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CATALYSTS FOR HYDROCRACKING AND REFINING HEAVY OILS AND TARS

PART 2: THE EFFECTS OF MOLYBDENUM CONCENTRATION AND OF ZINC TO
MOLYBDENUM RATIO ON DESULPHURIZATION AND DENITROGENATION

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PART 2: THE EFFECTS OF MOLYBDENUM CONCENTRATION AND OF
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by

R.J. Williams*, M. Ternan** and B.I. Parsons***

ABSTRACT

This report is the second in a series dealing with transition metal-molybdenum catalysts supported on alumina. Experimental catalysts of various zinc to molybdenum atomic ratios as well as several pure molybdenum-alumina catalysts were prepared by a surface layering technique. Impregnation was achieved through addition of the salts of the active ingredients in a mix-muller. The activity of the molybdenum-alumina catalysts increased with the percentage Mo. Sharp increases with concentration occurred for desulphurization up to 9.0 wt %. At higher concentrations the changes were much less pronounced. Similar results were observed for denitrogenation but the increase in activity was less rapid. No optimum ratio for desulphurization or denitrogenation was observed for the zinc-molybdenum series (as had previously been reported in the literature). In fact, the addition of zinc resulted in activities virtually the same as that achieved by molybdenum-alumina alone and very much less than cobalt-molybdate supported on alumina. Catalyst life studies were undertaken on the 9.0 wt % Mo-Al₂O₃ and a cobalt-molybdate catalyst of Co/Mo = 0.48. No measurable deactivation was detected.

All of the catalysts were evaluated using a 650 - 975^oF (345-525^oC) gas-oil made by thermally hydrocracking Athabasca bitumen. The experiments were carried out at 2000 psi (13.9 MPa) pressure and at a liquid-space-velocity of 2.0 hr⁻¹ (0.56 Ks⁻¹). Results are discussed relative to a commercially prepared cobalt-molybdate catalyst of Co/Mo = 0.48.

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CATALYSEURS POUR L'HYDROCRAQUAGE ET LE RAFFINAGE DES HUILES LOURDES
ET DES GOUDRONS

PARTIE 2: LES EFFETS DE CONCENTRATION DU MOLYBDENE ET DU RAPPORT
ZINC/MOLYBDENE SUR LA DESULFURATION ET LA DENITRIFICATION

par

R.J. Williams*, M. Ternan** et B.I. Parsons***

RESUME

Ce rapport est le deuxième d'une série qui traite des catalyseurs de transmission métalliques de molybdène sur alumine. Des catalyseurs de recherches de différents rapports atomiques zinc-molybdène ainsi que plusieurs catalyseurs de molybdène-alumine purs ont été préparés au moyen d'une technique de disposition en couches de surface. L'imprégnation s'est produite à la suite de l'addition des sels des ingrédients actifs contenus dans le broyeur-malaxeur. Les catalyseurs de molybdène-alumine s'avérèrent plus efficaces selon les différents taux de molybdène. Pendant l'élimination du soufre, qui atteignit un taux de 9.0%, en poids, un accroissement marqué de l'efficacité, accompagné d'une concentration, fut constaté. Par contre, celle-ci demeura stable en présence de fortes concentrations. La dénitrification donna des résultats semblables, mais avec un accroissement plus lent de l'efficacité. Aucun rapport optimum n'a été constaté à la désulfuration ou à la dénitrification de la série cobalt-molybdène (comme il avait déjà été mentionné dans certaines publications). En effet, l'addition de zinc n'a apporté aucun changement et l'action des catalyseurs s'est avérée pareille à celle obtenue avec le molybdène-alumine pur et plus faible que celle obtenue avec le molybdène de cobalt sur alumine. Les études de longue haleine ont été effectuées avec le $\text{Mo-Al}_2\text{O}_3$ à 9.0% en poids et un catalyseur de molybdate de cobalt d'un rapport Co/Mo de 0.48. Aucune désactivation mesurable n'a été signalée.

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INTRODUCTION

Many of the catalysts presently employed on a commercial scale for the hydrocracking and desulphurizing of high-boiling crudes and tars are of the cobalt-molybdate variety supported on alumina¹. The active ingredients represent approximately 12-15% of the total oxide concentration corresponding to a metal-molybdenum atomic ratio of approximately 0.3. In view of the relatively high cost of the cobalt and molybdenum required, increasing attention is being given to alternative systems and/or lower metal concentration.

The application to which the current studies are directed is the catalytic hydrocracking and refining of bitumens derived from the Athabasca and Cold Lake oil sands in Alberta and the Lloydminster oil fields of Saskatchewan². By virtue of the high concentrations of coke precursors and metals in these bitumens, catalyst life is relatively short (a few hundred hours) and processing is consequently expensive. In addition to economic concerns, the current world oil situation and the realization that Canadian conventional supplies are dwindling have reinforced the need for development of processing techniques for heavy oils and tars.

A previous investigation in our laboratories³ has shown that the overall metal oxide concentration in cobalt-molybdate catalysts may be reduced from 12% to approximately 3% by layering the active ingredients on the surface of the alumina support. It is to be noted that these results apply primarily to liquid phase systems. Part 1 of this series³ also found that the optimum cobalt to molybdenum ratio for effective desulphurization and denitrogenation appeared at or near 0.6 (with 2.9 wt % metal oxides). Above a ratio of 0.6 the activity was approximately constant. These results are in disagreement with the findings of de Beer et al⁴ who reported a sharp decrease in activity at Co/Mo atomic ratios in excess of 0.6.

In an effort to gain a better understanding of the role of promoter ions in combined metal-molybdenum systems, the present authors felt it necessary to examine a series of catalysts with molybdenum only as the active ingredient. Of particular interest was the need to determine the minimum concentration of molybdenum required for desired levels of sulphur and nitrogen removal. At each stage in the investigation the results with the experimental catalysts were compared to those with a commercially prepared cobalt-molybdate mixture of Co/Mo = 0.48.

The virtues of the Zn-Mo- γ -Al₂O₃ system for desulphurization and denitrogenation have not been as thoroughly investigated as other metal-molybdenum-alumina catalysts. The de Beer workers, using thiophene as a model sulphur compound, found that the zinc promoted molybdenum-alumina catalyst reached optimum activity at a Zn/Mo atomic ratio of 0.92. They reported a level of activity greater than that observed with Ni-Mo-Al₂O₃. The fact that nickel and cobalt are used much more extensively than zinc for hydrorefining in commercial operations casts suspicion on their results. Since different results for the cobalt system were obtained by the de Beer group⁴ and by the Energy Research Laboratories³, it was considered essential to re-examine the whole question of zinc promotion.

Therefore, the purposes of the present investigation were:

(a) to examine the effect of molybdenum concentration on sulphur and nitrogen removal as it applies to commercial-type hydro-treating systems, i.e. systems utilizing bituminous or heavy gas-oil feedstocks, and

(b) to determine the optimum zinc to molybdenum atomic ratio (if any) for effective desulphurization and denitrogenation.

It is to be noted that considerable emphasis has been placed here on the description of the analytical and evaluation techniques used for the tested catalysts. The feeling is that any discussion of experimental results may only be properly interpreted in conjunction with the experimental methods.

EXPERIMENTAL

Catalyst Testing Apparatus and Procedures

All of the experiments were undertaken on a laboratory scale using a bottom-feed, continuous-flow reaction system, i.e. the oil and hydrogen were directed upwards through the reactor over a fixed bed of catalyst. This arrangement was previously found to be more effective (from the standpoint of the desulphurization process) than the top-feed system^{2b, 5}. The reaction vessel was manufactured at the Energy Research Laboratories machine shops from 316 stainless steel and had internal dimensions of 1 inch by 12 inches long (25.4 mm x 0.305 m). Three inches (76.2 mm) of 6 mm porcelain berl saddles were placed in the bottom of the reactor to act as a preheater section. This was followed by 8 inches (0.203 m) of catalyst pellets. The final inch at the top of the reaction vessel was filled with berl saddles. Temperatures were monitored by a movable thermocouple located in a central well. A more complete discussion of the components of the reaction system has already been published⁶. As in Part 1 of this series³, the temperature distribution was found to be essentially the same in all experiments and no effort was made to estimate the average temperature across the reaction zone. The temperatures appearing in the tables and graphs are the maximum temperatures in the reaction zone.

Each catalyst was stabilized and presulphided by exposing it to the oil-hydrogen mixture for 6 - 7 hours (21.6 - 25.2 Ks) prior to the first experiment. This period consisted of 2 - 3 hours (7.2 - 10.8 Ks) as the reaction temperature was raised to 400°C, 3 hours (10.8 Ks) at 400°C and 1 hour (3.6 Ks) as the reaction temperature was raised from 400 to 420°C (the usual temperature selected for the first run). Subsequent 2-hour runs (7.2 Ks) were made at 420, 400, 380, 435, and 450, followed by a repeat experiment at 420°C. The constancy of activity was checked by comparing the initial experimental results obtained at 420°C with those from the final experiments at 420°C. All of the tests were made at 2000 psig (13.9 MPa), at a liquid-space-velocity of 2.0 hr⁻¹ (0.56 Ks⁻¹), and with a hydrogen flow rate of 5000 standard cubic feet per barrel (scf/bbl) (0.0718 l/s at STP). Further details of start-up and sample period procedures are given elsewhere⁶.

On some occasions the catalyst was presulphided with H₂S prior to the above gas-oil treatment. Briefly, the sulphiding procedure consisted of the following steps:

1. The reactor (at atmospheric pressure) was brought to 400°C slowly over a 3-hour period with 10-15% H₂S in hydrogen flowing through the catalyst bed. This ratio was maintained by visual inspection of two in-line gas bubblers. No oil was introduced to the system in the H₂S presulphiding experiments.
2. The temperature was held at 400°C for 1 hour with the H₂S-H₂ mixture passing continuously.
3. The reactor was allowed to cool to 250 - 300°C then was repressurized quickly with pure hydrogen at 2000 psi.

Feedstock

The feedstock used throughout all experiments was the 650 - 975°F (345 - 525°C) heavy gas-oil fraction derived by thermal hydrocracking Athabasca bitumen in an Energy Research Laboratories pilot plant⁹. The bitumen was supplied by Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta. The general properties of the feedstock are shown in Table 1 and the results of the distillation, sulphur and nitrogen analyses are shown in Table 2. As was the case in Part 1 of this series³, the digression from unrefined bitumen for the experimental work was to facilitate the nitrogen analyses which had previously been difficult² due to unreacted residuum and clay in the product samples.

Catalyst Preparation

Nine experimental catalysts were prepared for testing in this investigation. The results were compared to a commercial cobalt molybdate catalyst (Harshaw 0603T) and a pure alumina blank. The support material used in the preparation of the experimental catalysts was a mixture of two physical forms of monohydrate (boehmite). These were supplied to E.R.L. by the Continental Oil Company of Teterboro, New Jersey, under the trade names "Catapal N" and "Catapal SB" respectively. The SB alumina monohydrate hydrolyzed relatively quickly (in a matter of minutes) and the Catapal N alumina was highly resistant to hydrolysis. Table 3 shows the physical properties of the calcined support. The procedure followed in the preparation of the catalyst was as follows:

TABLE 1

GENERAL PROPERTIES OF THE GAS-OIL FEEDSTOCK

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 by wt)	< 1
Viscosity, Kinematic	(cst at 100°F)	108.8

TABLE 2

RESULTS OF DISTILLATION ANALYSES AND SULPHUR AND NITROGEN
DETERMINATIONS FOR THE GAS-OIL FEEDSTOCK

Boiling Range of Fraction equiv temp at 1.0 atm		Amount of Fraction (wt % of feed)	Specific Gravity (60/60°F)	Sulphur (wt %)	Nitrogen (wt %)
(°C)	(°F)				
IBP-200	IBP-392	0.2	-	-	-
200-250	392-482	0.5	-	-	-
250-275	482-527	1.1	-	-	-
275-332	527-630	3.2	0.932	2.91	0.13
332-361	630-682	13.6	0.954	3.11	0.17
361-391	682-736	14.5	0.970	3.26	0.23
391-421	736-790	19.9	0.986	3.47	0.32
+ 421	+ 790	46.9	1.027	3.97	0.51

1. 4000 grams of "N" alumina and 1000 grams of "SB" alumina were placed in a Simpson mix-muller (model LF). 600 ml of a solution of distilled H₂O and 14 ml 70% HNO₃ were added slowly; the mixture was muller for 3 minutes and left to stand for 7 minutes.
2. Appropriate amounts of concentrated solutions of reagent grade zinc nitrate Zn(NO₃)₂ · 6H₂O, and ammonium paramolybdate (NH₄)₆ Mo₇O₂₄ · 4H₂O were then added slowly to the support. Each ingredient was muller separately for 3 minutes with Zn(NO₃)₂ · 6H₂O added first. Previous experience^{2e} has shown that the order of adding solutions of the metal salts does not affect the resultant activity of the catalysts. In some cases the volume of distilled water used to prepare the salt solutions was adjusted to allow for water of hydration associated with the salts. This procedure was adopted to maintain an essentially constant total volume of water in the system. After mulling was completed the mixture was damp to the touch.
3. The mixture was crushed to break up large lumps, spread into a 1/2" layer in a stainless steel tray, and dried in air for 4-5 hours at 110°C. It was then calcined at 500°C for 4 hours.
4. The calcined mixture was crushed to pass a 20 mesh screen and finally formed into 1/8" x 1/8" pellets at 40,000 psi using 2 wt % stearic acid as a binder-lubricant. The pellets were recalcined at 500°C for 4-5 hours to remove the stearic acid.

The specifications of the experimental catalysts are shown in Table 4. The commercial cobalt molybdate catalyst used for comparative purposes contained 3.0 wt % CoO and 12.0 wt % MoO₃ resulting in a Co/Mo atomic ratio of 0.48. It was obtained from the Harshaw Chemical Company, Cleveland, Ohio as 1/8" x 1/8" pellets (catalyst No. 0603T).

TABLE 3

PHYSICAL PROPERTIES OF THE CALCINED ALUMINA SUPPORT

		<u>Catapal SB</u>	<u>Catapal N</u>
Crystal structure (uncalcined)		$\alpha - \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	$\alpha - \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Crystal structure (calcined)		$\gamma - \text{Al}_2\text{O}_3$	$\gamma - \text{Al}_2\text{O}_3$
Particle size	(microns)	30 - 100	100 - 1000
Surface area (B.E.T.)	(m^2/g)	250	180
Pore volume	(ml/g)	0.5	0.4

TABLE 4

SPECIFICATIONS OF THE TESTED CATALYSTS

Catalyst No.	ZnO (wt %)	MoO ₃ (wt %)	Zn/Mo
1	7.46	12.0	1.1
2	6.11	12.0	0.90
3	4.75	12.0	0.70
4	2.04	9.0	0.40
5	1.02	9.0	0.20
6	0.0	12.0	0.0
7	0.0	9.0	0.0
8	0.0	6.0	0.0
9	0.0	3.0	0.0

TABLE 5

DISTILLATION TEMPERATURE CHARACTERISTICS

Fraction No.	Pressure (mm Hg)	Boiling Range of Fraction (°C)	Boiling Range of Fraction (°F)	Equiv Temp (°C)	at 1.0 atm (°F)
1	760	IBP - 100	IBP - 212	IBP - 100	IBP - 212
2	760	100 - 200	212 - 392	100 - 200	212 - 392
3	760	200 - 250	392 - 482	200 - 250	392 - 482
4	760	250 - 275	482 - 527	250 - 275	482 - 527
5	40	IBP - 225	IBP - 437	275 - 332	527 - 630
6	40	225 - 250	437 - 482	332 - 361	630 - 682
7	40	IBP - 275	482 - 527	361 - 391	682 - 736
8	40	275 - 300	527 - 572	391 - 421	736 - 790
9	40	+ 300	+ 572	+ 421	+ 790

Analytical and Evaluation Methods

A modified version of the U.S. Bureau of Mines Hempel Distillation apparatus¹⁰ was used to characterize the distribution of light ends in the oil products. The object was to determine the extent to which hydrocracking took place during the desulphurization and denitrogenation reactions. A charge of 100 ml of oil was placed in a 500 ml petroleum distilling flask (Pyrex F4110) and the sample was distilled rapidly using a high temperature Meker burner. Each distillation was undertaken in 2 stages:

1. fractions collected at 760 mm Hg pressure
2. fractions collected at 40 mm Hg pressure

Table 5 shows the temperature range of the fractions collected and the equivalent temperature at a pressure of 1.0 atm. Each distillate fraction was characterized in terms of amount (wt % of feed), sulphur content, nitrogen content, and specific gravity.

The sulphur content of each fraction was determined by an X-ray fluorescence technique using an analyzer manufactured by Panametrics, a division of the Esterline Corporation of Waltham, Massachusetts^{11, 12}. The apparatus used iron 55 as the radioactive source. Irradiation of the sample caused bound electrons to be stripped from the sulphur atoms present. Subsequent refilling of these electron shells produced the fluorescence (characteristic X-rays) which were then measured by a detector and displayed as pulses per unit time. The apparatus was calibrated with oil samples having known sulphur concentrations.

The nitrogen concentration was determined using a pyrolysis-micro-coulometric apparatus developed by Dohrmann Instruments Co., a division of the Envirotech Corporation of Mountain View, California^{13, 14}. It was necessary in this investigation to dilute the samples by a factor of 20 to accommodate the working range of the instrument. The apparatus was calibrated by standard solutions of oil, 10 and 100 ng N/ μ l pyridine in toluene. After injection into the analyzer, the sample entered a hydrogen stream and was pyrolyzed and hydrogenated over a granular nickel catalyst at 700°C. The bound nitrogen present was converted to ammonia and the gas stream scrubbed to remove acid components. The remaining gases flowed to a pH balanced titration cell in which the ammonia was allowed to react with hydrogen ions of the cell electrolyte. The current required to coulometrically replace the hydrogen consumed was a measure of the nitrogen present in the sample.

EXPERIMENTAL RESULTS AND DISCUSSION

Pure Molybdenum - Alumina Catalysts

Much of the previous work in our laboratory^{2, 3, 5} has dealt with the investigation of cobalt molybdate catalysts for hydrocracking and desulphurizing bitumens and heavy gas-oils. To determine the catalytic contribution of the molybdenum alone in combined metal-molybdenum-alumina systems (without the complications of cobalt or other promoters) a series of supported catalysts containing only molybdenum were prepared and evaluated.

The results of this area of the investigation are summarized in Figures 1 through 4 and Tables 6 and 7. Figures 1, 2 and 3 illustrate the relationships of specific gravity, sulphur removal and nitrogen removal as functions of the concentration of molybdenum in the catalyst. Comparisons of the extent and efficiency¹ of desulphurization and denitrogenation are made in Figure 4. Distillate analyses for the reference commercial catalyst and typical prepared catalysts are shown in Tables 6 and 7 respectively.

The extent of sulphur removal from the gas-oil was strongly dependent upon the concentration of molybdenum in the catalyst. The results suggest that a maximum desulphurization concentration was reached at approximately 9% as the 12.0 wt % Mo catalyst showed no significant improvement in its capacity to remove sulphur (Figure 2). Experiments were not done at concentration levels greater than 12.0 wt % because of the economic penalties associated with high metal loadings. Figure 2 illustrates the nature of molybdenum as a promoter ion. The ability to remove sulphur increases sharply from 0-3.0 wt % (in the temperature range 380 - 450°C). From 3.0 to 9.0 wt % molybdenum the extent of desulphurization is greater but the slope of the curve is considerably less and, as mentioned previously, from 9.0 to 12.0 wt % the difference is minimal. It seems apparent that molybdenum has its most significant incremental effect in the 0 - 3.0 wt % range and reaches a maximum at or near 9.0 wt %.

1. Efficiency used here is defined as sulphur or nitrogen removal per unit weight of molybdenum.

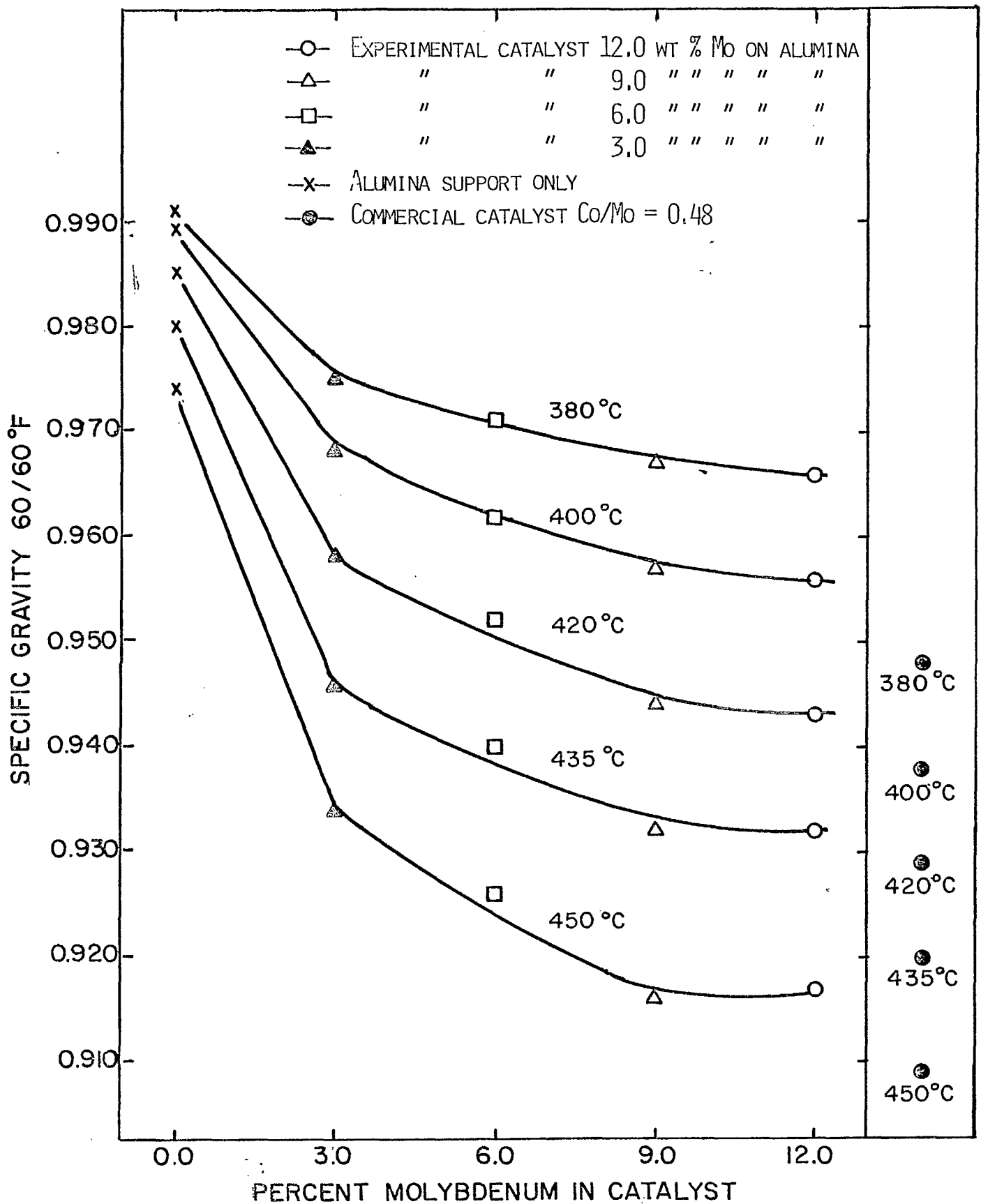


Figure 1. Effect of Molybdenum Concentration on the Specific Gravity of the Products.

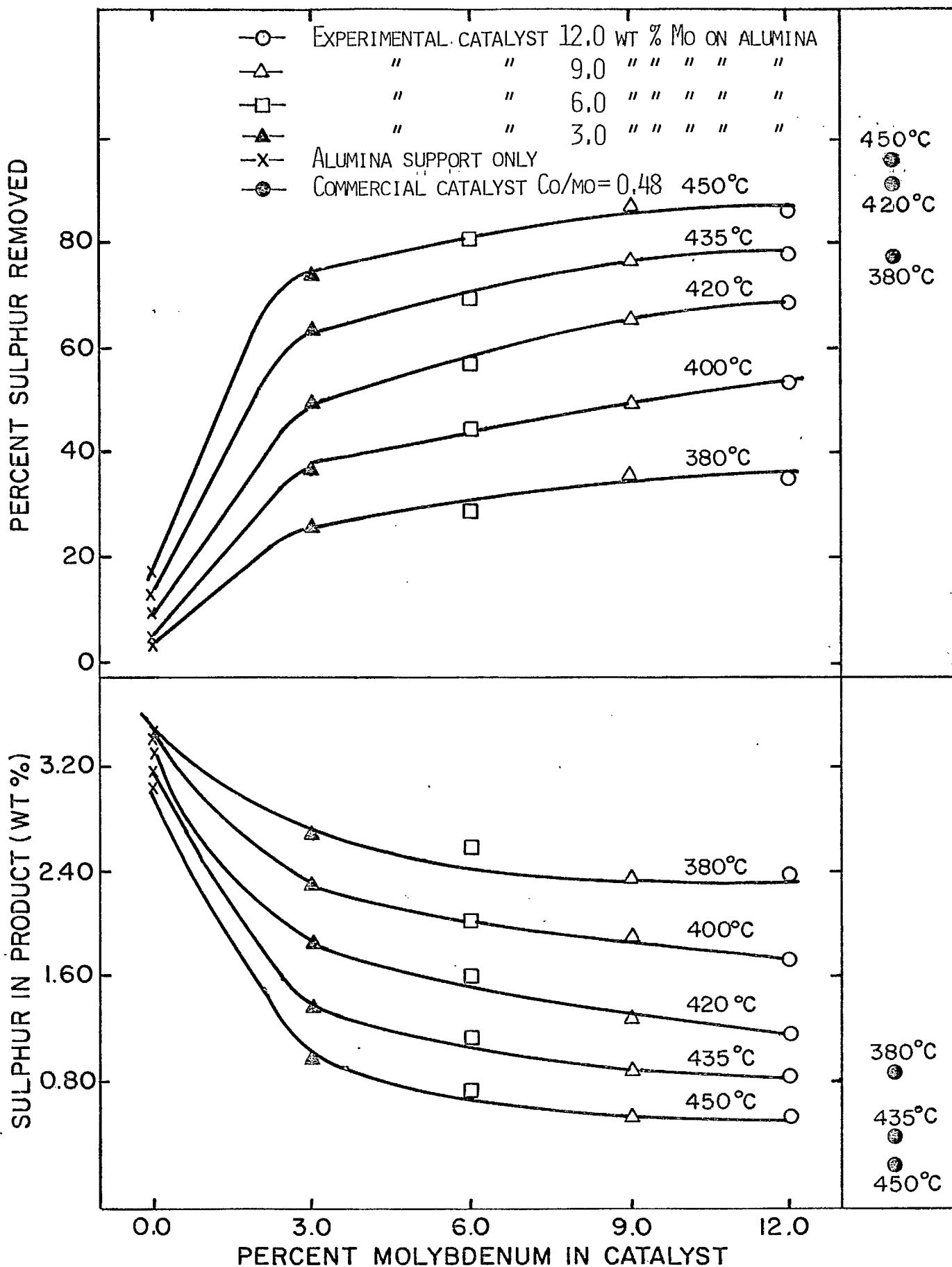


Figure 2. Effect of Molybdenum Concentration on Sulphur Removal.

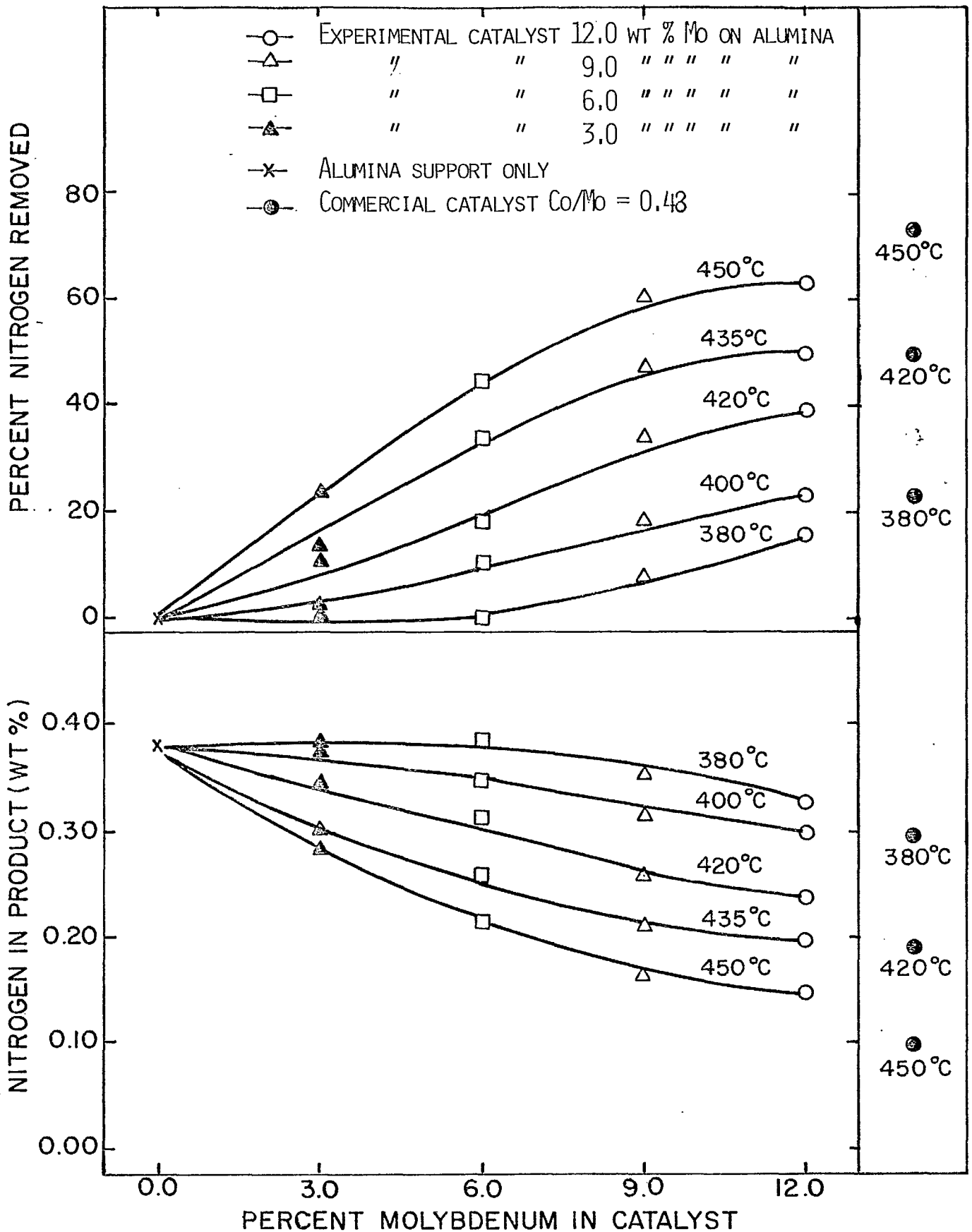


Figure 3. Effect of Molybdenum Concentration on Nitrogen Removal.

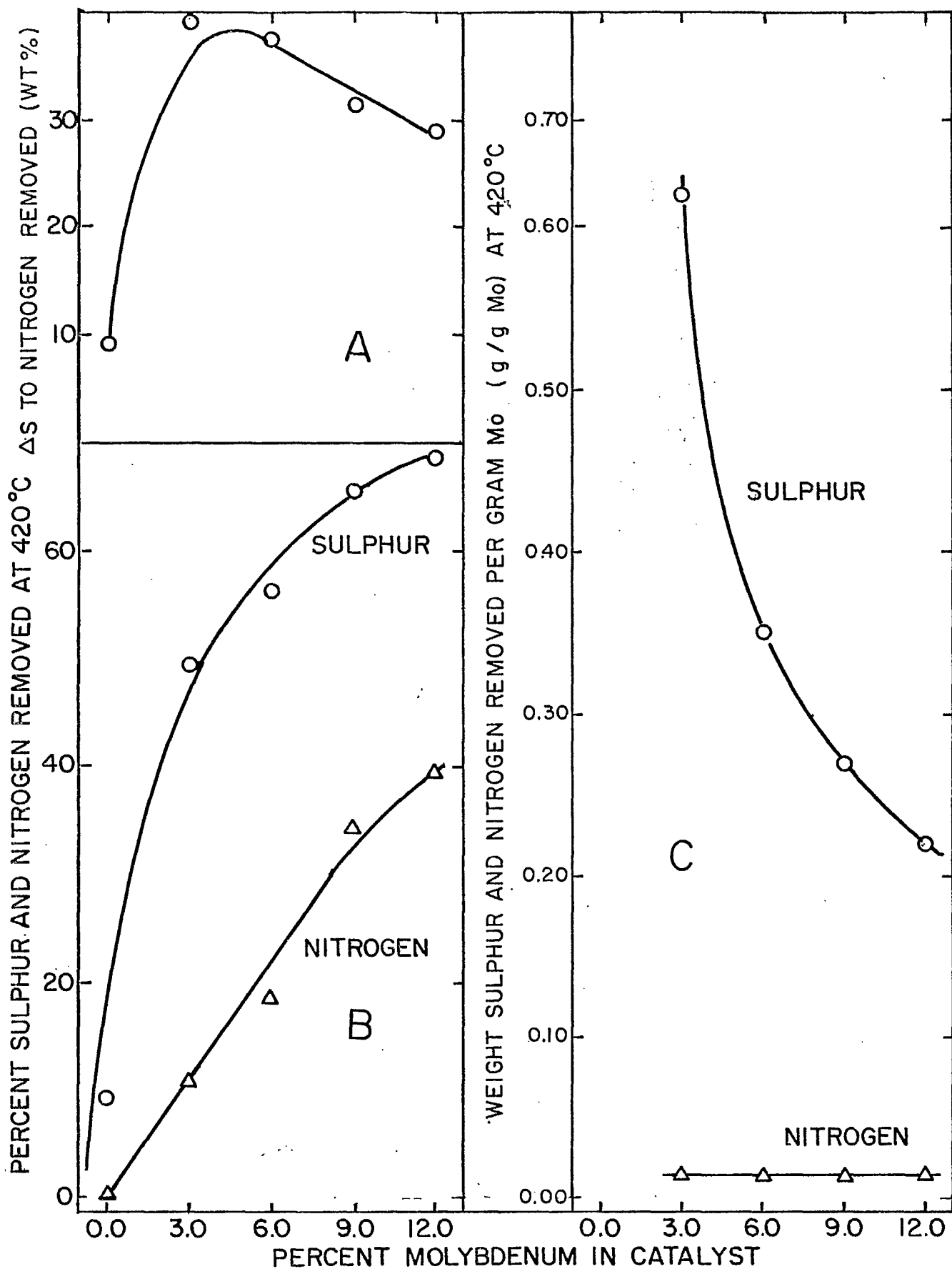


Figure 4. Comparison of Sulphur and Nitrogen Removal at 420°C.

TABLE 6

RESULTS OF DISTILLATION ANALYSES AND SULPHUR AND NITROGEN
DETERMINATIONS FOR THE COMMERCIAL CATALYST AT THE TEMPERATURES INDICATED

Boiling Range of Fraction (equiv temp. at 1.0 atm)		Amount (wt % of feed)	Sp Gr 60/60°F	Sulphur (wt %)	Nitrogen (wt %)
(°C)	(°F)	Commercial Catalyst Co/Mo = 0.48 (420°C)			
IBP-200	IBP-392	2.1	-	-	-
200-250	392-482	2.1	0.86*	0.04	0.04
250-275	482-527	2.6	0.89*	0.12	0.05
275-332	527-630	10.8	0.912	0.19	0.06
332-361	630-682	18.0	0.927	0.17	0.10
361-391	682-736	12.0	0.934	0.24	0.13
391-421	736-790	22.3	0.941	0.30	0.18
+ 421	+ 790	26.6	0.96*	0.41	0.27
Sulphur + Nitrogen removed		3.5	-	-	-
Total		100.0			
Commercial Catalyst Co/Mo = 0.48 (435°C)					
IBP-200	IBP-392	4.3	-	0.03	-
200-250	392-482	3.3	0.86*	0.06	0.04
250-275	482-527	4.7	0.89*	0.07	0.05
275-332	527-630	14.0	0.914	0.13	0.06
332-361	630-682	16.6	0.927	0.13	0.09
361-391	682-736	13.4	0.934	0.17	0.13
391-421	736-790	16.6	0.940	0.22	0.16
+ 421	+ 790	23.5	0.96*	0.28	0.23
Sulphur + Nitrogen removed		3.6	-	-	-
Total		100.0			
Commercial Catalyst Co/Mo = 0.48 (450°C)					
IBP-200	IBP-392	7.9	-	0.02	-
200-250	392-482	6.0	0.86*	0.03	0.02
250-275	482-527	5.6	0.89*	0.04	0.02
275-332	527-630	16.4	0.914	0.06	0.04
332-361	630-682	17.5	0.927	0.10	0.07
361-391	682-736	8.6	0.93*	0.14	0.11
391-421	736-790	17.1	0.941	0.17	0.14
+ 421	+ 790	17.2	0.96*	0.25	0.20
Sulphur + Nitrogen removed		3.7	-	-	-
Total		100.0			

Pressure = 2000 psig

H₂ Flow Rate = 5000 scf/bbl

* Qualitative values only

TABLE 7

RESULTS OF DISTILLATION ANALYSES AND SULPHUR AND NITROGEN DETERMINATIONS FOR THE 9.0 AND 12.0 WT % Mo EXPERIMENTAL CATALYSTS AT THE TEMPERATURES INDICATED

Boiling Range of Fraction (equiv temp. at 1.0 atm)		Amount (wt % of feed)	Sp Gr. 60/60°F	Sulphur (wt %)	Nitrogen (wt %)
(°C)	(°F)	Experimental Catalyst 9.0 wt % Mo, Zn/Mo = 0.0 (435°)			
IBP-200	IBP-392	3.9	-	0.07	-
200-250	392-482	3.7	0.86*	0.14	0.10
250-275	482-527	2.9	0.89*	0.38	0.11
275-332	527-630	11.7	0.920	0.62	0.11
332-361	630-682	17.8	0.935	0.75	0.14
361-391	682-736	7.9	0.952	0.85	0.18
391-421	736-790	24.1	0.952	0.91	0.24
+ 421	+ 790	25.1	0.96*	0.98	0.32
Sulphur + Nitrogen removed		2.9			
Total:		100.0			
Experimental Catalyst 9.0 wt % Mo, Zn/Mo = 0.0 (450°C)					
IBP-200	IBP-392	7.3	-	0.05	-
200-250	392-482	5.5	0.86*	0.12	0.07
250-275	482-527	5.4	0.89*	0.37	0.07
275-332	527-630	15.4	0.921	0.48	0.10
332-361	630-682	15.4	0.936	0.52	0.13
361-391	682-736	11.7	0.944	0.60	0.17
391-421	736-790	16.8	0.950	0.61	0.21
+ 421	+ 790	19.2	0.96*	0.69	0.27
Sulphur + Nitrogen removed		3.3			
Total:		100.0			
Experimental Catalyst 12.0 wt % Mo, Zn/Mo = 0.0 (450°C)					
IBP-200	IBP-392	7.4	-	0.05	-
200-250	392-482	5.9	0.86*	0.11	0.08
250-275	482-527	5.8	0.89*	0.20	0.07
275-332	527-630	14.0	0.921	0.46	0.08
332-361	630-682	17.0	0.935	0.50	0.13
361-391	682-736	12.1	0.943	0.58	0.17
391-421	736-790	15.4	0.949	0.61	0.20
+ 421	+ 790	19.1	0.96*	0.70	0.29
Sulphur + Nitrogen removed		3.3			
Total:		100.0			

Pressure = 2000 psig

H₂ Flow Rate = 5000 scf/bbl

* Qualitative values only

The process of denitrogenation showed similar results in some instances and somewhat different results in others. As in desulphurization, the extent of nitrogen removal appeared to be a function of the amount of molybdenum present, increasing as the concentration was raised (Figure 3). However, at lower temperatures, (380-420°C) the differences observed between the catalysts were smaller for nitrogen removal than for sulphur removal. Also, denitrogenation appeared to reach a maximum with respect to the percentage molybdenum added only under severe temperature conditions (435 and 450°C). At high temperatures the maximum occurred at or near 9.0 wt % as it did for sulphur (Figure 3). Furthermore, the effect of molybdenum on denitrogenation in the 0-9.0 wt % range was relatively constant in contrast to the sharp changes observed at low concentrations for desulphurization.

Only a small amount of hydrocracking was observed to occur in any of the experiments (increasing, of course, at the higher reaction temperatures) while the degree of hydrorefining remained quite high. For example, the product obtained after reaction in the presence of the commercial cobalt molybdate catalyst at temperatures of 420, 435 and 450°C contained only, respectively, 6.8, 12.3 and 19.5 wt % of material distilling at 275°C or lower. As shown in Table 7, at 450°C, the 9.0 and 12.0 wt % Mo catalysts exhibited almost equivalent concentrations of low-boiling material. Also at 450°C, sulphur removal was of the order of 86-87% with 61-63% nitrogen removed. These results are similar to those observed in Part 1 of this series³ for catalysts containing up to 3.3 wt % combined cobalt and molybdenum oxides.

Weight yields of product oil plus sulphur and nitrogen removed always exceeded 100% due to added H₂. At the higher reaction temperatures (435 and 450°C), the specific gravity was lowered considerably, hence the volume yields were well in excess of 100%. For example, at 435 and 450°C, a typical volume yield was in the 102-104% range.

In general, the level of impurity atom removal was always less for nitrogen than for sulphur. For example, at 420°C, the difference between the extent of desulphurization and denitrogenation varied from a minimum of 10% to a maximum of 40% for all the catalysts tested, as shown by Figures 4A and 4B.

One point worth noting is as follows: When operating at 420°C, as the metals concentration in the catalyst was increased, the weight of sulphur removed per gram of molybdenum present decreased while the weight of nitrogen removed remained constant. This does not mean that denitrogenation is as efficient as it might be, only that it is considerably more efficient than

desulphurization (for the Mo-Al₂O₃ system). The authors are aware that the relative values per gram Mo are quite different for each process. The point is that at 420°C at least one reaction maintains its rate of removal while the other does not. By examining the data in Figures 2 and 3 it is apparent that the phenomena shown in Figure 4C is temperature-dependent. This can be seen by comparing the 380°C and 450°C nitrogen removal results in Figure 3. At 450°C, molybdenum concentration had an effect from 0 to 9 wt % but little effect from 9 to 12 wt %. At 380°C, molybdenum concentration had no effect from 0 to 6 wt % but did have an effect from 6 to 12 wt %.

Catalyst Life Studies

The following paragraphs describe the results of the life studies undertaken on the commercial cobalt molybdate catalyst and the experimental catalyst containing 9.0 wt % molybdenum. Figures 5 through 7 show the relationship to "time on stream" (ie. the length of time for which the catalyst was exposed to the oil-hydrogen mixture at a temperature of 450°C) of specific gravity, sulphur removal and nitrogen removal respectively.

The weight percentage of sulphur removed from the gas-oil remained essentially constant over the 100 hour (360 Ks) testing period. (There was a small drift of approximately 2 wt % from the average value at some points.) Similar results were observed for the nitrogen removal and specific gravity data.

The time studies bring to light two points which, although not dramatic, are significant. First, the life runs were made at the highest temperature of any of the experiments performed in this investigation. Under these severe conditions no appreciable deactivation was noted for either catalyst over the time considered. This indicates, albeit superficially, some measure of stability over the long term. It is to be emphasized that the 100 hour (360 Ks) "time on stream" period refers only to the time at temperature. It does not include approximately 30 hours of catalyst exposure to oil and hydrogen during which the system was coming to or falling away from the sampling temperature of 450°C. Because of stiff limitations the life run was not undertaken as one continuous experiment. It was set up as the sum of several sections totalling 100 hours at temperature. Finally, at the conclusion of the tests, each catalyst was examined visually for gross deposits of coke and other impurities on the pellet surface. No such deposits were observed. It must be emphasized that the used catalysts did contain coke. However, there were no visual indications that the coke content of the 100 hour catalysts was different from that obtained during shorter experiments.

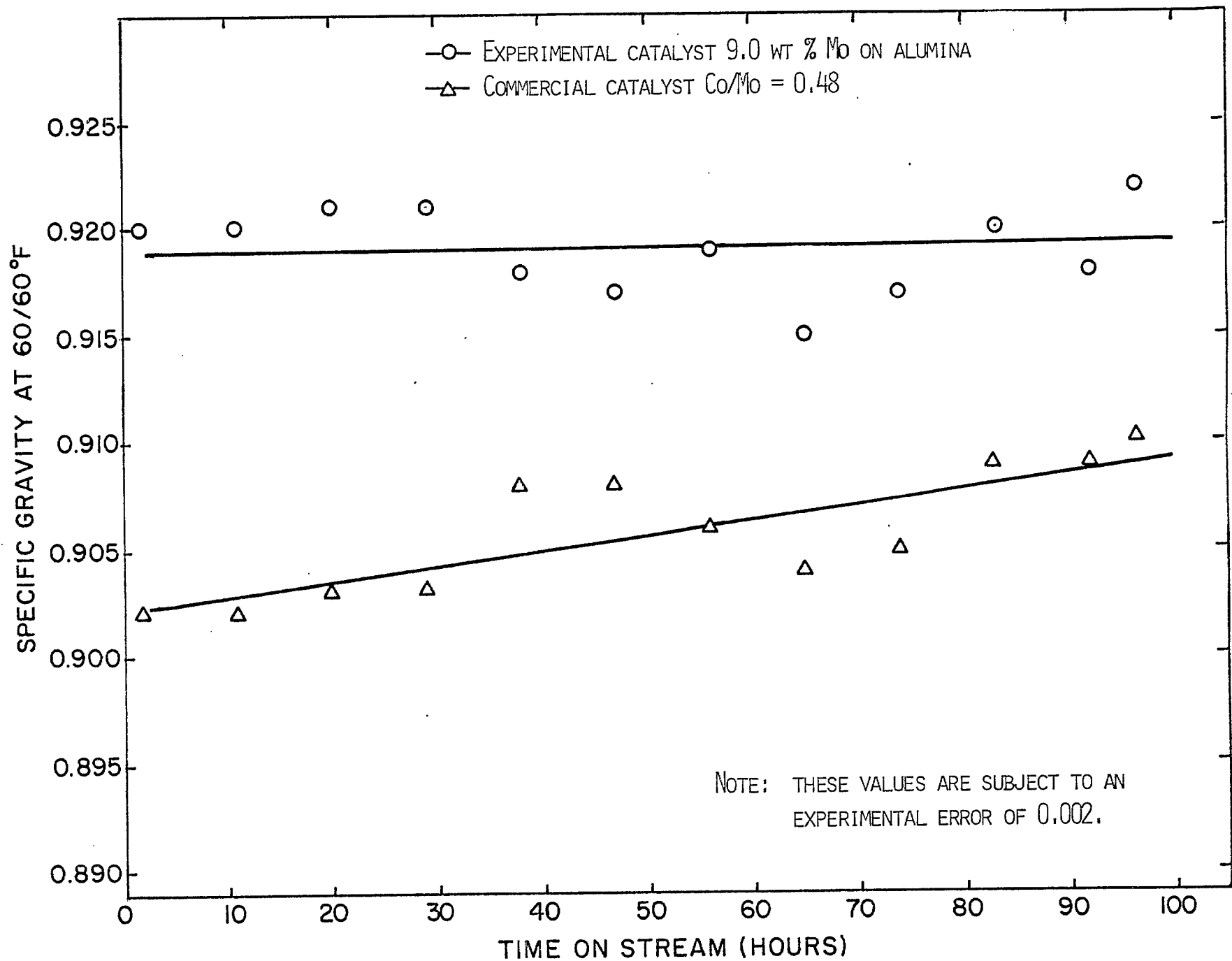


Figure 5. Effect of Time on Stream on the Specific Gravity of the Products.

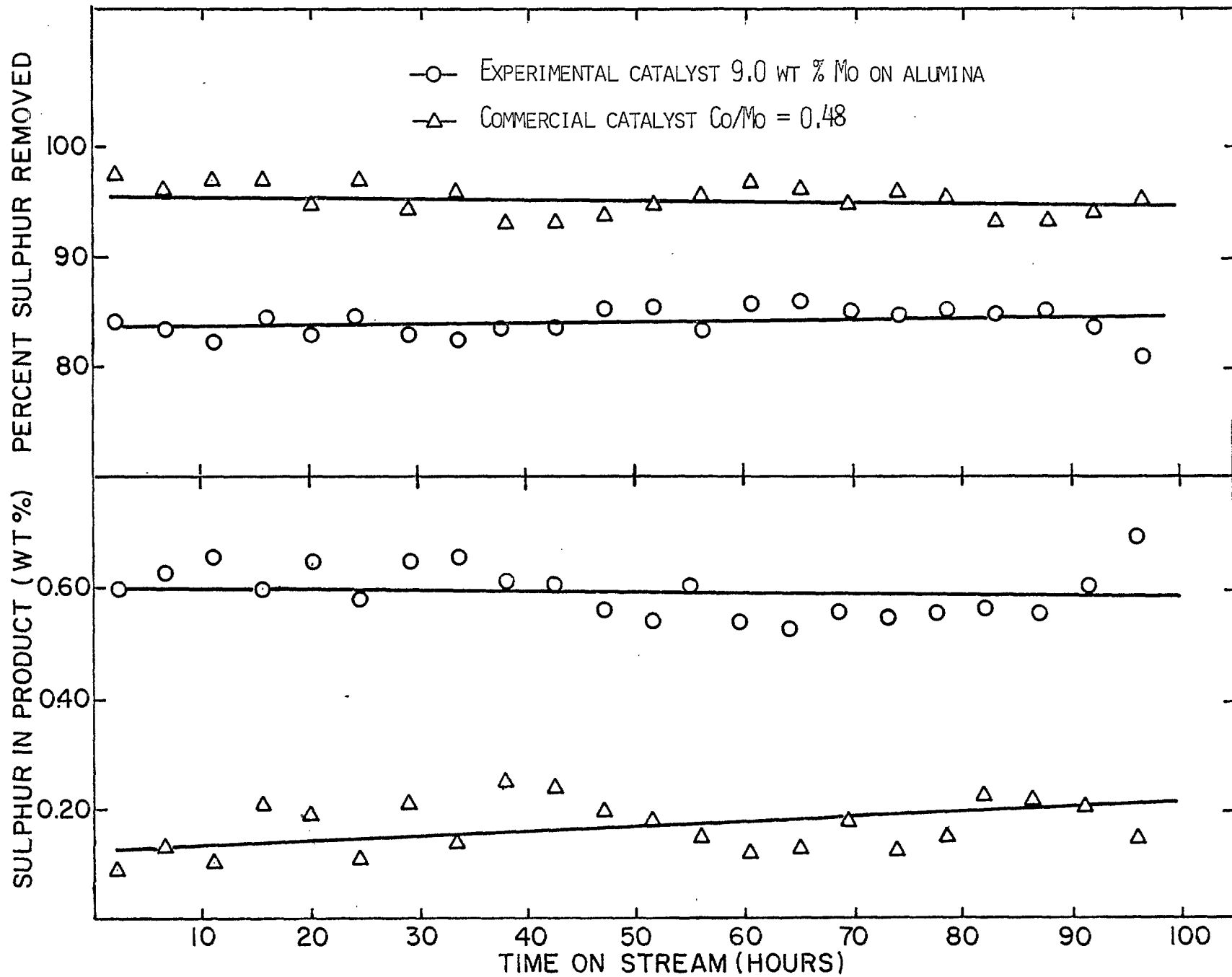


Figure 6. Effect of Time on Stream on Sulphur Removal.

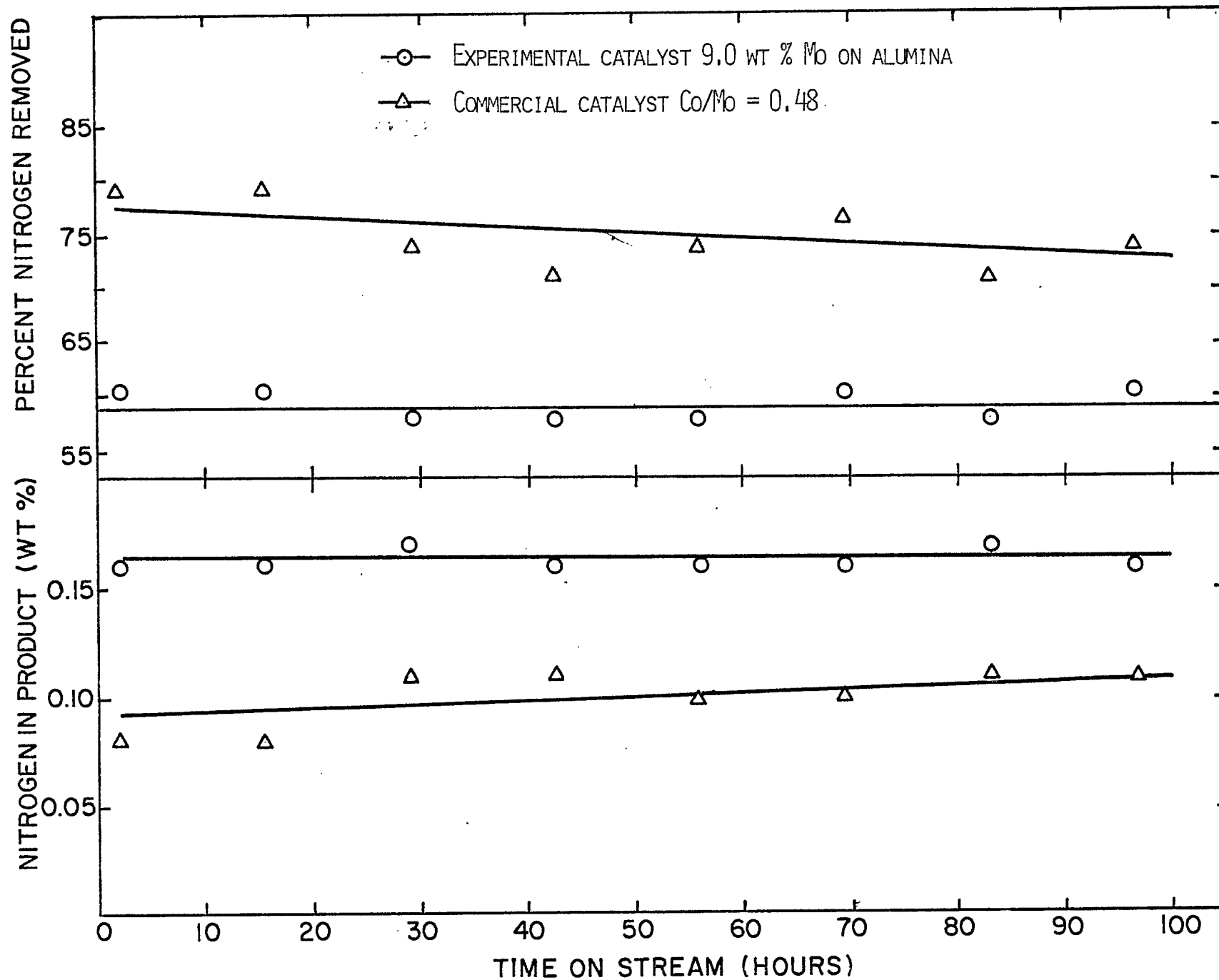


Figure 7. Effect of Time on Stream on Nitrogen Removal.

Zinc-Molybdenum - Alumina Catalysts

Figures 8 through 10 and Table 8 summarize the results of attempting to promote the Mo catalyst with zinc. The effect of zinc to molybdenum atomic ratio on specific gravity is shown in Figure 8. The extent of desulphurization and denitrogenation as a function of the Zn/Mo ratio are given in Figures 9 and 10 respectively. The results of distillation analyses and the sulphur and nitrogen determinations on typical products collected at 450°C are also summarized in Table 8.

It should be noted that the zinc-molybdenum on alumina catalysts having atomic ratios of 0.7, 0.9 and 1.1 were prepared with a base concentration of 12.0 wt % MoO₃ while the 0.2 and 0.4 mixtures contained only 9.0 wt % MoO₃. The point has already been made that the conversion levels of the unpromoted molybdenum on alumina catalysts were essentially the same for both the 9.0 and 12.0 wt % samples. Therefore, the results obtained with the 0.2 and 0.4 Zn/Mo catalysts are shown on the same graph as the results obtained using the 0.7, 0.9 and 1.1 catalysts.

There were only marginal differences in the performance of all the catalysts tested. No optimum Zn/Mo atomic ratio could be detected for either desulphurization or denitrogenation. In fact, the promoter effect of zinc at lower atomic ratios (0.0 - 0.4) was negative and there was only a small improvement between 0.9 and 1.1.

These results are in marked disagreement with the findings of de Beer and his co-workers⁴ who reported a sharp increase in conversion at a Zn/Mo ratio of 0.92 followed by a rapid decrease at Zn/Mo atomic ratios greater than 0.92. For example, at Zn/Mo = 1.12 de Beer found that the percentage conversion was lower than for the 12.0 wt % MoO₃-Al₂O₃ mixture and at the optimum ratio (0.92) it was slightly higher than the optimum Co/Mo atomic ratio. This is in contrast to the results of this investigation which showed that the zinc-promoted systems all had activities which were considerably less than those reported for cobalt in Part 1 of this series³. A subsequent de Beer paper⁸ published after this study was initiated concluded that, for a Zn-Mo-Al₂O₃ catalyst initially in the oxide form, the steady state level or working state was only reached after 6-7

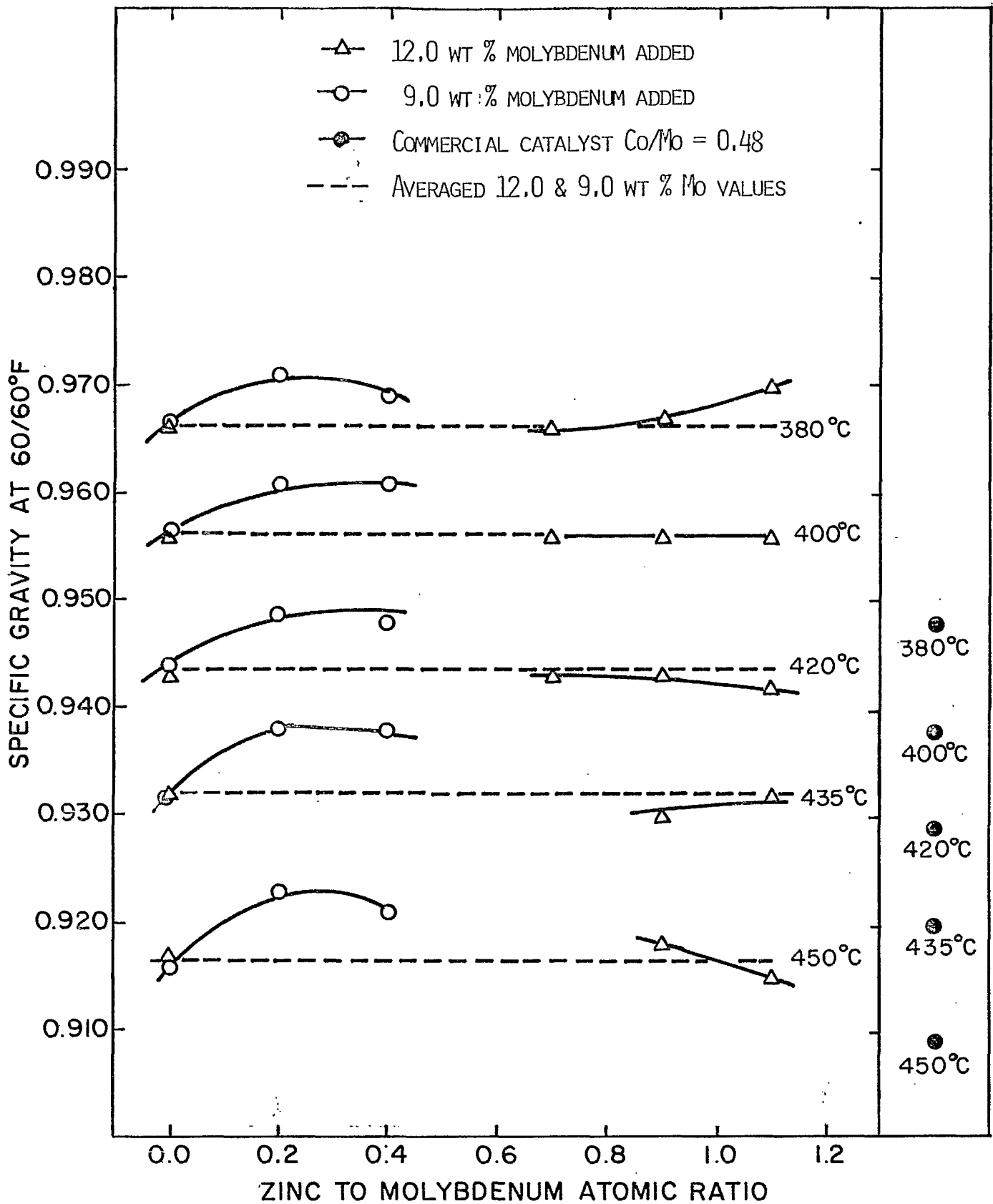


Figure 8. Effect of Zinc to Molybdenum Ratio on the Specific Gravity of the Products.

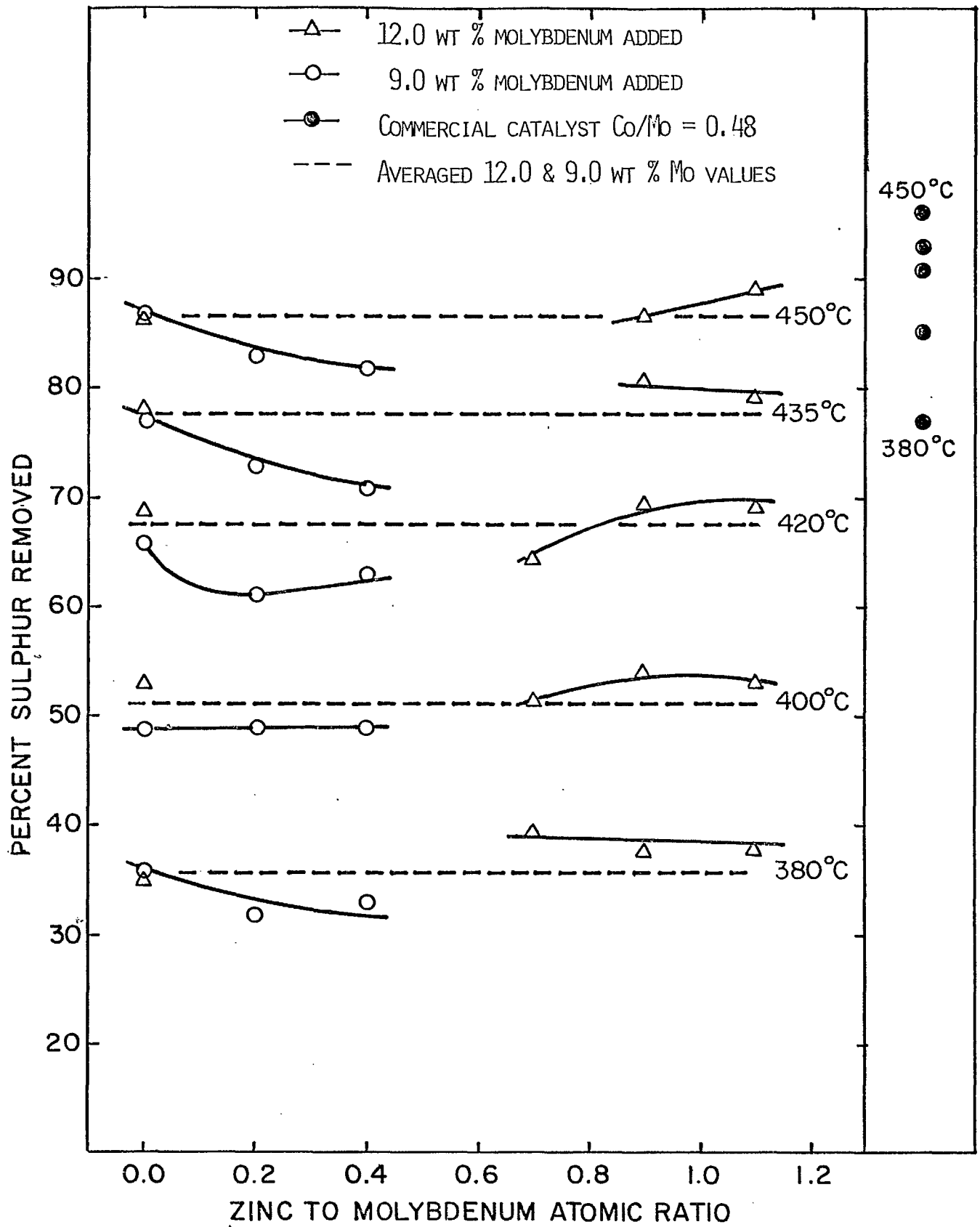


Figure 9. Effect of Zinc to Molybdenum Ratio on Sulphur Removal.

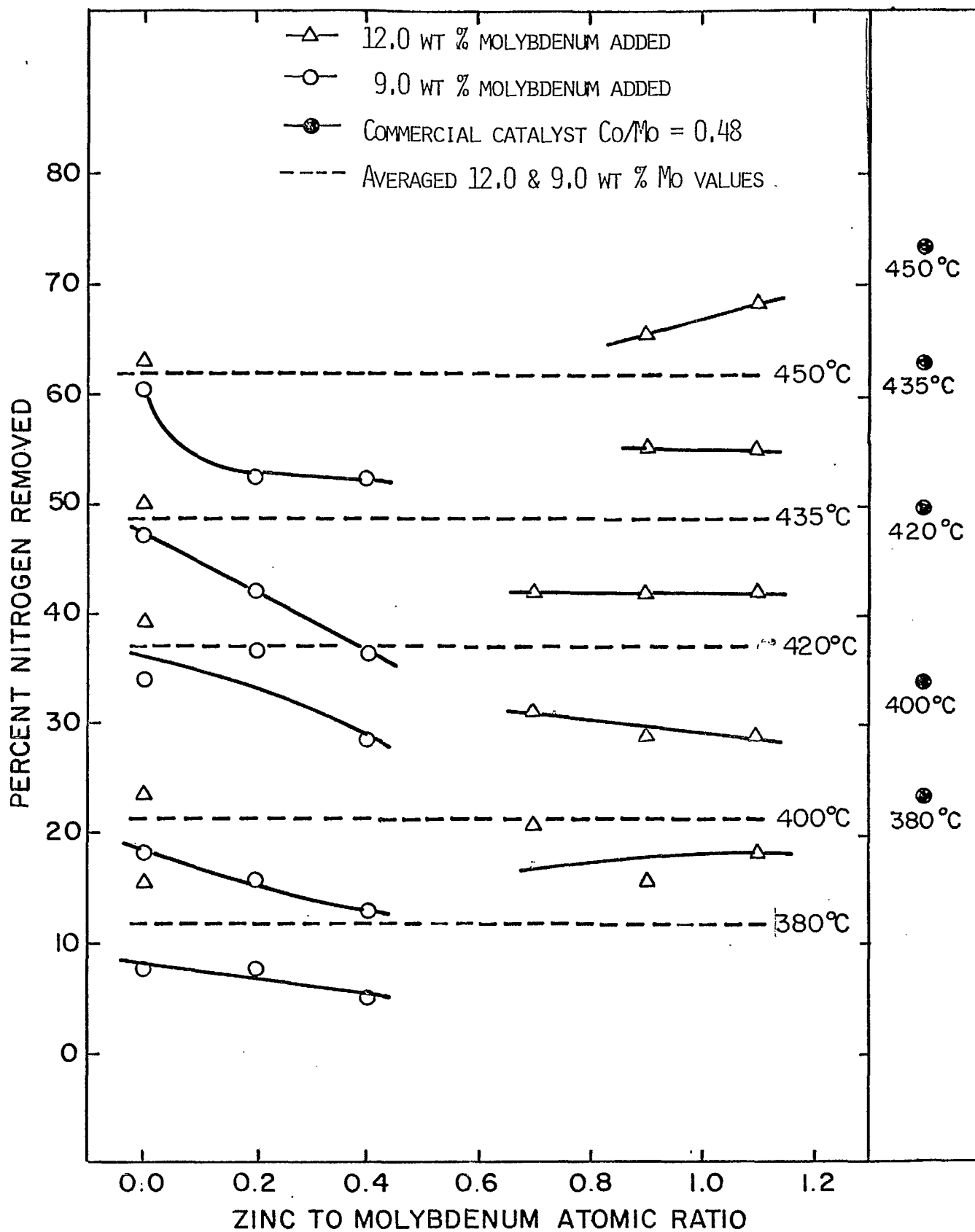


Figure 10. Effect of Zinc to Molybdenum Ratio on Nitrogen Removal.

TABLE 8

RESULTS OF DISTILLATION ANALYSES AND
SULPHUR AND NITROGEN DETERMINATIONS FOR
TYPICAL PRODUCTS COLLECTED AT 450°C

Boiling Range of Fraction (equiv temp at 1.0 atm)		Amount (wt % of feed)	Sp Gr 60/60°F	Sulphur (wt %)	Nitrogen (wt %)
(°C)	(°F)	Experimental Catalyst 9.0 wt % Mo, Zn/Mo = 0.20			
IBP-200	IBP-392	6.4	-	0.05	-
200-250	392-482	4.7	0.86*	0.14	0.10
250-275	482-527	5.1	0.89*	0.29	0.09
275-332	527-630	13.3	0.922	0.53	0.10
332-361	630-682	18.1	0.936	0.63	0.14
361-391	682-736	9.6	0.944	0.70	0.18
391-421	736-790	18.8	0.952	0.72	0.21
+ 421	+ 790	20.8	0.96*	0.79	0.29
Sulphur + Nitrogen removed		3.2	-	-	-
Total		100.0			
Experimental Catalyst 12.0 wt % Mo, Zn/Mo = 1.1					
IBP-200	IBP-392	8.1	-	0.08	-
200-250	392-482	5.9	0.86*	0.11	0.04
250-275	482-527	5.5	0.89*	0.18	0.05
275-332	527-630	15.4	0.918	0.45	0.07
332-361	630-682	16.6	0.934	0.46	0.11
361-391	682-736	11.4	0.941	0.50	0.15
391-421	736-790	15.3	0.948	0.53	0.18
+ 421	+ 790	18.3	0.96*	0.62	0.24
Sulphur + Nitrogen removed		3.5	-	-	-
Total		100.0			

Pressure = 2000 psig

H₂ Flow Rate = 5000 scf/bbl

Liquid Space Velocity = 2.0 hr⁻¹

*Qualitative values only

hours. The text of the earlier paper⁴ implied experiments of only 100 minutes in length after which time the steady state level was assumed to be attained. These discrepancies, in combination with the observations of this investigation, lend little support to the validity of the de Beer results alluded to in 4. The authors feel that an extremely cautious approach should be taken when interpreting de Beer's data.

All of the catalyst systems exhibited similar effects on the specific gravity of the product. Curves plotted over the 0.0 to 1.1 range (Figure 8) of zinc to molybdenum ratios indicated essentially equal spacing between the dotted lines. At the higher temperatures, specifically 435-450°C, a larger gap was observed. This resulted in the volume yields being somewhat greater than 100% (at the highest temperatures 101-103%).

Two of the experimental catalysts (the unpromoted 12% Mo catalyst and the systems containing Zn/Mo = 0.70 and 12.0 wt % Mo) were pretreated with H_2S/H_2 before testing with oil to determine any differences between the oxide and sulphide forms. In both cases the level of conversion noted with the sulphided system was slightly less than that observed with the oxide form. This is in contrast to the statement of de Beer⁸ that sulphidation of an $MoO_3-Al_2O_3$ catalyst reduced its activity by a factor of 0.6 but it agrees with their findings in that their sulphided zinc sample (Zn/Mo = 1.39) showed no promoter effect at all. The role of zinc as a promoter in oil systems is a complex one and much has yet to be learned in this field. It is well known that pure ZnO catalysts (which have been in production for more than twenty years) are moderately successful in the area of desulphurization²³. In the unsupported form, zinc oxide is slowly converted to zinc sulphide and once all of the oxide has been converted, the catalyst must be regenerated or replaced. Zinc oxide is the active phase in such systems and zinc sulphide is inactive. The results of the present study conform to these time-tested observations.

SUMMARY

The results obtained using a commercial-type gas-oil feedstock show that the molybdenum on alumina catalysts have a definite profile of desulphurization activity rising sharply from 0.0 to 3.0 wt % and levelling out at or near 9.0 wt %. To put the matter in perspective, it must be appreciated that the extent to which molybdenum on alumina can remove sulphur and nitrogen is

of the order of 30-50% less than our reference commercial cobalt molybdate catalyst.

The results of the catalyst life studies indicate that the 9.0 wt % Mo on alumina catalyst will maintain its desulphurization and denitrogenation activity for a prolonged period even at elevated temperatures. The results suggest that the unpromoted molybdenum on alumina catalyst has a catalytic lifetime comparable to commercial Co-Mo-Al₂O₃ systems.

The zinc to molybdenum ratio appears to have little or no significance where desulphurization or denitrogenation are concerned. All of the zinc-molybdenum-alumina catalysts exhibited activities comparable to the unpromoted molybdenum system. With all of the experimental catalysts only a small amount of hydrocracking took place.

From the standpoint of a practical industrial operation, it seems appropriate to compare all the experimental catalysts with the widely used commercial cobalt molybdate reference system. Considering first the process of desulphurization with the zinc-molybdenum on alumina catalysts, the results of the current investigation have shown that conversion levels of 78% or greater can be realized at temperatures of 380°C using the commercial cobalt molybdate mixture. By way of comparison, the same conversions can only be attained using the zinc-molybdenum catalysts by operating at temperatures in the vicinity of 430°C. It is also obvious that zinc is not a practical promoter for a commercial application.

Observations made with respect to denitrogenation were only slightly more encouraging. For the reference cobalt molybdate catalyst the removal of nitrogen reaches 35% at 400°C and 50% at 420°C. Temperatures of 420 and 435°C were required for equivalent conversions using any of the zinc-molybdenum-alumina or the 9.0 and 12.0 wt % Mo on alumina mixtures. Similar comparisons may be noted for the changes in specific gravities. The above statements reinforce the point that both Zn-Mo-Al₂O₃ and Mo-Al₂O₃ are much less active than Co-Mo-Al₂O₃.

Consideration of the applicability of a particular catalyst system for the hydrorefining of heavy oils and bitumens on a commercial scale encompasses many parameters. Little can be said in support of zinc-molybdenum or the unpromoted molybdenum system as suitable alternatives to cobalt molybdate. In presenting Mo-Al₂O₃ as a substitute for cobalt molybdate, however, the cost of generating the higher reaction temperatures required probably exceeds any advantages gained through less expensive catalyst preparation.

POSTSCRIPT

The listing of specific brand names for equipment and materials is made for information purposes only and does not imply endorsement by the Energy Research Laboratories.

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REFERENCES

1. J.C. Vlugter and P. Yan't Spijkev, "Catalysts for Hydrocracking of Distillates and Residuums", 8th World Petroleum Congress, Moscow, 4, 159 (1971).
2. E.C. McColgan, P.S. Soutar and B.I. Parsons, "The Hydrocracking of Residual Oils and Tars"
 - (a) Part 1 - Mines Branch Research Report R-246 (1971)
 - (b) Part 2 - Mines Branch Research Report R-253 (1972)
 - (c) Part 3 - Mines Branch Research Report R-256 (1972)
 - (d) Part 4 - Mines Branch Research Report R-261 (1973)
 - (e) Part 5 - Mines Branch Research Report R-263 (1973)
 - (f) Part 6 - Mines Branch Research Report R-273 (1974)
 Department of Energy, Mines and Resources, Ottawa, Canada.
3. R.J. Williams, R.G. Draper and B.I. Parsons, "Catalysts for Hydrocracking and Refining Heavy Oils and Tars, Part 1: The Effect of Cobalt to Molybdenum Ratio on Desulphurization and Denitrogenation", Mines Branch Technical Bulletin TB-187, Department of Energy, Mines and Resources, Ottawa, Canada (1974).
4. V.H.J. de Beer, T.H.M. Van Sint Fiet, J.F. Engelen, A.C. Van Haandel, M.W.J. Wolfs, C.H. Amberg and G.C.A. Schuit, "The CoO-MoO₃-Al₂O₃ Catalyst. IV: Pulse and Continuous Flow Experiments and Catalyst Promotion by Cobalt, Nickel, Zinc and Manganese", Journal of Catalysis 27, 357-368, (1972).
5. T. Takematsu and B.I. Parsons, "A Comparison of Bottom-Feed and Top-Feed Reaction Systems for Hydrodesulphurization", Mines Branch Technical Bulletin TB-161, Department of Energy, Mines and Resources, Ottawa, Canada (1972).
6. M.A. O'Grady and B.I. Parsons, "The Hydrogenation of Alberta Bitumen Over Cobalt Molybdate Catalyst", Mines Branch Research Report R-194, Dept. of Energy, Mines and Resources, Ottawa, Canada (1967).
7. A. Aoshima and H. Wise, "Hydrodesulphurization Activity and Electronic Properties of Molybdenum Sulphide Catalyst", Journal of Catalysis 34, 145-151, (1974).
8. V.H.J. de Beer, T.H.M. Van Sint Fiet, G.H.A.M. Van Der Steen, A.C. Zwaga and G.C.A. Schuit, "The CoO-MoO₃-Al₂O₃ Catalyst. V: Sulphide Catalysts Promoted by Cobalt, Nickel and Zinc", Journal of Catalysis 35, 297-306, (1974).
9. W.H. Merrill, R.B. Logie and J.M. Denis, "A Pilot Scale Investigation of Thermal Hydrocracking of Athabasca Bitumen", Mines Branch Research Report R-281, Department of Energy, Mines and Resources, Ottawa, Canada (1973).
10. N.A.C. Smith, H.M. Smith, O.C. Blade and E.L. Garton, "The Bureau of Mines Routine Method for the Analysis of Crude Petroleum", U.S. Bureau of Mines Bulletin No. 490 (1951).

11. "Panalyzer 4000 X-Ray Spectrochemical Analyzer Operating Manual", Panametrics, Esterline Corporation, Waltham, Massachusetts (1971).
12. G. Frechette, J.C. Hebert, T.P. Thinh and Y.A. Miron, "Hydrocarbon Processing", 43, (2), 109, (1975).
13. L.A. Fabbro, L.A. Filachek, R.L. Iannacone, R.T. Moore, R.J. Joyce, Y. Takahashi and M.E. Riddle, *Analytical Chemistry* 43, 1671-78 (1971).
14. H.V. Drushel, "Microcoulometric Determination of Sulphur and Chlorine by Combustion and Nitrogen by Hydrogenolysis", *Analytical Letters*, 3(7), 353-72, (1970).
15. N. Todo, K. Muramatsu, M. Kurita, K. Ogawa, T. Sato, M. Ogawa and Y. Kotera, "The Effect of Chemical Composition on Hydrodesulphurization Activity of Co-Mo-Al₂O₃ Catalyst", *Bulletin of the Japan Petroleum Institute*, 14, No. 1, 89-93 (1972).
16. S. Kolboe and C.H. Amberg, "Catalytic Hydrodesulphurization of Thiophene VI: Comparisons over MoS₂, CrMo and Chromia Catalysts", *Canadian Journal of Chemistry* 44, 283-302 (1965).
17. J.M.J.G. Lipsch and G.C.A. Schuit, "The CoO-MoO₃-Al₂O₃ Catalyst II: The Structure of the Catalyst", *Journal of Catalysis* 15, 174-178 (1969).
18. M. Dufaux, M. Che and C. Naccache, "Etude par résonance paramagnétique électronique de l'adsorption d'oxygène sur les oxydes de molybdène et de cérium supportés", *Acad. Sci. Paris Série c* 268, 2255-57 (1969).
19. M. Dufaux, M. Che and C. Naccache, *J. Chim. Phys.* 67, 527 (1970).
20. N. Giordano, J.C.J. Bart, A. Vaghi, A. Castellan and G. Martinatti, "Structure and Catalytic Activity of MoO₃ Systems 1: Solid State Properties of Oxidized Catalysts", *Journal of Catalysis* 36, 81-92 (1975).
21. M. Lo Jacono, A. Cimino and G.C.A. Schuit, "Magnetic and Spectroscopic Investigations of Cobalt-Alumina and Cobalt-Molybdenum-Alumina", *Gazzetta Chimica Italiana* 103, 1281-95 (1973).
22. M. Ternan and M.J. Whalley, "Catalysts for Hydrocracking and Refining Heavy Oils and Tars Part 3: The Effect of Presulphiding Conditions on Catalyst Performance", CANMET Report 76-9, Department of Energy, Mines and Resources, Ottawa, Canada (1976).
23. J.J. Phillipson, "Catalyst Handbook", Springer-Verlag, New York, p. 49, (1970).