



**CANADA CENTRE FOR MINERAL AND ENERGY TECHNOLOGY
(Former Mines Branch)**

THE HYDRODESULPHURIZATION AND HYDROCRACKING ACTIVITY
OF SOME SUPPORTED BINARY METAL OXIDE CATALYSTS

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CATALYSIS RESEARCH SECTION.

AUGUST 1975

For Submission to the Paper Selection Committee of the Sixth
International Congress on Catalysis.

NATIONAL ENERGY RESEARCH PROGRAM

ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 75-86 (J)

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Administrative Details

- (i) The Hydrodesulphurization and Hydrocracking Activity
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- (iv) Number of Illustrations = 4

**Paper to be considered for Congress theme number 9, Hydrocracking,
Hydroforming and Hydrodesulphurization.

THE HYDRODESULPHURIZATION AND HYDROCRACKING ACTIVITY
OF SOME SUPPORTED BINARY METAL OXIDE CATALYSTS

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ABSTRACT

The hydrocracking of heavy residual oils causes rapid catalyst deactivation. Catalysts containing low concentrations of metal oxides on gamma alumina were evaluated in an attempt to reduce the resulting high catalyst replacement costs. Hydrocracking, hydrodesulphurization and hydrodenitrogenation catalytic activity measurements were made at a pressure of $1.39 \times 10^7 \text{ N/m}^2$ (2000 psig) using a 345-525°C gas oil. Studies with unpromoted catalysts containing from 2.2 to 30 percent MoO_3 showed that the lower concentrations, 2.2 - 3.0 percent MoO_3 , produced significant hydrodesulphurization activity. Catalysts promoted by Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn oxides containing 2.2 percent MoO_3 and having metal/molybdenum atomic ratios of 1.0 were also studied. The results are discussed in terms of catalyst surface acidity, the role of hydrogen in the catalytic process, and the applicability of the intercalation model and the monolayer model. Some of the promoted catalysts containing 2.2 percent MoO_3 were found to compare favorably with a commercial catalyst containing 12 percent MoO_3 and 3 percent CoO .

INTRODUCTION

An investigation of the hydrodesulphurization and hydrocracking of heavy residual oils and bitumens has been in progress at

our laboratories for several years¹. When these heavy feedstocks are processed rapid catalyst deactivation occurs, due to the deposition of coke and of nickel, vanadium, and iron metals. At high conversions, of the high boiling hydrocarbons to lower boiling distillates, catalyst fouling caused by coke formation is several times greater than that caused by metals deposition^{1f}. Regeneration of the catalyst by burning off the coke restores a large part of the original activity. However, this process does not remove the metals; therefore, repeated use increases the extent of permanent deactivation. The rapidity and severity of catalyst deactivation cause catalyst replacement costs to be much greater for residual oil hydrocracking processes than for gas-oil or naphtha hydrorefining processes. One method of reducing catalyst cost is to decrease the concentrations of the active metal oxides impregnated in the alumina support. In our laboratory the hydrocracking and hydrodesulphurization activities of catalysts initially containing 2.2 wt % MoO₃ and 1.1 wt % CoO were found to be almost as good as that of a commercial catalyst containing 12 wt % MoO₃ and 3 wt % CoO^{1e}. Trifiro and co-workers² have also studied catalysts having lower than normal concentrations of cobalt oxide. Rovesti and Wolk³ found that acceptable hydrodesulphurization results could be obtained using a sequence of two different catalysts. They recommended that a catalyst containing 2 wt % Mo be used for demetallization in a first stage. Sulphur removal was to occur in a second stage using a catalyst containing 15 wt % MoO₃ and 3 wt % CoO.

The purpose of the present paper is to establish some of the characteristics of catalysts having low concentrations of active

metal oxides. Specifically, the effect of molybdenum concentration and the promotional effect produced by a number of fourth period transition metal oxides were investigated. The catalyst evaluation was performed using a high boiling gas oil (345-525°C) containing 3.64 percent sulphur. Previous studies in our laboratory showed that the same relative activities were obtained when catalysts were evaluated with this gas oil⁴ and with Athabasca bitumen^{1e}.

EXPERIMENTAL

The catalysts used in this study were prepared by spraying aqueous solutions of the appropriate metal salts onto 5000 grams of alpha alumina monohydrate powder (Continental Oil Company Catapal SB) which were being milled in a mix-muller. Initially a solution consisting of 14 ml of concentrated HNO₃ (70 wt %) and 1000 ml of distilled water was added to the powder. The first salt solution added contained one of the cations being tested as a catalyst promoter. The ammonium paramolybdate solution was added last. The following compounds, containing the promoter cations, were used: Zn (NO₃)₂ · 6H₂O, Cu SO₄ · 5H₂O, Ni(NO₃)₂ · 6H₂O, Co(NO₃)₂ · 6H₂O, Fe(NO₃)₃ · 9H₂O, MnSO₄ · H₂O, Cr(NO₃)₃ · 9H₂O, VOSO₄ · 2H₂O, and TiCl₄. All of the promoted catalysts had a metal promoter/molybdenum atomic ratio of 1.0 and contained 2.2 wt % MoO₃. The impregnated mixtures were dried at 120°C for 10.8 ks and calcined at 500°C for 10.8 ks. The catalyst promoted with chromium was also calcined at 900°C. The calcined powder was mixed with 2 wt % stearic acid and pressed into cylindrical pellets (L = D = 3.18 mm) in a continuous pelleting press. The stearic acid acted as a binder and lubricant during pelleting. The pellets were recalced at 500°C for 14.4 ks to remove the stearic acid.

Surface area and surface acidity measurements were made on the catalysts in their oxide form. A gravimetric quartz spring balance was used to perform the nitrogen adsorption measurements. The surface areas were calculated using the BET method. The method of Clark, Ballou, and Barth⁵ was used to determine surface acidities. One gram samples of catalyst powder, smaller than 74 μm (200 mesh U.S. Standard Sieve Series), were calcined at 500°C for 10.8 ks and slurried in acetonitrile. After a stable initial reading was obtained, the potentiometric titrations were performed by adding 5 ml increments of a 0.006 molar solution of n-butylamine in acetonitrile and waiting 0.3 ks before taking the reading. The potentiometric reading obtained after a total of 25 ml of n-butylamine solution had been added was used as an indication of catalyst acidity.

The feedstock used to evaluate catalyst activity was prepared in our pilot plant by thermally hydrocracking Athabasca bitumen obtained from Great Canadian Oil Sands at Fort McMurray, Alberta. The 345-525°C portion distilled from the hydrocracked product was used as the feed material. Typical compounds in this gas oil contained from three to six condensed rings. Properties of the feedstock are listed in Table 1.

The catalyst pellets were evaluated in a bench-scale fixed bed reactor having a volume of 155 ml and a length-to-diameter ratio of 12. The reactor was filled sequentially from the bottom with 42 ml of berl saddles, 100 ml of catalyst pellets and 13 ml of 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 $1.39 \times 10^7 \text{ N/m}^2$ (2000 psig), a liquid volumetric space velocity of 0.556 ks^{-1} (2.0 hr^{-1}) based on the reactor volume occupied by the catalyst pellets, and a hydrogen flow rate of 0.0718 l/s at STP (5000 cf/bbl). The catalyst was pre-sulphided and stabilized using the mixture of gas oil and hydrogen at 400°C . Subsequent experiments were performed sequentially at temperatures of 420°C , 400°C , and 380°C . Gas oil and hydrogen contacted the catalyst for 25.2 ks prior to the 420°C experiment. The reaction system was maintained at steady state conditions for 3.6 ks prior to, and for 7.2 ks during, the period in which each sample of liquid product was collected.

The liquid product was analyzed for sulphur, nitrogen, and the weight fraction boiling above 420°C . The sulphur content was determined using an X-Ray fluorescence technique⁶. The nitrogen analyses were performed using a hydrogenation-microcoulometric apparatus⁷. A modified version of the U.S. Bureau of Mines Hempel distillation analysis⁸ was used to distill the liquid product into nine fractions. The change in the amount of the heaviest fraction ($+420^\circ\text{C}$) was taken as an indication of the extent of hydrocracking.

RESULTS AND DISCUSSION

Measurements of surface area and surface acidity for the oxide form of the unpromoted and promoted catalysts are shown in Figures 1 and 2, respectively. The weight of the catalyst charge is also shown at the bottom of each figure. The surface areas of the unpromoted catalysts are comparable to those reported by Giordano

et al⁹ and by de Beer¹⁰ for catalysts prepared somewhat differently, that is by impregnating aqueous solutions of ammonium paramolybdate in gamma alumina powders and subsequently drying and calcining. The surface areas of the promoted catalysts, calcined at 500°C, did not vary enormously. However, the chromium promoted catalyst calcined at 900°C had a much lower surface area than the chromium promoted catalyst calcined at 500°C. Similar results (decreasing alumina surface areas with increasing calcining temperature) have been documented by Gitzen¹¹. The Cr promoted catalyst calcined at 500°C was yellow in colour indicating the presence of Cr⁶⁺ ions¹². In contrast the Cr promoted catalyst which was calcined at 900°C had a light green colour suggesting the formation of a Cr₂O₃ compound¹³.

All the potentiometric titration curves obtained during the surface acidity measurements had the same general shape as that reported by Clark, Ballou and Barth⁵ for F-10 alumina. The surface acidities of the unpromoted catalysts were found to increase fairly uniformly with MoO₃ content. This is in agreement with the finding of Kiviat and Petrakis¹⁴ that Bronsted acidity increased with increasing MoO₃ concentrations on γ -Al₂O₃. For the promoted catalysts in their oxide form, the Co, Ni and Zn promoted catalysts had almost the same acidity as the unpromoted catalyst containing 2.2 wt % MoO₃, the Fe and Cr (calcined at 900°C) promoted catalysts were slightly more basic, and the Ti, V, Cr (calcined at 500°C), Mn and Cu promoted catalysts were more acidic. Our results for the Co promoted catalysts are different than those obtained by Ratnasamy, Sharma and Sharma¹⁵ who found that both the distribution and the strength of acid sites on a catalyst prepared by the simultaneous impregnation of Co and Mo

salts were different than those of a comparable catalyst containing Mo only.

As shown in Figure 3, the extents of the three reactions, hydrocracking, hydrodesulphurization and hydrodenitrogenation, do not change in exactly the same way as the molybdenum content of the unpromoted catalyst increases. The reaction mixture converts the oxide form of the catalyst to a sulphide form. However for the sake of simplicity, all catalyst concentrations are referred to in their oxide form. The increases in hydrocracking and hydrodesulphurization with MoO_3 concentration were quite large up to 9 percent and 3 percent respectively, but more gradual at higher concentrations. The activity pattern for hydrodenitrogenation was considerably different. The activity increased up to 18 percent MoO_3 and then declined.

The change in the hydrocracking activity pattern at 9 percent MoO_3 may be related to the formation of an epitaxial layer of molybdenum on the alumina surface. Dufaux, Che and Naccache¹⁶ reported that molybdenum was bonded to gamma alumina forming a complete monolayer at concentrations of 10 percent MoO_3 . At higher concentrations of molybdenum in the catalyst, free MoO_3 was formed. Changes in activity patterns with $\text{MoO}_3\text{-Al}_2\text{O}_3$ catalysts have also been observed at 9-10 percent MoO_3 concentrations for reactions completely different from the ones considered here^{17, 18}.

To some degree, hydrodesulphurization and hydrocracking are related. When a sulphur atom is removed from a polycyclic thiophene type compound the number of rings is reduced by at least one and a lower boiling compound is formed. On this basis the hydrocracking

activity would be expected to follow the hydrodesulphurization activity pattern. The fact that from 3 to 9 percent MoO_3 the extent of hydrocracking increases markedly, while hydrodesulphurization activity does not, suggests that considerable hydrocracking not related to sulphur removal is occurring.

The hydrodenitrogenation reaction was the only one to show a decline in activity at high catalyst concentrations of MoO_3 . Giordano and co-workers⁹ found that an $\text{Al}_2(\text{MoO}_4)_3$ species began to form at MoO_3 concentrations of 20 percent and higher. The decline in hydrodenitrogenation activity shown in Figure 3 may be related to formation of this compound.

The surface acidity results in Figure 1 are not directly proportional to any of the reaction results in Figure 3. This suggests that the reaction rates are not limited by the concentration of acidic sites for all of the unpromoted catalysts. Presumably when a sufficient number of acidic sites are present the reaction rate is limited by some step in the reaction process which is not controlled by the number of acidic sites.

The activities of the promoted catalysts are shown in Figure 4 as a function of increasing atomic number of the promoter cation. The Co and Ni promoters produced the highest activities for all of the reactions. The Cr promoted catalyst (calcined at 900°C) also exhibited a relatively large hydrodenitrogenation activity. These results are somewhat different than those reported by de Beer and co-workers¹⁹. They found that Zn and Co promoted catalysts had the highest hydrodesulphurization activities and that Mn and Ni promoted catalysts had lower but comparable activities. Their experiments

were performed for shorter periods than ours and their promoted catalysts contained 12 weight percent MoO_3 whereas ours contained only 2.2 percent. These differences in experimental conditions were probably responsible for the different hydrodesulphurization results. The greater activities we obtained with the Co and Ni promoted catalysts are consistent with the fact that these materials are used extensively as promoters in commercial hydrodesulphurization catalysts.

The twin peak pattern in the hydrodenitrogenation activity shown in Figure 4 is similar to activity patterns reported for other reactions involving hydrogen. Twin activity peaks have been reported by Dowden, MacKenzie and Trapnell²⁰ for hydrogen deuterium exchange, by Dixon, Nicholls and Steiner²¹ for cyclohexane disproportionation and dehydrogenation, and by Harrison, Nicholls and Steiner²² for ethylene hydrogenation. The existence of the twin peak pattern for hydrodenitrogenation activity suggests that the role of the catalyst promoter involves hydrogenation which tends to support the suggestion of Smith²³.

According to the intercalation model, the catalyst promoter is located between layers of sulphur atoms. For example, Voorhoeve and Stuver²⁴ suggested that Ni atoms were inserted between adjacent sulphur layers of WS_2 , and that the role of the alumina support was only to disperse the catalyst. Farragher and Cossee²⁵ found that the increase in benzene hydrogenation activity using tungsten catalysts was proportional to the "goodness of fit" of the promoter in the octahedral holes between the WS_2 layers. Plausible cationic

radii of the catalyst promoters ($\text{Ti}^{4+} = 68$ pm, $\text{V}^{5+} = 59$ pm, $\text{Cr}^{3+} = 63$ pm, $\text{Cr}^{6+} = 52$ pm, $\text{Mn}^{2+} = 80$ pm, $\text{Fe}^{2+} = 74$ pm, $\text{Fe}^{3+} = 64$ pm, $\text{Co}^{2+} = 72$ pm, $\text{Ni}^{2+} = 69$ pm, $\text{Cu}^{2+} = 72$ pm, and $\text{Zn}^{2+} = 74$ pm) used in this study do not correlate with the activity patterns shown in Figure 4. The intercalation model may provide an explanation for systems in which the catalyst does not interact with the support. If the evidence¹⁶ for the interaction of molybdenum with gamma alumina is correct, only one sulphide layer will exist making intercalation impossible. A monolayer model incorporating some of the features proposed by Schuit and Gates²⁶, Massoth²⁷, or Ueda and Todo²⁸ might be more appropriate, especially when low concentrations of catalytic materials are used, as was the case in this study.

Finally, the catalytic activities of the Co promoted catalyst shown in Figure 4 can be compared with a Co promoted commercial catalyst. A pelleted commercial catalyst (Harshaw 0603T) containing 12 weight percent MoO_3 and 3 weight percent CoO was used to process the same feedstock at the same operating conditions⁴. The percent conversion of $+420^\circ\text{C}$ material, the weight percent sulphur removed, and the weight percent nitrogen removed were 31, 86 and 50, respectively. While the activities of the low-metals catalysts in Figure 4 are less than those of the commercial catalyst, they do approach it rather closely. The activities of low-metals catalysts compare just as favorably with that of the commercial catalyst when a heavier feedstock such as Athabasca bitumen is used^{1e}. The low-metals catalysts have the advantage that the cost for catalyst ingredients will be significantly less than for the high-metals commercial catalyst.

This feature may be of interest when processing heavy residual feedstocks which cause rapid catalyst fouling.

ACKNOWLEDGEMENTS

The authors wish to thank E.C. McColgan, P.S. Soutar, R.W. Taylor, M.J. Whalley, R.J. Williams and G.R. Lett for technical assistance.

TABLE 1

PROPERTIES OF THE HEAVY GAS OIL FEEDSTOCK

Property	Value
Boiling Range	345-525 ^o C
Specific Gravity 16/16 ^o C	0.992
Conradson Carbon	0.97 wt %
Sulphur	3.64 wt %
Nitrogen	3800 ppm
Kinematic Viscosity at 38 ^o C	108.8 mm ² /s

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LEGENDS TO THE FIGURES

- Figure 1. Surface Area (m^2g^{-1}), Surface Acidity (mV), and Weight of Catalyst Loaded into the Reactor (g) versus the Concentration of MoO_3 in the unpromoted molybdenum-alumina catalysts.
- Figure 2. Surface Area (m^2g^{-1}), Surface Acidity (mV), and Weight of Catalyst Loaded into the Reactor (g) versus the Catalyst Promoter Cation in the molybdenum-alumina catalysts. The circles represent catalysts calcined at 500°C . The square data points represent a catalyst calcined at 900°C .
- Figure 3. Conversion of Hydrocarbons Boiling Above 420°C to Lower Boiling Compounds, Weight Percent Sulphur Removed from the Liquid Hydrocarbon, and Weight Percent Nitrogen Removed from the Liquid Hydrocarbon Versus the Concentration of MoO_3 in the unpromoted molybdenum-alumina catalysts. All data points obtained at 400°C .
- Figure 4. Conversion of Hydrocarbon Boiling Above 420°C to Lower Boiling Compounds, Weight Percent Sulphur Removed from the Liquid Hydrocarbon, and Weight Percent Nitrogen Removed from the Liquid Hydrocarbon Versus the Catalyst Promoter Cation in the molybdenum-alumina catalysts. The circles represent catalysts calcined at 500°C . The square data points represent a catalyst calcined at

900°C. The atomic metal to molybdenum ratio was 1.0 in all the promoted catalysts. All data points obtained at 400°C.







