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ON THE CONVERSION OF ATHABASCA BITUMEN

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ON THE CONVERSION OF ATHABASCA BITUMEN

by

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INTRODUCTION

Catalytic hydrotreating of Athabasca bitumen using conventional, commercial catalysts is severely limited by the nature of the feedstock. Oil-sands bitumens have high concentrations of iron, vanadium and nickel metals, a high +525°C fraction, and high asphaltene components. These lead to rapid catalyst deactivation through the formation of "coke" on external and internal surfaces and to the precipitation of poisoning metals onto the active surfaces. Previous work (1) in this laboratory has indicated that metals deposition occurs mainly at, or near, the external catalyst skin. Some increase in catalyst life might be expected if the metals deposition and coke formation could be minimized and spread as uniformly as possible over the whole of the catalyst active surface area. Mass transfer limitations in the pore system are thought to be major inhibitors to higher catalyst effectiveness in view of the large asphaltene component. High average molecular weight (6000) and a relatively high concentration of polycyclic aromatic structures suggest that mass transfer in the system of intergranular cracks and intragranular pores limit the net chemical activity, i.e. the

catalyst effectiveness, η . Studies by other workers using coal slurries (2) and petroleum residua (3,4) have indicated that there is merit in using catalysts with pore sizes which permit enhanced mass transfer.

Several potential methods have been suggested for alleviating the short catalyst life and high operating cost expected for hydrotreating and hydrocracking bitumen. In this paper we report some results from the investigation of the effects of variation in catalyst physical parameters on several measures of conversion.

A series of catalysts have been prepared with surface areas in the range ($180 \text{ m}^2\text{g}^{-1}$ to $2 \text{ m}^2\text{g}^{-1}$), pore volumes in the range (0.60 to 0.20 ml^3g^{-1}) and median pore diameters ($\langle d \rangle$) from 7.5 nm to 3000 nm. Each sample was reacted with bitumen under a given set of conditions to determine pore size effects on sulphur removal, nitrogen removal, metals removals, catalyst coke level, and catalyst metal profile. As well, the effects on the aromatic carbon content, hydrogen-to-carbon ratio, and pentane-insoluble components were determined. The specific results discussed in this paper are for a nominal 2.2 wt% MoO_3 , 1.1 wt% CoO on alumina catalyst.

EXPERIMENTAL

The chemical and physical properties typical of the bitumen used in these experiments have been described previously (1).

The chemical preparation of the 2.2 wt% MoO₃, 1.1 wt% CoO catalyst gels involves solution impregnation of high purity SB alumina (boehmite, AlOOH) with acidified solutions of ammonium paramolybdate and cobalt nitrate. The resultant pastes were milled until the paste gave uniform, smooth and physically stable extrudates. The 3.17 mm extrudates were formed using a 2¼ inch Bonnot bench scale extruder.

Samples formed in this way were partially dehydrated in air at 383 K for 6.0 hours in a pre-heated oven. The extrudates were then sealed, stored and maintained dry until calcined.

In order to make catalysts with varying median pore sizes, these partially dehydrated extrudates were calcined at different set temperatures. Samples were loaded in a thin layer in shallow, vitrosil trays and these were placed directly into a muffle-furnace pre-heated to the desired temperature. After calcining for 2 hours the samples were cooled in air and stored in sealed jars. The catalyst with a median pore diameter of 1180 nm was calcined for 0.5 hours at 1323 K.

The extruded catalysts prepared in this way were physically characterized. The specific surface areas were determined by an N₂, BET, gravimetric method. Catalyst pore volume and median pore diameter (<d>) were measured by mercury penetration using a Micromeritics Model 910 porosimeter operating up to 348 MPa. After being weighed in the porosimetry cell, but before loading the cell into the high pressure chamber, the catalysts were dehydrated at 393 K for one hour. This helped to considerably

reduce the pump-down time of the catalyst and chambers.

The pore diameters are calculated using an assumed, constant angle of 130° , the applied hydrostatic pressure and a mercury surface tension of 474 dynes/cm. The mercury used in the porosimeter was a redistilled technical-grade product. Since the chemical composition of these catalysts is in principle constant, differences in contact angle are thought to be small. Variations in the mercury surface tension as a function of contamination during a series of determinations have not been taken into account.

The efficacy of each catalyst was tested using a bottom fed, fixed-bed reaction system which has been used in these laboratories for some time. A constant volume of catalyst (127 ml) is charged into a 28.4 mm i.d. stainless steel, continuous flow reactor 0.381 m long. The catalysts were presulphided by exposure to bitumen for 5 hours, including the periods for reactor heating, followed by a reaction experiment of 2 hours duration at steady reactor conditions. Presulphiding was effected at 13.9 MPa, 723 K, LHSV=1.2 and a hydrogen flow rate of 844 ℓ/ℓ feed. The reactor has an axial temperature profile of ± 5 K. The 2 hour experiments described here were conducted under the same reaction conditions as for presulphiding, except that the temperature was lowered to 713 K.

Liquid product for analysis was withdrawn from a single, sample receiver vessel. Sulphur and vanadium contents were analyzed by x-ray fluorescence using an Inax Instruments Ltd. model 311 spectrometer. Carbon, nitrogen and hydrogen contents were measured by sample combustion using a Perkin-Elmer model 240 analyzer. Nickel and iron in the liquids were determined by wet ashing, and atomic absorption spectrophotometry. The unconverted asphaltenes are, in this case, pentane insolubles determined by a modification of ASTM method 2042-76. References describing the above

procedures have been given previously (5). The percentage of total carbon present as aromatic carbon was determined by quantitative ^{13}C n.m.r. using a method recently developed in our laboratories (6).

Used catalyst samples were analyzed for residual carbon, hydrogen, nitrogen and metals after Soxhlet benzene extraction. The extraction was continued until the returning solvent was visually clear. The residual carbon, nitrogen and hydrogen contents of the "coke" on the dried catalyst were determined by combustion, as before.

Radial distributions for iron, nickel, vanadium, sulphur, molybdenum, cobalt were determined by microprobe analysis using a JEOL JXA-3 instrument. The latter is equipped with a CPS high voltage power supply and ORTEC electronics. The profile traces for element pairs were made at 20kV. The electron beam traversed the samples at 0.5 mm/min whilst the chart speed was chosen to be 2 cm/min. Simultaneously the x-ray counts and digitized current, integrated over 10 second intervals, were printed out every 14 seconds. A beam size of 25 microns was employed as a compromise appropriate to the detail sought and the resolution on the chart. Pure metals and iron pyrites were used as reference materials.

Samples were prepared for microprobe examination as follows: short lengths were cut from central portions of the extrudates and were then impregnated with Araldite epoxy resin at 69.5 MPa cured, cross-sectioned radially and then polished in conventional fashion. For conduction purposes a 40 nm layer of carbon was evaporated onto the finished surface. The concentrations of the metals iron, nickel and vanadium on the catalyst were relatively low and this limited the statistical accuracy of the data.

Interference between the observed S K_{α} and Mo L_{α} x-ray lines in sulphided, used catalysts was taken into account by comparison with results from similar, but oxidized, "unused" catalysts.

RESULTS AND DISCUSSION

The median pore size in each catalyst was determined from the penetration branch of the porosimetry curve. Examples of the curves for three catalysts are shown in Figure 1. The distribution of mesopores (2-50 nm) was quite narrow in each catalyst. In contrast the catalysts containing large macropores ($d_p > 50$ nm) had wide distributions of pore size. In this study the median pore diameter corresponded to the point at which half of the mesopore volume was filled. For the two catalysts which only contained macropores, the median pore diameter corresponded to one-half of the macropore volume in excess of 0.15 ml/g.

From Figure 1 and scanning electron micrographs, it is apparent that the pore system can be described as having two regimes: (a) the large, interparticle pores corresponding mainly to intergranular voids greater than 3000 nm (3μ); and (b) the intra-particle pore system with void passage dimensions less than 3000 nm (3μ), usually in the range below 50 nm. In general, the pore system (< 50 nm) is unimodal, with a relatively narrow range of pore sizes. One catalyst, with a median pore diameter near 50 nm, has a distinct, bimodal pore system with approximately 25% of the intra-particle pores being twice as large as the overall average.

Catalysts with different pore diameters were prepared through variations in calcining temperature and time. The catalyst pore diameter, surface area and bulk density for each calcining temperature is shown in Figure 2. The enormous decrease in surface area with increasing pore

diameter should be noted.

The variation of the catalyst specific surface area as a function of median pore diameter is shown in Figure 2a. There is a very rapid drop in area from 7.5 to 16 nm; this decrease lessens in the ($\langle d \rangle$) range up to 50 nm, and becomes much less pronounced above 50 nm. From Figure 2b, ($\langle d \rangle$) versus calcining temperature, one sees that the catalysts with $\langle d \rangle$ less than 16 nm have been calcined at less than 1148 K, the temperature above which pure $\gamma\text{-Al}_2\text{O}_3$ begins to transform to $\Delta\text{-Al}_2\text{O}_3$. The two samples with very large pores were calcined above 1298 K, the lower limit for transformation of pure $\Delta\text{-Al}_2\text{O}_3$ to $\theta\text{-Al}_2\text{O}_3$. Identification of the solid alumina phases actually present in the catalysts has not been completed.

The total pore volumes were all found to lie in the range 0.60 to 0.45 mlg^{-1} , Table I. The calcining treatments during catalyst preparation led to variations of bulk-density as shown in Figure 2c. This bulk-density variation led to different weights of catalyst charged to the reactor.

Sublimation of some molybdenum trioxide undoubtedly occurred at higher calcining temperatures. However, MoO_3 sublimation at pore surfaces may have provided sufficient potential for MoO_3 in the bulk to diffuse to the surface. This replenishment would help to compensate for any surface depletion caused by vapourized MoO_3 . As calcining temperature increased the surface concentration of MoO_3 should decrease with increasing pore diameter.

An alternative preparative method would have been to pre-calcine the support and add the molybdenum and cobalt by solution impregnation. This method would have ensured that the same bulk analysis of molybdenum and cobalt would have been obtained for every catalyst. However the decreases in surface area would cause the surface concentration of molybdenum and cobalt to increase greatly with increasing pore diameter. Therefore solution

impregnation is considered inappropriate.

Since a surface analysis on the pore walls could not be obtained readily, neither of the above catalyst preparation techniques could be shown to cause the least variation in surface concentration. However the catalyst preparation and calcining method used here is likely to cause decreasing surface molybdenum concentration with increasing pore diameter. In contrast, solution impregnation of a calcined support would cause increasing surface concentration with increasing pore diameter for a constant bulk concentration. When Figure 7 is discussed it will be apparent that our catalyst preparation method was more appropriate for this study.

The efficacy of the set of 2.2 wt% MoO₃, 1.1 wt% CoO catalysts was gauged by observation of their activities for specific reaction types. The variations in activities as a function of median pore diameter are shown in Figure 3 for sulphur and nitrogen removal. The conversion of asphaltenes is indicated in Figure 4. The variation of the atomic H/C ratio is shown in Figure 5b, while Figure 5a gives the values for changes in atomic percent aromatic carbon C (of total carbon only) present in the product.

For removal of (the following heteroatoms), sulphur, nitrogen, nickel and vanadium heteroatoms, the curves in Figures 3 and 6 all have somewhat similar shapes. More of each heteroatom is removed with the catalysts having the smaller pore diameters, and fewer with the large pore diameter catalysts. The decrease in extent of reaction with increasing pore size may have been caused by the loss in catalyst surface area shown in Figure 2. The nickel and vanadium in organometallic compounds are probably deposited on the catalyst surface near the reaction site. At steady state sulphur and nitrogen normally leave the reactor as hydrogen sulphide and ammonia and do not cause catalyst fouling.

The conversion of asphaltenes shown in Figure 4 is likely related to the changes in hydrogen content of the liquid product shown in Figure 5. The asphaltenes may be converted to oils and perhaps resin type compounds. These classes of compounds generally have higher hydrogen contents and smaller proportions of aromatic structures than asphaltenes. In that case, the higher hydrogen content obtained with the small pore catalysts is consistent with the higher asphaltene conversions. Once again, however, the smaller surface areas present in the large pore catalysts were probably responsible for the lesser extents of reaction

The metals-removal activities are given in Figure 6. Removal of vanadium and nickel follow a trend similar to that found for sulphur and asphaltenes removal. There is a range of relatively constant demetalization activity from 7.5 to 50 nm. Once again there may be maxima near 20 nm but the activity drops by a factor of about 3 from 50 to 3000 nm.

For iron removal, Figure 6c, there is a distinct maximum near 40-50 nm. It is believed that the bulk of the iron in the feed is present in colloidal clay platelets. This maximum may be due to increased adherence of the platelets onto the exterior surfaces of the catalyst.

It is interesting to see the effect of pore size on the catalytic reaction rates per unit surface area. It is generally accepted that both thermal and catalytic mechanisms operate simultaneously during most reactions in this system. An attempt was made to subtract the effect of the thermal processes numerically. A base line experiment was performed with extrudates composed primarily of alumina which were considered to have little or no catalytic effect. The extent of reaction occurring in the base line experiment was subtracted from the extent of reaction occurring in each of the

experiments performed with catalysts of varying pore size. The reaction rates per unit surface area were then calculated.

The results for sulphur and nitrogen removal are shown in Figure 7. Two factors contribute to the scatter in the data for pore diameters greater than 1000 nm. The extents of sulphur and nitrogen removals for the large diameter catalysts approach those obtained in the base line experiment. A decrease in significance always occurs when a difference between two similar values is computed. Secondly the apparatus used to measure the surface areas in this study does not produce accurate results for low surface area materials, i.e. those with large pore diameters. When both of these factors are considered, the data scatter for the large pore catalysts in Figure 7 seems quite reasonable.

Figure 7 shows that the reaction rate per unit area increases as the pore diameter increases. It is evident that mass transfer controls the reaction rate when the median pore diameter is less than 50 nm. It was mentioned previously that some molybdenum in the catalyst probably sublimes at elevated calcining temperatures. Figure 7 shows that the increase in reaction rate caused by improved mass transfer more than compensates for molybdenum sublimation from the catalyst surface.

It should be possible to relate these results to the catalyst effectiveness factor, η . Equation 1 gives the Thiele modulus ϕ , for an assumed first order reaction and straight, round catalyst pores (7),

$$\phi = L \left(\frac{4k_s}{\langle d \rangle D_{eff}} \right)^{1/2} \quad (1)$$

where L is the pore length, $\langle d \rangle$ is the pore diameter, D_{eff} is the effective diffusion coefficient, and k_s is the rate constant in terms of unit surface area. The diffusion coefficient may be a function of the pore diameter, if

if the pores are sufficiently small. This might be expressed as

$$D_{\text{eff}} = (\langle d \rangle)^m \cdot G \quad (2)$$

where m is a constant and G is a function which is independent of the pore diameter. For large values of the Thiele Modulus, the effectiveness factor, η , can be represented by equation 3,

$$\eta = \frac{1}{\phi} \quad (3)$$

In this study everything was held constant except the pore geometry. With that assumption, one can represent all the other parameters, and functions by a constant, C_A . If this is done, Equation 2 can be substituted into Equation 1 and the result substituted into Equation 3 to obtain Equation 4.

$$\eta = \frac{r_D}{r_{DF}} = C_A (\langle d \rangle)^{\frac{m+1}{2}} \quad (4)$$

where r_D is the diffusion controlled reaction rate and r_{DF} is the diffusion free reaction rate. Equation 4 can be expressed in terms of logarithms

$$\log (r_D) = \frac{m+1}{2} \log (\langle d \rangle) + \log (C_A R_{DF}) \quad (5)$$

The value of the constant m can be determined from the slopes of the lines in the log-log plot in Figure 7.

It is conceivable that the effective diffusion coefficient will be influenced by the pore diameter, if the pores are sufficiently small. This effect could be caused by frequent interaction between the diffusing species and the pore wall. In principle, in this reaction system both vapour and liquid phases can exist in any pore. For the case of weak molecule-molecule, and molecule-wall interactions the slowest diffusing species should be high molecular weight components in the liquid phase. Speight (9) has suggested

that asphaltene micelles in Athabasca bitumen have dimensions of approximately 1 to 2 nm. The collision frequency and integrated interaction times for such micelles should decrease as the median pore diameter increases from 7.5 nm to 3000 nm.

The two lines in Figure 7 have slopes which are close to 0.7, corresponding to an m value of 0.4. This can be compared to the case where the diffusion coefficient is not a function of pore diameter. The value of m in Equation 5 for the latter case is then zero and the slope of the line is 0.5. The data points corresponding to the smallest pore catalysts fall below the line. This may indicate that the value of m increases considerably for pores smaller than 10 nm, i.e. the effective diffusion coefficient is affected by the pore diameter. Such a conclusion is reasonable when the relative dimensions of the pores and the asphaltene micelles are compared.

Analyses of the coke (carbon, hydrogen and nitrogen) on the catalysts are shown in Figure 8. The amount of carbon per unit surface area increases considerably with increasing pore diameter. Since carbon is the major constituent in coke, it can be considered to be a measure of the amount of coke on the catalyst. The atomic hydrogen-to-carbon ratio in the coke decreases and the nitrogen content increases with increasing pore size.

One explanation for the increased carbon on the large pore catalysts would be that more reactions per site occurred on these surfaces. Figure 7 specifically illustrated that the reaction rate per unit area was greater for the large pore surfaces. While this explanation may be valid in this case, it is not universally true. For example in other studies (9) the reaction rate on the catalyst increased considerably while the catalyst coke content remained constant or decreased.

There is an alternative explanation for the data in Figure 8. In principle the larger pore catalysts should provide access to greater quantities of larger species of higher molecular weight. In general such species will contain a greater proportion of condensed aromatic rings and will have a greater tendency to be coke precursors. The presence of more coke precursors in a pore would explain the carbon curve. The decreasing hydrogen-to-carbon ratio would be explained by the fact that the larger species tend to be more aromatic. Coke would be expected to have a lower hydrogen content if it was formed from a more aromatic species. Finally the nitrogen content of the feedstock is known to increase with molecular weight. Therefore the larger the species which can enter a pore the greater the possibility of a polar material, such as nitrogen, being adsorbed strongly onto the catalyst surface. Thus all three curves are consistent with the suggestion that the coke in the larger pores may be formed from species which do not penetrate very far, if at all, into the smaller pores.

The radial profiles of vanadium, nickel and iron in the catalyst are shown in Figure 9. The results for iron and nickel, Figures 9c and 9b, are tenuous because the general level of poisoning with these elements after only 8 hours total reaction time is too low for a satisfactory rapid survey. A more detailed examination is planned for the immediate future. The results for vanadium are considerably better, Figure 9a. A plot of vanadium relative peak height versus r/R shows a regular shift of the peak maximum towards the centre of the extrudate (r denotes beam position and R the catalyst radius). Typical r/R vs peak counts per second values are: 7.5 nm/0.92; 16.0 nm/0.88; 50 nm/0.85; and 1180 nm/0.78. The two extreme cases are shown here. In all catalysts observed for this work the iron is found in a relatively sharp band near the catalyst skin.

The profiles of cobalt and molybdenum across "new" and "used" catalysts were relatively constant, as was sulphur for the "used" samples.

It can be hypothesized that the nickel and vanadium exist in the bitumen feedstock as organometallic compounds and that the iron is bound in clay particles. The data in Figure 9 can be explained in terms of this hypothesis. When the pore diameter was increased the organometallic vanadium penetrated much farther into the catalyst. However the iron (present as clay particles) deposited on the exterior of the catalyst extrudate regardless of the catalyst pore diameter.

The net effect of increasing pore diameter on metals deposition is a positive one. The larger pores permit the metals to be spread more evenly throughout the catalyst. This reduces fouling at the pore mouth, which normally makes the most accessible catalyst sites the most inactive ones. If fouling due to metals deposition was the predominant fouling mechanism, the larger pores would tend to extend catalyst life.

CONCLUSIONS

The data for sulphur removal, asphaltene removal, and hydrogen to carbon ratio in Figures 3, 4, and 5 all indicate that similar reaction rates are obtained with catalysts having pore diameters between 7.5 nm and 50 nm. The increase in rate of mass transfer with the larger pores, shown in Figure 7, is accompanied by a decrease in surface area, shown in Figure 2. These two effects combined to produce the relatively constant reaction rate. However the data does suggest that higher reaction rates would have been obtained if a large pore catalyst (say 50 nm) having a high surface area (say 150 m²/g) could have been prepared.

Another advantageous feature of large pore catalysts is the increased dispersion of metals which foul the catalyst. Figure 9 shows that with small pore catalysts vanadium is deposited predominantly at the exterior surface of the extruded catalyst particle. As the pore diameter increases vanadium tends to be dispersed more evenly throughout the catalyst. Since the deposition of metals is a phenomenon which decreases catalyst life, spreading the metals throughout the catalyst is desirable. In catalysts with small diameter pores, due to mass transfer limitations, the exterior of the extrudate is the region most likely to catalyze a reaction. Simultaneously it is the region most likely to be fouled by metals. By increasing the pore diameter mass transfer limitations are decreased and the metals are spread more evenly throughout the catalyst. This means that fewer metal atoms are deposited per unit area and that the catalyst life will be longer.

Coke deposition on the catalyst can also decrease catalyst life. The data in Figure 8 indicate that more coke is formed on catalysts with large pores than on catalysts with small ones. As the hydrogen to carbon ratio in the coke decreases (with increasing pore size) there is a diminishing possibility of the coke being hydrogenated and leaving the catalyst surface. Both the greater quantity of coke and the lower hydrogen to carbon ratio suggest that large pore catalysts would have shorter useful lifetimes.

The optimum pore size would have to be established by a series of life tests. Mass transfer effects and metal foulant dispersion would be improved with large pore catalysts. Conversely the quality and quantity of coke on the small pore catalysts would be preferable. One of these effects could be more important than the others in choosing the optimum pore size for a hydrocracking catalyst.

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TABLE I

Catalyst Pore Volumes

Catalyst	<d> nm	Total Pore Volume	Pore Volume <2 μ
1	7.5	58.5 mlg ⁻¹	45.0 mlg ⁻¹
2	8.5	60.0 mlg ⁻¹	46.0 mlg ⁻¹
3	10.0	52.5 mlg ⁻¹	43.5 mlg ⁻¹
4	12.5	50.0 mlg ⁻¹	43.0 mlg ⁻¹
5	16.0	46.5 mlg ⁻¹	40.0 mlg ⁻¹
6	28.5	53.0 mlg ⁻¹	37.0 mlg ⁻¹
7	37.5	54.8 mlg ⁻¹	40.0 mlg ⁻¹
8	50.0	46.5 mlg ⁻¹	37.5 mlg ⁻¹
9	1180	53.0 mlg ⁻¹	35.0 mlg ⁻¹
10	3000	54.0 mlg ⁻¹	31.0 mlg ⁻¹

FIGURE CAPTIONS

- Figure 1: Representations of the penetration curves for 3 typical 2.2 wt% MoO₃, 1.1 wt% CoO on alumina catalysts: A - median pore diameter 7.5 nm; B - 28.5 nm; and C - 1180 nm. In all cases the initial penetration of the very large macropores is excluded from the calculation of median pore diameter.
- Figure 2: Properties of the catalysts. 2A - the gravimetrically determined N₂ BET surface areas; 2B - the calcining temperature vs median pore diameter correlation for 2 hour calcining. The open circle represents calcining at 1298 K for 0.5 hours; 2C - bulk density for non-uniform length extrudates as a function of median pore diameter.
- Figure 3: Conversion of sulphur and nitrogen: A - wt% sulphur removed from the bitumen feedstock which had a base sulphur concentration of 4.48 wt%; B - wt% nitrogen removed as a function of <d>. The base nitrogen concentration was 0.35 wt%.
- Figure 4: Asphaltene conversion as a function of median pore diameter, <d>. The feed bitumen has 15 wt% asphaltenes, which are defined as pentane insolubles for this work.
- Figure 5: Effects on hydrogen-to-carbon ratio and aromatic carbon content of the products for the series of catalysts with increasing median pore sizes. The wt% aromatic carbon is the proportion of total carbons only.
- Figure 6: Demetalization of the bitumen: 6A - removal of vanadium from a feed containing 174 ppm V; 6B - removal of nickel from a feed concentration of 76 ppm; 6C - wt% iron removed from the feed.
- Figure 7: Reaction rates for desulphurization and denitrogenation of Athabasca bitumen as a function of catalyst pore diameter.
- Figure 8: Coke analysis results for "used" catalysts after benzene Soxhlet extraction: A - weight of residual nitrogen on the eight catalysts having median pore sizes in the range 7.5 to 50 nm. B - the hydrogen-to-carbon ratio of the coke residues; C - the weights of carbon in the insoluble coke residues on the catalysts.
- Figure 9: Profiles of the relative intensities of vanadium, nickel and iron across the catalyst for two extreme pore diameter ranges: circles are derived from the scans of the 8.5 nm catalysts; squares are derived from scans of the 1180 nm catalyst. In each case the intensity values represent the average of the smoothed curves through the two sides of the catalysts. For nickel, the limits of confidence are low.

RELATIVE INTENSITIES

















