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NEW AND IMPROVED DISPERSION AND RECOVERY TECHNIQUES
FOR SLURRY PHASE CATALYSIS

Report Period: October 1–December 31, 1983

Work Performed Under Contract No. AC22-83PC60044

Auburn University
Auburn University, Alabama

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**NEW AND IMPROVED DISPERSION AND RECOVERY
TECHNIQUES FOR SLURRY PHASE CATALYSIS**

Report Period: 10/1/83—12/31/83

Under Contract No. DE-AC22-83PC60044

**Auburn University
Department of Chemical Engineering
Auburn University, Alabama**

New and Improved Dispersion and Recovery Techniques for Slurry Phase Catalysis.

Task 2.1 - 2.5

Introduction. This quarterly report covers an extensive review of the literature in the area of catalyst deactivation and regeneration. The literature review, which is presented here in three sections, namely, carbonaceous deposit formation, metal deposit formation and methods of analysis and regeneration, served as an invaluable aid in the initiation of experimental work required to fulfill the task objectives. Since the literature survey is applicable to all five tasks, no attempt has been made to divide it in terms of contract tasks.

A. Carbonaceous Deposit Formation

Carbonaceous deposits are responsible for early catalyst deactivation (that is, substantial carbonaceous deposits occur before metal laydown). The main sources of these deposits are polycondensed aromatic structures (e.g. naphthalene, phenanthrene, pyrene, chrysene, dibenzofuran, carbazoles, dibenzothiophene and many of the alkyl derivatives of these), of which many are combined with heterocyclic rings (1,2).

In their study of catalytic cracking, Appleby et al (2) reacted 20 different model compounds including naphthalene, quinoline, carbazole, pyrene, dibenzofuran, etc. The catalysts used were synthetic silica-zirconia-alumina (86.2/9.4/4.3 wt%, UOP type B), synthetic silica-alumina (90/10 wt%) and a low alumina content silica (Al < .001%, Ca .02%). The reactions were carried out in a fixed bed bench scale reactor between 400° and 500°C.

They claim that the side chains (> ethyl) and the naphthene rings are removed from the feed molecules on the cracking catalyst, leaving small aromatic molecules. These aromatics are the bulk of the reactants in the coke forming reactions. The monoaromatics are mainly tetralin and indane types, the diaromatics are mainly naphthalenes, the triaromatics are phenanthrenes, and the higher compounds include pyrene, chrysene and perylene. Aromatics are involved at all stages of the coking reactions from the newly adsorbed materials through intermediate ring systems to the polycyclic layer structures which are precursors of turbostratic graphite.

Olefins such as propene, butene and pentene were also present and may contribute to coke formation by reacting with adsorbed species and acting as a hydrogen shuttle (2). The fact that coke formation conversion was higher in mixtures of olefins and aromatics than for either pure component supports this point. It was shown that coke formation increases as the molecular weight of the precursors increase. Coke formation also increases as unsaturation increases for a given aliphatic carbon skeleton (2). N-butane was nearly inert at 500°C whereas n-butenes and 1,3-butadiene reacted extensively at 400°C to form coke (2). Coke formation involves condensation-hydrogen elimination reactions in which the H/C ratio of the coke decreases as the time spent by

the catalyst particle in reaction increases (2). The coke deposit on the spent cracking catalyst was determined to be a mixture of solid coke deposit left from the prior regeneration: a solid or semiliquid mixture of polynuclear aromatics--e.g., dimers and trimers of naphthalene, phenanthrene, chrysene, etc.--and the more strongly adsorbed components of the product. The cokes contained 2-8% ash (2).

The cracking of n-butene and phenanthrene showed active surface area losses of about 22 and 33%, respectively, for 2.8 and 10.4 weight% coke on the catalyst (2). This data indicates that the active surface area loss is due to the blocking off of pores by the coke deposits (pore mouth plugging). An increase in coke formation of almost 400% caused only a 50% increase in active surface area loss. The initial coke deposit clogs and covers the pores rendering a 22% loss of active surface area. The majority of the additional coke piles up on top of the initial deposit and does not decrease the available surface area at all. Only some of this additional coke deposits onto uncovered pores and causes the additional active surface area loss (up to 33%).

The catalysts used in the liquefaction reactions have acidic active sites, and the ability of the aromatics to form coke depends on their basicity (2). It has been suggested (10) that aromatic rings with higher electron density (such as n-containing rings) will have a higher affinity towards adsorption.

Furimsky (1) separately reacted heavy gas oil and bitumen over a Co-Mo catalyst (3% CoO₃-12% MoO₃) in a fixed bed reactor at 2000 psi and 400° and 450°C respectively. Heteroring-containing compounds (mainly asphaltenes) were strongly adsorbed on the surface due to their polar nature. Because the

coke-forming reactions occur on the surface, these heterocyclics will play a more dominant role than nonpolar hydrocarbons as coke precursors. The rate of asphaltene adsorption onto the catalyst reaches a steady state in the early stages of the reaction. The time it takes to reach this steady state is determined by the physical properties of the catalyst (e.g., pore and pellet sizes). These adsorbed asphaltenes then react to form coke.

The S, N and O may be eliminated during the above reaction through the splitting off of unstable groups, e.g., carboxylic, amine, thio, etc. Mochida et al (11) have shown that N and O accumulate in the coke (for dibenzofuran and carbazole reactions) significantly more than S in dibenzothiophene reactions. This difference may be because the C-S bonds are weaker than the C-N and C-O bonds (1). The easy cleavage of the C-S bonds results in the removal of S and H₂S, but the strength of the C-N and C-O bonds keep the heteroatoms in the molecule and hence on the catalyst. Nitrogen compounds are especially poisonous due to their strong basicity. They deplete the surface of protons, thus destroying some proton-donating sites (Bronsted acidity) and decrease catalyst activity (3).

The amount of coke deposited from different feeds may not differ much due to the assumption that a maximum coke layer exists (a saturation level). That is, the reaction ceases after a maximum amount of coke deposits, regardless of the reactant make-up, due to the inaccessibility of the catalyst (1).

Ocampo et al (9) used 18 different catalysts (11 Co-Mo, 4 Ni-W, and 3 Ni-Mo all on alumina or alumina-silica) all of which were presulfided with H₂S at 644K and 18.3 mpa for 3 hours. The reactions were carried out in a

commercial magne-drive 2-liter autoclave at 630, 658, and 687K and 13.9 mpa using Kentucky No. 11 and Wyodak and Illinois No. 6 coals. The higher temperature runs showed higher initial activities; however, all of the runs asymptotically reached the same activity after 72 hours of reaction. The higher initial activities are due to increased cracking and enhanced hydrogenation of the heavy fractions at higher temperatures.

Nickel-molybdates were found to have the highest resistance to carbonaceous deposit deactivation in coal liquefaction (9). Decreasing the coal to catalyst ratio from 12:1 to 2:1 and the coal to solvent ratio from 1:3.3 to 1:20 had little effect on reducing catalyst deactivation. This data reiterates Furimsky's theory (1) that a maximum coke layer exists on the catalyst (a saturation level). The three different coal feedstocks did not exhibit much difference in deactivation characteristics. This study concluded that only a very slight improvement of catalyst activity occurs by using "ash-less" coal, however, this study only dealt with deactivation due to carbonaceous deposits and not metals.

In Ocampo's study (9), carbonaceous deposits were found throughout the pore structure, preferentially within the smaller pores with radii less than 3.0nm. The catalysts which showed the highest activity (Ni-Mo on alumina) may have higher hydrogenation capabilities with Ni in the sulfided form (as opposed to other metals) and high surface areas and pore volumes. Additionally, a significant amount of the surface areas and pore volumes are found in desirable (large) pore size ranges. Examination of the pore volume distributions of catalysts with high and low activity indicates that the high activity catalyst had 73% of its surface area in pores greater than 6nm, and

the lower activity catalyst (Co-Mo) had less than 12% of its surface area in pores of this size. None of the Ni-Mo catalysts studied had small pores; hence, the determination of Ni as the best metal is incomplete (9).

The thickness of the deposits ranged from 0.5 to 2nm, with the thickest layers being in the smallest pores (9). Frequently, pores with radii less than 3.0nm were almost completely filled. Hence, catalysts with large fractions of their surface area in small pores experienced the highest degree of deactivation.

While the carbonaceous deposits rapidly deactivate the catalyst, they also act as adsorption barriers for the inorganic metallics that permanently deactivate the catalyst (9). Since a significant amount of the carbonaceous coke deposits before the metals, some of the metals will adsorb onto a thick layer of coke. During the regeneration process, these metals may be removed since they are not attached to the catalyst surface. The metals are permanently poisonous when they are on or near the catalyst surface.

In all of the above studies, the catalysts lost reactive surface area and pore volume, some of which was regained by regeneration (to be discussed later). A common conclusion reached by researchers in this field is that catalyst life can be improved by increasing the intraparticle diffusional resistance of the catalyst. The degree of diffusional resistance for a given reaction system is dependent on the catalyst productivity, lifetime and physical characteristics (pore and pellet sizes). The diffusional resistance to reaction is exemplified by a pore-mouth plugging mechanism of poisoning. The pore mouths are covered and deactivated by coke deposits.

Stiegel et al (4) studied the effect of catalyst diameter, and to some extent pore diameter, on the deactivation of presulfided catalysts. These are

all cobalt-molybdenum supported on alumina (HDS-1442A and B, HDS-2 with different pellet diameters). Coal was treated in a continuous SRC-II liquefaction process at 663 K. From examining the plots of the catalyst efficacy versus the pellet effectiveness factor for varying degrees of catalyst activity (efficacy, E = amount of feedstock processed per gram of catalyst; effectiveness factor, η = actual catalyst reactivity/catalyst reactivity without any diffusional resistance, and F = amount of initial catalyst activity remaining in catalyst), it is evident that the activity decreases as the amount of coal processed increases. For values of F greater than 0.3, an optimum effectiveness factor exists for a given value of F . Hence, the extent that a catalyst is allowed to deactivate must be selected for a given catalyst size ($E \propto$ pellet diameter) and η value. The efficacy decreases for effectiveness factors greater than 0.6, and the catalyst lifetime goes to zero as η goes to one (no diffusional resistance). Hence the diffusional resistance of the pellet increases the catalyst lifetime.

The small diameter pellets (.8mm) had a higher initial activity (10-20%) than pellets with 1.6mm diameter (4). However, the smaller pellets deactivated much more rapidly and lost almost two-thirds of their initial activity after 50 hours of reaction. This rapid deactivation renders the smaller diameter catalyst with a lower efficacy (4). That is, the large pellets are able to process more coal per weight of catalyst due to diffusional resistance. The smaller pellets may have higher reaction rates which enhance the dissolution of the coal by rapid hydrogenation. The higher initial activity of the smaller pellets can be attributed to these factors.

No difference was observed between 1.6 and 3.2mm diameter pellets in the same experiment. This suggests that an optimum diameter may be obtained due

to the trade-off between catalyst lifetime and intraparticle diffusion. That is, even though the inner portion of the catalyst is still active, the reactants are unable to reach it due to diffusional resistance. In other words, the catalysts have poor effectiveness factors.

Stiegel et al (4) performed a similar experiment reacting catalysts with different average micropore diameters, 5 and 10 nm, and holding all other variables constant. The larger pore catalysts had a higher initial activity but they deactivated faster. After 25 hours of reaction, the catalyst with the higher diffusional resistance (smaller pores) is more active. As was stated earlier, it is the pore-mouth poisoning mechanism that influences the results, and a change in pore structure which changes the deactivation mechanism could yield different or opposite results.

In his review of coal liquefaction catalysts, Gavin (5) states that in some reacting situations the small pores are about the same size as the large asphaltene molecules which are coke precursors. In this case the small pores protect the active sites and act as a molecular sieve to coking. He also cited a study by Hardin (21) in which constant conversions were observed for catalysts with pores between 7.5 and 50nm. These constant conversions were attributed to the trade off between increased mass transfer rate and decreased surface area of the different pore sizes. It should be noted that the pore-mouth poisoning mechanism plays a big part in the diffusional resistance of the reacting pellet. Altering the pore structure such that the deactivation mechanism changes could yield opposite results (12).

B. Metal Deposit Formation

It is strongly agreed to in the literature that metals deposit on the catalyst at a later time than the carbon deposits. Like carbon deposits, the

rate of metal deposition is strongly controlled by the diffusional resistance of the pellet. Measurement of asphaltenes often reveal molecule sizes which are larger than typical catalyst pore diameters. At temperatures approaching reaction temperature, depolymerization of the asphaltenes occurs. This makes the catalyst accessible to at least some of the asphaltenes(13).

Stanulonis et al (18) and Holloway et al (19) measured significant concentrations of Si, Fe, Na, K, Mg, Al, Si, and Ca in and on used CoMo hydrodesulfurization catalysts with alumina-silica supports.

Spry and Sawyer (14) proposed a relationship between the effective diffusivity and the ratio of the reactant diameter and the catalyst pore diameter. They used this to predict the size distribution of the reactant molecules and correlated the demetallization activities (reactivity in reactions where metal containing compounds are deposited onto the catalyst) of catalysts with different pore diameters. Their model implies that because of size differences in the metal-containing molecules found in different crudes, there should be an optimum pore size catalyst for each crude.

In their study of metals contamination, Tamm et al (7) hydrotreated petroleum residuum in a fixed bed reactor. The petroleum residuum contained vanadium, nickel and iron, vanadium often being the most abundant.

Iron was found primarily outside the catalyst particle as a thin scale, although in some cases the iron showed some penetration. Both Ni and V display a maximum concentration inside the edge of the particle, and the point of maximum concentration approached the edge of the catalyst near the outlet of the reactor. The nickel always penetrated the catalyst more than the vanadium.

The amount of vanadium deposited decreased from the inlet to the outlet of the reactor, and nickel shows the reverse behavior.

The distribution of metal in a deposit is controlled by the reactivities and diffusivities of the organometallic compounds present (7). It has been suggested by Beuther and Schmidt (15) that the vanadium compounds are more reactive because the vanadium is coordinated with a protruding oxygen atom, and this makes them subject to attack. However, Tamm found the ratio of reactivities, V/Ni, equal to 0.63 at the reactor inlet and 0.92 at the outlet (under the assumption of second order kinetics). Thus the vanadium compounds are less reactive than the nickel, but they found the concentration of vanadium deposits on the catalyst to be six times that of nickel. The reason for this difference may be the diffusivities of the compounds. In Furimsky's study of bitumen (1), the V/Ni ratio in the feed was 3 but the ratio of V/Ni adsorbed on the catalyst was 9. This shows that vanadium has a higher affinity for adsorption than Ni.

In Tamm's study (7), a reaction temperature of 750°F yielded a maximum vanadium deposit closer to the edge of the pellet ($R = .97$) than at 700°F reaction ($R = .90$). A hydrogen partial pressure of 1825 psia yielded lower maximum vanadium concentration ($.12 \text{ g/cm}^3$) than 2700 psia ($\text{CMAX} = .185$). Thus higher hydrogen pressure ultimately decreases the lifetime of the catalyst. It has been stated in other literature, however, that increasing the hydrogen pressure decreases the amount of coke deposited and increases the catalyst lifetime. Perhaps this discrepancy stems from the fact that Tamm dealt with metal deposits and the other literature dealt mainly with carbonaceous deposits.

As should be expected, different feeds exhibit different metals distribution in the pellet. Small pores showed a higher maximum V concentration ($.23 \text{ g/cm}^3$) than large pores where $C_{\text{max}} = .15$ (7). The small pores had the effect of concentrating the metals closer to the outer surface of the catalyst particle (again exemplifying diffusional resistance). The pore structure directly determines the maximum local deposit which can be tolerated before intraparticle transport of reactants and products is significantly affected. The more uniform the radial metal distribution, the lower the concentration at the maximum, and therefore, the slower the initiation of pore plugging (7). Tamm's study showed the same effect of metal distribution or concentration with different sized catalyst pellets as Stiegel's study(4) done on carbonaceous deposits. The observed radial distributions strongly support the theory of a pore diffusion controlled reaction due to pore-mouth plugging.

The deposited metals are always found in the form of sulfides (eg. V_3S_4), hence the presence of hydrogen sulfide may be necessary for the demetallation reaction to occur (7). At the reactor inlet, there is little H_2S in the external gas phase. The reaction occurs inside the pores, and subsequently H_2S accumulates inside the pellet. This will increase the rate of reaction and metals will deposit inside the pellet. Hydrogen sulfide diffuses out of the pores and is carried downstream. Near the reactor outlet, the H_2S concentration outside the pellets is sufficient for the demetallation reaction to occur at or near the outer pellet diameter, and the metals deposit will show a maximum there. This is supported by the experimental radial distribution. The point of maximum metal concentration nears the edge of the pellet at the reactor outlet .

The maximum deposit concentrations of both Ni and V decreased by about 80% from reactor inlet to outlet, showing that the reaction does not follow a simple first order mechanism (7). In fact, the data almost fits second order kinetics. However, it is suggested that the metals reside in a spectrum of molecules, each having a different reactivity.

Kovach et al (6) studied metal deposition on CoMo catalysts on alumina supports during liquefaction of Western Kentucky No. 11 coal. The catalytic activity was determined by exposure to single organic and inorganic salts in an isolated system followed by a standardized hydrogenation activity test. Na, Ca, Mg, Fe, Ti, and Si were all identified on the used catalysts.

Different metal complexes revealed different deactivation characteristics (6). For example, doubling the concentration of Fe_2O_3 had no effect on the catalyst deactivation. However, when the concentration of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ was doubled, the catalyst deactivated three times as much. Additionally, titanium showed little poisoning behavior as a deposited oxide, but was very poisonous as an organometallic salt. The results indicate that inorganic forms of titanium have no poisoning effects, but organometallic forms are easily absorbed from even low concentrations in coal liquids and lower the hydrogenation activity substantially.

Holloway et al (19) found that the distribution of Ti in the "Synthoil" reactor catalysts varied with the position of the pellets in the reactor. At the reactor inlet, Ti penetration into the pellets reached 200 μm , but at the center and outlet, penetration was only 25 μm . This is probably because the liquid is essentially pure solvent at the inlet and does not hinder the transport of the Ti-complexes. Further downstream the concentration of heavy coal liquids is higher, and these hinder the transport of the Ti-complexes into the

pellet. In general, inorganic metallics are essentially insoluble in the coal-liquids, and are less able to diffuse into the narrow mouth pores. Initially their deactivation effect should be limited to the outer surfaces. However, for long reaction times, they could diffuse deeper into the pores (7).

C. Methods of Analysis and Regeneration

In their catalytic cracking study, Appleby et al (2) dissolved the used silica-alumina catalyst with hot concentrated sodium hydroxide to separate the coke from the catalyst. From this the weight of the coke deposited was determined. The coke was then analyzed by X-ray diffraction. Some of the coke was dissolved in benzene and chromatographed over alumina to separate the wash into fractions. Ultraviolet spectra of these fractions showed many compounds, the main ones being fluoranthene, perylene, benzofluoranthene, 1,2-benzanthracene, chrysene and pyrene. This showed that part of the coke had formed a turbostratic graphite structure. The conclusion that condensed systems of fused aromatic rings are the major component of coke was also made. The coke formation was 14.8% of the feed and contained 4.0 weight % hydrogen. The feed contained 14.3 weight % hydrogen.

After the reactor was drained, it was purged with nitrogen gas for at least 20 minutes to remove unreacted feed and volatile products. The temperature was then raised from the reaction temperature (usually 500°C) to the regeneration temperature of 550°C. A mixture of air and nitrogen was used to keep the temperature from rising above 575°C (2).

Furimsky(1) hydrotreated heavy gas oil and bitumen over cobalt molybdate (3% CoO₃-12% MoO₃) 1/8 x 1/8 inch cylindrical pellets. Extractions of pellets were carried out in a Soxhlet apparatus. A clean solvent indicated the end of

extraction. After evaporation of the solvents, the extracts and catalyst pellets were subjected to high vacuum at 100°C to remove any remaining solvent. Analysis for carbon, hydrogen, nitrogen and oxygen were performed on a Perkin-Elmer 240 analyzer and a Dohrman microcoulometer. Sulfur was determined by either Leco or an X-ray fluorescence technique. Atomic absorption spectroscopy was used to determine metals content.

Preextraction with benzene was chosen as a basis of carbonaceous deposit identification, assuming that the light fractions and soluble asphaltenes are removed by the benzene. Pyridine extractions followed benzene in an attempt to remove any remaining deposits. The chemical analysis of the extract indicated significant amounts of metal. The amount of metal removed depends on the solvent used. Strong solvents, such as quinoline are expected to remove more metals than pyridine (1). The high amount of N and O from the gas oil is unexpected and may be due to the fact that some pyridine might have been left in the extract (1).

Ocampo et al (9) studied the deactivation of many different catalyst during coal liquefaction in a pressurized autoclave. After a given reaction time, the reaction was stopped and the reactor contents dumped. All heavy hydrocarbons were removed from the catalysts by washing each one for 15 minutes, once with tetralin and then with a reference standard. Charges of the latter were then used to evaluate the catalyst's hydrogenation activity.

Researchers have determined activity by either measuring the amount of unconverted coal and the liquid product distribution or the amount of sulfur removed. These methods mask the true activation mechanism by using the overall process data. A more sensitive method of evaluation is to

periodically determine the residual catalyst activity by a carefully controlled hydrogenation of a standard aromatic hydrocarbon (9). The extent to which this standard reaction occurs is then measured by the refractive index of the reaction mixture.

The catalysts were analyzed by X-ray diffraction and atomic absorption after the reaction and after regeneration to determine the metals content (9). Unsulfided, sulfided, used and regenerated catalysts were examined for surface area, pore volume, and carbon-hydrogen deposits. The used catalysts were soaked in tetralin and cooled to room temperature. All catalysts were degassed at 353K for at least 8 hours at 0.0001 torr before pore characterization. Surface areas and pore volumes and their distribution with pore radii were evaluated from nitrogen adsorption-desorption isotherms at 77K. The pore volume distributions results were confirmed by mercury intrusion. The catalysts were regenerated in air at 770K. Another technique consisted of oxidizing the catalyst with air, but the temperature was raised by 1 K/min from the reaction temperature to 777K. This technique resulted in the removal of carbonaceous deposits from even the small pores (9). The pore characteristics were recovered and increased slightly with a distribution tending toward the larger pore sizes. In addition to re-oxidizing the molybdate and carbon-hydrogen deposits, the regeneration caused some of the pore walls to collapse. The regenerations restored the catalysts to their initial activity, even after repeated regenerations. It should be noted that the coal feedstock used had a low metals content (metal deposits = permanent deactivation).

In their study of the effect of catalyst diameter, Stiegel et al (4) used cobalt-molybdenum catalysts supported on alumina. Samples of the liquid

product were collected and subjected to a microfiltration technique. This technique classifies the conversion of coal based on the solubility of the products in various solvents. Tetrahydrofuran, ethyl acetate and cyclohexane were used to determine total conversion, conversion to asphaltenes plus oils, and oil conversion, respectively. X-ray diffraction analyses of the catalysts in their oxidic and sulfided states were unable to provide information on the dispersion of the cobalt and molybdenum on the catalyst surface. No peaks were observed which could be attributed to either cobalt or molybdenum.

Mercury porosimetry was used to determine the pore volume before and after the run. Mercury porosimetry was chosen instead of nitrogen BET because it is better for analyzing the larger pores. The smaller pores (less than 3 nm) which are best measured by BET are rapidly filled early in the liquefaction run.

Regeneration was conducted by subjecting the catalyst to increasing levels of oxygen in nitrogen (0.5 to 21%) at a rate of 3.75×10^{-8} m³/s for 9 hours at 723K (8). The regeneration did not fully restore the pore volume, surface area or pellet density to their initial states. The longer the catalyst was in the reactor, the bigger the difference in the properties of the new and regenerated pellets. X-ray analysis showed that sintering of the catalyst occurred in the form of a growing molybdenum sulfide crystallite during the liquefaction reaction. Regeneration was done under mild conditions in order to prevent any additional sintering (6).

In their study of metal deposition, Tamm et al (7) used gel permeation chromatography to measure the molecular size of the asphaltenes in the reactant (petroleum residuum). Some asphaltenes were larger than the small pore diameters of the catalyst. An applied research laboratories model EMX/

SM electron microprobe was used to measure metal composition profiles through the pellet radius. In most cases, 50 data points were taken over the radius of the pellet.

Thomas and Sample (16) used a variety of methods to characterize the catalysts used in the H-coal bench scale process. Illinois No. 6 coal was processed at 454°C and 15.5 mpa. The catalysts used were NiMo and CoMo on alumina supports. Emission spectroscopy was used to determine the concentrations of the major metal components on the coke. Fe, Ti, B, Mg, Ca, and Si were deposited in concentrations greater than 0.1 wt%, and the different catalysts showed different affinities for the contaminants. The total metal deposit amounted to several weight percent of the catalyst. It was found that the highest concentration of contaminants came from the most abundant species in the coal. However, the major metal-contaminant concentrations were not proportional to their respective concentrations in the coal.

Optical and scanning electron microscopes were used for preliminary scanning of the catalysts (16). Optical observations (50-5000X) of used catalysts in cross-section (longitudinal and lateral), revealed regions of higher reflectivity near the surface. These extended in the range 5-20% of the diameter of the catalyst. For many of the pellets, the penetration from the end was one to four times greater than from the sides, and for all catalysts, there was an abrupt boundary. The deeper penetration could be a result of the combined diffusion from the sides and ends.

These optically observed reflective surface regions were clearly seen with a scanning electron microscope. A smooth external surface of the spent catalyst is in contrast to the rough, porous nature of the fresh catalyst.

Upon magnification above 2000x, crystallites were observed in spent samples, but none are seen in fresh samples (16).

The above crystallites were identified by three methods: morphological comparison, transmission electron microscopy (TEM), and energy dispersive X-ray analysis. The largest crystallite mass observed had dimensions of approximately $5 \times 0.5 \times 1 \mu\text{m}$ and was identified as MoS_2 . Use of energy dispersive X-ray analysis allowed direct identification of the larger crystallites. X-ray diffraction confirmed the presence of MoS_2 in the bulk sample, but the broadness of the X-ray lines suggested small crystals. Electron diffraction of the particles suggested some noncrystalline agglomerates.

Quantitative electron microprobe analysis provided depth profiles of metal-oxides and sulfides. The stoichiometry of Mo and S, on an atomic ratio, was consistent with MoS_2 (16). Further surface characterization by the electron microprobe partially defined the spent catalysts chemical characteristics. The major alkaline earths, Ca and Mg, were deposited in the outer $50 \mu\text{m}$. This type of surface deposition was not seen for the alkali metals and their concentrations were much lower. Ti and Fe compounds penetrated the catalyst much more than other metals. The depth of this penetration was consistent with the observations of the optical and electron microscopes mentioned above. There may be a relation between the concentrations of Ca and Ti in some regions of the pellet, possibly due to perovskite, CaTiO_3 . Electron diffraction was used to positively identify TiO_2 , MoS_2 , FeS , FeS_2 and CaSO_4 .

It should be noted that zinc was not observed as a contaminant, even though it was present in the processed coal. However, boron was found in much

higher proportions in the catalyst than in the coal. This difference may be due to the fact that boron is highly associated with the organic part of the coal whereas zinc is associated with the inorganic (insoluble) part (17). The lack of zinc deposition disagrees with a study conducted by Ternan and Brown (8), in which they also hydrotreated coal using CoMo catalysts on an alumina support. X-ray photoelectron spectroscopy (XPS) was used to determine zinc in that study.

Thomas and Sample regenerated the catalysts by ignition at 775° and 450°C. This removed 18-23% and 13-18% of the deposited metals from the catalyst, respectively. A higher percentage of metals was removed from the NiMo catalysts than from the CoMo catalysts at each temperature.

In his characterization of catalysts by petroleum asphaltenes adsorption, Saint-Just (20) continuously monitored the color of the solution by visible spectrometry. The reaction solution was recycled from the bottom of the vertical, tubular reactor, through the spectrometer cell, and back into the top of the reactor. A wavelength of 550 nm was used in the spectrometer, since the absorbance at 550 is a function of the vanadium content. This was confirmed by measuring the vanadium content of the solution by X-ray fluorescence. Nitrogen absorption was used to determine the average pore radius. The amount of vanadium adsorbed in the pellet increases as the pore radius increases (the vanadium containing molecules diffuse more easily into the larger pores). This reiterates the concept of diffusional limitation.

The diffusional resistance was again attributed to pore-mouth plugging. This was shown by running the reaction with standard catalyst pellets and with crushed pellets. The crushed pellets showed a fivefold increase in

reactivity. It was concluded that the crushing revealed large volumes of pores that would otherwise be "sealed off" from the reaction solution due to pore-mouth plugging.

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