# Diffusion and Catalytic Activity Studies on Resid-Deactivated HDS Catalysts

Three different pore size CoMo/$Al_2O_3$ catalysts, which had been deactivated to the same extent during bench-scale tests with an atmospheric resid, were examined for coke and metal deposits, diffusivity, and intrinsic activity for hydrodesulfurization, hydrogenation, and hydrodenitrogenation using model compounds. The aged catalysts had very low effective diffusivities and lower intrinsic activities than the fresh catalysts. Both metals and coke deposits were responsible for lowering diffusivity, but activity reduction appears to be predominantly due to metal deposits.

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## SCOPE

Supported CoMo/$Al_2O_3$ catalysts have been used for many years to hydroprocess light to moderate molecular weight refinery feedstocks. Application of these catalysts to heavier feedstocks has been less successful because of catalyst deactivation. Residuum hydroprocessing catalysts must be replaced every six months to one year depending on the feedstock properties. The economic feasibility of such hydroprocessing is markedly affected by catalyst costs.

The catalysts deactivate due to deposition of coke and metals from the feedstock onto the catalyst surface. These deposits cause lower intrinsic surface activity by covering active catalyst sites and cause lower catalyst effectiveness factors by pore constriction or blockage.

It has been shown that the effective catalyst lifetime is a function of the catalyst support pore structure. Nielsen et al. (1981) and Hannerup and Jacobsen (1983) have shown that there is an optimum catalyst pore size giving a maximum lifetime for any particular feedstock and processing condition. Understanding the principles behind catalyst deactivation can lead to better designed catalysts with longer lifetimes.

The objective of this study was to assess the role of the structural properties of the support on hydroprocessing catalyst deactivation. The physical properties of the fresh and aged forms of three different pore size CoMo/$Al_2O_3$ catalysts were measured and compared. The catalysts were tested for room temperature effective diffusivity of a polyaromatic model compound using a method developed by this laboratory (Chantong and Massoth, 1983). High-pressure activity testing was used to determine the residual activity of the deactivated catalysts.

## CONCLUSIONS AND SIGNIFICANCE

Catalyst deactivation lowered the effective diffusivity of coronene at room temperature by a factor of over 500. This was a result of the buildup of an outer edge diffusion barrier, which was high in metals deposits. This diffusion barrier may significantly affect the catalyst effectiveness near the end of a hydroprocessing run.

Metals and coke deposits lowered catalyst diffusivities by forming wedge-type deposits at pore mouths throughout the catalyst particles. Complete blockage of pore mouths by deposits did not occur in these catalysts.

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**Intrinsic catalytic activities for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation were significantly lower in the aged catalysts, compared to the fresh catalysts. The metals deposits were solely responsible for loss of HDS activity and mainly responsible for loss of HDN and hydrogenation activities.**

**Catalyst lifetime under the hydroprocessing conditions of this study is not related to the total metal or coke deposition, but rather to the catalyst pore size.**

## Introduction

Hydroprocessing catalysts gradually become deactivated during processing of heavy feedstocks (resids). In commercial operation, the catalyst loss in activity is usually compensated for by increasing the reactor temperature to maintain a constant conversion at the desired reactant feed rate. The deactivation curve, in terms of temperature vs. time on-stream, typically exhibits an S-shaped curve (Tamm et al., 1981; Nielsen et al., 1981; Hannerup and Jacobsen, 1983). The curve shows a sharp initial increase in temperature, followed by a slower, gradual rise in temperature, and finally another rapid temperature rise, requiring termination of the run when the temperature required to maintain catalyst activity exceeds a prescribed maximum operational temperature.

The three stages of catalyst deactivation have been ascribed (Tamm et al., 1981; Bridge, 1982) to:

1. Rapid coke formation with attendant loss in catalyst active sites
2. Gradual buildup of metal deposits, notably vanadium and nickel, causing further loss in catalyst intrinsic activity
3. Constriction or blockage of pore mouths by continued deposition of metals with additional loss of catalytic activity due to diffusional limitations.

In addition to loss of catalytic activity by these processes, preferential metals deposition near the exterior surface of the catalyst particle may contribute to an additional diffusion barrier to reactants entering the interior of the catalysts (Tamm et al., 1981; Dautzenberg et al., 1978; Newson, 1975).

In order to assess the role of coke and metals deposits on the activity of hydrodesulfurization (HDS) catalysts, and especially the influence on intraparticle diffusion, three catalysts, which contained different pore structures and had been tested in a bench-scale flow reactor for HDS of an atmospheric resid (Nielsen et al., 1981), were examined in this study. Inspection of the aged catalysts from the runs included physical properties of the catalyst, coke and metals deposits, thermogravimetric analysis, catalyst diffusivities, and catalytic activities for model compounds representative of HDS, hydrogenation (HYD), and hydrodenitrogenation (HDN). Fresh, aged, and aged-regenerated catalysts were studied.

## Experimental

### *Catalysts*

The catalysts in this study contained about 2% Co and 7% Mo on different activated alumina supports. Properties of the supports and fresh catalysts are given in Table 1. The catalysts had a range of average pore diameters from 10 to 17.5 nm, which encompasses those generally used in resid hydrotreating applications (Gajardo et al., 1982).

The catalysts, $7.9 \times 10^{-4}$ m (1/32 in.) extrudates, were tested at the Topsoe laboratory for HDS of an atmospheric resid in a $5.0 \times 10^{-5}$ $m^3$ trickle-bed reactor described elsewhere (Nielsen et al., 1981). Reactor conditions were 17.2 MPa pressure, a LHSV of 2, and 70% HDS conversion. The runs were terminated at 80 K above base temperature. Temperature-time deactivation curves for the catalysts *E*, *A*, and *F* exhibited typical S-shape patterns, with run duration (lifetime) varying in the ratios *E*:*A*:*F* = 0.74:1.0:0.85. The spent catalysts, taken from the middle half-section of the reactor, were Soxhlet-extracted

**Table 1. Physical Properties of Catalysts**

| Catalyst | Surface Area $\times 10^{-3}$ $m^2/kg$ | Pore Vol. $\times 10^3$ $m^3/kg$ | Avg. Pore Dia. nm | Particle Dens. $\times 10^{-3}$ $kg/m^3$ |
|---|---|---|---|---|
| Support* | | | | |
| E | 238 | 0.68 | 11.4 | 1.02 |
| A | 185 | 0.67 | 14.5 | 1.03 |
| F | 144 | 0.66 | 18.3 | 1.04 |
| Fresh | | | | |
| E** | 219 | 0.57 | 10.4 | 1.17 |
| A† | 194 | 0.60 | 12.3 | 1.13 |
| F‡ | 125 | 0.54 | 17.3 | 1.21 |
| Aged | | | | |
| E | 92 | 0.21 | 9.1 | 1.75 |
| A | 60 | 0.20 | 13.3 | 1.94 |
| F | 57 | 0.20 | 14.0 | 1.88 |

*Proprietary aluminas
**2.1% Co, 6.9% Mo
†1.9% Co, 6.9% Mo
‡1.7% Co, 6.9% Mo

with xylene followed by an acetone wash and drying at 393 K to remove adsorbed materials. The aged catalysts were regenerated by heating overnight in a muffle furnace at 773 K. Physical property data of the aged catalysts are also given in Table 1.

### *Physical property measurements*

Surface areas were determined by the standard BET method using $N_2$. Pore volumes were measured by Hg porosimetry. Determination of carbon was made by combustion and of metals by wet chemical analysis and atomic absorption.

Radial distribution plots of metals in aged catalyst extrudates were obtained *with* an Applied Research Laboratories EMX electron microprobe. Samples were imbedded in plastic and were ground down to expose a radial cross section at about one-half of the extrudate length; this was followed by polishing.

### *Diffusion experiments*

Diffusivity measurements on the catalysts were carried out as described previously (Chantong and Massoth, 1983) using coronene (1.11 nm critical dia.) as the solute. Basically, the technique involved measurements of the residual coronene concentration (in a cyclohexane solution) with time during exposure of the catalyst to the solution in a stirred-tank batch reactor at ambient temperature and pressure. Catalyst charges of about 0.2 to 1.0 × $10^{-3}$ kg with 4.00 × $10^{-4}$ $m^3$ of 23 × $10^{-3}$ kg/$m^3$ coronene in cyclohexane were used. The coronene (Aldrich) was of the highest purity commercially available. Spectrograde (99+%) cyclohexane was pretreated with calcined 13X zeolite to remove water and other impurities. Runs were carried out on both extrudates and on 2.1–4.2 × $10^{-4}$ m (35–65 mesh) crushed samples of these. Because of the extremely slow diffusion and low coronene uptake of the aged extrudate catalysts, these runs were carried out in sample bottles rather than in the stirred reactor, taking periodic samples of solution for analysis and then replacing the solution in the bottle; because of the slow diffusion in the catalyst, stirring was not required. Solution concentrations were measured with a Beckman Model 25 UV spectrometer at a wavelength of 328.8 nm, calibrated with known mixtures.

The basis for calculating diffusivities has been given elsewhere (Chantong and Massoth, 1983). Material balance allows calculation of the amount of solute uptake by the catalyst at equilibrium. The adsorption constant, $K$, can be calculated from the equilibrium uptake divided by the final concentration. A fractional approach to equilibrium is calculated for each point and the overall solution fractional depletion calculated. A dimensionless parameter $\tau_t$ for each point is then determined from tables of Rudloff (1965) and $\tau_t$ is plotted vs. sample time. The slope of this plot is given by

$$\text{Slope} = \frac{D_e}{R^2(\epsilon + \rho K)} \tag{1}$$

where $R$ is the catalyst particle size, $\epsilon$ the fraction void volume, and $\rho$ the density. From Eq. 1, the effective diffusivity $D_e$ can be calculated. The above analysis pertains to spherical particles (crushed samples) having three-dimensional coordinates. For the extrudate samples, an analogous analysis was carried out based on two-dimensional cylindrical coordinates in the basic differential equations (Crank, 1975), equivalent $\tau_t$ Rudloff tables being generated by a computer program. Because of the very slow attainment of equilibrium with the aged and regenerated extrudate samples, final uptake values were not obtained, the values for the comparable crushed samples being used to calculate diffusivities. In all cases, a linear adsorption isotherm was assumed.

### *Thermogravimetric analysis (TGA)*

TGA was performed on the catalysts in a temperature-programmed flow microbalance. The catalyst was crushed to less than 6 × $10^{-5}$ m (>250 mesh) and 100 mg placed in the balance bucket. The temperature was raised at a rate of 0.05 K/s in a $N_2$ flow until reaching 673 K. Catalyst weight loss as a function of temperature was continuously monitored.

### *High-pressure activity testing*

Model compound catalytic activity tests were carried out in a fixed-bed, vapor-phase flow reactor (Liu et al., 1984) at 3.5 MPa pressure. The catalysts were tested for dibenzothiophene hydrodesulfurization, naphthalene hydrogenation, and indole hydrodenitrogenation. The stainless steel tube reactor of 6.4 × $10^{-3}$ m ID was located in a 5 × $10^{-2}$ m OD by 0.46 m long copper jacket, which was heated by a furnace. A sintered stainless steel disk (100 $\mu$m pore) held the catalyst bed in place.

The catalyst (5.00 × $10^{-4}$ kg based on the amount of fresh catalyst present) was mixed with 5 × $10^{-3}$ kg of 5 × $10^{-4}$ m glass beads. The catalyst-glass bead mixture was preceded in the reactor by 0.19 m of a 1 × $10^{-3}$ m glass bead preheating section, and followed by 5 × $10^{-2}$ m of 5 × $10^{-4}$ m glass beads and 0.19 m of 1 × $10^{-3}$ m glass beads. The catalyst was first sulfided *in situ* with a 10% $H_2S/H_2$ mixture at 673 K for 7.2 × $10^3$ s, after which the reactor was cooled to 548 K and pressurized to 3.5 MPa $H_2$. A liquid feed containing 2 wt. % dibenzothiophene and 1.2 wt. % dimethyldisulfide in *n*-heptane solvent was fed to the reactor at 1.1–1.4 × $10^{-9}$ $m^3/s$ with a hydrogen flow of 2.33 × $10^{-6}$ $m^3/s$ and held overnight. The hydrodesulfurization (HDS) activity was then measured at four different liquid feed rates with 7.2 × $10^3$ s intervals between sampling. The liquid products were condensed and collected for analysis. After HDS testing, the liquid feed was replaced with one containing 2% naphthalene and 1.2% dimethyldisulphide, held overnight, and then sampled the next day as before. Following this, the reactor temperature was increased to 623 K, and a 2% indole and 1.2% dimethyldisulfide feed was passed over the catalyst overnight and was sampled the next day. Liquid products were analyzed by gas chromatography with a flame ionization detector, employing a 6% OV-17 on chromosorb column. Under the reaction conditions employed, reactants and products were in the vapor phase. Estimates of effectiveness factors (Satterfield, 1981) were virtually unity for all reactions. Further experimental details are given elsewhere (Johnson, 1985).

## Results

### *Catalyst inspections*

Physical properties of the aged (spent) catalysts are given in Table 1. These samples had appreciably lower surface areas and pore volumes compared to the fresh catalysts, and lower average pore diameters. Table 2a presents elemental analyses of deposits on the aged catalysts. Aged catalyst $E$ had higher coke but lower metal deposits than *F*, while catalyst *A* was intermediate. Assignment of deposits to the expected compounds, given in Table 2b, shows that the total deposits were about the same for all aged catalysts. Table 2c gives the estimated volumes of deposits assuming normal densities and a value of 1.8 × $10^3$ kg/$m^3$ for coke (Levinter et al., 1967). Coke formation was approximately proportional to the surface area of the fresh catalyst, whereas depositions of V and Ni were roughly proportional to the average pore diameter of the fresh catalyst.

Color photographs of sectioned, aged-regenerated extrudates taken under a light microscope revealed a brownish yellow ring at the outer 10–20% periphery of the extrudates. Also, the higher metals-loaded *F* catalysts showed deeper penetration of the metals toward the extrudate center. Electron microprobe analyses of the aged extrudates showed this ring to be due to vanadium and nickel deposits. An example of a microprobe analysis is given in Figure 1, where high concentrations of V and Ni near the extrudate outer edge are evident.

**Table 2a. Elemental Analyses of Aged Catalysts**

| | Catalyst, Wt. % of Element | | |
|---|---|---|---|
| Element | E | A | F |
| C | 11.5 | 9.5 | 4.3 |
| V | 9.0 | 11.8 | 13.7 |
| Ni | 2.5 | 3.4 | 4.1 |
| Fe | 0.14 | 0.14 | 0.2 |
| Na | 1.5 | 1.0 | 1.3 |

**Table 2b. Proposed Composition of Aged Catalysts**

| | Catalyst, Wt. % of Component | | |
|---|---|---|---|
| Component | E | A | F |
| $CH_{0.7}$ (coke) | 12.1 | 10.0 | 4.5 |
| $V_2S_3$ | 17.4 | 22.9 | 26.6 |
| NiS | 3.9 | 5.3 | 6.4 |
| FeS | 0.2 | 0.2 | 0.3 |
| NaCl | 3.8 | 2.5 | 3.2 |
| Total | 37.4 | 40.9 | 41.0 |
| Correction factor* | 1.63 | 1.70 | 1.70 |

*Factor to correct catalyst weight to fresh catalyst basis. Corrections are based on total deposits and conversion of catalyst from sulfide to oxide (fresh) basis.

**Table 2c. Estimated Volume of Deposits on Aged Catalysts**

| Assumed Component | Assumed Density × $10^{-3}$ kg/$m^3$ | Vol. of Deposit × $10^3$ $m^3$/kg Aged Cat. | | |
|---|---|---|---|---|
| | | E | A | F |
| $CH_{0.7}$ (coke) | 1.8 | 0.07 | 0.06 | 0.03 |
| $V_2S_3$ | 4.7 | 0.04 | 0.05 | 0.06 |
| NiS | 5.5 | 0.01 | 0.01 | 0.01 |
| FeS | 4.7 | 0 | 0 | 0 |
| NaCl | 2.2 | 0.01 | 0.01 | 0.01 |
| Total deposits | — | 0.13 | 0.13 | 0.11 |
| Equiv. pore vol. of fresh cat.* | — | 0.35 | 0.35 | 0.31 |
| Net pore vol. of aged cat. | — | 0.22 | 0.22 | 0.20 |
| Measured pore vol. | — | 0.21 | 0.20 | 0.20 |

*Equiv. vol. = (vol. fresh cat.) × (1 − % deposits/100)

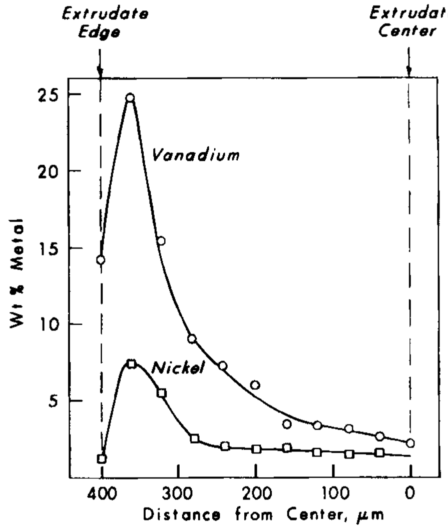

**Figure 1. Electron microprobe of aged *E* extrudate.**

### *Thermogravimetric analysis (TGA)*

TGA was performed on the aged catalysts in order to determine the temperature at which the catalysts should be heated to remove adsorbed water and any residual solvent from the extraction, as these would be expected to lower considerably the adsorption of coronene in the diffusion experiments (Moora, 1977). It was anticipated that heating the aged catalysts at too high a temperature might volatilize some of the carbonaceous surface species. Therefore, it was desirable to find a temperature at which the excess solvent and most of the water is removed without loss of coke species.

The test results of the aged catalysts are shown in Figure 2. A

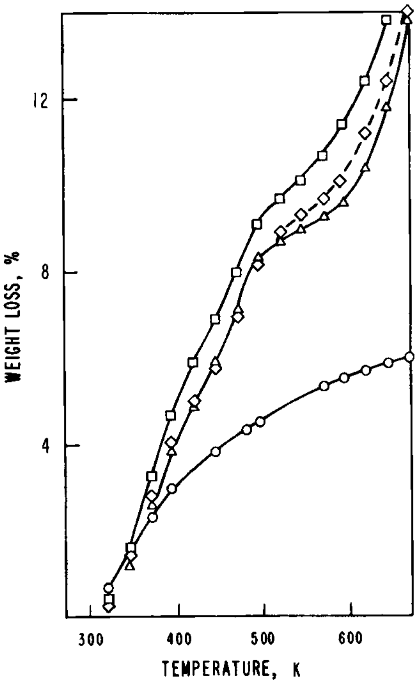

**Figure 2. TGA results for catalysts in $N_2$; heating rate 0.5 K/s.**

Catalysts: ◇ *A*, aged; □ *E* aged; △ *F*, aged; ○ *A* fresh

fresh catalyst was run for comparison. The aged catalysts showed a sharp initial weight loss of about 8% up to 500 K. A leveling off of the rate of desorption occurred until about 573 K, followed by another sharp increase that continued past 673 K. The fresh catalyst had initially the same rate of desorption up to 373 K but then asymptotically leveled off at around 6% weight loss. The difference in weight loss between the aged and fresh catalysts is probably due to solvent retained from the cleaning of the aged catalysts after use. The rise in weight loss of the aged catalysts after 573 K may be due to volatilization of some surface carbonaceous material. From these results, it was decided to heat the aged catalysts to 523 K in nitrogen before use in the diffusion runs. This should remove most of the water and solvent present without altering the catalyst surface. The other catalysts were calcined at 523 K also to give comparable results.

### *Diffusion runs*

Fractional uptake plots for crushed and extrudate catalyst *A* are given in Figures 3 and 4, respectively. The different time scales for these plots are to be noted. The extrudate uptakes are slower because of their larger particle size. Previous studies with different aluminas have shown that the uptake is diffusion-controlled, the diffusivity being inversely proportional to the square of the particle radius (Chantong and Massoth, 1983). Of significance are the lower relative uptake rates for the aged and regenerated vs. fresh samples for the extrudate catalysts, compared to the crushed catalysts. Thus, the presence of the metals at the outer portion of the extrudate causes a severe lowering in the uptake rate and consequently the diffusivity. The uptake data were worked up in terms of the dimensionless parameter $\tau_t$ vs. $t$ (see the Experimental section). From the slope, the effective diffusivity $D_e$ is calculated from Eq. 1. A summary of the results is presented in Table 3.

Effective diffusivities varied from 4 to 6 × $10^{-10}$ m$^2$/s for the supports and fresh catalysts. Although the sensitivity of the analysis is 0.01 × $10^{-10}$ m$^2$/s, repeat runs gave a standard deviation for these runs of 0.5 × $10^{-10}$ m$^2$/s (10% relative error). The fresh catalysts were also run as extrudates and gave diffusivities within experimental error of the crushed catalyst values when diffusivities for the former were calculated based on cylindrical coordinates.

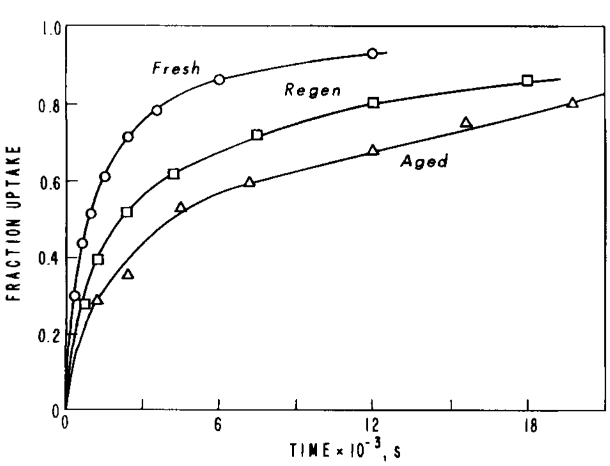

Figure 3. Fraction uptake vs. time for crushed catalyst *A* in coronene.

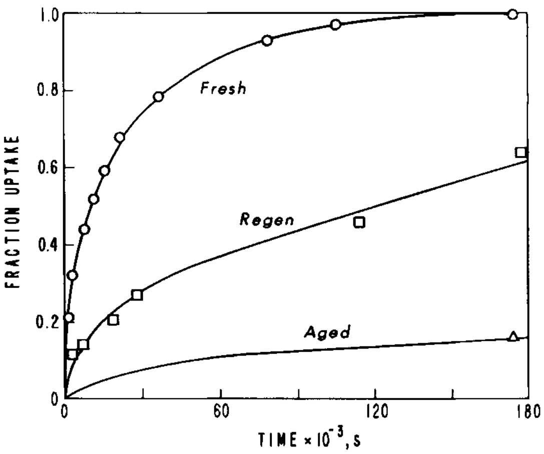

Figure 4. Fraction uptake vs. time for catalyst *A* extrudates in coronene.

The aged extrudates exhibited diffusivities more than 500 times slower than the fresh catalysts. Since the aged extrudate diffusion experiments proceeded so slowly, an arbitrary cutoff time of three weeks was chosen for these runs and the equilibrium uptakes of the comparable crushed catalysts were used to estimate their diffusivities. Regenerating the aged extrudates increased their diffusivity appreciably, but the regenerated extrudates still exhibited 20 to 50 times slower diffusion than the fresh catalysts. Crushing the aged extrudates increased the diffusivity substantially. Crushing the regenerated extrudates also improved the diffusivity, but not to the level of the fresh catalysts. It is estimated that the relative error in diffusivities of aged and regenerated catalysts is about 30%.

It is recognized for the cases of aged and aged-regenerated catalysts that the void fraction and density will vary with position in the extrudate, and thus the diffusivity according to Eq. 1 will vary. (The contribution of the void volume in Eq. 1 is negligible.) It is expected that the diffusivity would be limited by the high metal deposits at the outer edge. Therefore, the density at the outer edge should properly be used to calculate the diffusivity in Eq. 1, instead of the average values used. This would result in larger diffusivity values by perhaps a factor of two to four (density at exterior not known) for the extrudates. This does not apply to the crushed catalysts, whose diffusivities represent an average value. Taking account of density, however, will not raise

**Table 3. Effective Diffusivities and Uptakes of Coronene**

| | $D_e$ × $10^{10}$, m$^2$/s | | | Uptake × $10^3$, kg/kg | | |
|---|---|---|---|---|---|---|
| Catalyst | E | A | F | E | A | F |
| Crushed | | | | | | |
| Support | 4.3 | 5.0 | 5.9 | 11.6 | 8.8 | 6.9 |
| Fresh | 4.0 | 4.9 | 5.3 | 14.6 | 11.3 | 7.4 |
| Aged | 0.3 | 0.2 | 0.1 | 2.3 | 1.8 | 1.5 |
| Regen. | 1.3 | 1.2 | 0.5 | 7.2 | 5.7 | 5.2 |
| Extrudates | | | | | | |
| Fresh | 4.3 | 5.1 | 5.1 | 11.6 | 10.9 | 8.3 |
| Aged* | ** | <0.01 | <0.01 | — | — | — |
| Regen.* | 0.2 | 0.1 | 0.1 | — | — | — |

*$D_e$ values based on uptake values for crushed catalysts.
**Too slow to measure.

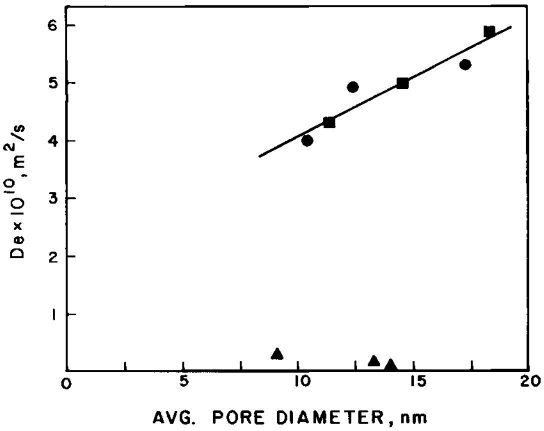

**Figure 5. Effective diffusivity vs. average pore diameter.**
▲ aged; ● fresh; ■ support

the very low diffusivities of the aged extrudate catalysts to those of the crushed catalysts.

Figure 5 shows a plot of effective diffusivity vs. average pore diameter for the crushed catalysts. The support and fresh catalysts show a trend of increasing effective diffusivity with increasing pore diameter. The aged and regenerated catalysts have average pore diameters in the same range as the support and fresh catalysts, but have much lower diffusivities.

Coronene uptake by the catalysts in the diffusion experiments is related to their surface area. Figure 6 is a plot of coronene uptake vs. surface area. The slopes of the lines are related to the number of coronene adsorption sites per unit area of catalyst surface. The slope increases according to aged < support < fresh. This demonstrates that coronene adsorbs on the Mo and/or Co phase(s) present, as well as the alumina.

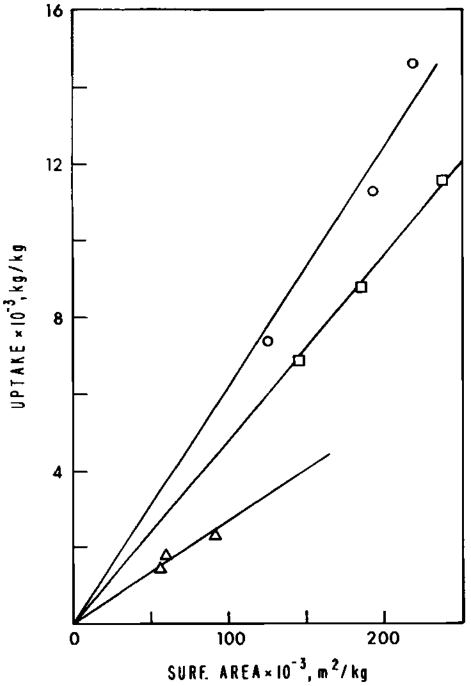

**Figure 6. Coronene uptake vs. BET surface area.**
△ aged; ○ fresh; □ support

Table 4. Catalyst Activities for HDS, HYD and HDN

| Catalyst | Rate Constant × $10^3$* (Rel. Activity**) HDS | HYD | HDN |
|---|---|---|---|
| E | | | |
| Fresh extrudate | 4.22(1.0) | 3.35(1.0) | 1.13(1.0) |
| Aged extrudate | 0.65(0.15) | 0.30(0.09) | 0.18(0.16) |
| Aged crushed | 0.65(0.15) | 0.30(0.09) | 0.18(0.16) |
| Regen. extrudate | 0.65(0.15) | 0.70(0.21) | 0.30(0.26) |
| F | | | |
| Fresh extrudate | 4.92(1.0) | 4.33(1.0) | — |
| Aged extrudate | 0.13(0.03) | 0.02(0.01) | — |

*First-order rate constant at a liquid feed rate of $2.78 \times 10^{-9}$ $m^3/s$. Units are $m^3$ feed/s kg catalyst.

**Activity relative to the fresh catalyst in terms of ratios of rate constants.

### *Catalytic activities*

Table 4 lists activities for catalysts *E* and *F* in terms of pseudofirst-order rate constants at a liquid feed rate of $2.78 \times 10^{-9}$ $m^3/s$, as well as relative activities compared to the fresh catalyst. The justification for employing first-order kinetics for relative activity comparisons is given elsewhere (Liu et al., 1984). In order to obtain a direct comparison between activities, sample weights were adjusted by applying the correction factors given in Table 2b for the aged catalyst and a value of 1.48 for the regenerated *E* catalyst, so that the same amount of fresh catalyst exclusive of deposits was used in each run. This more closely simulates activity in a pilot-plant run (which is obtained on a single charge of fresh catalyst) than using the same sample weight for all catalysts. As expected, activities of the aged catalysts were considerably lower than the fresh catalyst for all the reactions. Somewhat surprisingly, the aged extrudate and aged crushed samples had the same relative activities for all reactions, deactivation being greatest for HYD. Whereas regeneration had no noticeable effect on HDS, it did improve HYD and HDN to some extent.

Only the fresh and aged extrudates of catalyst *F* were tested for HDS and HYD. As seen in Table 4, the fresh *F* catalyst was somewhat more active than the *E* catalyst. However, the aged *F* catalyst was appreciably less active than the aged *E*, especially for HYD.

## Discussion

The estimated volume of deposits on the aged catalysts ranged from 1.1 to $1.3 \times 10^{-4}$ $m^3/kg$. Table 2c gives calculations on the volume balance of deposits. From this table, it is seen that the calculated net pore volumes of the aged catalysts agree well with the measured pore volumes, indicating that blocking of pores by deposits located at pore mouths, Figure 7a, is negligible. If a significant fraction of pores were blocked, the volume in the blocked pores would not be measured, and thus the experimental pore volume would be appreciably lower than the calculated values.

The diffusion measurements showed considerably lower diffusivities for the aged crushed samples as compared to the fresh catalysts. Based on the pore diameter plot of Figure 5, the aged catalyst diffusivities should only be marginally lower. If the deposits completely blocked some pores (either by complete fill-

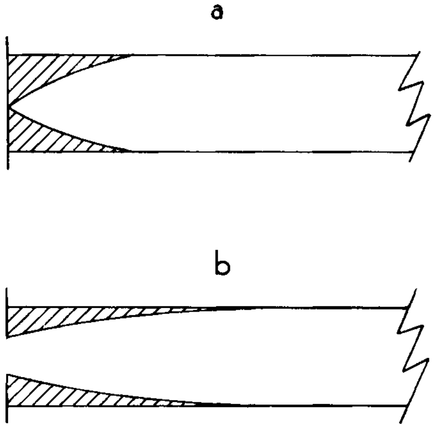

**Figure 7. Idealized models: (a) pore plugging, (b) pore wedging.**

ing or pore mouth coverage) and did not affect the remaining pores, the diffusivity in the remaining pores should be unchanged from that of the fresh catalysts (although the uptake would be lower), since the average pore diameter would remain the same.

In view of these arguments, it appears that most of the deposits are concentrated near the pore mouths, but not completely blocking the pore, with some penetration into the pore. By "pore mouths" we refer to the micropores within the catalyst structure, which consists of both macropore and micropore regions (Smith, 1970), and not exclusively to external pore mouths. The macropores can be envisioned as spaces between the basic particles containing the micropores. Nitrogen adsorption/desorption isotherms of the fresh and aged catalysts showed an increase in the size of the hysteresis loop for the aged catalysts, similar to the results of Fleisch et al. (1984), lending support for the existence of pore mouth constriction by deposits. This restricted pore may be visualized according to Hughes and Mann (1978) as a somewhat wedgeshaped pore, as illustrated in Figure 7b. The reduced dimension of the pore entrance from the high concentration of V and Ni will result in a decreased diffusivity of coronene. It should be noted that diffusivities can be appreciably lower than that of normal pore diffusion, by reason of a restrictive effect when the size of the diffusing molecule is greater than 10–20% of the pore diameter (Chantong and Massoth, 1983; Satterfield et al., 1973). Both factors can account for the low diffusivity values obtained for the aged crushed catalysts. Prasher et al. (1978) report diffusivities at 298 K for a number of aromatic compounds to be lowered by a factor of four to five for a catalyst exposed to resid for several days (probably containing mostly coke and little metals).

Aged extrudates showed drastically lower diffusivities than their crushed counterparts. The higher diffusivity for the crushed catalysts suggests that the high metal level at the outer edge of the aged extrudates, Figure 1, creates a diffusion barrier. In order to explain this, we visualize a catalyst structure consisting of an assemblage of porous microspherical particles, the macropore volume being the voids between the particles. The large deposits of metals in the external region of the extrudate, which constrict the micropore mouths, can also cause partial fusion of the microparticles by buildup of deposits on the outer portions of the microparticles. Thus, penetration of coronene through the macropores would be severely restricted by this barrier. Crushing the extrudates allows exposure to internal pores, whose pore mouths are less affected by the metal deposits, increasing the observed diffusivity. In summary, we believe that the very low diffusivities of the aged extrudates are due to a localized constriction of the macropores, while the low diffusivities of the crushed aged catalysts are due to micropore mouth constriction.

The diffusion barrier could also significantly affect diffusion into the catalyst for large reactant molecules in a liquid phase during a hydroprocessing run, assuming that the same relative diffusivities of aged to fresh catalysts apply at reaction temperatures as for coronene at room temperature. Thus, a lowering in the overall catalyst effectiveness factor would be expected due to the barrier effect, but not necessarily proportional to the diffusivity ratio, since the effectiveness factor is not directly related to $D_e$ (Satterfield, 1981).

Regeneration improves diffusivities, demonstrating that coke as well as metals deposits affects diffusivity. This is evident for both crushed and extrudate samples. Thus, coke as well as metals contributes to micropore mouth constriction and to restriction in the macropore diffusion barrier. This is especially evident in the regenerated *E* catalyst, where the increase in diffusivity from the aged catalyst is the highest, reflecting the removal of the higher coke content of this catalyst. The lower diffusivity of the regenerated crushed *F* catalyst is in line with its higher metal content. However, this does not apply to the regenerated extrudates, which all likely contain about the same amount of metal deposits at the outer part of the extrudates and exhibit the same diffusivities, Table 3.

Activities of the aged catalysts were low for all reactions. The crushed aged catalysts were no more active than the extrudates, consistent with the lack of a diffusional effect on the model reactions, i.e., the model compound activities represent intrinsic activities. Thus, intrinsic catalyst deactivation appears to be predominantly due to loss of active sites from coverage by deposits. Regeneration had no effect on the HDS activity, signifying that the metal deposits are entirely responsible for permanent deactivation of the HDS sites in the aged catalysts. On the other hand, regeneration somewhat improved HYD and HDN activity, indicating a partial contribution of coke to deactivation of these sites. The observation of different relative extents of deactivation and regeneration for the different reactions is consistent with the supposition that these reactions take place on different active sites (Massoth and Muralidhar, 1982).

Catalyst *F*, having a larger pore diameter than catalyst *E*, allows further penetration of metal deposits into the pores. Thus, more of the catalyst sites are covered with metal deposits, accounting for the lower intrinsic activity of the aged *F* catalyst compared to the *E* catalyst, Table 4. The fact that both catalysts exhibited the same HDS activity at the end of the bench-scale runs signifies that the intrinsically more active aged *E* catalyst was more affected by diffusional limitations of the resid feed than the aged *F* catalyst, presumably because of a smaller residual pore opening caused by the deposits in the external diffusion barrier. Thus, the higher intrinsic activity of catalyst *E* as compared to *F* must be counterbalanced by its greater diffusional restriction, because both catalysts exhibited the same effective HDS activity at the end of the process runs.

Although the total deposits and pilot plant HDS activities were the same at the end of the runs, the lifetimes of the catalysts were appreciably different, being in the order $A > F > E$. Neither the order in coke deposits ($F < A < E$), nor in metals deposits ($E < A < F$) is consistent with the lifetime pattern; nor is the pattern reflected in diffusivities of coronene at room temperature ($E > A > F$). It is interesting that the longest life is obtained with the catalyst having an intermediate average pore diameter. This is in line with the existence of an optimum pore size giving a maximum life, as proposed by Jacobsen and coworkers (Nielsen et al., 1981; Hannerup and Jacobsen, 1983).

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## Notation

$D_e$ = effective diffusivity, $m^2/s$
$K$ = adsorption constant, $m^3/kg$
$R$ = catalyst particle radius, m
$t$ = reaction time, s
$\rho$ = catalyst density, kg/m
$\epsilon$ = catalyst void fraction, $m^3/m^3$
$\tau_t$ = dimensionless time parameter

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