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AND ITS EFFECT ON HYDROTREATING CATALYSTS

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SURFACE LAYERING WITHIN THE GRAINS OF AN ALUMINA
SUPPORT AND ITS EFFECT ON HYDROTREATING CATALYSTS

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ABSTRACT

Earlier studies (McColgan et al. 1973) on hydrocracking catalyst development alluded to a surface layering effect of catalytic material within the particles or grains of the alumina catalyst support. This paper presents evidence that surface layering can occur during the preparation of hydrotreating catalysts. An enhancement of the surface layering effect was observed when larger particles of alumina monohydrate were used. In contrast, during the impregnation of the catalytic material into the alumina monohydrate, the presence of an excessive amount of acid promoted gelling of the alumina and tended to eliminate surface layering. The effect of surface layering on sulphur and nitrogen conversion was measured. Other variations in the catalyst support such as the type of alumina monohydrate had no effect on conversion.

INTRODUCTION

A method for preparing hydrotreating catalysts was developed in our laboratories a few years ago (McColgan et al. 1973). When catalysts containing 1.1 wt % CoO and 2.2 wt % MoO₃ were prepared using this technique, their activities approached those of commercially available catalysts containing 3 wt % CoO and 12 wt % MoO₃. One possible explanation for these results (McColgan et al. 1973) alluded to a surface layering phenomenon which might have occurred in the particles or grains of the catalyst pellets. Later studies (Parsons and Ternan 1976), performed with catalysts in which surface layering was much less likely, produced similar results. The validity of the surface layering hypothesis was then questioned. The purpose of this work was to determine whether or not surface layering occurred when this technique was used and, if so, its influence on catalyst activity. Variables investigated included the type of alumina monohydrate, the particle size of the alumina monohydrate and the procedure used to impregnate the catalytic ingredients into the support.

EXPERIMENTAL

The catalyst preparation method developed earlier (McColgan et al. 1973) involved several steps. 5000 grams of alpha alumina monohydrate (80% Catapal SB and 20% Catapal N, obtained from the Continental Oil Company, Peterboro, New Jersey) were placed in a mix-muller. The SB material had been manufactured by spray drying and consisted of particles which were predominantly from 30 to 100 μm in diameter. The N material had been dried in a kiln and consisted of particles having diameters from 100 to 500 μm . A solution of 1000 ml of distilled water and 14 ml of nitric acid (70%) was added slowly to 5000 g of alumina monohydrate in a mix-muller. The mixture was mulled for 0.18 ks (3 min) and allowed to stand for 0.42 ks (7 min). Then with the mix-muller in operation, 1600 ml of a solution of the pre-determined quantity of ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in water were added and mulled for 0.18 ks (3 min). In the cases when both cobalt and molybdenum salts were added, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the paramolybdate, both dissolved in separate 800 ml quantities of water, were added successively.

The impregnated mixture was then spread as a layer approximately 1.5 mm thick in a stainless steel tray and dried in air at 80°C for 21.6 ks (6 h) and 110°C for 21.6 ks (6 h). The lumps of dried mixture were crushed and calcined at 500°C for 21.6 ks (6 h). The calcined alumina was pressed into 3.2 x 3.2 µm cylindrical pellets (1/8 x 1/8 in.) using 2 wt % stearic acid as a binder-lubricant. The pellets were subsequently recalcined at 500°C for 18 ks (5 h).

In this work three series of catalysts were prepared. Each series consisted of two types of catalyst. In the first series the first type was made by a method described above except that 60 wt % SB and 40 wt % N was used. The second type was identical to the first except that excess acid (4000 mls containing 100 mls of 70% HNO₃) was added to alumina monohydrate during the mulling stage of preparation.

The second series of catalysts was prepared using particles of alpha alumina monohydrate of fairly uniform size. The alumina monohydrate was crushed and sieved into fractions having U.S. Standard mesh sizes of -60+100, -100+200, -200+325, and -325 (or in µm 250-149, 149-74, 74-44, and smaller than 44 respectively). One type of catalyst was made from SB and the other from N alumina monohydrate. All the catalysts in the first and second series contained 12 wt % MoO₃.

The third series of catalysts contained both MoO₃ and CoO in a Mo:Co atomic ratio of 1.0. In the first type, N alumina monohydrate was used and no acid was added to the formulation. In the second type, SB alumina monohydrate was used and excess acid (4000 mls of solution containing 100 mls of 70 wt % HNO₃) was added. The above catalysts were prepared at two concentration levels, a total of 2 wt % MoO₃ and CoO and a total of wt % MoO₃ and CoO.

The hydrotreating activities of the above catalysts were evaluated using heavy gas-oil. This oil was prepared by first thermally hydrocracking Athabasca bitumen, obtained from Great Canadian Oil Sands at Fort McMurray, Alberta, in a pilot plant reactor. The 345-525°C portion was subsequently distilled from the hydrocracked product and used as the feedstock. Properties of the feedstock are listed in Table 1.

The reaction equipment used for the hydrotreating experiments was described previously (O'Grady and Parsons 1967) in detail. The catalyst pellets were evaluated in a bench-scale fixed bed reactor having a volume of 155 cm³ and a length:diameter ratio of 12. The reactor was filled sequentially from the bottom with 42 cm³ berl saddles, 100 cm³ catalyst pellets and 13 cm³ berl saddles. The heavy gas-oil, mixed with hydrogen (purity = 99.9 wt %), flowed continuously into the bottom of the reactor and up through the catalyst bed. The product leaving the top of the reactor flowed to receiver vessels where the liquid and vapour were separated. Each experiment was performed at a pressure of 13.9 MPa, a liquid volumetric space velocity of 0.556 ks⁻¹ (2.0 h⁻¹) based on the reactor volume occupied by the catalyst pellets, and a hydrogen flow rate of 46.9 cm³ s⁻¹ at STP (5000 cu ft/bbl). The catalyst was presulphided and stabilized using the mixture of gas-oil and hydrogen at 400°C. Subsequent experiments were performed sequentially at temperatures of 400, 420 and 380°C. Gas-oil and hydrogen were in contact with the catalyst for 18 ks (5 hr) prior to the 420°C experiment. The reaction system was maintained at steady state conditions for 3.6 ks (1 h) prior to, and for 7.2 ks (2 h) during, the period in which each sample of liquid product was collected.

Concentration profiles in catalyst pellets were measured using a modified JEOL model JXA-3 electron microprobe having an ORTEC Si(Li) detector. The catalyst pellets were prepared by cutting the pellets radially, mounting them in trans-optic-organic mounting media, polishing with silicon carbide paper Linde C(1 µm) and Linde A(0.3 µm) alumina at 10 rev/sec in a conventional manner, and finally coating with a 200 Å layer of carbon. The traces were run at 20 KeV and 0.333 µm/sec using 10 µm beam diameter to reduce sample heating and to smooth out the effects caused by catalyst porosity (cracks and holes). The optical microphotographs were taken with reflected light using a Zeiss metallographic microscope.

RESULTS AND DISCUSSION

Series I catalyst pellets were analyzed with both an optical microscope and an electron probe microanalyzer. Figures 1 and 2 are typical optical micrographs. The straight black lines in the photographs show the trajectories of the electron beam from the electron probe microanalyzer. Profiles of the molybdenum concentration in the two catalysts are shown in Figures 3 and 4.

Figure 1 is typical of catalysts prepared by the method of Parsons and co-workers (McColgan et al. 1973). The right hand half of the photograph shows a reasonably well defined grain. The outer shell of the grain appears to be rather smooth. The interior contains two rather rough looking areas.

Figure 2 is typical of catalysts in the first series which were prepared with excess acid. This surface appears to contain a large number of holes and cracks. Nevertheless its texture is reasonably homogeneous across the entire surface. That is, there does not appear to be any grain structure or rough area comparable to that in Figure 1.

The structure in Figures 1 and 2 can be related to the molybdenum concentration profiles in Figures 3 and 4. In Figure 3 the molybdenum concentration was much higher on the left hand half than on the right hand half. The lower concentrations of molybdenum in the right half of Figure 3 can be associated with the grains in the right half of Figure 1. Conversely the higher concentrations of molybdenum in Figure 3 can be associated with the area having a relatively smooth appearance in Figure 1. In contrast the molybdenum concentration profile shown in Figure 4 is relatively uniform throughout. This corresponds to the reasonably homogeneous surface (ignoring cracks and holes) shown in Figure 2.

One explanation of these observations would involve the gel forming tendencies of colloidal particles (Iler 1973). The addition of acid (low pH values) promotes gel formation. In contrast peptization occurs at high pH values. The smooth areas could have been penetrated by acid to form gel and subsequently penetrated by the aqueous solution of molybdenum ions during impregnation. The areas having the rough appearance could be ones which had less contact with acid. Gel formation would not

have occurred and penetration by molybdenum ions during the impregnation step could have been hindered.

The variation in sulphur removal rate caused by particle size is shown in Figure 5. The particle size effect was measured for both SB and N types of alumina monohydrate. The data in the top of Figure 5 indicate that particle size had no effect on per cent sulphur removal, with either type of alumina monohydrate. Results obtained at other temperatures (Kriz et al. 1977) confirm this finding.

The reaction rate expressed per unit weight of catalyst (bottom of Figure 5) instead of conversion (top of Figure 5) was definitely higher for the catalysts made from SB material than for those from the N material. The catalysts made from SB had bulk densities which were at least 10 per cent lower (higher porosity) than those made from the N material. Measurements of specific surface areas showed that the lower densities are associated with larger surface areas. Although the SB catalysts had a greater reaction rate per unit catalyst weight, the fact that they had a lower density meant that a smaller weight of material could be loaded into the reactor. When the SB and N types of catalysts were compared on the basis of conversion the results were similar because the reactor contained different weights of catalyst. The low density catalyst would only have an advantage if both catalysts had the same cost per unit weight. In this instance a smaller weight of the low density catalyst would have to be purchased to fill the reactor.

The reasons the catalysts made from SB alumina monohydrate had lower densities than those made from the N type are not known. Since the SB material was spray dried and the N type was kiln dried, it is highly likely that the two materials will have had different time-temperature histories. Generally speaking, solid residence times in spray driers are shorter than those in kilns. Also temperature profiles in spray driers are more uniform than in kilns. It is likely that both the longer residence times and the sporadic higher temperatures in a kiln would tend to cause sintering and therefore higher densities.

The third series of catalysts was chosen to determine the maximum effect of surface layering on reaction rate. The results are shown in Figure 6. The square data points represent catalysts prepared with N alumina and no acid. The larger sized particles present in the N material combined with the absence of acid, would tend to hinder the penetration of solution into the alumina and enhance the surface layering effect which was shown in Figures 1 and 3. On the other hand, extensive gelling, which occurred in the smaller particles of the SB material when contacted with excess acid, resulted in a catalyst represented by the circular data points. In Figure 6 it appears that the surface layered catalysts may have caused higher sulphur removals and lower nitrogen removals. In both events the differences were minor and were only observed for low concentrations of catalytic ingredients. It also appears that on increasing these concentrations the differences between surface layered and gelled catalysts may have decreased.

The findings in this work may be summarized as follows. The surface layering effect alluded to in earlier work was found to actually occur. The surface layering was found to have very little effect on sulphur and nitrogen conversion. This technique might be useful when supported catalysts of very low concentrations are to be prepared. Other variables such as the type of alumina monohydrate had no effect on conversion. However the time-temperature history (spray drying versus kiln drying) of the alumina monohydrate did alter the density and porosity of the catalyst pellets. This in turn was reflected in the reaction rate per unit weight of catalyst (Figure 5).

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TABLE 1

Properties of Gas-oil Feedstock

Boiling range	345-525°C
Specific gravity, 16/16°C	0.992
Conradson Carbon	0.97 wt%
Sulphur content	3.60 wt%
Nitrogen content	3000 ppm ₂
Kinematic viscosity at 38°C	108.8 mm ² sec ⁻¹

LIST OF CAPTIONS FOR FIGURES

- Figure 1: Final appearance of a catalyst prepared by surface layering (125-fold magnification)
Grain of approximate size 0.5 x 0.3 mm visible on the right side of the photograph
- Figure 2: Final appearance of a catalyst prepared by complete gel formation (125-fold magnification)
- Figure 3: Electron microprobe recorder trace of catalyst prepared by surface layering.
- Figure 4: Electron microprobe recorder trace of catalyst prepared by complete gel formation.
- Figure 5: Weight per cent sulphur removal (a) and reaction rate per unit catalyst weight (b) as a function of alumina monohydrate particle size. Dashed lines for kiln-dried N alumina. Solid lines for spray-dried SB alumina.
- Figure 6: Weight per cent of sulphur removal and nitrogen removal as a function of temperature, total concentration of molybdenum and cobalt oxides being 1 wt % (a) and 2 wt % (b). Solid lines for catalysts prepared by surface layering, dashed lines for catalysts prepared by extensive gelling.



Figure 1



Figure 2

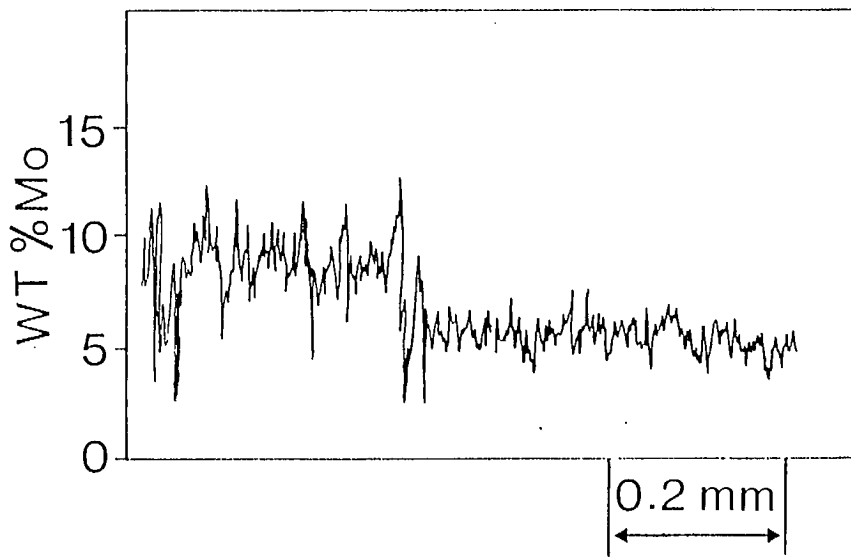


Figure 3

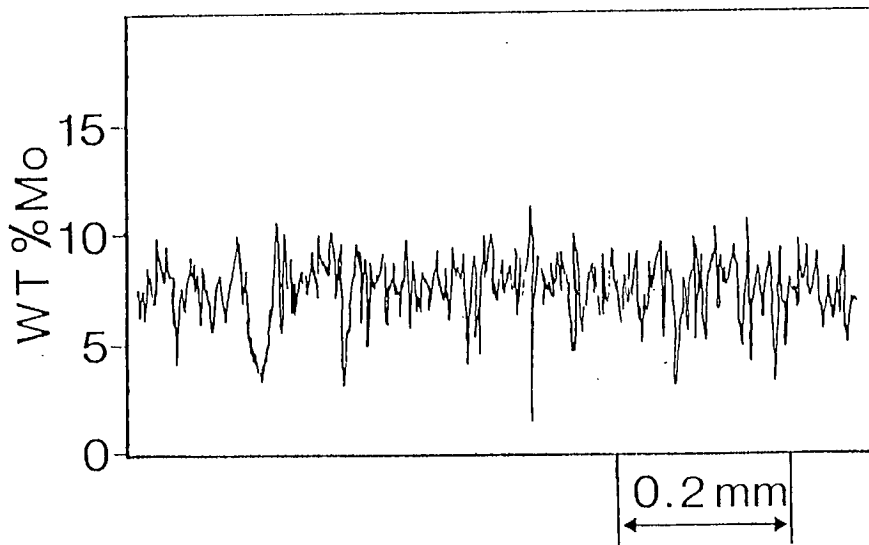


Figure 4

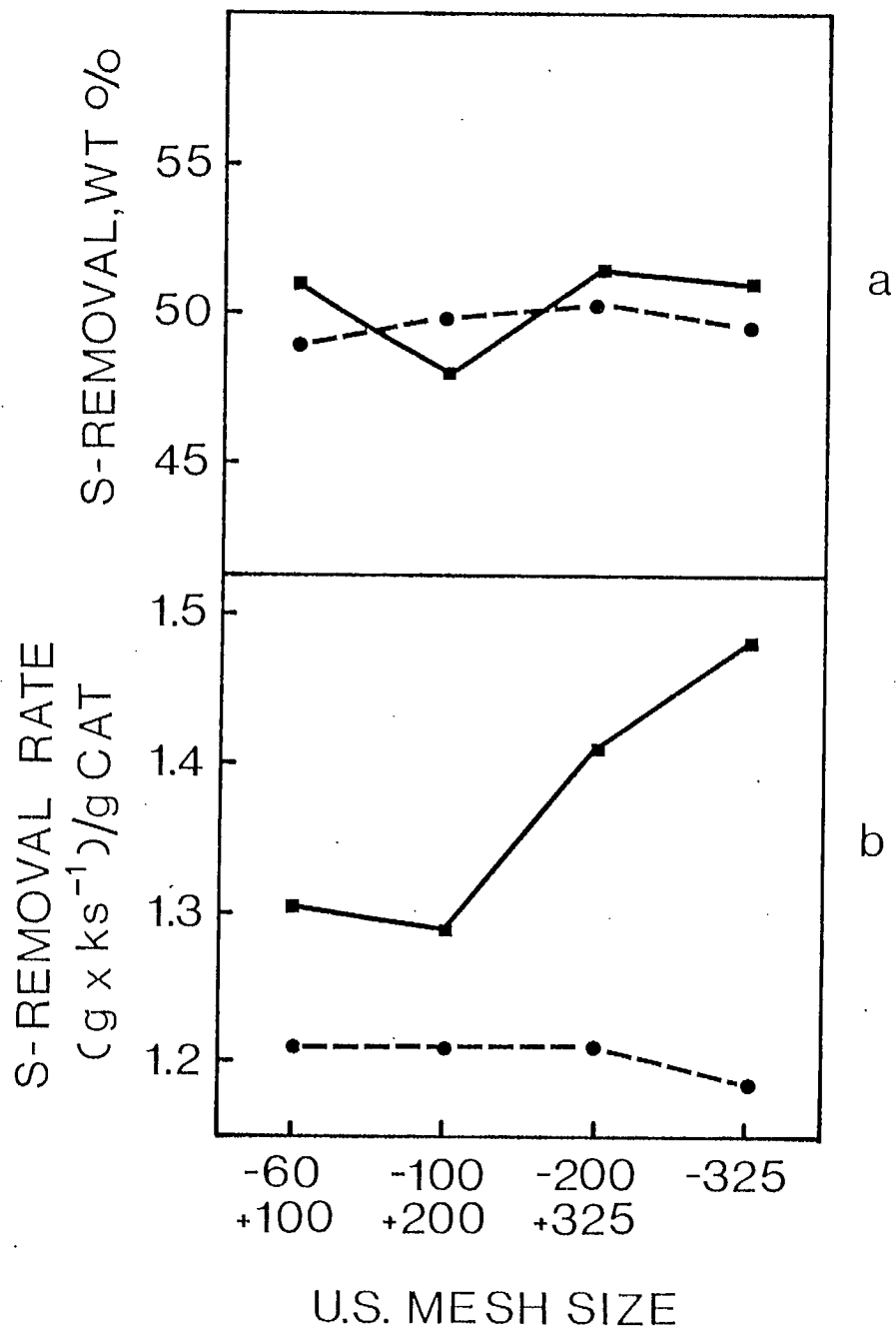


Figure 5

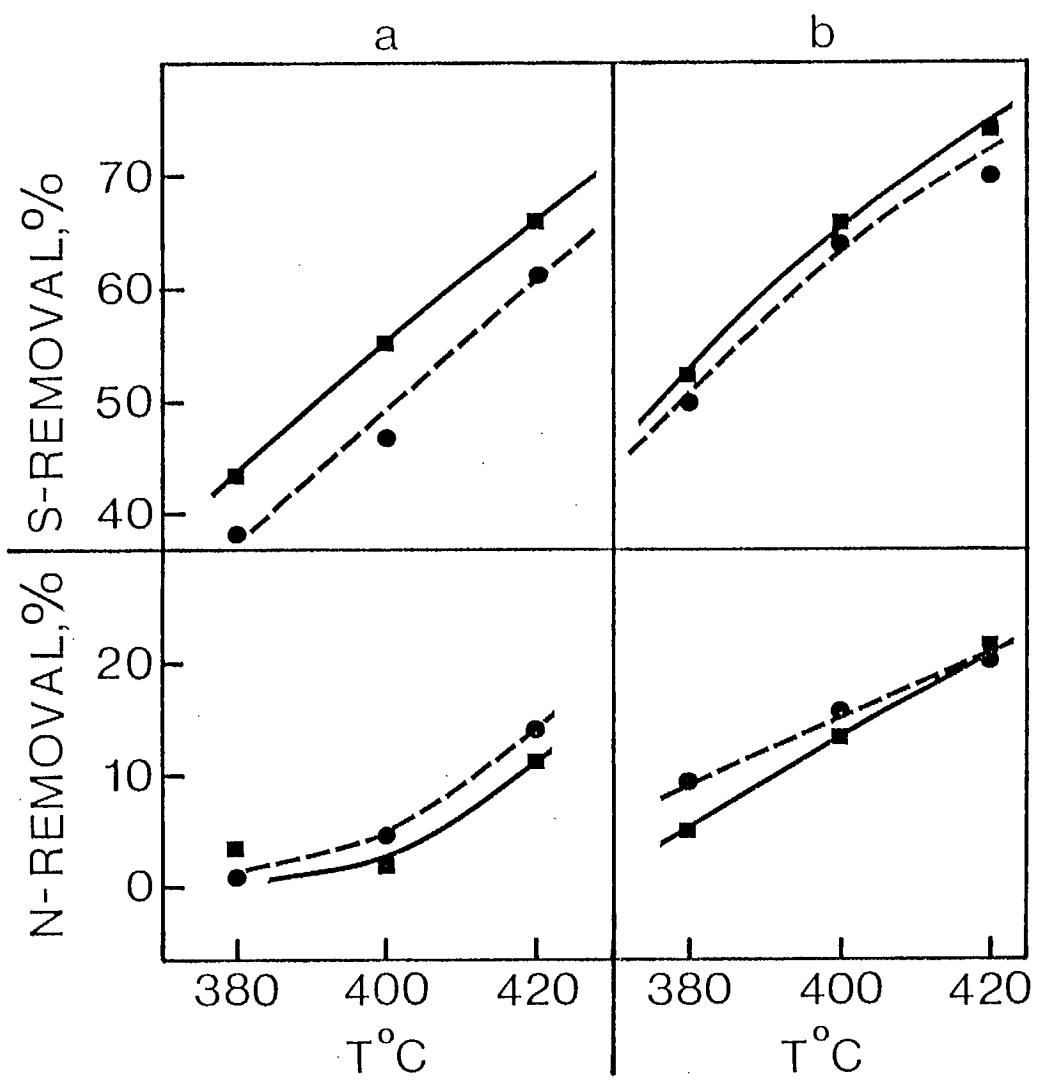


Figure 6