DEPARTMENT OF
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MINES BRANCH

OTTAWA

CATALYSTS FOR HYDROCRACKING AND REFINING HEAVY OILS AND TARS PART 1: THE EFFECT OF COBALT TO MOLYBDENUM RATIO ON DESULPHURIZATION AND DENITROGENATION

R. J. Williams, R. G. Draper and B. I. Parsons

FUELS RESEARCH CENTRE

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ABSTRACT

This report is the first in a series on an investigation of the factors involved in the preparation of effective, low-cost catalysts for the hydrocracking and refining of high-boiling gas-oils and bitumens. Active catalysts of the "cobalt molybdate on alumina" type, containing 3% and 13% combined metal-oxides were prepared by a surface layering technique using a mix-muller. A gradual leveling out, or plateau, of activity for both sulphur and nitrogen removal was observed beginning at, or near, a cobalt to molybdenum atomic ratio of 0.6. The denitrogenation activity of the cobalt molybdate catalysts increased more slowly with the overall concentration of metals than did the desulphurization activity.

The effectiveness of the catalysts for sulphur and nitrogen removal was determined with a 650-975°F gas-oil distilled from Athabasca bitumen that had been thermally hydrocracked in a Mines Branch pilot plant. The tests were undertaken at 2000 psi pressure in a bench-scale flow system with bottom feed at a liquid-hourly-space-velocity of 2.0. The results of the study are discussed relative to those observed by others using different methods of catalyst preparation.

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CATALYSEURS POUR L'HYDROCRAQUAGE ET LE RAFFINAGE DES HUILES LOURDES

ET DES GOUDRONS

PARTIE 1: L'EFFET DU RAPPORT COBALT/MOLYBDENE SUR

LA DESULFURATION ET L'ELIMINATION DE L'AZOTE

par

R.J. Williams*, R.G. Draper**, et B.I. Parsons***

RESUME

Ce rapport est le premier d'une série sur l'étude des facteurs qui entrent en ligne de compte dans la préparation de catalyseurs efficaces et peu coûteux pour l'hydrocraquage et le raffinage de gas-oils et de bitumes à point d'ébullition élevé. Les catalyseurs actifs de type "molybdate de cobalt sur alumine" contenant 3% et 13% d'oxydes combinés de métaux ont été préparés au moyen d'une technique de disposition en couches de surface faisant usage d'un broyeur-malaxeur. Il se produit dans l'élimination du soufre et de l'azote une stabilisation ou un plateau d'activité commençant lorsque le rapport atomique cobalt-molybdène est de 0.6 ou près. La capacité d'élimination de l'azote par les catalyseurs de molybdate de cobalt s'accroît plus lentement que le processus de désulfuration lorsqu'il s'agit d'une concentration générale de métaux.

L'efficacité des catalyseurs dans l'élimination du soufre et de l'azote a été déterminée à l'aide d'un gas-oil à point d'ébullition de 650 - 975°F provenant de la distillation de bitume de l'Athabasca soumis à l'hydrocraquage dans une usine pilote de la Direction des mines. Les essais ont été faits sous une pression de 2000 livres par po² à l'aide d'un système d'alimentation par le bas en régime liquide à une vélocité horaire spatiale de 2. L'auteur traite des résultats de l'étude par rapport aux résultats obtenus par d'autres personnes utilisant des méthodes différentes pour la préparation des catalyseurs.

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INTRODUCTION

The emphasis in the research program on catalytic processing at the Fuels Research Centre is currently on the development of <u>cheaper</u> forms of hydrodesulphurizing and hydrocracking catalysts for upgrading heavy oils and tars. The system of particular interest is the catalytic hydrocracking (at 1000 to 2000 psi) of bitumens separated from the Athabasca and Cold Lake oil sands in Alberta and from the Lloydminster oil field in Saskatchewan(1). Effective catalyst life with these bitumens is only a matter of a few hundred hours because of the high carbon residue and metals content of the feed stock. Various approaches to reducing catalyst cost are being examined with a view to developing a liquid-phase slurry-bed type of process(2) for hydrocracking the residuum (+975°F) into stable, relatively-low-sulphur distillate fractions which can then be readily pipelined from the northern locations to existing refineries in the south and east of Canada. The ultimate objective is to generate a true "synthetic crude"* from bitumen which can be substituted for conventional crude as supplies decline in Western Canada.

To summarize progress to date, it has been found that for <u>liquid-phase systems</u> the overall metal oxide concentration of an alumina-supported cobalt molybdate catalyst can be reduced to approximately 3% (from 12%) by layering the active ingredients on to the exterior surface of boehmite particles prior to calcination. It is to be emphasized that the lower metals concentration is only effective in predominantly liquid-phase systems where the internal pore structure of the catalyst particles does not contribute significantly to the reaction process (by virtue of the low rates of diffusion of liquids or, in the case of high residuum feed stocks, because the internal structure becomes plugged by coke and tar residues).

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*As compared to the refined product such as is presently being produced by Great Canadian Oil Sands Ltd.(3) or as proposed by Syncrude Canada Ltd.(4).

The purposes of the present work are:

a)   to determine the optimum atomic ratio of cobalt to molybdenum in
     the preparation of the catalyst by the surface layering technique
     as it applies to the desulphurization process, and

b)   to investigate the effect of metals concentration and atomic ratio
     on nitrogen removal.

Previous investigations of the effect of cobalt to molybdenum ratio on the
desulphurization process are not in agreement. Todo et al(5), working
with a reduced Khafji crude, report that the optimum ratio depends to a
large extent on the molybdenum concentration ..... ranging from an atomic
ratio of cobalt to molybdenum of greater than 0.7 for molybdenum trioxide
concentration of 6.5% to Co:Mo = 0.2 at MoO_3 concentrations of 13-14%.
These findings are in marked contrast with the many commercial forms of
cobalt molybdate catalyst produced in North America most of which have a
cobalt to molybdenum atomic ratio in the vicinity of 0.6. DeBeer et al(6),
working with a pure compound, thiophene, confirm that the optimum ratio is
about 0.6 but suggest a much reduced activity at Co:Mo ratios in excess of
0.6.

In view of the rapidly increasing interest in cobalt molybdate
catalysts for the hydrogen-treating of bitumens and other such crudes, it
seemed to the authors to be an appropriate time to re-examine the system,
using a high-boiling, high-sulphur commercial feed stock, to establish the
optimum cobalt to molybdenum ratio and to determine whether or not this
ratio is sharply defined.

Cobalt molybdate catalysts are also effective for nitrogen
removal(7). The effect of the cobalt to molybdenum ratio on denitrogena-
tion has largely been ignored in all previous investigations and it was
felt that this aspect of its catalytic action should be explored as well.

EXPERIMENTAL

In very general terms, it has been found that heavy crudes are best hydrogen treated in flow systems in which the oil and hydrogen are fed into the <u>bottom</u> of the reactor, i.e. the reactor is operated as a mixed three-phase system with the heavy oil fraction predominantly in the liquid phase, rising and flowing slowly through the catalyst bed by displacement, and the lighter vapours and hydrogen rising rapidly by buoyancy. By operating the system in a bottom-feed arrangement the residence time of the high-boiling fractions in the catalyst bed is maximized (which enhances hydrocracking) and the residence time of the lighter fractions produced in the process is minimized (which greatly reduces gas formation and hydrogen consumption). Temperature control in the reaction bed is much better in a bottom-feed system because of the ability of the liquid-phase oil to distribute the exothermic heat of reaction, and the working temperatures and pressures required are sub-stantially lower because of the much increased contact time. Properly engineered, these things result in better catalyst activity, less coke and catalyst fouling and longer catalyst life.

<u>Catalyst Preparation</u>

The support material used in the preparation of the catalysts was an alumina monohydrate (boehmite) produced by the hydrolysis of aluminum alkoxides in the manufacture of alcohols. It was supplied to the Fuels Research Centre by the Continental Oil Co. of Teterboro, New Jersey, and was designated (trade name) "Catapal SB". Most of the particles occurred in the size range 30-100 microns. In the monohydrate form the alumina possessed little or no effective surface or pore structure in the catalytic sense. It is only on calcination that the active surface area and pore structure are developed*. To ensure that the catalytic ingredients were

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*The surface area and pore volume of the calcined alumina are reported by the manufacturer to be of the order of 200 m^2/g and 0.5 ml/g respectively.

dispersed primarily on the outer surfaces of the particles, the pores
of the alumina monohydrate were first saturated with water in a mix-
muller, the active ingredients added, and <u>then</u> the mixture was calcined.
The details of the procedure used in the preparation of the catalysts
were briefly:

1. 5000 grams of the alumina monohydrate was placed in a
   Simpson mix-muller (model LF), 1500 mls of distilled water
   were added slowly and the mixture was mulled for 5 minutes.

2. Appropriate amounts of concentrated solutions of reagent-
   grade cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$ and ammonium paramolybdate,
   $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$, were added slowly. The usual procedure
   was to add the cobalt solution first. (Previous experience......
   see Research Report R-263 in reference 1, indicated that the
   order in which the solutions were added to the support material
   did not affect the end result.) The mixture was mulled for 3
   minutes after the addition of each ingredient. The concentration
   and volume of the solutions used were adjusted so as to keep
   the total volume of water added to the system approximately
   constant. At the end of the mulling operation the mixture was
   damp to the touch. No significant change (peptization) of the
   alumina monohydrate appeared to have occurred.

3. The impregnated mixture was spread as a half-inch layer in
   a stainless steel tray and dried in air at 110°C for 3 hours,
   crushed lightly with a wooden rolling pin to break up lumps,
   then calcined at 500°C for 3 hours.

4. The calcined sample was formed into 1/8 x 1/8 inch pellets at
   40,000 psi in a continuous pelleting press using 2% stearic
   acid as a binder-lubricant. The pellets were recalcined at
   500-550°C for 4 hours to remove the stearic acid.

The concentrations of cobalt and molybdenum oxides in the catalysts that were prepared and tested are as follows:

Catalyst Number	Source	CoO (wt %)	MoO_3 (wt %)	Co:Mo
1	Commercial	3.0	9.0	0.64
2	Experimental	4.4	8.6	1.0
3	"	1.1	2.2	1.0
4	"	0.73	2.2	0.64
5	"	0.52	2.2	0.45
6	"	0.37	2.2	0.32
7	"	0.23	2.2	0.20
8	"	0.0	2.2	0.00

The catalyst numbers correspond to the graph designations used in the figures describing the experimental results. In addition to the above, a batch of the pure support material was put through the preparative procedure (adding distilled water in place of the salt solutions) for "zero" metals baseline experiments. The commercial cobalt molybdate catalyst used for comparison purposes was manufactured by the Harshaw Chemical Co. of Cleveland, Ohio. It was supplied in the form of 1/8 x 1/8-inch pellets and used as received.

Apparatus and Procedure for Evaluating the Catalysts

The evaluation work was undertaken in a bench-scale flow system with the oil and hydrogen percolating up through a fixed bed of catalyst. The major components of the apparatus are described in Mines Branch Research Report R-194(8). The general advantages of bottom feed over top feed have been outlined in previous Bulletins(9). The

reaction vessel was 12 inches long by 1 inch in diameter. The first three inches of the reactor were filled with porcelain berl saddles to act as a pre-heater section, and the following 8 inches (100 ml) were filled with catalyst pellets. The remaining one inch of reactor length were filled with berl saddles.

All of the experiments were undertaken at 2000 psi, at a liquid-hourly-space-velocity (LHSV) of 2.0, with a hydrogen flow-rate of 5000 standard cubic feet per barrel (scf/bbl). A series of experiments with each catalyst consisted of a bedding-in run for 4 hours at 400°C (to dampen the initial high activity of the catalyst characteristic of the first few hours of operation), followed by 4 experiments of 4 hours each at 420, 400, 380 and 360°C. The activity of the catalyst after each series of tests was checked by repeating the first run at 420°C and comparing the results.

Feed Stock

The feed stock used was a heavy gas-oil (650-975°F) derived from Athabasca bitumen by thermal hydrocracking. The general properties of the gas-oil are shown in Table 1. Much of the previous work in this laboratory(1) was done using unrefined bitumen separated from the Athabasca Oil Sands. The reason for changing the feed stock in the present experiments was simply to facilitate the analytical work ..... specifically, the nitrogen analyses, and the assessment of the ability of the catalysts to remove nitrogen. In the earlier work, considerable difficulty had been encountered in analysing for nitrogen because of the presence of the dregs of the unreacted residuum and clay in the products. It is appreciated that there is considerable difference between separated bitumen and a distillate gas-oil, but it was felt that for catalyst evaluation purposes the gas-oil was sufficiently high boiling to simulate the action of the bitumen in a bottom-feed reactor and indicate, at least in a relative way, the changes taking place with changes in catalyst composition.

TABLE 1

The General Properties Of The Feed Stock

Physical Properties and Chemical Analyses	Thermally Hydrocracked Gas-Oil
Boiling Range (°F)	650-975
Specific Gravity 60/60°F	0.992
Conradson Carbon (wt %)	0.97
Sulphur (wt %)	3.59
Nitrogen (wt %)	0.38
Ash (wt %)	trace
Vanadium (ppm)	<1
Viscosity, Kinematic (cSt) at 100°F	108.8

The gas-oil was distilled from bitumen that had been thermally hydrocracked in a pilot plant at the Mines Branch(10). The average conversion level of the residuum (+975°F) in the hydrocracking experiments was about 75% and the operating pressure was 2000 psi. The bitumen was supplied by Great Canadian Oil Sands Ltd. from their plant on the Athabasca River, north of McMurray, Alberta.

Analytical Procedures

The extent of hydrocracking which took place, i.e. the amount of light-ends formed in the course of desulphurization and denitrogenation, was determined using a modification of the U.S. Bureau of Mines Hemple Distillation Analysis(11). A charge of 100 mls of oil was placed in a

Hemple distillation flask and, using a large fan-like flame burner, distilled rapidly in two stages at, a) atmospheric pressure and b) 40 mm pressure. The temperature cuts collected are shown in Tables 2 and 3.

The sulphur content of the oil products was determined by X-ray fluorescence using a Model 4000 Panalyzer manufactured by Panametrics, a subsidiary of the Esterline Corporation of Waltham, Massachusetts. The source of the X-rays was Fe-55. The apparatus was calibrated in an absolute sense by the direct addition of pure sulphur compounds to sulphur-free oils and, in a relative sense, by comparing results with those obtained independently by an oxygen-bomb technique (ASTM Procedure D129).

The concentration of nitrogen in the oil samples was measured using a hydrogenation-microcoulometric apparatus developed and manufactured by the Dohrmann Division of Envirotech Corp., Mountain View, California(12). A measured amount of oil is introduced with flowing hydrogen into a reaction tube containing nickel catalyst. Complete hydrogenation of the sample takes place, converting all bound nitrogen present in the sample into ammonia, which is passed through a scrubber for acid-gas removal and then into a titration cell. The Dohrmann procedure was developed for oils containing 10-100 ppm and was calibrated using research-grade standards of pyridine, carbazole and acetanilide. The gas-oil samples of the present investigation were diluted to reduce the nitrogen concentration to the working range of the instrument.

EXPERIMENTAL RESULTS AND DISCUSSION

General Observations

The results of the investigation are summarized in Figures 1 to 4 and Tables 2 and 3. The effect of reaction temperature and catalyst composition on the specific gravity of the product is shown in Figure 1, and the effect on sulphur and nitrogen removal in Figures 2 and 3 respectively. The overall trend of the changes observed with changes in the cobalt to molybdenum ratio in the low-metals series of catalysts is indicated in Figure 4. Summaries of the results of the distillation analyses and sulphur and nitrogen determinations on products formed at $400^{\circ}C$ are given in Tables 2 and 3.

The effects of the composition of the catalyst on nitrogen and sulphur removal were similar in some respects and markedly different in others. For nitrogen removal, the most important feature of the catalyst composition was the overall metals loading, i.e. the higher the concentration of either of the component metals the more nitrogen was removed. There was no obvious optimum atomic ratio of cobalt to molybdenum (in the range 0 to 1) though the incremental improvement between the catalysts with atomic ratios of 0.64 and 1.0 was small. For desulphurization, on the other hand, there were only marginal differences between the high-metals and low-metals forms of the catalyst, and there was an optimum in the atomic ratio of cobalt to molybdenum at, or near, 0.64. The decrease in desulphurization measured at atomic ratios greater than the optimum was small .....for practical purposes the optimum is better described as the minimum ratio required for effective desulphurization. This observation is in general agreement with the many claims put forward in the North American patent literature; however, it is in disagreement with the papers of Todo and DeBeer, who reported sharp decreases in conversion at atomic ratios greater than the optimum.

1	—o—	commercial catalyst
2	—●—	Exptl. catalyst, high metals, Co/Mo = 1.0
3	—□—	" " low metals, Co/Mo = 1.0
4	—■—	" " " " " = 0.64
5	—△—	" " " " " = 0.45
6	—▲—	" " " " " = 0.32
7	—o—	" " " " " = 0.20
8	—●—	" " " " " = 0.00
9	—x—	Alumina support only

Figure 1 - The effect of reaction temperature on the
specific gravity of the products.
(Metals concentrations shown on page 5)

Figure 2 - The effect of reaction temperature on
sulphur removal.
(Metals concentrations shown on page 5)

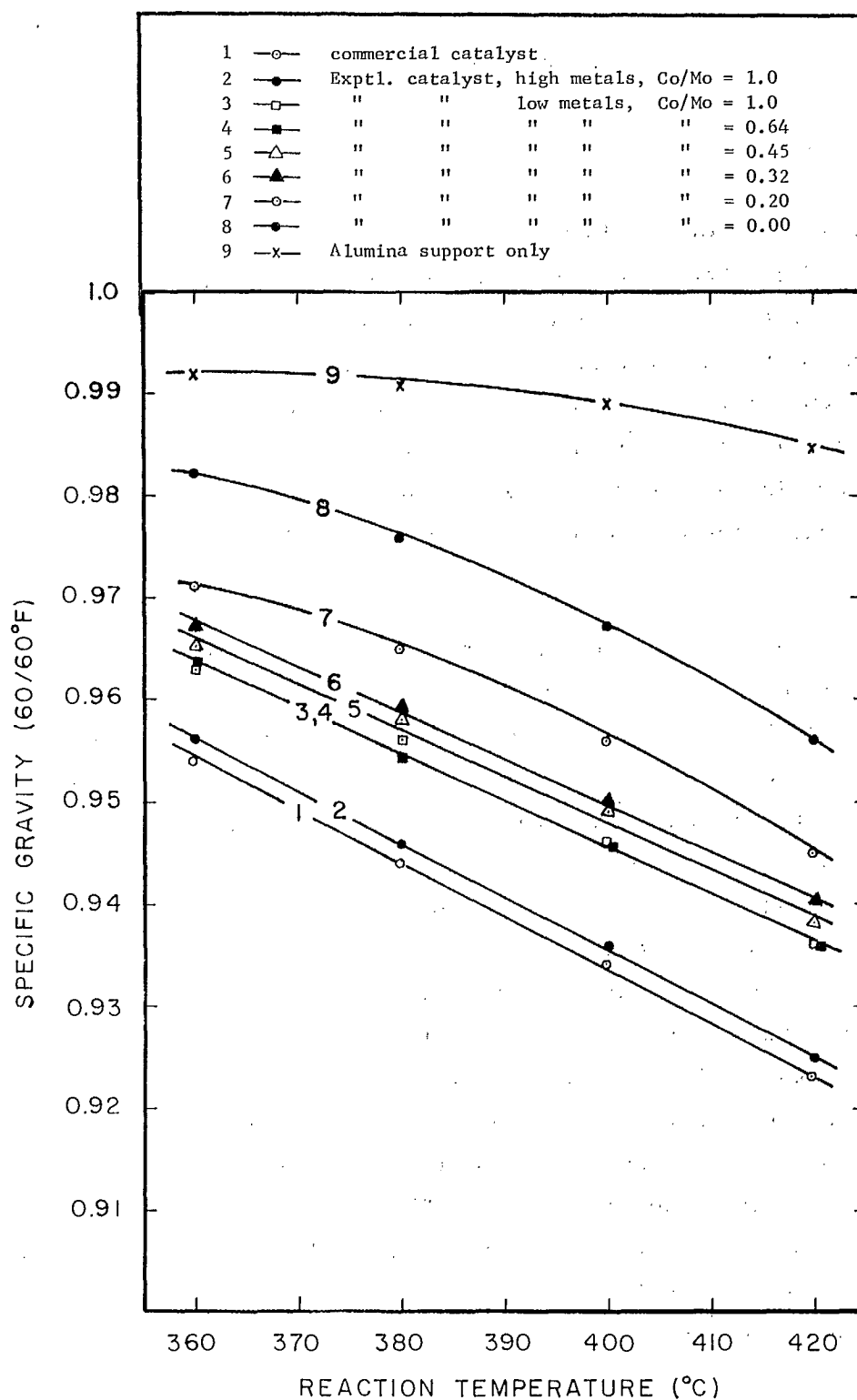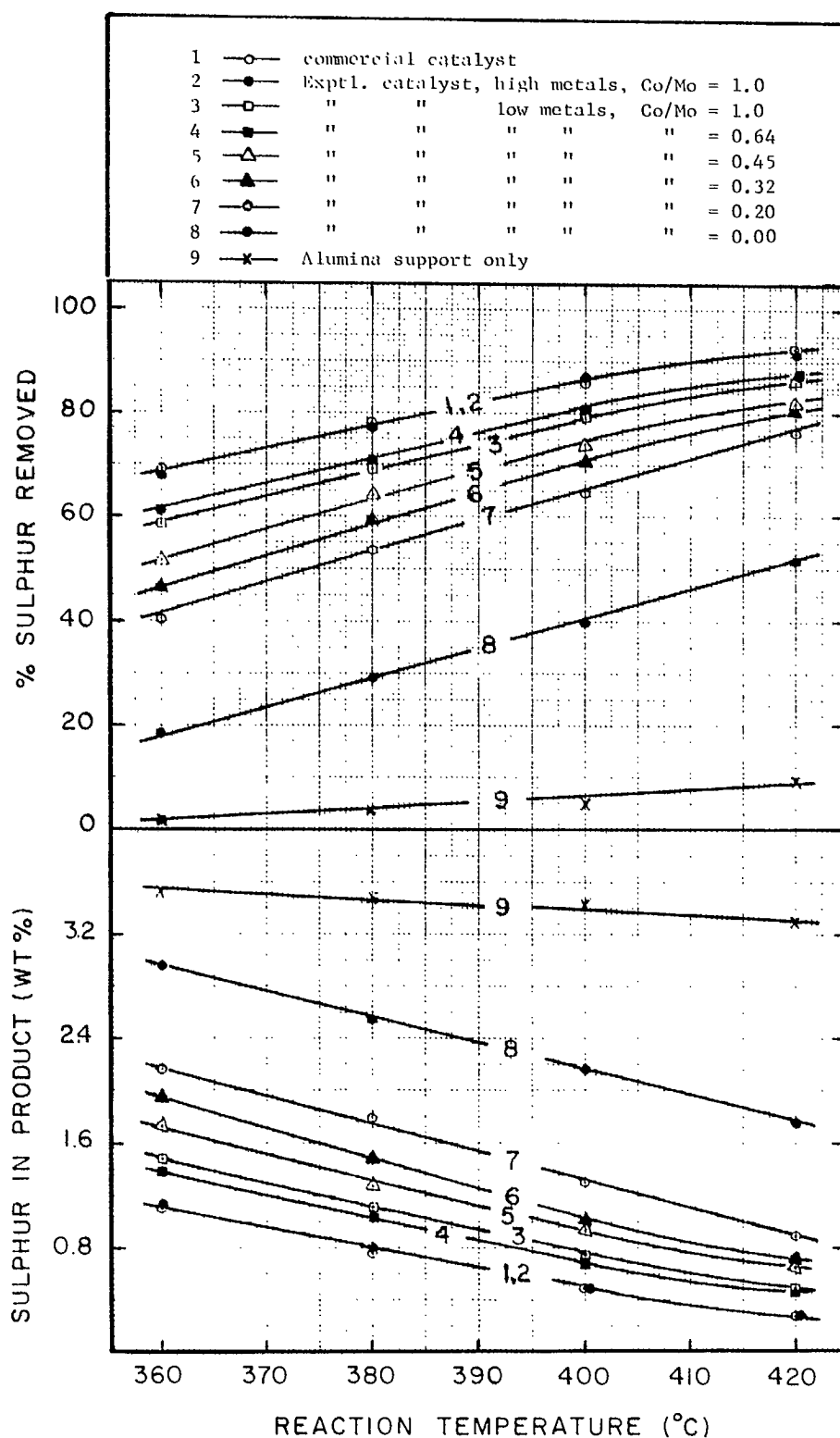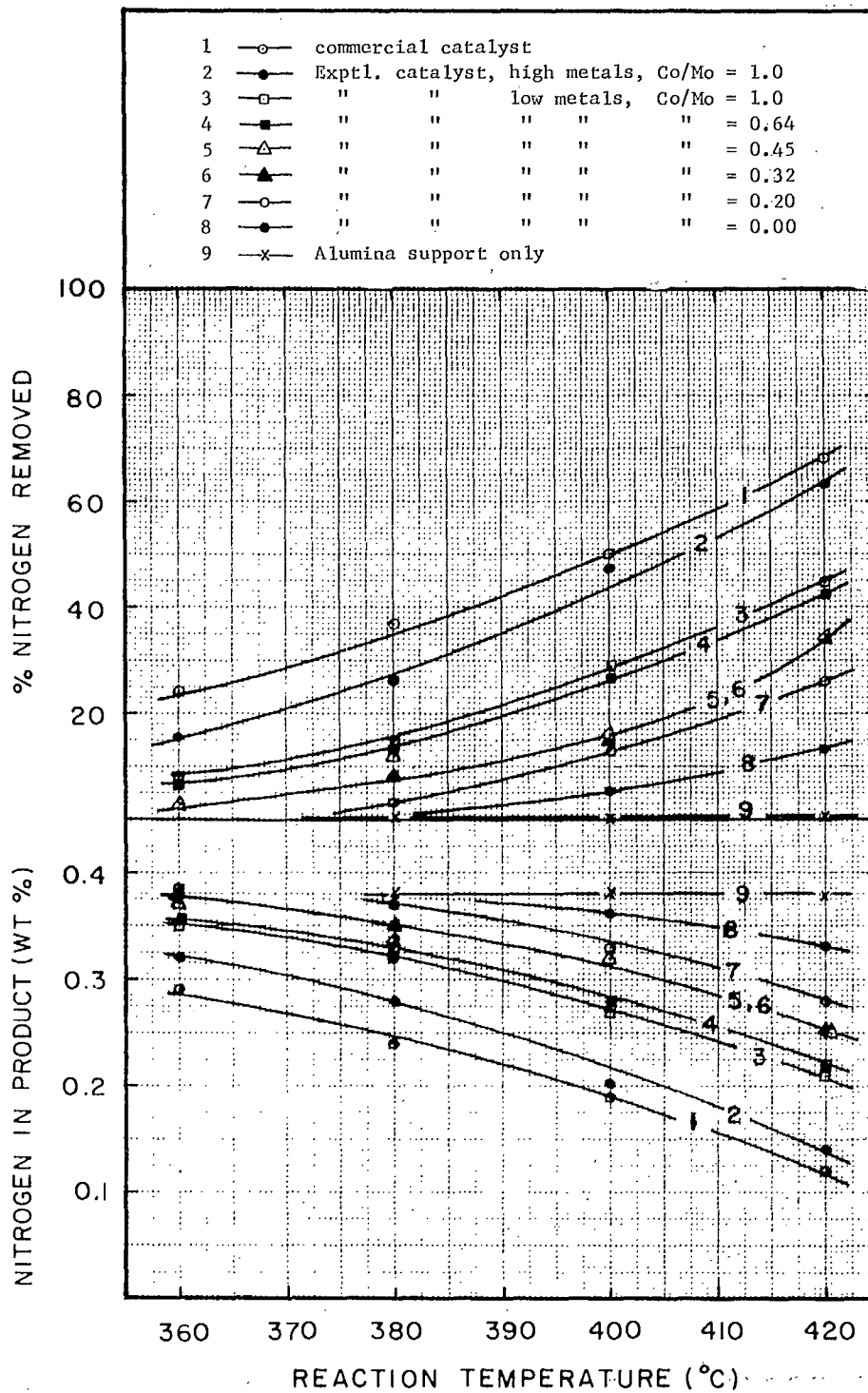| 1 | —o— | commercial catalyst |
2	—●—	Exptl. catalyst, high metals, Co/Mo = 1.0
3	—□—	" " low metals, Co/Mo = 1.0
4	—■—	" " " " " = 0.64
5	—△—	" " " " " = 0.45
6	—▲—	" " " " " = 0.32
7	—o—	" " " " " = 0.20
8	—●—	" " " " " = 0.00
9	—x—	Alumina support only

Figure 3 - The effect of reaction temperature on
nitrogen removal.
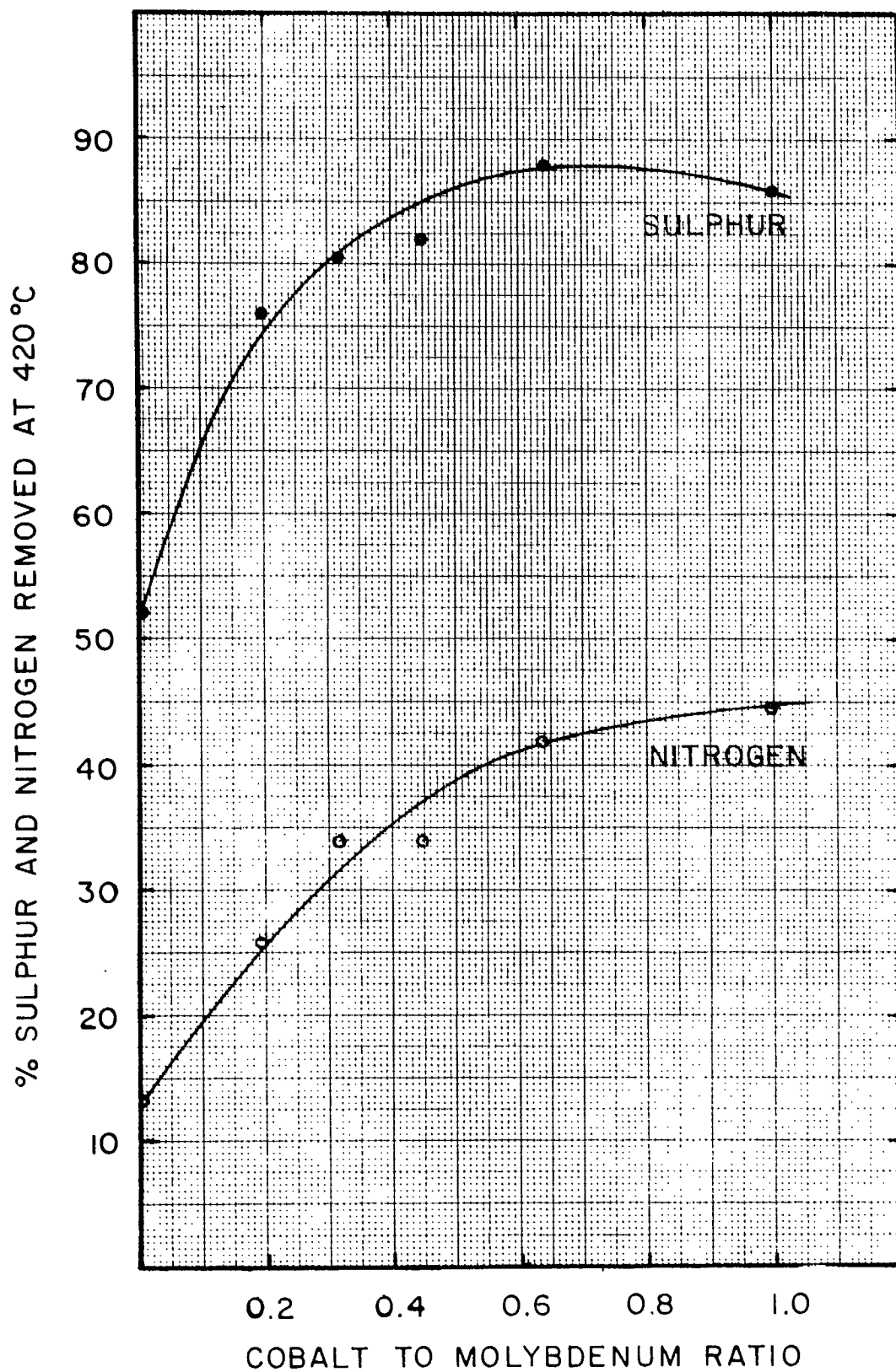(Metals concentrations shown on page 5)

Figure 4 - The effect of the cobalt to molybdenum ratio
in the low-metals series of catalysts on
sulphur and nitrogen removal.

TABLE 2

Summary of the Results of the Distillation Analyses and the Sulphur and Nitrogen Analyses on
the Feed Stock and on Products formed at 400°C over the commercial and high metals catalysts
and the alumina support.

(Metals concentrations shown on page 5)

Boiling Range of Fraction Equiv. Temp. at one atm. (°C)	(°F)	Amount (wt.% of feed)	Specific Gravity 60°/60°F	Sulphur (wt. %)	Nitrogen (wt. %)	Amount (wt.% of feed)	Specific Gravity 60°/60°F	Sulphur (wt. %)	Nitrogen (wt. %)
		GAS OIL FEED STOCK				COMMERCIAL CATALYST Co/Mo = 0.64			
IBP-200	IBP-392	0.3	-	-	-	1.3	-	-	-
200-250	392-482	0.5	-	-	-	2.0	0.861	0.00	0.06
250-275	482-527	1.1	-	-	-	2.4	0.888	0.18	0.07
275-332	527-630	3.2	0.932	2.91	0.13	11.3	0.916	0.14	0.08
332-361	630-682	13.6	0.954	3.11	0.17	16.0	0.930	0.23	0.12
361-391	682-736	14.5	0.970	3.26	0.23	13.4	0.939	0.34	0.16
391-421	736-790	19.9	0.986	3.47	0.32	19.6	0.948	0.44	0.22
+421	+790	46.9	1.027	3.97	0.51	30.7	0.964	0.56	0.31
Sulphur and Nitrogen Removed		0.0	-	-	-	3.3	-	-	-
Totals		100.0				100.0			
		HIGH METALS CATALYST Co/Mo = 1.0				ALUMINA SUPPORT			
IBP-200	IBP-392	1.5	-	-	-	0.4	-	-	-
200-250	392-482	2.1	0.862	0.07	0.06	0.4	-	-	-
250-275	482-527	3.5	0.892	0.16	0.08	1.0	-	2.17	0.13
275-332	527-630	10.6	0.916	0.11	0.09	4.7	0.932	2.75	0.17
332-361	630-682	16.2	0.930	0.20	0.12	14.2	0.953	2.88	0.19
361-391	682-736	13.4	0.939	0.31	0.17	14.8	0.970	3.10	0.21
391-421	736-790	18.0	0.948	0.37	0.21	17.9	0.985	3.19	0.32
+421	+790	31.4	0.963	0.51	0.30	46.4	1.024	3.79	0.51
Sulphur and Nitrogen Removed		3.3	-	-	-	0.2	-	-	-
Totals		100.0				100.0			

PRESSURE = 2000 psi   H$_2$ FLOW RATE = 5000 scf/bbl   LHSV = 2.0   REACTION TEMPERATURE = 400°C

TABLE 3

Summary of the Results of the Distillation Analyses and the Sulphur and Nitrogen Analyses on
Products formed at 400°C over the low metals catalysts with varying Cobalt to Molybdenum ratio
(Base concentration of molybdenum trioxide = 2.20 wt.%)

Boiling Range of Fraction Equiv. Temp. at one atm. (°C)	(°F)	Amount (wt.% of feed)	Specific Gravity 60°/60°F	Sulphur (wt. %)	Nitrogen (wt. %)	Amount (wt.% of feed)	Specific Gravity 60°/60°F	Sulphur (wt. %)	Nitrogen (wt. %)
		Co/Mo = 1.0				Co/Mo = 0.64			
IBP-200	IBP-392	1.0	-	-	-	1.0	-	-	-
200-250	392-482	1.8	0.859	0.03	0.12	1.5	0.858	0.01	0.12
250-275	482-527	2.1	0.887	0.08	0.13	2.3	0.889	0.10	0.13
275-332	527-630	9.4	0.917	0.25	0.13	9.2	0.916	0.23	0.13
332-361	630-682	16.0	0.934	0.41	0.16	16.3	0.933	0.39	0.17
361-391	682-736	14.8	0.945	0.59	0.21	14.8	0.945	0.59	0.22
391-421	736-790	18.1	0.956	0.70	0.27	17.1	0.956	0.71	0.28
+421	+790	33.9	0.974	0.89	0.38	34.8	0.974	0.86	0.38
Sulphur and Nitrogen Removed		2.9	-	-	-	3.0	-	-	-
Totals		100.0				100.0			
		Co/Mo = 0.45				Co/Mo = 0.32			
IBP-200	IBP-392	1.0	-	-	-	0.9	-	-	-
200-250	392-482	1.6	0.864	0.05	0.13	1.8	0.862	0.08	0.15
250-275	482-527	2.0	0.886	0.11	0.15	2.4	0.890	0.19	0.16
275-332	527-630	10.5	0.920	0.38	0.15	9.8	0.920	0.47	0.18
332-361	630-682	14.4	0.935	0.57	0.19	15.3	0.936	0.67	0.19
361-391	682-736	16.7	0.948	0.79	0.24	13.6	0.948	0.87	0.24
391-421	736-790	15.1	0.959	0.95	0.29	18.6	0.960	0.98	0.30
+421	+790	35.9	0.979	1.14	0.39	35.0	0.980	1.24	0.38
Sulphur and Nitrogen Removed		2.8	-	-	-	2.6	-	-	-
Totals		100.0				100.0			
		Co/Mo = 0.20				Co/Mo = 0.00			
IBP-200	IBP-392	0.9	-	-	-	1.0	-	-	-
200-250	392-482	1.7	0.864	0.17	0.18	1.0	-	-	-
250-275	482-527	1.8	0.890	0.31	0.18	1.7	0.896	1.36	0.23
275-332	527-630	9.3	0.921	0.66	0.19	7.3	0.929	1.76	0.21
332-361	630-682	14.6	0.938	0.93	0.20	14.0	0.946	1.85	0.21
361-391	682-736	14.8	0.951	1.11	0.25	14.1	0.959	2.06	0.25
391-421	736-790	18.3	0.963	1.25	0.30	19.6	0.973	2.18	0.31
+421	+790	36.3	0.986	1.54	0.41	39.9	0.999	2.41	0.46
Sulphur and Nitrogen Removed		2.3	-	-	-	1.4	-	-	-
Totals		100.0				100.0			

PRESSURE = 2000 psi   H$_2$ FLOW RATE = 5000 scf/bbl   LHSV = 2.0   REACTION TEMPERATURE = 400°C

A surprising feature of both the sulphur and nitrogen removal processes was that neither seemed particularly dependent on the extent of cracking that took place. From Tables 2 and 3 it can be seen that only 3-4% light-ends were produced in any of the experiments, yet the amount of hydro-refining which took place was quite considerable. For example, with the commercial catalyst at 400°C the overall sulphur removal was 87% and the overall nitrogen removal was 50%. This result is in complete disagreement with numerous claims in patent disclosures and in the review literature(13) which imply that extensive hydrogenolysis must accompany hydro-desulphurization and denitrogenation. This is not to be taken as an indication that no cracking takes place, because the sulphur and nitrogen present in the feed stock occur predominantly in cyclic hydrocarbon configurations(14), high molecular weight thiophenes etc., and ring opening must accompany the hydro-refining process. The point the authors wish to make is that there does not appear to be extensive hydrocracking before or after the desulphurization or denitrogenation reactions which results in a major lowering of the average boiling point beyond that which would be expected with the removal of the impurity atoms. The absence of excessive cracking (which is the main consumer of hydrogen in the process) is a strong point in favour of the bottom-feed arrangement for the operation of a catalytic hydro-treating reactor.

In all of the experiments, with all of the catalyst systems, the weight yield of oil product and the sulphur and nitrogen removal was always slightly greater than 100%. Where the extent of desulphurization and denitrogenation was high there was considerable lowering of the specific gravity with the result that the volume yield of oil product always exceeded 100%. At the 80 to 90% desulphurization levels the volume yield was generally in the region of 103-104%. No measurable catalyst deactivation occurred in the experimental series and no deposits, tar or coke, were detected on any of the catalysts at the conclusion of the tests.

Catalyst Preparation and Metals Disposition

Several aspects of the present study have important implications with respect to catalyst preparation. The high activity of the low-metals form of the catalyst for desulphurization, relative to denitrogenation, suggests strongly that the general nature of the catalytic surface prepared by the present procedure is extremely effective. Originally(1), it was believed that the high activity of the 3%-catalyst (compared to the 13% metal loading) was due entirely to the mode of operation of the reactor, i.e. as a liquid-phase system in which only the external surfaces of the catalyst would be expected to be effective. If this hypothesis was completely true, the activity of the low-metals catalyst for denitrogenation should also be comparable to that of the high-metals catalyst. However, the results of the nitrogen analyses summarized in Figure 3 indicate that there is a measurable short-fall in the activity of the low-metals catalyst for denitrogenation. The near-equal activity of the 3%- and 13%-catalysts for desulphurization would seem to be due, at least in part, to a higher surface activity relative to conventional catalyst preparation methods.

Solution impregnation techniques described in the patent literature usually begin with the alumina support in the calcined, or gamma, form. A calcined alumina has a well-defined pore structure, and the nature of the surface is more or less fixed. In the work described here the support was impregnated as the alumina monohydrate (boehmite) and the calcination process was accomplished after impregnation. The structuring of the alumina surface, and the cobalt and molybdenum oxides from their respective salts, all occurred simultaneously in the calcination process. From the point of view of desulphurization this appears to be a very effective way of creating the active sites and surfaces. There are obviously other factors relating to denitrogenation that we have yet to learn.

As mentioned previously, the gradual leveling off of the catalyst activity at the higher cobalt to molybdenum ratios generally disagrees with the observations of Todo(5) and DeBeer(6), who report considerable decreases

in activity beyond sharply defined optima.   Todo does not describe the
preparation of his catalysts and consequently an evaluation of his
observations is not possible. DeBeer et al used a solution impregnation
technique, placed the molybdenum on the catalyst first, and calcined the
catalyst between impregnation steps. This procedure differs considerably
from commercial practice where the two solutions are usually added to the
support together, or consecutively, with no intermediate calcination. As
pointed out by the DeBeer group of investigators themselves, the rapid decrease
in activity following the apparent optimum cobalt to molybdenum ratio is
possible due to poisoning by excess cobalt oxide.

Two other groups of researchers, Lipsh and Schuit(15) and Ashley
and Mitchell(16) examined extensively the magnetic
and spectroscopic properties of cobalt and molybdenum impregnated gamma-
alumina systems. It is interesting to view the results of the present
work (obtained with a high-boiling feed stock) in the light of their
observations with pure compounds and analytically clean surfaces. In the
case of a simple impregnation with cobalt they conclude that part of the
cobalt becomes incorporated by adsorption and dehydration into the
tetrahedral sites of the alumina and that the remainder exists in an
octahedral crystalline form in the pore structure of the alumina (due to
the occlusion and subsequent evaporation of the impregnating solution in
the pores). Where the cobalt and molybdenum are present together, Ashley
and Mitchell note a synergic effect in the adsorption process ..... the
percentage of tetrahedral cobalt decreasing with increasing molybdenum
concentration. If, for desulphurization, the most effective sites of the
promoted cobalt-molybdenum association are the tetrahedral form then, at
a fixed molybdenum concentration (as used here), one would expect the
activity of the combined catalyst system to rise to a plateau as the cobalt
concentration is increased, rather than a sharp maximum. There is also
the obvious inference from the effect of the overall metals concentration

on denitrogenation, that the effective form of the catalyst for nitrogen removal is the occluded crystalline form which would predominate at high metals loading.

POSTSCRIPT

The mention of specific brand names for equipment and materials is made for information purposes only and does not imply endorsement by the Mines Branch.

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