can be minimized by using low primary beam currents.

The present article deals with such an AES study of an actual spent catalyst consisting of small amounts of Co and Mo on a high-surface area γAl_2O_3 that has been used in the hydrodesulfurization of a hydrocarbon test feed containing vanadium-bearing asphaltenic species. In this process, appreciable amounts of carbon, sulfur, and vanadium are deposited on the catalyst surface. Using AES, we succeeded in analyzing the concentration profiles of these elements throughout the spent catalyst pellets and in semiquantitatively interpreting the spectroscopic results.

EXPERIMENTAL

The experimental procedure used consisted in measuring the freshly fractured catalyst extrudates on at least 10 points along the diameter of the fracture face. To this end, the catalysts extrudates were cleft by making a small notch on the extrudate using a scalpel blade and applying a slight force on one end of the extrudate while holding the other. Care was taken to ensure that the fracture face was touched neither by tools nor by hand so as to preserve the original element distribution. Four pellets of each particular catalyst sample from a specific desulfurization run were mounted on a multisample handling manipulator by means of a conductive silver-containing glue specially adapted for (ultra) high vacuum applications. The pellets were

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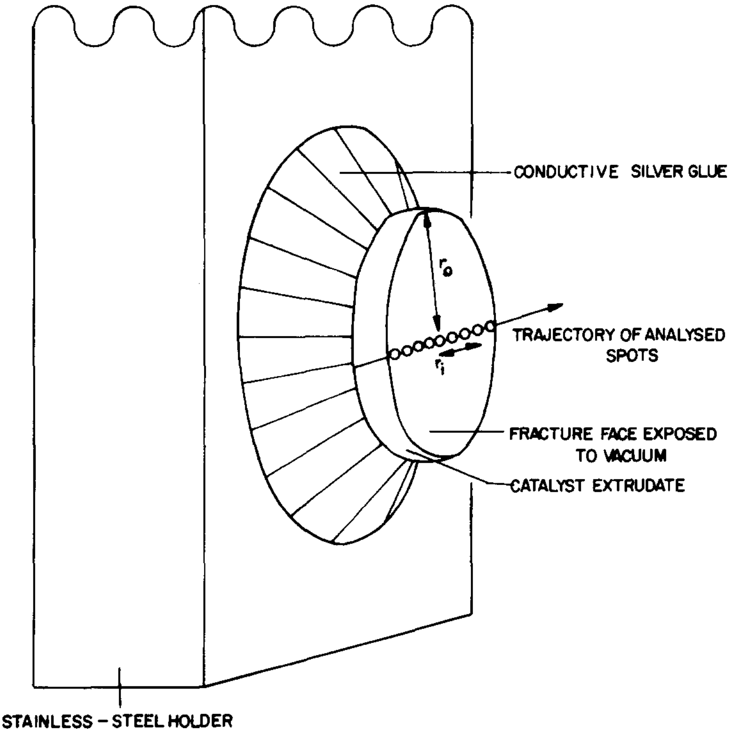

FIG. 1. Schematic arrangement of the fractured catalyst extrudate in the analyzer.

mounted in such a way that the primary electron excitation beam would hit the fracture face perpendicularly, the pellet being completely surrounded by silver glue (Fig. 1). This mounting procedure allows easy alignment of the primary electron beam at the periphery of the exposed fracture face. Spectra were taken with the Phi Single Pass Cylindrical Mirror Analyzer at a primary excitation energy of 5 keV, at incident beam currents between 100 and 500 nA, and at a modulation amplitude of 10 V peak-to-peak.

After the samples had been mounted in the analyzing chamber, which was pumped to about 10^{-8} Torr (1 Torr = 133.3 N m^{-2}), spectra were taken of each catalyst pellet at about 10 positions equally spaced from each other along the diameter of the pellet. Figure 2 shows two Auger spectra taken at the periphery and at the center of the fracture face of one and the same (arbitrarily chosen) extrudate. Each spectrum was analyzed for the carbon (KLL), oxygen (KLL), vanadium ($L_{2,3}M_{2,3}M_{2,3}$), sulfur (LMM), and aluminium (KLL) Auger lines. The I_α/I_{Al} line intensity ratios (α = C, V, S) at the various radial positions were determined by averaging the values obtained from four pellets of each batch. The results were put on a semiquantitative basis by measuring the line intensity ratios of the following calibration compounds: Al_2O_3, V_2S_3, V_2O_3, and VC. This set of compounds affords the relative atomic abundances or relative atomic sensitivities (*5*).

RESULTS AND QUANTITATIVE TREATMENT

The atomic Auger sensitivities as measured for carbon, sulfur, oxygen, and vanadium, relative to aluminium, are given in Table 1. As a typical example, data of one of the catalysts are presented in Table 2. There are two main problems to be solved: (1) What is the composition of the deposited layer? (2) What is the total layer thickness of the deposit? The data collected in Table 2

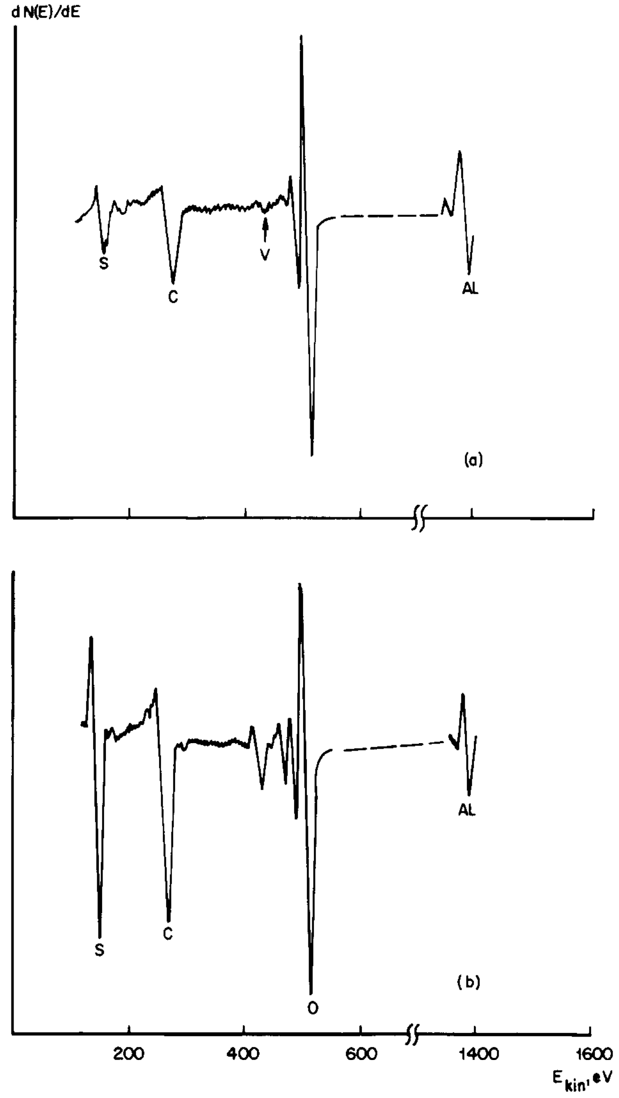

FIG. 2. Auger spectra of a catalyst taken at the center and at the periphery of an extrudate.

contain information on both questions. In the following we shall briefly indicate how the desired information was extracted from the raw data.

Electrons escaping from the solid are exponentially attenuated along their path within the solid. The mean free path of electrons in the energy range of our experiments is such (*2*, *4*) that the information contained in the spectra stems from a layer with total thickness somewhere between 1 and 5 nm. This implies that the built-up (morphology

TABLE 1

Atomic Sensitivities of the C (KLL), O (KLL), S (LMM), and V ($L_{2,3}M_{2,3}M_{2,3}$) Auger Lines Relative to That of the Al (KLL) Transition

Transition	Sensitivity
C (KLL)	1.35
O (KLL)	2.15
S (LMM)	2.15
V($L_{2,3}M_{2,3}M_{2,3}$)	1.35

TABLE 2

Results Obtained from a Catalyst[a] after a Desulfurization Test

Distance from center of pellet[b] r/r_p	$Q(I)_\alpha$[c]		
	C/Al	S/Al	V/Al
0	1.38	0.29	0.12
1/6	1.56	0.28	0.14
1/3	2.10	0.32	0.19
1/2	2.93	0.44	0.26
2/3	4.01	0.64	0.33
5/6	6.99	1.23	0.46
1/1	(17.8)	3.13	0.59

[a] Catalyst No. 3 of Table 4.

[b] Relative to particle radius, r_p.

[c] $Q(I)_\alpha$ (α = C, S, V) is a normalized intensity ratio $Q(I)_\alpha = (I_\alpha/I_{Al})$ observed/(I_α/I_{Al}) calibrated.

and composition) of the exposed solid surface region, i.e., the region of some 1–5 nm thickness, is of importance for the further analysis of the experimental data. For instance, if the deposited material were homogeneously distributed throughout the γ-Al_2O_3 matrix, on an atomic scale, then one could easily determine the C, V, and S contents directly from the I_α/I_{Al} values (α = C, S, V . . .) using the I_α/I_{Al} values obtained from suitable reference compounds (*6*). However, we deal rather with one of the following situations: (a) stratified layers deposited on the surface of γ-Al_2O_3; (b) agglomerates scattered across the surface of the γ-Al_2O_3; (c) a combination of (a) and (b), e.g., a stratified layer whose thickness varies considerably over short distances across the surface of the carrier.

We will first consider case (a). The implications of cases (b) and (c) will be dealt with in the Discussion.

In order to calculate the thickness of the total deposited layer it is necessary to make certain assumptions about the structure of the catalyst and the type of fracture as exposed to the analyzer. As regards the structure of the catalyst, we propose a model by which the catalyst is represented as a plurality of particles interconnected by thin "necks," e.g., the points where the particles touch. The space left between the network of particles is the pore space. For mathematical convenience we assume the particles to be cubes of uniform size (edge length d_0). These cubes are coated by a layer of deposit with thickness d, consisting of various components α that are assumed to be homogeneously mixed throughout the deposit.

From the specific surface area of the γ-Al_2O_3 used we calculate d_0 to be 9 nm. This cube size is so large that we can neglect any contribution to I_α which originates from the bottom part of the cubes. Furthermore we consider only electrons that escape in a direction perpendicular with respect to the surface. Finally, we assume that the catalyst system is isotropic for electron scattering, and that the mean free path of electron scattering is matrix-independent. Now we can consider two cases: (1) the fracture made to prepare the sample for AES analysis leaves the particles untouched and thus runs along the particle connectors ("necks") (model I); (II) the fracture also affects the particles (model II). A schematic representation of model I is given in Fig. 3. For reasons of mathematical convenience we neglect the necks and thus represent the catalyst as a collection of "untouched" free particles. Two different parts are now exposed to the analyzer: (1) a part (a) of deposit with thickness d, on top of γ-Al_2O_3 which is considered to be infinitely thick, occupying a fraction f_a of the fracture face;

$$f_a = (d_0)^2/(d_0 + 2d)^2 \qquad (1)$$

(2) a part (b) consisting of pure deposit, occupying a fraction, f_b, of the surface,

$$f_b = \{(d_0 + 2d)^2 - d_0^2\}/(d_0 + 2d)^2 \quad (2)$$

Since we have assumed that the components α are homogeneously mixed in the deposit, we may write the following general

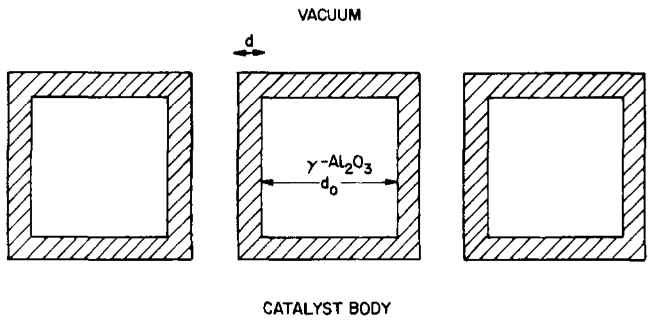

FIG. 3. Model I. A collection of catalyst particles with γ-Al_2O_3 cube length d_0 and total cube length $(d_0 + 2d)$.

expression for the observed intensity ratio I_α/I_{Al} for the total system (a + b):

$$(q_{obs})_\alpha = \frac{I_\alpha}{I_{Al}} = \frac{I_{0,\alpha} \cdot x_\alpha \left\{ f_a \int_0^d e^{-z/\lambda_\alpha} dz + f_b \int_0^\infty e^{-z/\lambda_\alpha} dz \right\}}{I_{0,Al} \cdot x_{Al} \cdot f_a \int_d^\infty e^{-z/\lambda_{Al}} dz}, \qquad (3)$$

where I_0 is the Auger electron flux per unit depth, the subscript α denotes the element (either C, S, or V) concerned, x_α is the molar fraction,[1] z is the depth below the vacuum-exposed surface from which the Auger electrons originate, and λ_α is the mean free path of inelastic scattering ($\lambda_S = 0.5$ nm; $\lambda_C = 0.7$ nm; $\lambda_V = 0.8$ nm; and $\lambda_{Al} = 1.5$ nm). Integration of Eq. (3) gives:

$$(q_{obs})_\alpha = \left(\frac{I_{0,\alpha} \cdot \lambda_\alpha}{I_{0,Al} \cdot \lambda_{Al}}\right)\left(\frac{x_\alpha}{x_{Al}}\right) \left[\frac{f_b + f_a\,(1 - e^{-d/\lambda_\alpha})}{f_a \cdot e^{-d/\lambda_{Al}}}\right]. \qquad (4)$$

For a system of components α homogeneously distributed throughout the γ-Al_2O_3 on an atomic scale, i.e., a system for which the atomic sensitivities are obtained, we may write:

$$(q_{cal})_\alpha = \frac{I_\alpha}{I_{Al}} = \frac{I_{0,\alpha} \int_0^\infty e^{-z/\lambda_\alpha} dz}{I_{0,Al} \int_0^\infty e^{-z/\lambda_{Al}} dz} = \frac{I_{0,\alpha} \cdot \lambda_\alpha}{I_{0,Al} \cdot \lambda_{Al}}. \qquad (5)$$

Using Eq. (5), Eq. (4) can be rewritten as:

$$Q(I)_\alpha = \frac{(q_{obs})_\alpha}{(q_{cal})_\alpha} = \frac{x_\alpha}{x_{Al}} \left[\frac{1 - e^{-d/\lambda_\alpha} + f_b/f_a}{e^{-d/\lambda_{Al}}}\right]. \qquad (6)$$

At this point, it should be remarked that Eq. (6) is characterized by two unknowns for each α, viz. x_α and d[f_b/f_a has a fixed relation to d, cf. Eq. (1) and (2)]. If the λ-values of the characteristic Auger electrons of each α would be the same, then x_α could be easily determined, because in that case [see Eq. (6)]:

$$x_\alpha = \frac{Q(I)_\alpha}{\Sigma Q(I)_\alpha}. \qquad (7)$$

In our case, however, $\lambda_C \neq \lambda_V \neq \lambda_S$, and therefore the x_α values cannot be determined directly from the $Q(I)_\alpha$ values.

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[1] I_α is linearly proportional to the fraction of component α, present per unit volume. Since there is uncertainty about the chemical state of the components α in the deposit, and thus also about the atomic volumes occupied by vanadium, sulfur, and carbon, we assume for reasons of convenience that all elements have the same atomic volume and take I_α to be linearly proportional to x_α.

TABLE 3

Composition Distribution of Catalyst[a] Expressed in Atomic Fractions $x_\alpha (\alpha = \mathrm{C, S, V})$, Total Deposit Thickness d, and "Partial" Thickness of Each Component Expressed in a Number of Atomic Layers

Distance from center of pellet[b] r/r_p	Atomic fractions[c]			d (nm)	Number of atomic layers		
	x_C	x_S	x_V		n_C	n_S	N_V
0	0.74	0.13	0.07	0.37	1.0	0.2	0.09
1/6	0.73	0.11	0.07	0.42	1.1	0.2	0.19
1/3	0.79	0.10	0.08	0.51	1.4	0.2	0.14
1/2	0.77	0.10	0.07	0.69	1.9	0.3	0.48
2/3	0.78	0.11	0.07	0.88	2.4	0.4	0.21
5/6	0.77	0.13	0.05	1.31	3.5	0.6	0.24
1/1	0.80	0.14	0.03	(2.15)	6.0	1.0	0.80

[a] Catalyst No. 3 of Table 4.

[b] Relative to particle radius, r_p.

[c] Calculated from $Q(I)_\alpha$, cf. Table 2.

Consequently, we have to solve the following set of equations:

$$Q(I)_{\mathrm{carbon}} = \left(\frac{x_C}{x_{Al}}\right) F_C(d), \quad (8)$$

$$Q(I)_{\mathrm{sulfur}} = \left(\frac{x_S}{x_{Al}}\right) F_S(d), \quad (9)$$

$$Q(I)_{\mathrm{vanadium}} = \left(\frac{x_V}{x_{Al}}\right) F_V(d), \quad (10)$$

and

$$x_C + x_S + x_V = 1, \quad (11)$$

where

$$F_\alpha(d) = \left(\frac{1 - e^{-d/\lambda_\alpha} + f_b/f_a}{e^{-d/\lambda_{Al}}}\right). \quad (12)$$

A calculation along these lines yielded the x- and d-values presented in Table 3.

The carbon, vanadium, and sulfur contents within the catalyst pellet, expressed as a particle layer thickness, n_α, is given by:

$$n_\alpha = x_\alpha \cdot d \cdot \phi_\alpha^{-1}, \quad (13)$$

where ϕ_α is the atomic diameter of element α. Values for n_α are presented in Table 3 and Fig. 3.

Similar calculations of x and d have been performed along the lines of model II (Fig. 4). In this model, which allows also transgranular fracture of alumina, three different parts are exposed to the analyzer: (a) a part consisting of deposit with layer thickness d on top of an "infinitely" thick γ-Al_2O_3 crystal, occupying a fraction, f_a, of the surface

$$f_a = d_0^2/2(d_0 + 2d)^2 \quad (14)$$

(b) pure deposit, occupying a fraction, f_b, of the surface

$$f_b = \{(d_0 + 2d)^2 - d_0^2\}/(d_0 + 2d)^2 \quad (15)$$

(c) pure γ-Al_2O_3 occupying a fraction, f_c, of the surface

$$f_c = d_0^2/2(d_0 + 2d)^2. \quad (16)$$

For this system, q_{obs} is written as:

$$(q_{\mathrm{obs}})_\alpha = (q_{\mathrm{cal}})_\alpha \left(\frac{x_\alpha}{x_{Al}}\right) \left\{\frac{f_b/f_a + (1 - e^{-d/\lambda_\alpha})}{1 + e^{-d/\lambda_{Al}}}\right\}. \quad (17)$$

Processing our data according to formulas (17) and (11) leads to unrealistically high values of d and therefore we discard this model.

From plots such as those given in Fig. 5 one can calculate the total sulfur, vanadium, and carbon contents of the catalyst.

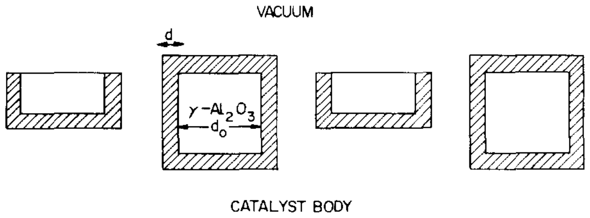

FIG. 4. Model II as model I, with 50% of the particles transgranularly fractured.

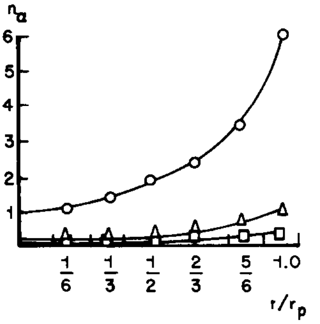

FIG. 5. Number of atomic layers, n_α, of component α as a function of the distance, r, from the center, along the radius of the catalyst pellet: —O— carbon; —△— sulfur; —□— vanadium.

We have compared these "Auger-derived" C, V, and S contents with the total C, V, and S contents as found by conventional bulk analysis methods. To make this comparison, we calculated the average thickness d_α of the stratified α-layer, assuming only component α to be present, as:

$$d_\alpha = f_i d_{\alpha,i}, \qquad (18)$$

where

$$f_i = \frac{(r_i + 0.0625)^2 - (r_i - 0.0625)^2}{r_0^2} \qquad (19)$$

in which f_i is the fraction of the core of the catalyst extrudate that is analyzed at location r_i (with respect to the center of the catalyst pellet), r_0 is the radius of the pellet, the value 0.0625 is half the distance between two locations of analysis, and $d_{\alpha,i} = n_{\alpha,i} \cdot \phi_\alpha$. From d_α the total weight of the material, W_α, deposited per gram of Al_2O_3 pure carrier material is calculated by:

$$W_\alpha = S_{Al_2O_3} \cdot d_\alpha \cdot \rho_\alpha \cdot 10^{-2}, \qquad (20)$$

where $S_{Al_2O_3}$ is the specific surface area of the alumina in $m^2\ g^{-1}$ ([illegible] = 200 $m^2\ g^{-1}$) and ρ_α is the density of the component α (in g cm^{-3}). For carbon (which we assumed to be present in the elemental, amorphous state), sulfur, and vanadium we inserted ρ-values of 2, 2, and 6, respectively. As sulfur and vanadium may well be present as a vanadium sulfide, we also calculated W_S and W_V using a ρ-value of 4 for the compound VS. The results of these calculations are given in Table 4.

There are some points of interest. For carbon we observe a reasonably good agreement between the bulk-analysis values and the Auger-derived values for five out of eight catalysts, but there is no general trend in the difference between the two sets of values. Quite a different picture emerges for vanadium and sulfur: the Auger-derived overall contents for these elements are systematically lower than those obtained by bulk analysis.

DISCUSSION

The results indicate that the method of "scanning" the surface of a fractured

TABLE 4

A Comparison between the Carbon, Sulfur, and Vanadium Bulk Analysis Values and the Integrated, Auger-Derived Values, Processed According to Catalyst Model I

Catalyst number	Carbon analysis (%w)		Sulfur analysis (%w)			Vanadium analysis (%w)		
	Bulk	$\rho_C = 2$	Bulk	$\rho_S = 2$	$\rho_S = 4$	Bulk	$\rho_V = 6$	$\rho_V = 4$
1	20.2	14.9	9.4	2.9	5.7	5.0	2.4	1.6
2	15.3	22.9	11.5	4.5	8.6	16.0	7.9	5.4
3	17.4	20.4	21.5	5.0	9.6	24.0	6.5	4.4
4	19.4	20.6	8.4	3.1	5.9	8.9	3.3	2.2
5	11.7	12.2	18.9	8.2	15.1	17.2	8.8	6.0
6	12.2	6.8	18.4	7.1	15.3	16.0	6.7	4.6
7	11.8	14.1	19.1	4.1	7.8	18.3	4.8	3.3
8	13.5	17.6	19.5	2.8	5.5	18.2	4.9	3.3

catalyst pellet is in principle useful, providing qualitative or semiquantitative information. However, there is a large number of limitations and assumptions that make a quantitative interpretation of the results difficult. In the following the most important of these are reviewed and discussed:

(1) The catalyst pellets taken from the sample need not be representative of the total catalyst batch.

(2) The catalyst model as proposed by us is a very simplistic approximation of the true state. It does not allow for a particle size distribution and neglects transgranular fractures.

(3) The deposit is assumed to be present as a smooth layer rather than as a collection of agglomerates.

(4) The analyzed electrons are supposed to be scattered isotropically throughout the catalyst.

(5) In the calculation of d, it is assumed that the deposit is homogeneous within the escape depth region of the Auger electrons.

Re (*1*). It is impracticable to take many catalyst pellets of one and the same sample. The reliability of the analysis, however, can be greatly increased for these catalyst systems by carefully selecting samples from the reactor and subjecting each of them (if possible) to the various analyses to be performed.

Re (*2*) *and* (*3*). What are the trends to be expected if we allow for a particle size distribution and transgranular fracture? It is easily seen that transgranular fracture results in a lower I_α/I_{Al} intensity ratio because of the presence of an additional amount of Al_2O_3 not considered in model I. Introduction of a particle size distribution would result in a higher I_α/I_{Al} intensity ratio, the reason being twofold. First, if we allow for a size distribution around $d_0 = 9$ nm we calculate a higher f_b/f_a ratio in Eq. (6). Secondly, in model I, the γ-Al_2O_3 particles are considered to be infinitely thick for those Auger electrons that are created in the regions directly opposite to the vacuum-exposed side. In consequence, the material deposited onto the "bottom" side of these particles is not "seen" by the spectrometer. The actual situation, however, is different for particles of sizes of the order of λ: for these, there is an extra contribution to I_α, which is not allowed for in formula (6). The extent to which the two extra contributions to I_{Al} and I_α compensate each other remains unknown until a more detailed picture of the fracture face is available.

Considerations of a similar nature apply to the third comment. Agglomeration of deposited material gives rise to reduced I_α values due to "selfshadowing" effects.

Re (*4*). The assumption of isotropic scattering was made on the basis of literature data (*2*, *4*) which suggest that the mean free path of inelastic scattering of electrons is not much different for a wide range of materials (Al_2O_3, carbon, metals). We do realize that the literature data refer to ideal systems which, unlike the systems of our study, have a well-defined crystallography. However, in view of the fact that we only wish to make a semiquantitative estimation, we consider this assumption to be justified.

Re (*5*). The comment concerning the homogeneity of the deposit can be checked in more detail. Assuming that our semiquantitative approach is reasonable and that the elements (C, S, and V) are homogeneously distributed throughout the deposit, then one would expect to calculate, from the Auger spectra, total carbon, sulfur, and vanadium contents of the catalyst that are in line with data from the bulk analysis values. If, however, one of the elements were concentrated at the γ-Al_2O_3/deposit interface, then one would obtain Auger signals from it that had been more attenuated than the Auger signals from the other elements. Consequently, the Auger-derived content of that element would fall below the true bulk analysis data.

As Table 3 shows, there is a reasonably good agreement between the Auger-derived carbon contents and the bulk analysis values. For sulfur and vanadium, however, there is a systematic discrepancy. Whether calculated from elemental densities ($\rho_S = 2$ and $\rho_V = 6$) or from a common density ($\rho_{VS} = 4$), the sulfur and vanadium contents as derived from the Auger spectroscopic data are invariably below the true bulk analysis values. We therefore tentatively conclude that sulfur and vanadium are concentrated at the γ-Al_2O_3/deposit interface rather than being distributed homogeneously throughout the deposit. The simultaneous occurrence of sulfur and vanadium at the interface possibly points to the presence of vanadium sulfide(s).

CONCLUSIONS

(1) The Auger spectroscopic technique is suitable for determining the concentration profiles of materials deposited on the surface of catalyst pellets.

(2) Quantitative treatment of the experimental data yields results that give confidence in the method used. The agreement between the Auger-derived overall carbon content and that found from true bulk analysis is satisfactory.

(3) The results suggest that carbon forms an "overlayer" on top of the vanadium and sulfur. The amount of carbon deposited in the pores is smallest in the center and increases toward the periphery of the catalyst extrudate particles.

REFERENCES

1. Pentenero, A. A., *Catal. Rev.* **5,** 199 (1971).
2. Brundle, C. R., *in* "Surface and Defect Properties of Solids," Vol. I, p. 171. Chemical Society, London, 1972.
3. Todd, C. J., *Vacuum* **23,** 195 (1973).
4. Bouwman, R., *Ned. Tijdschr. Vacuumtechn.* **11,** 37 (1973) (in English).
5. Wagner, C. D., *Anal. Chem.* **44,** 1050 (1972) and *in* "Quantitative Surface Analysis of Materials" (N. S. McIntyre, Ed.). ASTM Special Technical Publication 643, 1978.
6. Bouwman, R., Toneman, L. H., and Holscher, A. A., *Surface Sci.* **35,** 8 (1973).