Catalyst Aging in a Process for Liquefaction and Hydrodesulfurization of Coal

Aged $CoO/MoO_3/SiO_2/Al_2O_3$ catalyst pellets, used in a pilot plant for the single-stage liquefaction and hydrodesulfurization of coal, were analyzed with an electron microprobe and scanning electron microscope. The results demonstrate the occurrence of catalyst aging processes which could lead to bed plugging and pore mouth blocking.

J. J. STANULONIS
B. C. GATES
and
J. H. OLSON

Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

SCOPE

To meet the need for new sources of clean fuels, processes are being developed for liquefaction of coal and catalytic hydrodesulfurization of the derived liquids. In some of these processes, the liquefaction and catalytic hydrodesulfurization take place in a single reactor. Catalyst aging evidenced by declining conversions is expected to result from formation of coke, deposition of metal sulfides, and/or accumulation of mineral components of coal. The origin of the aging has been undefined in the literature, however. This study provides a preliminary characterization of the physical processes of catalyst aging by analysis of a used pilot plant catalyst with an electron microprobe and a scanning electron microscope.

CONCLUSIONS AND SIGNIFICANCE

Pellets of the hydroprocessing catalyst used in the Synthoil process (sulfided $CoO/MoO_3/SiO_2/Al_2O_3$) accumulated inorganic and organic contaminants both on the exterior surface and in the pore mouths. The inorganic (carbon free) deposit found in the upstream end of the fixed-bed reactor has been identified as primarily ferrous sulfide, $Fe_{14}S_{15}$. This material covered 50 to 70% of the catalyst's peripheral surface and penetrated into the catalyst pores to a depth of about 100 μm. The total accumulated deposit caused a 70% reduction in catalyst surface area and pore volume. The inorganic deposit found in the downstream end of the reactor was mainly aluminum and silicon and covered 10 to 20% of the catalyst's peripheral surface. Titanium penetrated about 150 μm into the pores. All of these deposits caused a 40% loss of pore volume. These results imply that deposition in coal hydroprocessing reactors could lead to bed plugging and pore mouth blocking.

Conversion of coal to clean liquid fuels can be accomplished by processes being developed for liquefaction (a reductive depolymerization of the organic coal matrix) followed by catalytic hydroprocessing of the derived liquid, which removes sulfur and increases the H/C ratio. The liquefaction and hydroprocessing steps typically have been carried out in separate stages, with interstage removal of the mineral matter of the coal. Alternatively, in processes such as Synthoil (Yavorsky, 1973), both liquefaction and hydroprocessing are carried out in a single reactor. The fixed-bed reactor of the Synthoil process is fed with a slurry of coal in coal derived liquid which flows concurrently with hydrogen through a preheater, reaching a temperature of about 720°K at a pressure of 1.4×10^7 N/m^2. The organic coal matrix is largely liquefied in the preheater, and the resultant gas-liquid-solid mixture flows through a packed-bed reactor containing particles of $CoO/MoO_3/SiO_2/Al_2O_3$ hydrodesulfurization catalyst. Highly turbulent flow is used with the intention of preventing plugging of the catalyst bed by deposition of inorganic material, coke, and unconverted coal.

The research described here was undertaken to evaluate catalyst aging in reactors used for coal liquefaction and hydroprocessing. The aging problem is unidentified in the literature, but data from a Synthoil pilot plant operated continuously for about 1.3×10^6 s show that there was a significant loss of hydrocracking activity of the catalyst, as indicated by increasing product viscosity with increasing time on stream (Sternberg et al., 1975).

EXPERIMENTAL

The 0.35 m long entrance and exit sections of a 20.7 m long tubular Synthoil pilot plant reactor were obtained, including imbedded pellets of catalyst which has been used continuously for 1.3×10^6 s. The catalyst was Harshaw #0402T, initially containing 3% CoO, 15% MoO_3, 5% SiO_2, and 77% Al_2O_3 by weight, according to the manufacturer's specifications.

The catalyst pellets were carefully removed from 0.3 m long sections of the 7.9 mm I.D. reactor by splitting the sections longitudinally. The particles were analyzed with an electron microprobe and with a scanning electron microscope (SEM) equipped with an energy dispersive x-ray analyzer (EDAX) at the facilities of Micron, Inc., of Wilmington, Delaware. The pellets were prepared for microprobe and SEM analysis by vacuum impregnation in epoxy resin in a 2.5×10^{-2} m diameter mold. A circular cross section of each particle was exposed by

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Correspondence concerning this paper should be addressed to J. J. Stanulonis.

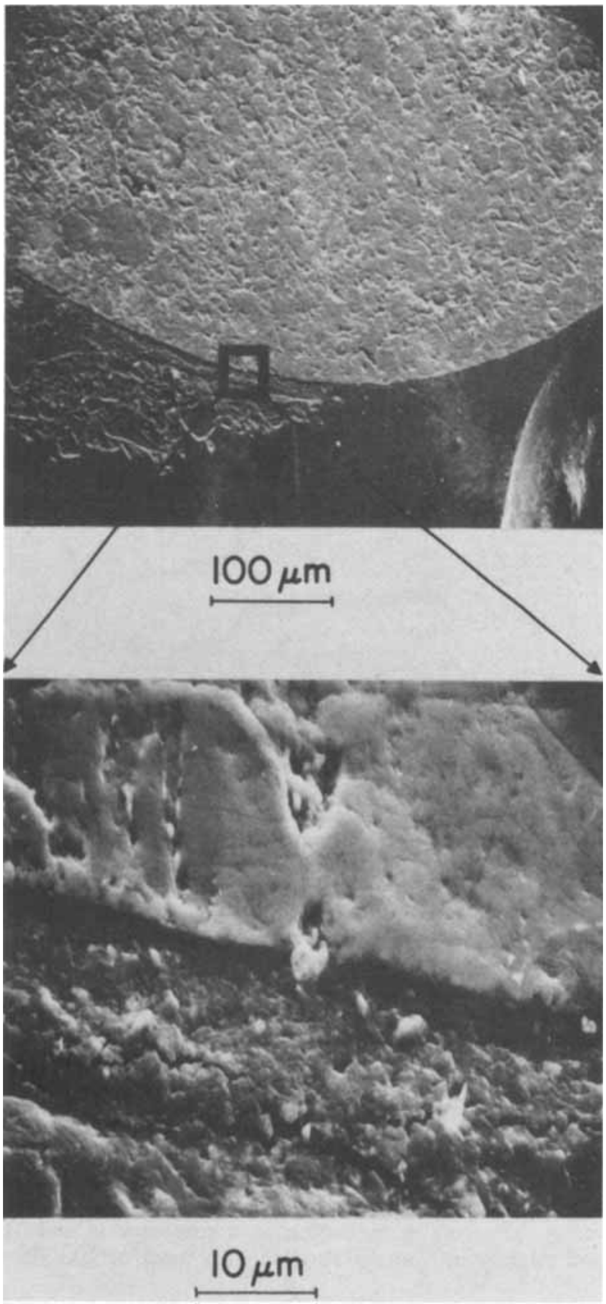

Fig. 1. Scanning electron micrograph of a catalyst particle from the upstream end of the reactor. The catalyst was sectioned along a radial plane. In the upper picture, a crust of inorganic deposit about 60 μm thick is evident on the exterior of the catalyst. Organic material forming an irregular additional deposit about 1 000 μm thick is evident in the lower righthand corner of the micrograph. The lower micrograph shows details of the interfaces separating the catalyst, the inorganic deposit, and the organic deposit. EDAX results showed that the crust at the location indicated was primarily ferrous sulfide, containing small amounts of calcium, titanium, and zinc.

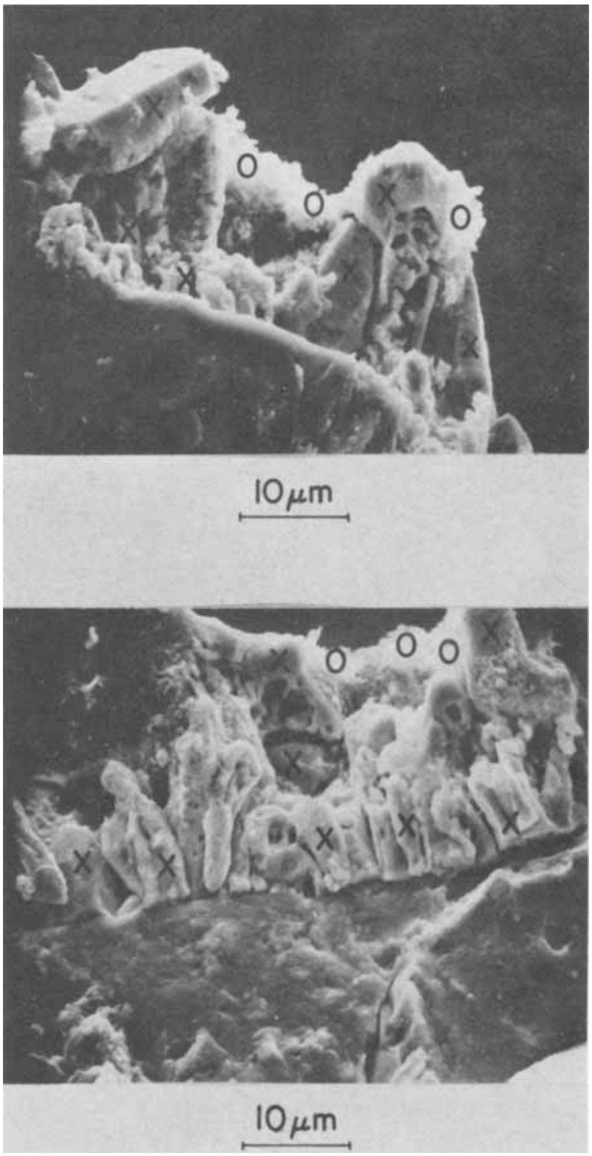

Fig. 2. Scanning electron micrograph of a fractured and plasma etched cross section of a catalyst particle from the upstream end of the reactor. Each picture shows the different structures observed in the inorganic crust. The catalyst is at the bottom of each picture. The areas marked (X) were shown by EDAX to be made up primarily of iron and sulfur. The trace elements, aluminum, silicon, calcium, titanium, chromium, and zinc, varied randomly from region to region. The areas marked (0) were determined by EDAX to be primarily aluminum and silicon. The trace elements in this structure were found to be iron, sulfur, calcium, titanium, and zinc, varying from site to site.

grinding in a sequence beginning with 80 and ending with 400 grid silicon carbide paper. The exposed surface was then polished in a sequence beginning with 6 and ending with 0.25 μm diamond paste.

To provide EDAX analyses of only the inorganic constituents of some catalyst particles, the organic material was removed by plasma etching, a low temperature ashing technique in which a gas plasma is generated from oxygen, producing free radicals to oxidize the organic material. Some particles were fractured radially, plasma etched, and mounted on a post prior to analysis, and others were plasma etched after being embedded and lapped. The latter particles were particularly useful for EDAX analysis.

Catalysts were initially investigated by EDAX, which is capable of detecting all elements from sodium to uranium, and the results were used to identify the major constituents. These data determined the elements to be analyzed subsequently with the electron microprobe. Since EDAX signals usually were neither calibrated against similar standards nor corrected for x-ray self-absorption, the elemental concentrations were determined only qualitatively.

Deposits containing iron and sulfur, however, were analyzed quantitatively by comparison of the data to those obtained with a suitable set of reference standards mounted and polished in the same way. Samples prepared for determination of pore size distribution were extracted with boiling benzene and dried at 420°K and ~1 N/m^2. The pore size distribution was determined by the standard mercury penetration method.

RESULTS AND DISCUSSION

Representative results are shown in Figure 1 to 4 for catalyst samples taken from the upstream end of the

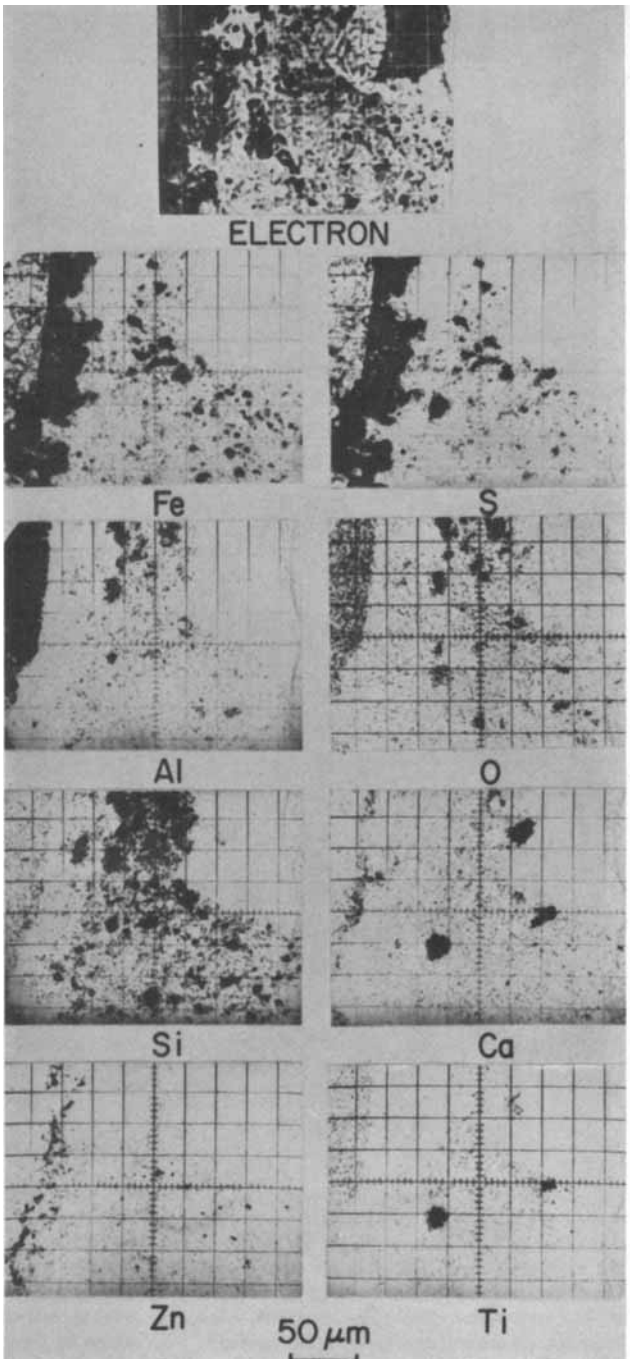

Fig. 3. Electron microprobe x-ray images showing a catalyst particle from the upstream end of the reactor and the inorganic and organic crusts. These pictures indicate the qualitative distribution of selected elements. The catalyst is shown in the upper left. The light area in the upper right is part of the mounting and is included as a reference location. The inorganic crust, which in this example measures ~40 μm wide, is concluded to be primarily FeS_x since the x-ray images for iron and sulfur are similar. This material also penetrated into the macropores of the catalyst and was distributed as 5 to 10 μm diameter particles in the organic crust. AlO_x, identified from the good correlation between the aluminum and oxygen images, is inferred to have been in the catalyst and dispersed through the organic layer as 10 to 15 μm diameter particles. Silicon is evident in high concentration in the organic phase, its image correlating to some degree with the aluminum and oxygen images, and it is found at a lower concentration in the catalyst. Small quantities of calcium and titanium are indicated, probably present as TiS_x and CaS_x since their images are similar to the sulfur image. Zinc is observed in small quantities in the inorganic layer near the catalyst surface. Titanium appears in small clumps in the inorganic crust as a trace component of the ash as defined by the calcium image. Titanium is also evident in a finer dispersion near the catalyst surface.

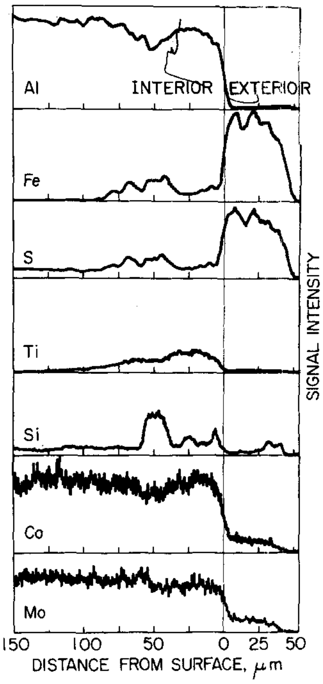

Fig. 4. Electron microprobe concentration profiles of a catalyst particle from the upstream end of the reactor. The aluminum profile serves to identify the exterior catalyst surface and shows variations in the interior, in part because the signals have not been corrected for varying local absorption of x-rays. The iron concentration is shown to be approximately proportional to the sulfur concentration in the crust with the sulfur/iron ratio being much higher in the interior of the catalyst, which is a sulfide in operation. The irregularities indicate variations in the macropore structure. Titanium was deposited primarily in the interior of the catalyst, and the concentration profile shows the presence of finely dispersed titanium. The irregular silicon profile suggests the incorporation of mineral constituents of the coal within the macropores. The cobalt and molybdenum profiles show large variations inside the catalyst, which may be attributed to low dispersion of these components. These two elements penetrate into the inorganic crust.

reactor and in Figures 5 to 8 for samples taken from the downstream end. These figures are accompanied by detailed captions giving a nearly complete statement of the results. The following section is a summary of only the most important general results, with most of the details omitted for brevity.

The catalyst particles in the upstream reactor section were firmly cemented in place by a 0 to 700 μm thick black organic residue. A thinner layer of residue (0 to 250 μm) was presented in the downstream section. This organic layer was probably not present under reaction conditions but instead was formed at least in part by solidification of reaction products during shutdown. On the pellets from both the upstream and downstream sections, the organic layer provided a matrix for the support of small (1 to 5 μm), randomly dispersed inorganic particles containing calcium, silicon, aluminum, zinc, titanium, iron, and sulfur; these were mineral components of the coal.

The upstream catalyst pellets also had a thin (0 to 90 μm) inorganic crust inside of the organic layer. This deposit, which covered 50 to 70% of the available catalyst surface, appeared to have grown from relatively large (5 to 10 μm) fissures in the catalyst. The crust consisted primarily of coarse, rodlike crystals covered with small amounts of fine, polycrystalline material. The rodlike crystals, when analyzed with reference to suitable standards, were shown to be ferrous sulfide; the atomic ratio of iron to sulfur remained constant at 14:15, but the

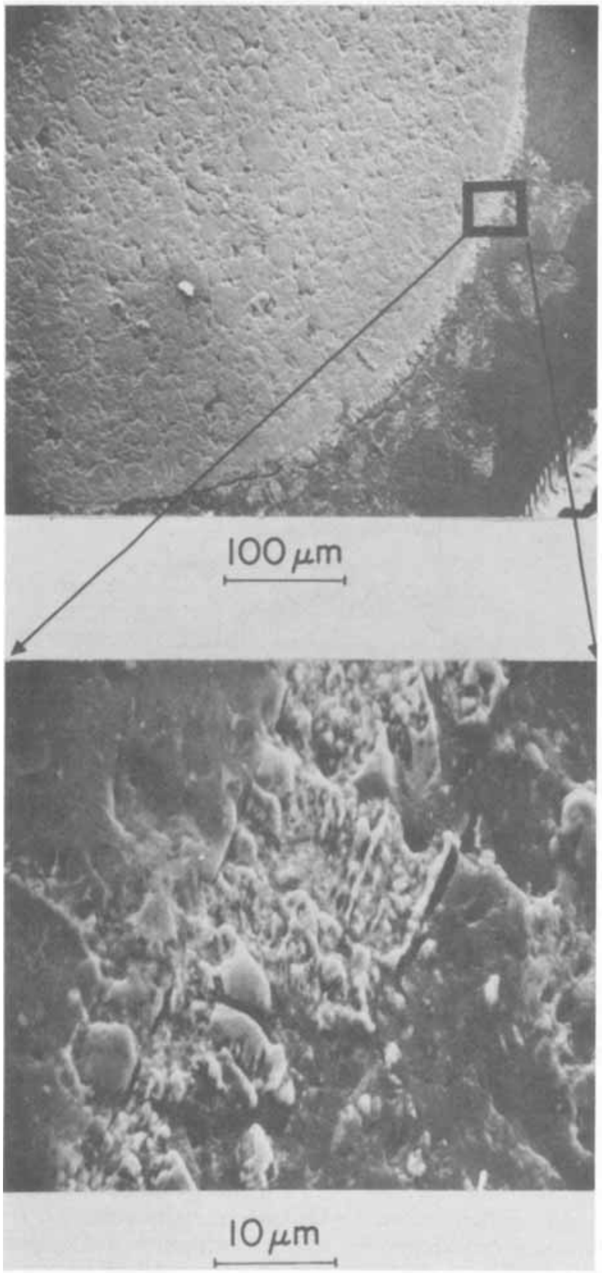

Fig. 5. Scanning electron micrographs of a catalyst particle from the downstream end of the reactor. These pictures parallel those in Figure 1 for the upstream samples. The upper picture shows a polished section of the catalyst. The catalyst is the upper portion; the inorganic crust below is a thin band attached to the surface. The organic deposit further below is irregular with a maximum thickness of 1 200 µm. The lower micrograph shows a small region of the inorganic crust at higher magnification. EDAX data indicated that this zone contained primarily silicon and aluminum, with some titanium, iron, and sulfur.

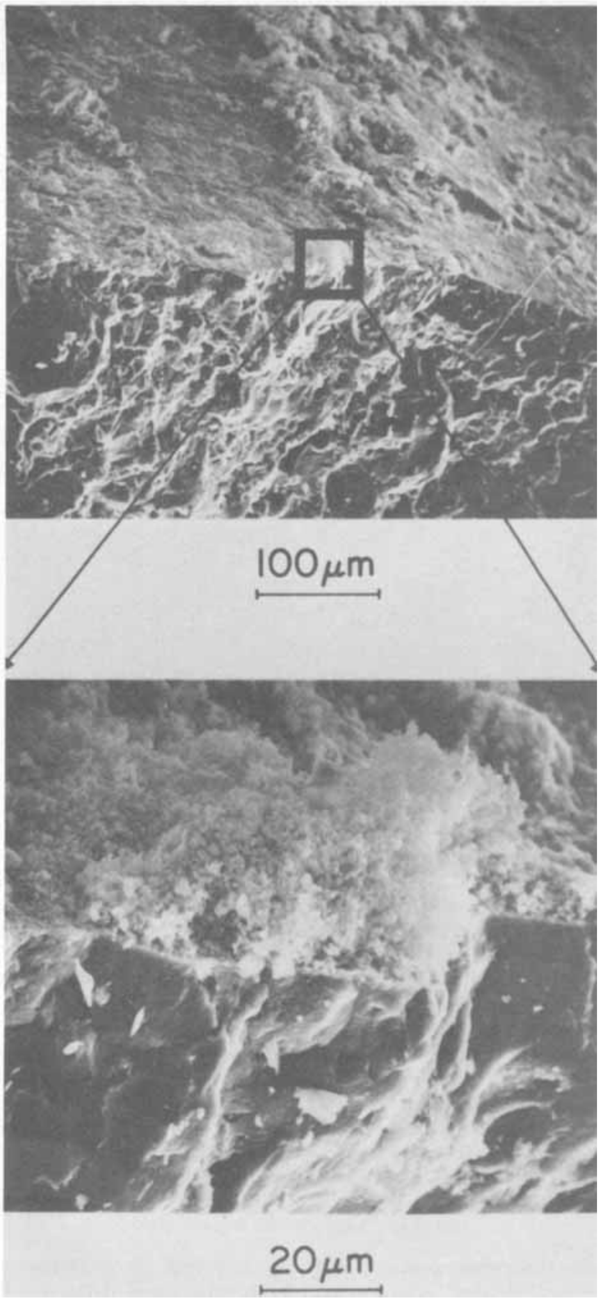

Fig. 6. Scanning electron micrographs of a fractured and plasma etched catalyst particle from the downstream end of the reactor. These pictures are comparable to those of Figure 2, but the sample was tilted to reveal much more of the catalyst surface; the surface was much less encrusted than that of the upstream sample. The lower picture shows a region having high concentrations of silicon and aluminum; this is similar to the regions marked (0) in Figure 2.

amounts of trace aluminum, silicon, calcium, titanium, chromium, and zinc were variable. The fine deposit was largely aluminum and silicon. The amounts of trace elements iron, sulfur, calcium, titanium, and zinc, varied depending on the location analyzed. Cobalt and molybdenum were also present in the crust.

Downstream, an inorganic crust consisting primarily of aluminum and silicon covered about 10 to 20% of the exterior surface. The morphology of this aluminum-silicon deposit was similar to that of the fine, polycrystalline deposit found on the upstream catalyst. The ferrous sulfide crust was entirely absent, and iron and sulfur as well as potassium, calcium, titanium, and zinc were present only in trace amounts.

Besides being deposited on the peripheral catalyst surfaces, inorganic components were also deposited within the interior pore structure. The penetration depth was less than 150 µm. Upstream, the pore mouths accumulated major quantities of iron and sulfur and traces of silicon, calcium, and titanium. Downstream, large quantities of titanium and silicon but very little iron, sulfur, or calcium were found in the pore mouths.

The nature and location of the deposits point to the following conclusions about their sources. The mineral matter of the coal is inferred to have been the source of calcium, potassium, silicon, and zinc. The aluminum may have come from the same source, but it could alternatively have been attrited catalyst. The cobalt and molybdenum found in the exterior crust presumably diffused out from the catalyst. We infer that the titanium found within the

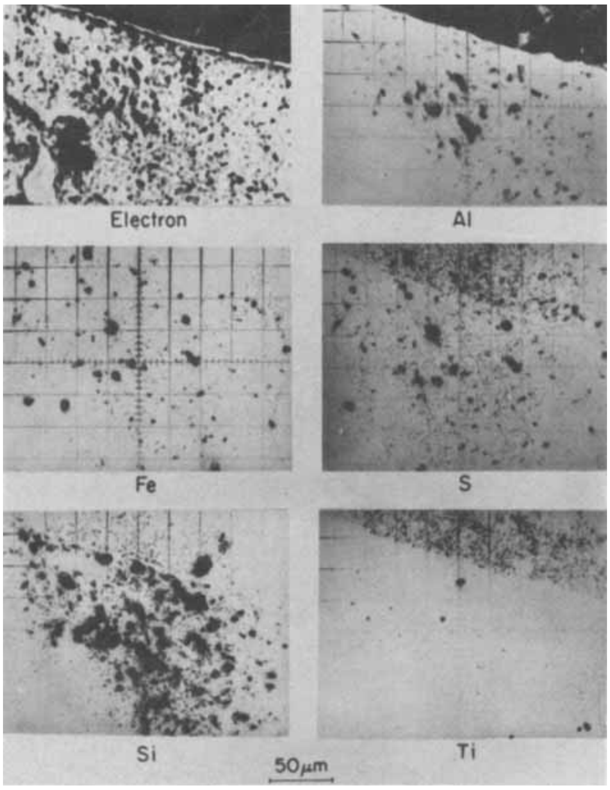

Fig. 7. Electron microprobe x-ray images of the downstream crust. These pictures parallel those of *Figure 3 for the upstream crust*. The electron image shows a roughly 200 μm thickness of the organic crust. A large number of particles less than 10 μm in size are indicated in the crust. The iron and sulfur images show a direct correspondence to one another; a higher background level of sulfur is evident in the interior of the catalyst. In contrast to the catalyst from the upstream section, the downstream catalyst gives evidence of macropores which were not blocked by FeS_x. The ~10 μm pits in the interior, however, were apparently partially filled with FeS_x. A few particles in the organic crust are shown to contain iron but not sulfur. These might be identified as tramp iron. A large number of relatively small particles containing silicon and aluminum are indicated in the organic deposit. These were probably mineral components of the coal. Silicon evidently penetrated into the interior of the catalyst, as did titanium, which appears to have been concentrated in clusters in the organic crust.

pore structure accumulated as a result of reactions of organotitanium compounds from the coal matrix; the entry of these components into the pore structure, especially of the upstream catalyst, was hindered by the exterior crust. Iron might have come from the pyritic components of the coal, or it might have been tramp iron. The sulfur deposits could have originated from either pyritic or organic precursors. Additional sulfur was deposited in the interior of the catalyst during presulfiding before the start of the pilot plant run.

The results demonstrate that solid deposits formed on the peripheral surface of the catalyst and grew into the interstices of the fixed-bed reactor. Such deposits might be expected to accumulate to such an extent in long runs that pressure drops across the fixed bed could become unacceptably high. Within the short run time of the pilot plant experiments, however, no change in pressure drop was observed. Since the inorganic layers covered no more than 50 to 70% of the catalyst surface, it is possible that the turbulent flow to some extent served the desired purpose of abrading deposits (Yavorsky, 1972). Evidence in support of the suggestion of effective scouring by the agitated coal slurry is given in Figure 9, which shows sections of crust partly broken away from catalyst particles.

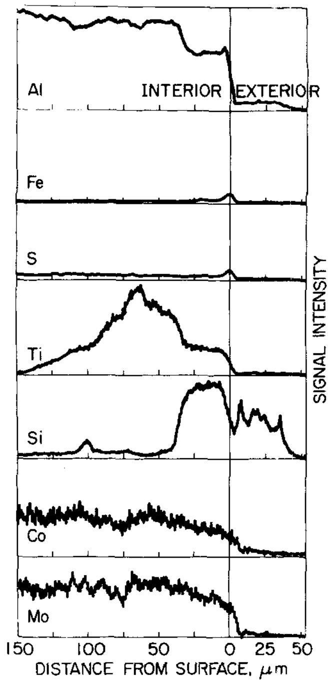

Fig. 8. Electron microprobe concentration profiles of a catalyst particle from the downstream end of the reactor. These profiles parallel those shown in Figure 4 for the upstream sample. The aluminum profile shows a 25 μm wide notch at the interior surface. The silicon profile indicates a correspondingly large inclusion of mineral matter. *Aluminum is indicated in the exterior*, and it also is attributed to mineral matter. The iron and sulfur profiles indicate formation of FeS_x in small quantities. The interior sulfur concentration is above the background. The titanium concentration is much greater for the downstream catalyst than for the upstream catalyst. The notch at the surface corresponds to that indicated by the aluminum profile. The silicon profile is irregular, suggesting that the mineral components were incorporated as 1 to 10 μm particles. The cobalt and molybdenum profiles show that there was transport of catalytically active material toward the exterior of the crust.

The inorganic deposit in the entrance section of the reactor was largely ferrous sulfide, which might well have been formed from pyritic matter, which Akhtar et al. (1975) demonstrated to be preferentially removed from the coal slurry. Since the reaction of pyrites was evidently not complete in the slurry entering the catalyst section, we infer that the process design might be improved by the inclusion of guard-bed reactors to trap a large fraction of the deposits and extend the life of the catalyst. A similar design has been suggested for desulfurization of petroleum residua and is suggestive of the two-stage coal liquefaction/hydroprocessing schemes in which mineral matter is removed between stages.

The changes in the catalyst surface area and pore volume are summarized in Table 1 and Figure 10. The results of the electron microprobe determinations have shown that the physical processes of aging include deposition of

TABLE 1. CATALYST PHYSICAL PROPERTIES DETERMINED BY MERCURY PENETRATION

	Fresh catalyst	Aged catalyst from upstream end of reactor	Aged catalyst from downstream end of reactor
10^{-5} × surface area, m^2/kg	1.74	0.58	1.01
10^4 × pore volume, m^3/kg	2.73	0.89	1.29

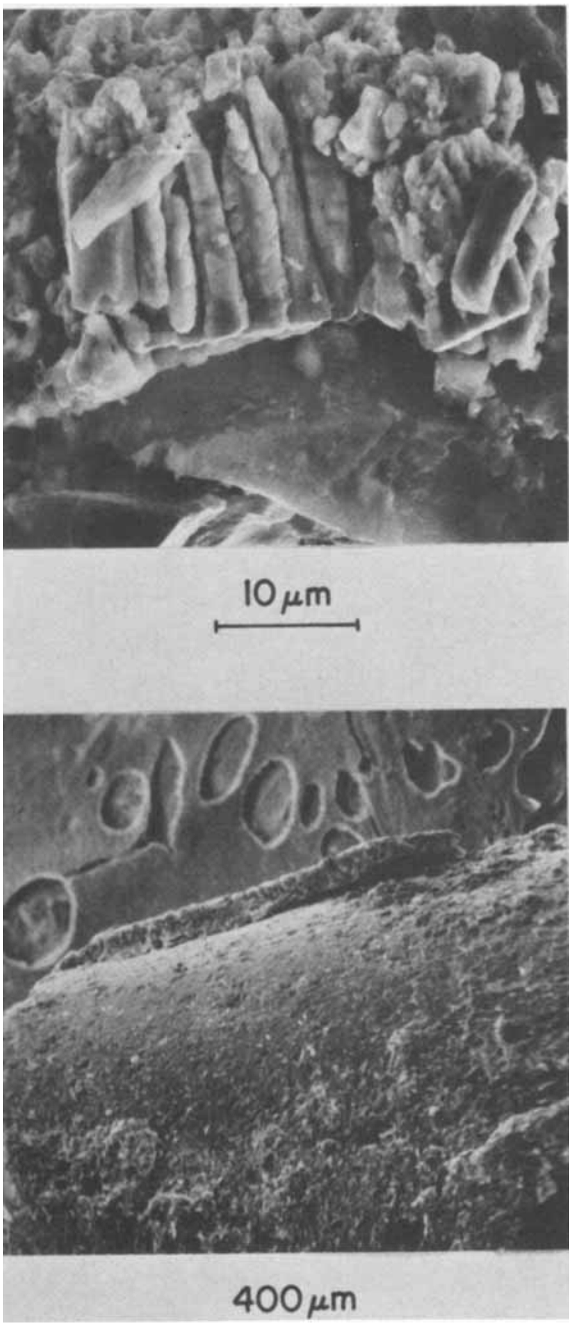

Fig. 9. Scanning electron micrographs of two plasma etched catalyst particles. The upper picture shows a pellet from the upstream section of the reactor at high magnification. The catalyst surface is shown at the bottom of the picture. The fluted structure above, identified as ferrous sulfide, appears to have been partially broken away from the catalyst. The lower picture was taken at low magnification and shows the round surface of a catalyst particle taken from the downstream end of the reactor. The pocked surface behind the particles is indicative of the potting compound. The small piece of crust at the outer surface of the catalyst appears to have been partially broken away from the surface. Both photographs suggest the occurrence of a process such as the scouring of the surface by the turbulently flowing slurry.

solids not only on the exterior catalyst surface but also on the interior surfaces near the pore mouths. The porosimetry data demonstrate that most of the internal deposition occurred in micropores with diameters less than 6 nm. The upstream catalyst sample suffered an overall loss of 70% of both the pore volume and the surface area. The downstream catalyst sample experienced a 40% decrease in surface area and a 50% decrease in pore volume. Further, the upstream sample shows pore mouth blockage by ferrous sulfide, and the downstream sample shows blockage by silicon, aluminum, and titanium. A similar process, involving formation of sulfides of vanadium and nickel, takes place in hydrodesulfurization of petroleum residua. This pore mouth deposition can limit the life of a catalyst by ultimately preventing access of reactant molecules through the narrowed pore mouths. A quantitative definition of the problem could lead to design of optimal pore size distributions for coal processing catalysts.

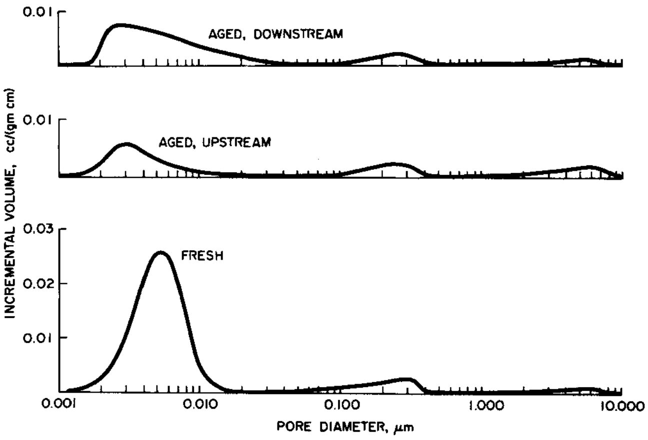

Fig. 10. Pore size distributions of the fresh and aged catalysts. Three kinds of pores are indicated, micropores in the range 2 to 8 nm, macropores in the range 0.1 to 0.4 µm, and cracks of about 5 µm. Most of the area of the original catalyst was in the micropores. The upstream catalyst sample shows a greater loss in micropore volume than the downstream sample, and the micropore size distribution is shifted to lower pore sizes. The pore volume of cracks was greater in the aged catalysts, especially the upstream sample.

The results do not define the chemical processes of catalyst aging, but they provide a basis for speculation about the surface structures of aged hydrodesulfurization catalysts. Surprisingly, these maintain a large fraction of their initial activity even after accumulating massive deposits of coke and metal sulfides. The observed migration of cobalt and molybdenum through the inorganic crust of the coal processing catalyst suggests that the catalytic sites on the surface of the fresh catalyst might even be present on the surface of the deposit. This provides an alternate route to the extended hydrodesulfurization activity of the catalyst than abrasion of the deposits on the catalyst with reactant slurry.

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