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CATALYTIC COAL LIQUEFACTION

Final Report

MASTER

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ABSTRACT

This report summarizes the results obtained on Contract DE-AC22-76ET-10518, from June 1979 to September 1981. The research program consisted of several tasks centered on the use of catalysts in coal liquefaction. These were: to develop improved catalysts containing supported molybdena; to extend the use of O_2 chemisorption as a measure of molybdena area; to explore the chemical role of unsupported liquefaction catalysts; and to study the hydrotreating of methyl naphthalene as a multifunction screening test for liquefaction catalysts. The following studies were carried out:

Monolith catalysts of MoO_3-CoO-Al_2O_3 were prepared and tested for coal liquefaction in a stirred autoclave. Pure γ-Al_2O_3 monolith (Corning) having 200 square channels/in^2 and an average pore diameter of 225 A was used as substrate. The monolith catalyst was tested both as whole pieces (oriented with channels parallel to the direction of stirring) and as a crushed particulate. Each catalyst was prepared with two loadings of MoO_3 and CoO, and each was tested in the oxide or in the presulfided form. A blank run with the empty catalyst holder in place showed higher conversion of asphaltene to oil than a blank run without catalyst holder; this may be evidence for a mechano-chemical effect in oil production. An effect of stirring speed was also found with monolith catalyst: liquefaction and H_2 consumption were notably less at 400 rpm than at 950 rpm. Presulfiding had little effect on the effectiveness of monolith catalysts, but low loading of MoO_3 and CoO on the support gave better results than high loading, for equal weights of MoO_3 and CoO charged. Whole monolith pieces showed slightly lower liquefaction than their crushed counterparts. In general, the monolith catalysts were not as good as particulate catalysts prepared on Corning alumina supports.

Measurement of O_2 chemisorption and BET surface area have been made on a series of Co/Mo/Al_2O_3 catalysts obtained from PETC. The catalysts were derived

from Cyanamid 1442A and had been tested for coal liquefaction in batch autoclaves and continuous flow units. Catalyst samples (fresh, heat-treated, or after use and regeneration) were presulfided before determination of O_2 chemisorption. O_2 chemisorption values give the same rank-ordering as do the short-term liquefaction tests (batch autoclave, or initial behavior in a continuous unit).

MoO_3-Al_2O_3 catalysts over the loading range 3.9 to 14.9 wt% MoO_3 have been studied with respect to BET surface (before and after reduction), O_2 chemisorption at -78°C, redox behavior at 500°C, and activity for cyclohexane dehydrogenation at 500°C. The BET areas for the unreduced catalysts are consistent with a monolayer model for MoO_3 on Al_2O_3; for reduced catalysts, the appropriate model would be porous or finely crystalline MoO_2. Catalysts with $<11\%$ MoO_3 are incompletely reduced to MoO_2 after 6 hours in flowing H_2 at 500°C. After correction is made for the actual extent of reduction, plausible relations are obtained for both O_2 chemisorption and cyclohexane dehydrogenation vs. MoO_3 loading (corrected). The sites responsible for both O_2 chemisorption and for dehydrogenation activity may be surface Mo^{4+} ions.

In connection with the fate of tin catalysts during coal liquefaction, calculations have been made of the relative thermodynamic stability of $SnCl_2$, Sn, SnO_2, and SnS in the presence of H_2, HCl, H_2S and H_2O. It is concluded that, under typical liquefaction conditions, it is thermodynamically possible for $SnCl_2$ to be reduced by H_2 to metallic Sn, or to be oxidized by H_2O to SnO_2; however, SnS appears to be the ultimately stable phase. Uncertainties in the thermodynamic data for $SnCl_2$ and SnS, and possible variations in the extant partial pressures of HCl, H_2S, and H_2O, prevent unequivocal conclusions to be drawn for some of the reactions considered.

Batch autoclave experiments have been completed for the comparison of SnS, SnS + NH_4Cl, and $SnCl_2$ as catalysts in the liquefaction of West Virginia coal under hydrogen pressure with a tetralin-naphthalene solvent. SnS alone behaves as poorly as no catalyst. By contrast, the combination of SnS + NH_4Cl is as effective as $SnCl_2$. These results are in agreement with old (ca. 1950) experiments done in the absence of any added solvent. They leave unanswered the question of why SnS, presumably stable under autoclave conditions, should act as a hydrogenation catalyst during coal liquefaction.

Ferrous sulfate dispersed in methylnaphthalene has been shown to be reduced to ferrous sulfide under typical coal hydroliquefaction conditions (1 hour, 450°C, 1000 psi initial p_{H_2}). This suggests that ferrous sulfide may be the common catalytic ingredient when either (a) ferrous sulfate impregnated on powdered coal, or (b) finely divided iron pyrite is used as the catalyst. Old research on impregnated ferrous sulfate, impregnated ferrous halides, and pyrite is consistent with this assumption.

Eight $Co/Mo/Al_2O_3$ catalysts from commercial suppliers, along with $SnCl_2$, have been studied for the hydrotreating of 1-methylnaphthalene (1-MN) in a stirred autoclave at 450° and 500°C. The predominant catalyzed reaction at 450°C is ring hydrogenation (RHG); at this temperature hydrodemethylation (HDM) is appreciable but little affected by catalysts, and ring hydrocracking (RHC) is very low. With presulfided catalysts at 500°C, HDM predominates and RHC becomes appreciable; the extent of RHC is much less at 500° than at 450°C. $SnCl_2$ slightly catalyzes HDM, but it is a very poor catalyst for both RHG and RHC. The RHG activity is much greater at 450°C for all the presulfided catalysts than for the as-received ones. Final autoclave pressure correlates well with the extent of 1-MN conversion by RHG and RHC.

I. Objectives and Scope of Work

This research has the following scope and objectives:

1. To develop improved coal liquefaction catalysts containing supported molybdena, by establishing the effects of pore size and composition in particulate catalysts, composition in monolith catalysts, and shell thickness in shell catalysts.

2. To extend the O_2 chemisorption technique for determination of specific surface area of molybdena to a temperature of -78°C rather than -195°C, to sulfided catalysts, to monolith and "shell" catalysts, and to used, regenerated catalysts.

3. To explore the role of unsupported catalysts in coal liquefaction.

4. To use hydrotreating of methylnaphthalene and/or other aromatic compounds as a convenient means of screening several catalytic functions of liquefaction catalysts.

II. Task No. 1: Improved Supported Catalysts

In earlier research the effect of catalyst pore diameter, over the range 100 to 1000Å, was studied for particulate $Co/Mo/Al_2O_3$ catalysts in the liquefaction of West Virginia coal. Catalysts were tested at two loadings of CoO and MoO_3, and in both oxide and presulfided condition. The results of this research have now been published [P. N. Ho and S. W. Weller, Fuel Process. Technol. 4, 21 (1981)]. Comparable experiments have now been made with monolith, rather than particulate, alumina supports.

Monolith catalysts are extensively used in automotive catalytic converters. The reason is two-fold: the catalytic "effectiveness factor" is high because the small web thickness makes the diffusion distance for the reacting molecules short. At the same time, the open channels of the monolith configuration result in pressure drops that are two or three orders of magnitude lower, for the same bed length and gas flow rate, than for a comparable bed of particulate catalyst (1).

The utility of monolith as a catalyst support was reported by Stopka in 1950 (2). In 1974, we proposed the use of monolith catalysts with controlled pore sizes for the catalytic hydrogenation of coal slurries (3). A preliminary assessment of monolith catalyst performance was published by Scinta and Weller (4). They obtained the most favorable liquefaction and hydrodesulfurization with a monolith catalyst having a nominal configuration of 200 square cells per in^2. Crynes has compared cobalt molybdate catalysts of monolithic and particulate configurations for the HDS of anthracene oil (5). Although he reported a poorer performance for the monolithic catalyst, the differences in surface areas and other properties of his catalysts makes it difficult to generalize the results. The present study compares the behavior of a single alumina-base monolith at two different loadings of MoO_3 and CoO, in oxide or in sulfide form, and tested either as whole pieces of monolith or crushed to small particles.

Catalysts were prepared on an experimental sample of pure γ-Al_2O_3 monolith obtained through the courtesy of Corning Glass Works; the configuration consisted of 200 square channels/in^2. The characteristics of this monolith support are summarized in Table 1. Of particular interest were the average pore diameter, 225Å, and the surface area, 72 m^2/g.

Monolith catalysts were prepared with MoO_3 concentrations of 6.97 wt% and 3.25 wt%; the wt. ratio of CoO:MoO_3 was maintained at 1:5. The MoO_3 loadings corresponded to 9.7×10^{-4}g MoO_3/m^2-Al_2O_3 and 4.5×10^{-4}g $MoO_3/m^2 Al_2O_3$.

The problem of mounting the monolith samples in the stirred Magnedrive autoclave was solved in the following manner. Four 1/2" x 1/4" catalyst holders were fabricated from 0.020" stainless steel sheet and were mounted symmetrically on the lower end of the stirring shaft just above the paddle impeller. The arrangement is shown in Figure 1. The front end of each holder, facing the direction of stirring, was completely open; the rear end of each holder was also open except for a thin nichrome wire that acted as a retainer for the catalyst

Table 1

Characteristics of Alumina Monolith

Surface Area (m^2/g)	72
Pore Volume (cc/g)	0.649
Avg. Pore Diameter (A)	225
Porosity (%)	68.1
Apparent Density (g/cc)	1.05
Skeletal Density (g/cc)	3.29
Channels	200 square/in^2
Web Thickness (in.)	0.010 - 0.013

sample. The monolith catalyst was cut to give pieces 1/2" x 1/4" in cross section. Each piece was slipped into its holder so that the monolith channels were aligned with the direction of stirring.

The catalyst charge, based on maf coal, was 0.91 wt% for the "High Loading" catalysts and 1.94 wt% for the "Low Loading" catalysts. This resulted in the same weight of MoO_3 (0.0315g) and of CoO (0.0064g) being charged in every run. Each catalyst was tested both as whole pieces of monolith and as a crushed particulate (40-60 mesh). Runs with crushed monolith were conducted with the catalyst holder on but empty. Each catalyst was also tested either in the oxide form, as prepared, or after presulfiding in a 15% H_2S/H_2 stream at 400°C. All tests were for 1 hour (nominal time at temperature) and 400°C.

Two "blank" runs were first made, without catalyst addition to the coal-methylnaphthalene charge. The results are summarized in Table 2. In Run 1, the catalyst holders were not used at all; in Run 2, the catalyst holders were mounted on the stirring shaft but left empty. A surprising difference was noted between these two blank runs. Although there was not much difference in total liquefaction, H_2 consumption, or S content in the product fractions, the blank with catalyst holders present (Run 2) showed a markedly higher conversion of asphaltenes to oil. We have no explanation for this effect other than to raise the possibility that mechanical stress, arising from the presence of the rotating catalyst holders, may play a role in this difficult conversion. Yang (6) has recently published data indicating that grinding of anthracite coal under H_2 pressure increases the extent of hydroliquefaction. Guin and Tarrer (7) also have recently presented evidence for a mechano-chemical effect in coal liquefaction when Kentucky or Amax coal is ground under tetralin.

Table 3 summarizes the results for the monolith catalyst with "High Loading" of MoO_3 and CoO; corresponding results for the "Low Loading" catalyst are in Table 4. In view of the difference between the two blank runs shown in

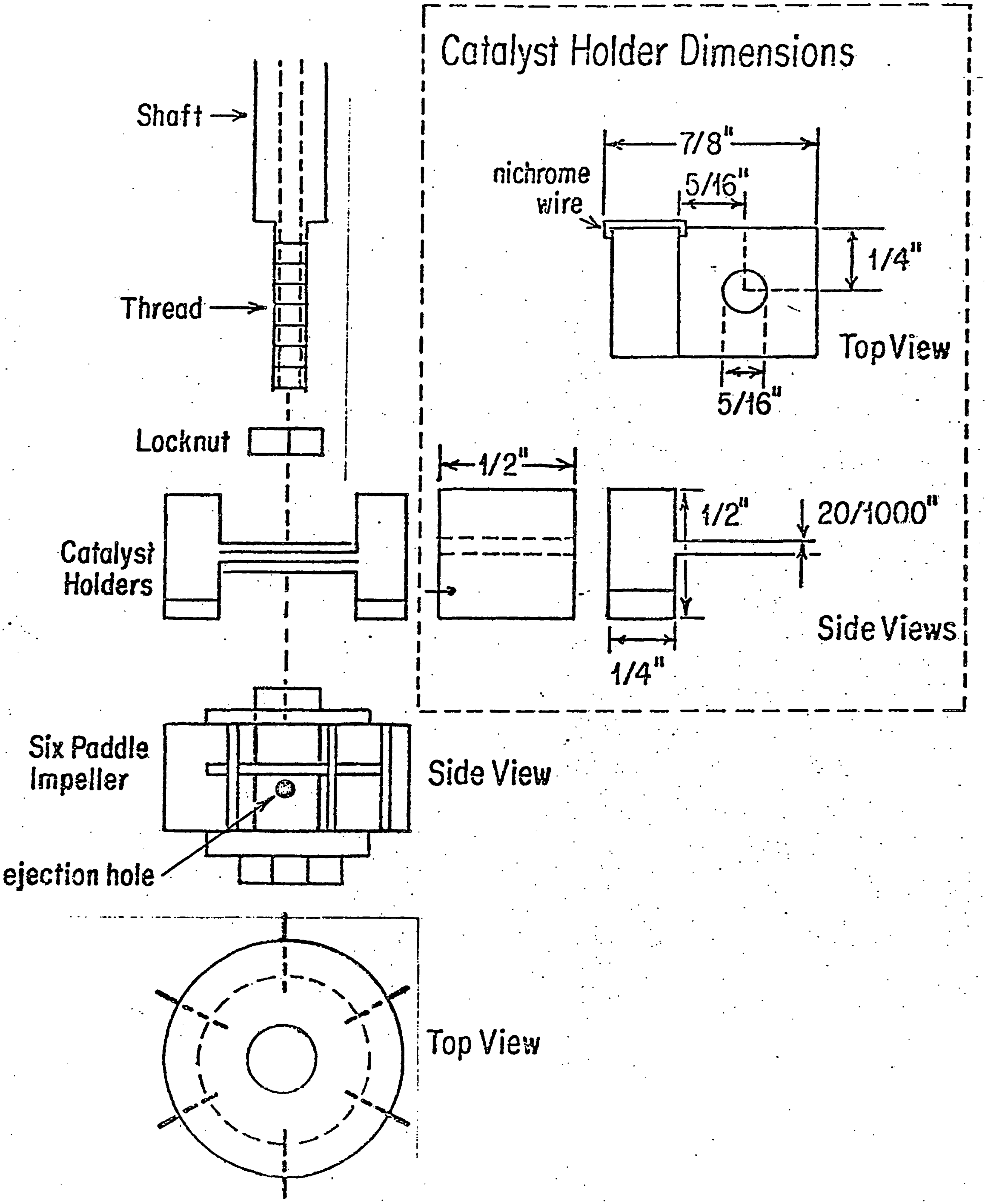

Figure 1. Monolithic Catalyst Holder

Table 2

Product Distribution and Sulfur Analysis of Blank Runs

Run No.	1[a]	2[b]
Liq'n., % maf coal[c]	71.9	70.1
A, %	49.8	42.7
O, %	22.1	27.4
H_2 Consumption	1.73	1.68
O/(O+A)	0.307	0.391
S (wt %) in:		
SI	5.1	5.2
A	2.0	2.0
O	2.1	2.2

(a) No catalyst holder used

(b) Empty catalyst holder used

(c) % Oil(O) = % Liquefaction - % Asphaltenes (A).
Gas production was $\leq$ 3% for all runs.

Table 3

Product Distribution and Sulfur Analysis with "High Loading" Catalysts[a]

	Sulfide Form		Oxide Form	
Run No.	3	4	5	6
Monolith Condition	Whole	Ground	Whole	Ground
Liq'n. %[b]	72.2	73.9	72.4	73.2
A, %	43.6	45.2	44.2	44.9
O, %	28.6	28.8	28.2	28.3
H_2 Cons., %	1.93	1.89	1.87	2.01
S (wt. %) in:				
SI	5.5	5.5	5.6	5.3
A	1.9	1.9	1.9	2.0
O	1.7	2.0	1.5	1.8

(a)Stirrer speed 950 rpm in all runs.

(b)Wt. % based on maf coal charge.

Table 4

Product Distribution and Sulfur Analysis with "Low Loading" Catalysts

	Sulfide Form		Oxide Form		
Run No.	7	8	9	10	11
Monolith Condition	Whole	Ground	Whole	Whole	Ground
Stirrer Speed, rpm	950	950	950	400	950
Liq'n., %	73.8	75.1	72.0	67.8	75.2
A, %	44.6	46.6	44.6	41.1	47.2
O, %	29.2	28.6	27.5	26.7	28.1
H_2 Cons., %	1.86	2.01	1.94	1.52	2.10
O/(O+A)	0.397	0.380	0.381	0.394	0.373
S (wt %) in:					
SI	5.8	5.9	5.5	5.4	5.8
A	1.9	1.8	1.9	1.9	1.8
O	1.4	1.5	1.7	2.0	1.6

Table 2, the catalytic runs should probably be compared with the blank Run 2, in which the empty catalyst holder was present. All experiments, with the notable exception of Run 10 in Table 4, were conducted with the stirrer rotating at 950 rpm. The stirrer speed was 400 rpm in Run 10, which was otherwise a duplicate of Run 9. Inspection of the data from run 10 quickly shows the poor results: the liquefaction is even less than that in the blank runs, and the H_2 consumption is correspondingly less. Unfortunately, it was not possible to operate the stirrer reproducibly at a speed greater than 950 rpm. The effect of stirrer speed shown in the comparison of Runs 9 and 10 may not be important at 950 rpm and higher, but it would be desirable to investigate this. The poor results at 400 rpm may derive partially from failure of coal slurry to flow properly through the small monolith channels at this speed; however, this could not explain a liquefaction even lower than with no catalyst present (Table 2). The most likely cause of the low conversion and H_2 consumption in Run 10 is a failure to maintain gas-liquid equilibration at the lower speed.

The major conclusions to be drawn from Tables 3 and 4 are the following:

1. Each monolithic catalyst shows a slightly lower (1-3%) liquefaction value than its crushed counterpart. The cause is probably the bypassing of the viscous reactant around the pieces of whole monolith.

2. Higher liquefaction is reflected mainly in higher yield of the asphaltene fraction. The yield of the oil fraction is quite stable at 27-29%.

3. With the exception of Run 10, H_2 consumption in the catalytic runs was also almost constant within the range 1.9 - 2.1%.

4. Presulfiding the catalyst had very little effect in these experiments.

5. As was the case for the particulate catalysts reported previously, monolith catalysts with "Low Loading" of MoO_3 and CoO performed somewhat better than those with "High Loading". The effect is less prominent with the monolith

samples, possibly because of the flow bypassing in the case of monolith testing.

6, The liquefaction and asphaltene yields were generally lower in all the runs with monolith catalysts (Tables 3 and 4) than in the runs previously reported with particulate catalysts. This may be the result of the test method employed for monolith samples. We are not encouraged to do further testing of monolith in autoclaves.

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III. Task No. 2: Specific Surface Area of Molybdena

Previous work in this laboratory has led to the development of a method, based on O_2 chemisorption at low temperature (-78°C), for measuring the specific area of molybdena in a reduced sample of MoO_3/Al_2O_3 (1,2). Attention has now been given to the implications of such measurements for two questions: (1) for a series of catalysts with varying MoO_3 loading on an Al_2O_3 support, what can be said about the nature of the molybdena both before and after reduction?; and (2) how do the O_2 chemisorption values relate to activity in a test catalytic reaction?

This report contains a study of MoO_3-Al_2O_3 catalysts over the loading range of 3.9 to 14.9 wt% MoO_3. Measurements have been made of: (1) BET surface areas in the oxidized (MoO_3) condition and after reduction in H_2 for 6 hours at 500°C; (2) O_2 chemisorption at -78°C after reduction at 500°C; (3) H_2 and O_2 consumption in redox experiments at 500°C; and (4) activity for dehydrogenation of cyclohexane at 500°C after reduction at 500°C. Catalysts were prepared by impregnation of 60-80 mesh Houdry Type 200S Al_2O_3 with the desired concentration of ammonium molybdate, vacuum drying at 110°C, and calcination in air for 12 hours at 500°C. Details of the procedures for O_2 chemisorption and for the redox studies are contained in Refs. 1 and 2. Cyclohexane dehydrogenation was studied in a pulsed microcatalytic reactor with a catalyst charge of 0.400g. Each pulse of cyclohexane was 1 $\mu\ell$ in He carrier gas flowing at 35cc/min through the reactor (1/4" O.D. stainless steel tube). No deactivation was observed during 10 pulses, and the activity, calculated from the steady-state value of benzene produced per pulse during this period, was expressed as "moles benzene produced/mole cyclohexane injected."

The results of surface area measurements on the oxidized and on the reduced samples are given in Table 1. Areas are expressed on two bases: m^2/g catalyst, and m^2/g Al_2O_3 in the catalyst. For samples in the oxidized

Table 1. BET Area of Oxidized and Reduced MoO_3/Al_2O_3 Catalysts

	Oxidized MoO_3/Al_2O_3		Reduced MoO_3/Al_2O_3	
Wt% MoO_3	BET area (m^2/g.cat.)	BET area (m^2/g.Al_2O_3)	BET area (m^2/g.cat.)	BET area (m^2/g.Al_2O_3)
0.0	-	144	-	-
3.9	136	141	142	148
5.7	-	-	147	156
7.5	137	148	147	159
10.8	-	-	144	161
11.4	128	145	146	163
13.2	-	-	143	165
14.9	124	146	141	166

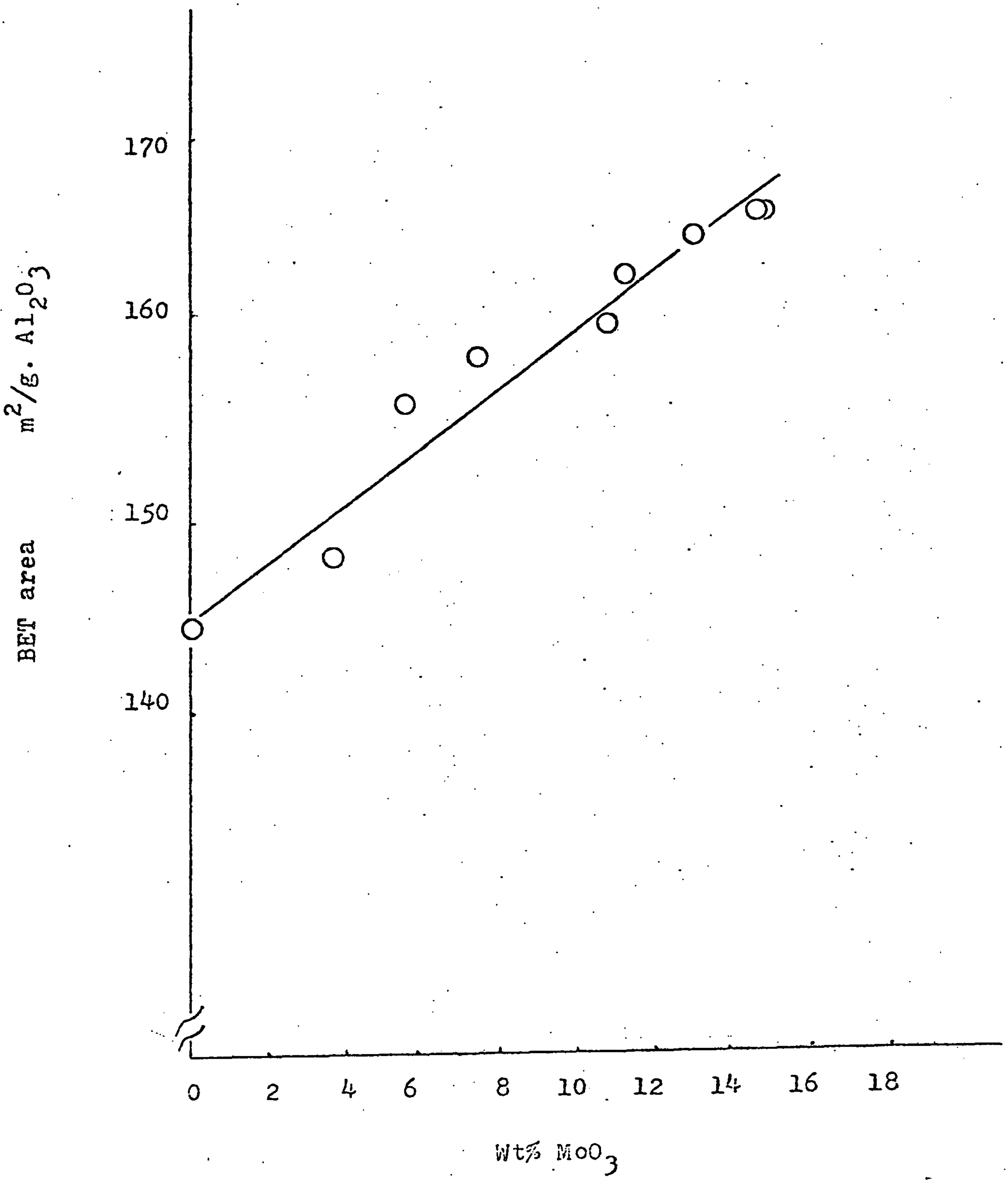

Figure 1 BET area of reduced MoO_3/Al_2O_3 vs. MoO_3 loading in unreduced catalyst

condition, the area/g catalyst decreases with increasing loading of MoO_3, but the area/g Al_2O_3 remains constant. These results are consistent with a monolayer model for MoO_3 on Al_2O_3.

The reduced catalysts present a different picture. The area/g catalyst remains essentially constant over the loading range, and the area/g Al_2O_3 increases almost linearly with loading. This behavior is shown more clearly in Figure 1. It is not consistent with a monolayer model for the reduced catalyst. However, it would be consistent with the existence of small crystallites of molybdena in the reduced catalyst, if the crystallites were sufficiently small (or sufficiently porous) to possess surface area comparable with that of the alumina support. Such a model has been previously suggested for MoO_2-Al_2O_3 (1).

Measurements of O_2 chemisorption at -78°C were then used to estimate the relative surface areas of the reduced molybdena in catalysts after 500°C reduction. The results are shown in Figure 2. The shape of the curve was somewhat puzzling. O_2 chemisorption may be a measure of the specific surface area of the MoO_2 formed by reduction, in the same way as H_2 chemisorption is used to measure the specific surface area (or dispersion) of Pt in Pt-Al_2O_3. Since the dispersion in supported catalysts is normally highest with low loading, the curve for O_2 chemisorption vs. MoO_3 loading might be expected to be linear or convex upward. The actual curve is concave upward.

A partial explanation was found in redox studies at 500°C, the results of which are summarized in Table 2. H_2 and O_2 consumption for the 14.9% MoO_3 sample are in close agreement with those reported by Parekh and Weller (1) for a 15.0% MoO_3 sample. For this sample, the difference between the total H_2 consumed and that required for $MoO_3 + H_2 \rightarrow MoO_2 + H_2O$ was attributed by Parekh and Weller to either the total H_2 chemisorbed on MoO_2 or, alternately, partial reduction of Mo beyond the Mo^{IV} stage. The difference in this case between the total O_2 consumed on re-oxidation and that required for $MoO_2 + 1/2\ O_2 \rightarrow MoO_3$ is

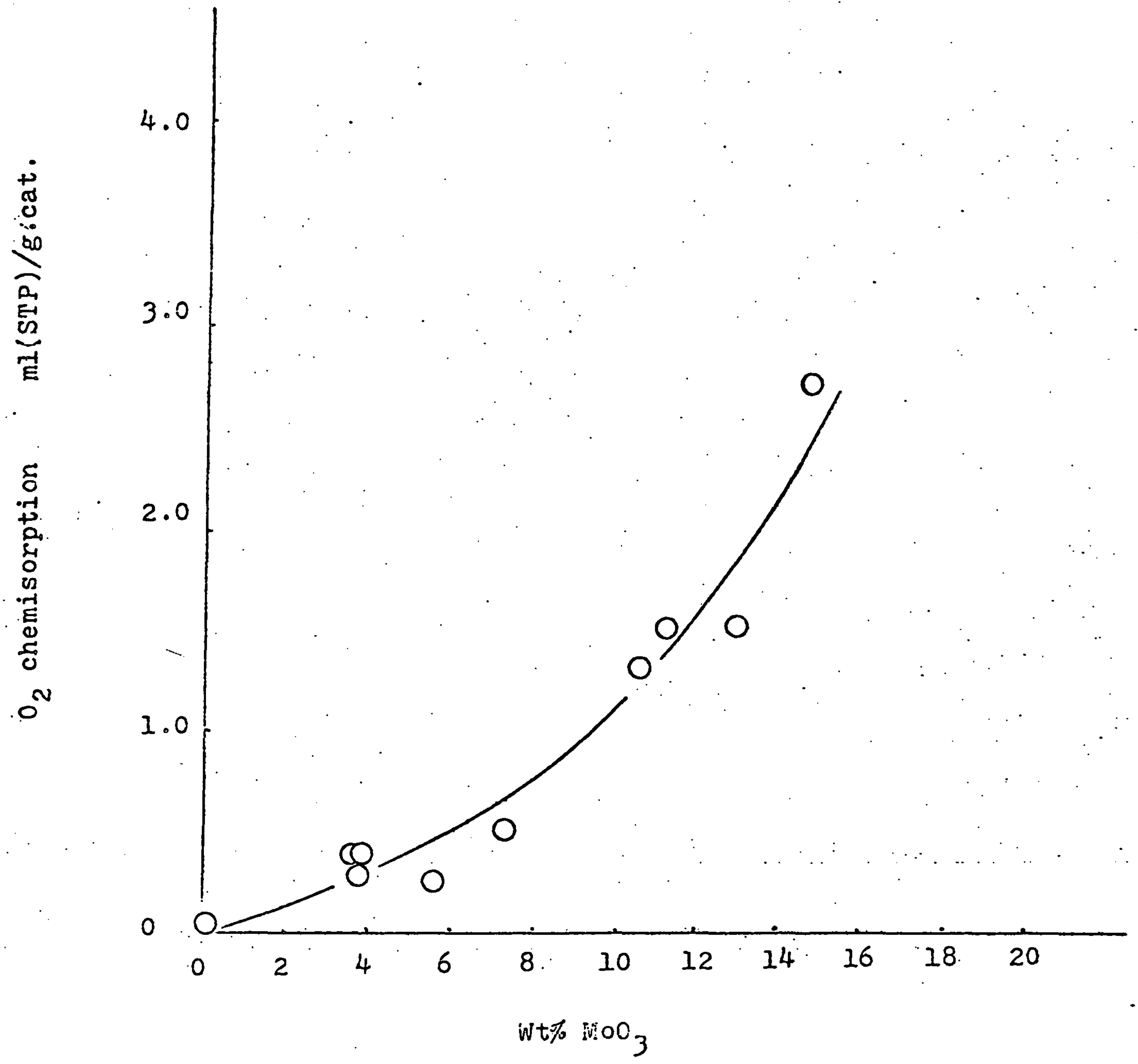

Figure 2 O_2 chemisorption at -78°C on reduced MoO_3/Al_2O_3 vs. MoO_3 loading in unreduced catalyst

Table 2. Redox Study of MoO_3/Al_2O_3 Catalysts

Wt% MoO_3	H_2 consumed [ml(STP)/g.cat.]	Theor. H_2 for $MoO_3 \rightarrow MoO_2$	O_2 consumed [ml(STP)/g.cat.]	Theor. O_2 for $MoO_2 \rightarrow MoO_3$	"Extent of reduction"*
14.9	28.52	23.19	12.48	11.59	1.08
11.4	13.01	17.74	7.34	8.87	0.83
7.5	10.55	11.67	4.55	5.84	0.78
3.9	4.61	6.07	1.67	3.03	0.55

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*"Extent of reduction" ≡ O_2 consumed (actual)/O_2 consumed (theor.) = atomic ratio of actual O_2 consumed: total Mo in sample.

attributed to oxidation of irreversibly adsorbed hydrogen which is retained after evacuation at 500° or, alternately, to re-oxidation of any Mo that had been reduced beyond Mo^{IV}. These alternatives are not distinguished by the present redox experiments. The last column in Table 2 is the atomic ratio of oxygen consumed on 500° re-oxidation to total molybdenum in the sample; for any given sample, this ratio is taken as a measure of the extent of reduction of MoO_3 to MoO_2. The ratio is 1.08 for the 14.9% MoO_3 sample.

The situation is different for the samples with lower loading of MoO_3. For the 11.4% MoO_3 sample, the total H_2 uptake is still slightly in excess of the theoretical for $MoO_3 \rightarrow MoO_2$, but the subsequent O_2 uptake is significantly less than theoretical for $MoO_2 \rightarrow MoO_3$. The extent of reduction, calculated from O_2 uptake, is only 0.83 (Table 2). On the basis of this interpretation, the excess H_2 consumption [18.01 - 2(7.34)] for this sample is attributed to reversible H_2 adsorption accompanying the reduction process.

Measured in this way, the extent of reduction after 6 hours in flowing H_2 at 500°C is 0.78 for the 7.5% MoO_3 sample and 0.55 for the 3.9% MoO_3 sample. Whatever the reason may be for this incomplete reduction, it is plausible to associate the values for O_2 chemisorption at -78° (Figure 2) with the actual amount of reduced molybdena, rather than with the total MoO_3 loading as in Figure 2. Figure 3 is a re-plot of Figure 2 for the four samples listed in Table 2, where the abscissa for each point is not the MoO_3 loading in the unreduced catalyst, but that loading corrected for the extent of reduction given in the final column of Table 2. With the exception of one point, the values now fall almost on a straight line through the origin, suggesting a dispersion of the MoO_2 that is independent of loading.

The reason for incomplete reduction at low MoO_3 loading is unclear. Much has been made of the stabilization of MoO_3 by reason of chemical interaction

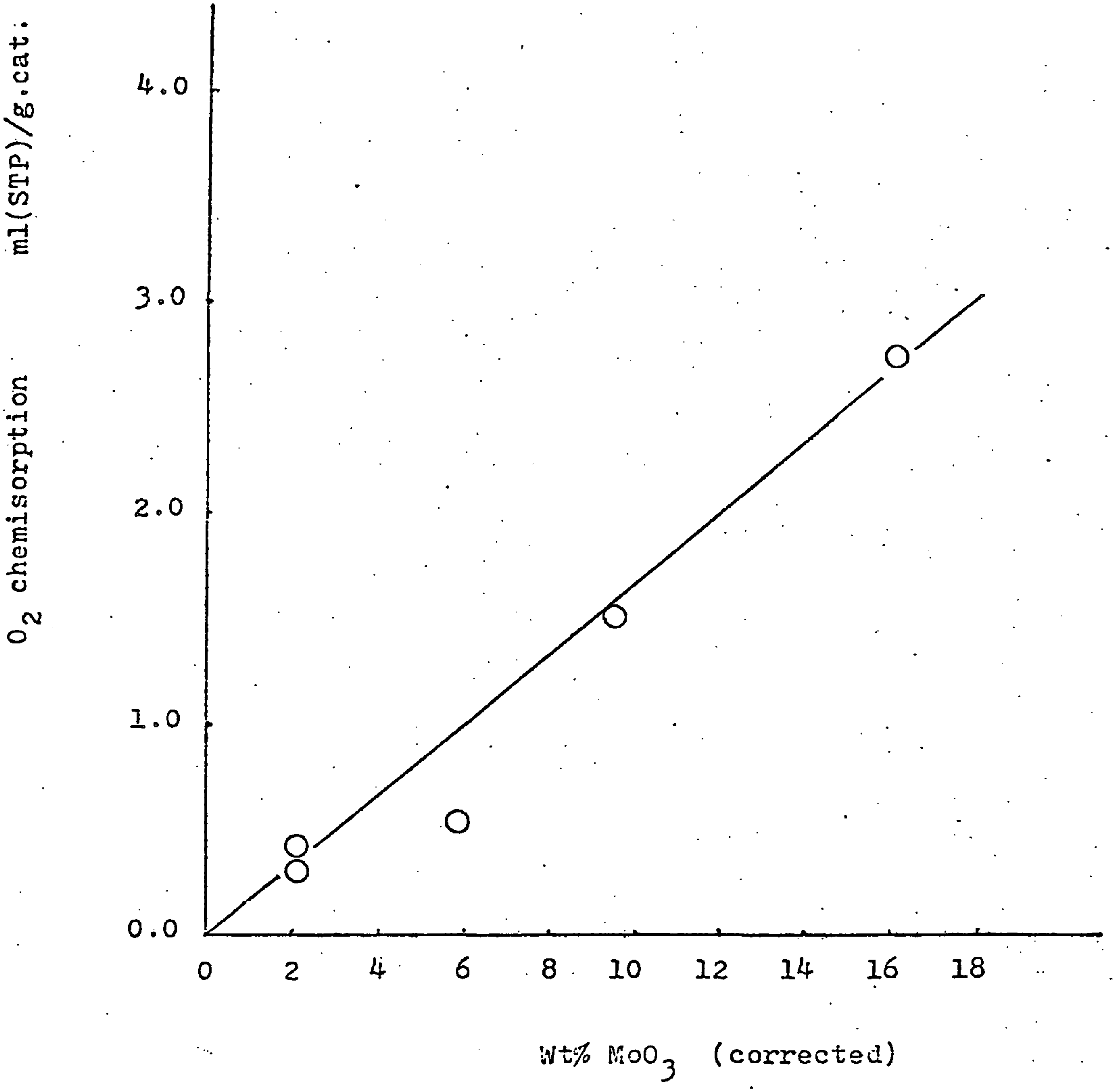

Figure 3 O_2 chemisorption vs. MoO_3 loading, corrected for extent of reduction with an Al_2O_3 surface. The data in Table 2 are compatible with this but imply a more complex model. Complete reduction (to MoO_2) is possible in 6 hours at 500°C with 15% MoO_3-Al_2O_3 but not with 11% MoO_3 or lower, although all the MoO_3 loadings should fall within the limits of monolayer coverage.

Differences in reduction behavior at low loading of MoO_3 on Al_2O_3 have been previously reported by Kabe et al. (3) and by Massoth (4); both followed the course of reduction gravimetrically. Kabe et al. studied loadings of 5%, 12.5%, and 27% MoO_3 at 550°C. Catalysts with lower MoO_3 reduced more slowly, but at 550°, in contrast, the 12.5% MoO_3 sampled appeared to be reduced to about MoO_2, even after 20 hours. Lower loading was not studied at 500°, and the sensitivity to temperature makes it difficult to compare our results with theirs. Massoth studied catalysts containing 2% to 25% Mo. A 10% Mo (15% MoO_3) catalyst was reduced to ca. MoO_2 in 2 hours at 500°C. However, the extent of reduction of a 6% Mo (9% MoO_3) catalyst was only ca. 0.50 after 2 hours at 500° (based on MoO_2; 0.17 based on reduction from MoO_3 to Mo), and the corresponding value for a 2% Mo (3% MoO_3) catalyst was ca. 0.20 (or 0.07, based on reduction to Mo). The data in Table 2 for 6 hour reductions are roughly compatible with those of Massoth.

Our sample of 3.9% MoO_3-Al_2O_3 was analyzed by a solution-titration method to confirm that the expected amount of Mo was present in the finished catalyst; it was. Another experiment was made to see if the low O_2 chemisorption (Figure 2) was simply the result of unusually slow reduction at 500°C. One sample of this material was subjected to the standard pre-reduction of 6 hours in flowing H_2 at 500°C and then used for O_2 chemisorption at -78°C. After the chemisorption, the same sample was again reduced for a second 6 hours in flowing H_2 at 500°C and again used for O_2 chemisorption at -78°C. The O_2 chemisorption value was the same after 12 hours of reduction as after 6 hours.

The catalytic activity of each MoO_3-Al_2O_3 catalyst was measured, after a 6 hour pre-reduction in flowing H_2, for the dehydrogenation of cyclohexane to benzene at 500°C. Figure 4 shows the activity (expressed as moles benzene produced per mole cyclohexane injected) for the pre-reduced samples, plotted against the gross composition (wt% MoO_3) of the samples before reduction. The curve is again concave upward, as in Figure 2. However, if correlation is sought not with gross composition but with MoO_2 content after reduction, it is more sensible to examine activity vs. O_2 chemisorption, taken as a measure of MoO_2 content (see Figure 3). Figure 5 is the plot of activity vs. O_2 chemisorption for the entire series of samples. Now the curve is convex upward; the correlation, though quite good, is not linear.

Recently Millman and Hall (5) have applied low temperature O_2 chemisorption for the assay of a MoO_3-Al_2O_3 catalyst of fixed MoO_3 loading but reduced to varying extents. Smooth correlations were found between amount of O_2 chemisorbed and extent of reduction, anion vacancy concentration, and catalytic activity for propylene hydrogenation. Their plot of hydrogenation rate vs. O_2 chemisorption was, like Figure 5, not quite linear; the range of O_2 chemisorption shown in their Figure 3 corresponded to extents of reduction from 0 to about 1.5 e/Mo (2e/Mo $\simeq$ MoO_2). It is not yet clear what relation the results of Millman and Hall bear to those in this paper. Since catalysts with different MoO_3 loading exhibit different reducibility (cf. Table 2), samples with a single loading but reduced to different extent are not necessarily comparable, even for like values of O_2 chemisorption.

Consideration of Figures 3 and 5 suggests that activity for cyclohexane dehydrogenation, for the samples studied here, may be associated with the amount of reduced molybdena (or equivalent MoO_2), the surface area of which can be estimated by O_2 chemisorption at low temperature. It is tempting to identify the catalytically active sites with Mo^{4+} species in the surface. The usual caution is in order, however: correlation does not necessarily imply causality. Activity, extent of reduction, and O_2 chemisorption may change in a parallel way,

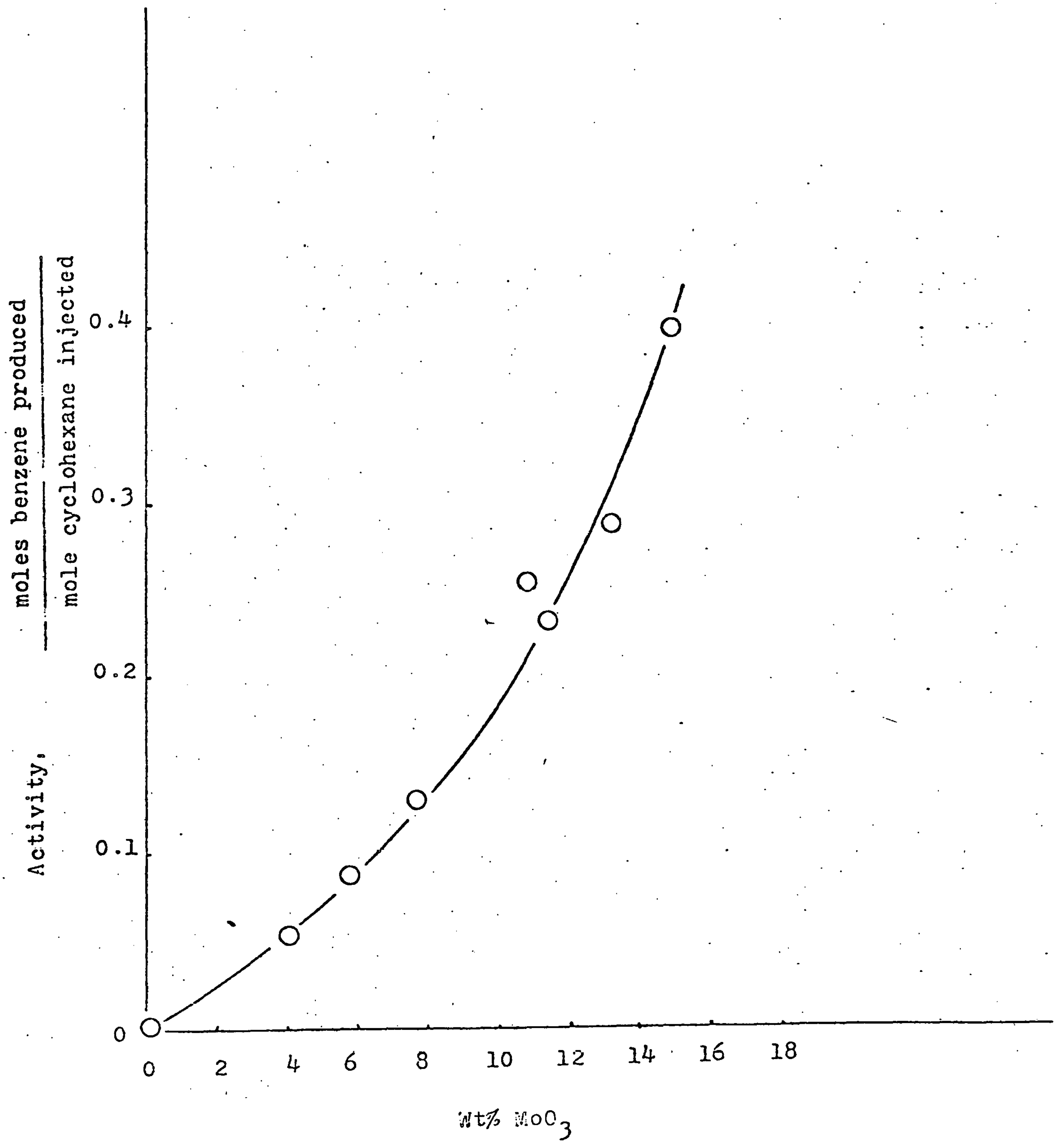

Figure 4 Activity of reduced MoO_3/Al_2O_3 vs. MoO_3 loading in unreduced catalyst

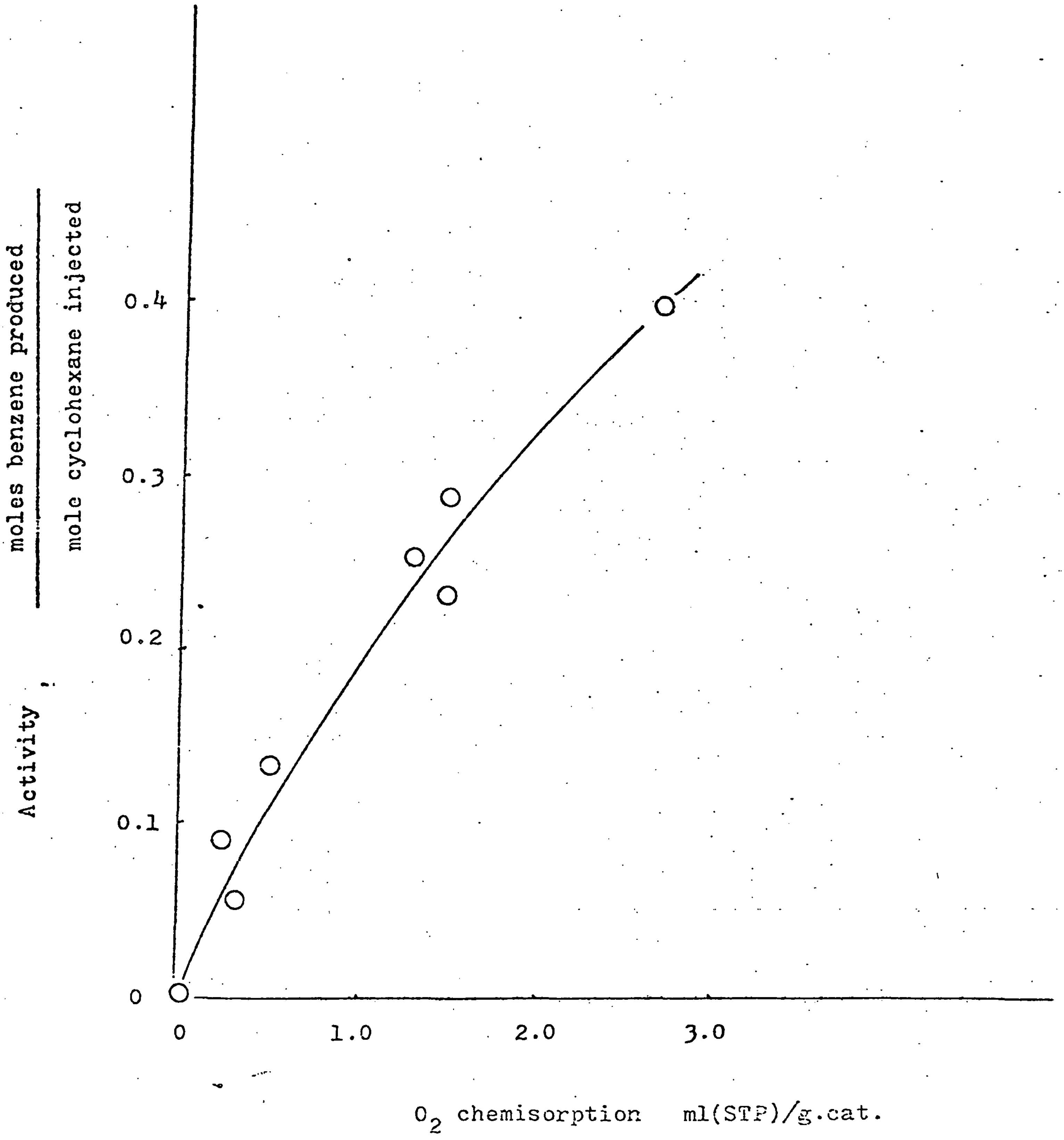

Figure 5 Activity and oxygen chemisorption of reduced MoO_3/Al_2O_3

but surface Mo^{4+} ions are not necessarily the sites responsible for dehydrogenation activity.

Measurements of O_2 chemisorption and BET surface area were also made on a group of $Co/Mo/Al_2O_3$ catalysts obtained from PETC. The catalyst designations and descriptions are summarized in Table 3. Table 4 lists the characterization of these samples, after presulfiding and reduction, for total (BET) surface area and O_2 chemisorption (at -78°C).

TABLE 3

Description of $Co/Mo/Al_2O_3$ Catalyst Samples

Sample No.	Description
1442A	American Cyanamid, as-received (A.R.)
XP-1	1442A, heat-treated at 725°C
SCR-4	1442A, used (103 hrs.), regenerated
SCR-6	XP-1, used without presulfiding (77 hrs.), regenerated
SCR-7	XP-1, used after presulfiding, regenerated

TABLE 4

Catalyst Characterization*

Sample No.	Surface Area (BET), m^2/g	O_2 Chemisorption, ml(STP)/g
1442A	229	2.04
XP-1	180	3.12
SCR-4	196	1.31
SCR-6	217	2.62
SCR-7	188	2.70

*All samples presulfided (15% H_2S-85% H_2, 2 hrs. at 500°C), reduced (H_2, 4 hrs. at 500°C), and evacuated (1 hr. at 500°C) before determination of O_2 chemisorption at -78°C. Surface area (N_2 at -195°C) determined immediately after O_2 chemisorption.

Autoclave screening tests (performed at PETC, Bruceton), in conjunction with the characterization data in Table 4, give interesting results in the comparison of 1442 (A.R.) and the heat-treated XP-1. In autoclave testing (coal + Panasol + catalyst, 30 minutes, 430°C), XP-1 shows higher conversion (THF solubility), higher asphaltene yield, and higher oil yield than does 1442A. The heat treatment at 725°C decreases total surface area and increases average micropore size. Oxygen chemisorption, which is taken as a relative measure of the (reductively sulfided) molybdena area, indicates that the available molybdena area is higher in the heat-treated catalyst than in the as-received sample. The higher initial liquefaction activity of XP-1, indicated by the autoclave tests, is also consistent with the initial behavior (up to ca. 10 hours on stream) of these catalysts in a continuous unit (Bruceton). Both the larger micropore diameter and the higher available molybdena area should contribute to the superior initial performance of XP-1 in liquefaction. For longer on-stream periods (t > 10 hours), 1442 (A.R.) becomes superior to XP-1. This "crossover" behavior is not predicted by the physical characterization data for the fresh catalysts and may be associated with accumulated metals poisoning in continuous operation. It is interesting (Table 4) that after regeneration, the XP-1 samples used in Runs SCR-6 and SCR-7 do not exhibit a marked drop-off in either BET surface area of O_2 chemisorption. By contrast, comparison of O_2 chemisorption for 1442 and SCR-4 shows a decline of ca. 1/3 after use (and regeneration).

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IV. Task No. 3: Role of Unsupported Catalysts.

There has been a recent resurgence of interest in iron pyrite as a coal liquefaction catalyst. The contemporary literature has been reviewed by Guin, et al. (1) and by Bickel, et al. (2). The fact that pyrite is a catalyst has been known for at least 30 years. Weller et al. (3) showed, for example, that the % liquefaction of Rock Springs, Wyo. coal under arbitrary conditions (3700 psi initial H_2 pressure, 1 hr., 450°C) is increased from 71% to 83% by the addition of 1% Fe as pyrite. Interestingly, "red mud" (Bayermasse) is at least equally effective and at least as inexpensive. Both were recommended for use.

In studies of the effect of catalyst distribution, Weller and Pelipetz (4) noted remarkable differences in the effectiveness of ferrous salts for the liquefaction of Rock Springs coal in the absence of added vehicle. A few of their results are extracted in the following table:

Catalyst	Mode of Distribution	% of maf Coal		
		Liq'n.	Asphaltene	Oil
None	----	33.4	2.8	10.4
$FeSO_4$ (1% Fe)	Powder	38.9	6.9	8.1
$FeSO_4$ (1% Fe)	Ball-milled w. coal	66.2	24.1	21.2
$FeSO_4$ (1% Fe)	Impregnated	84.9	38.9	21.7
$FeCl_2$ (1% Fe)	Impregnated	44.8	4.8	12.2
$FeBr_2$ (1% Fe)	Impregnated	50.4	7.7	17.9

Two major conclusions may be drawn from these data:

1. The catalytic effect of ferrous sulfate is enormously increased if it is brought into intimate contact with the ground coal by impregnation (from aqueous solution).

2. The catalytic effect is not a generic one of all ferrous salts. The halides are poor catalysts even when impregnated on the coal.

Although these conclusions from batch autoclave research were subsequently confirmed in continuous pilot plant studies (5), they have not been explained. A possible explanation could be that: (a) ferrous sulfate is reduced to ferrous sulfide under liquefaction conditions, (b) ferrous sulfide is a liquefaction catalyst but the ferrous halides are not, and (c) ferrous sulfide is a liquefaction catalyst only when intimately contacted with the coal. In the case of iron pyrite, it is already known (2) that reduction to ferrous sulfide (pyrrhotite) occurs rapidly at $T \geq 400°C$.

We have now done an experiment to check on the possible reduction of ferrous sulfate to ferrous sulfide. A mixture of 2g powdered $FeSO_4$ (nominally anhydrous) and 200 ml I-methylnaphthalene was charged to an autoclave equipped with glass liner, and the autoclave was filled with H_2 to an initial pressure of 1000 psia and then heated for 60 minutes at 450°C. After the autoclave was cooled, the contents of the liner were filtered, weighed, and subjected to x-ray diffraction analysis. The strongest x-ray lines, in order of decreasing intensity, were at d values of 2.07, 2.98, and 2.64 A. These correspond closely to the strongest lines reported (ASTM file) for pyrrhotite or troilite: 2.06 - 2.09, 2.97 - 2.98, and 2.65 - 2.67 A.

It thus appears that even in the absence of coal, ferrous sulfate is indeed reduced to ferrous sulfide under typical liquefaction conditions. The activity of both ferrous sulfate and iron pyrite as liquefaction catalysts is probably the result of a common reaction product, ferrous sulfide.

The tin-halogen acid-hydrogen sulfide catalyst system is an interesting one to study for coal liquefaction. It is a very efficient system, being effective at concentrations ≤ 1 %. The two catalytic functions--tin or tin sulfide as the presumed hydrogenation catalyst, halogen acid as the presumed splitting catalyst--can be studied separately, or they can be combined by the use of stannous chloride. Finally, Shibaoka and coworkers [Fuel <u>59</u>, 11 (1980)] have recently made substantial progress in clarifying the fate of stannous chloride when it is used as the catalyst in liquefaction of dry, powdered coal.

Using optical microscopy and scanning electron microscopy (with an energy-dispersive x-ray analysis system), Shibaoka et al. have followed changes in morphology of the Sn catalyst, as well as the distribution of Sn, Cl, and S in hydrogenated vitrinite. Both Sn and Cl penetrate the coal early, to differing depths. Under some conditions, the $SnCl_2$ is reduced to globules of metallic tin, and these in turn act as a sulfur scavenger so that SnS is finally formed as a crystalline phase. Sometimes stannic oxide (SnO_2) is formed, which is surprising. Long ago, it was claimed that under normal autoclave conditions, SnS would be the stable catalyst phase in the liquefaction of a typical Eastern bituminous coal [Weller, unpublished calculations, 1949; Weller and Pelipetz, Proc. IIIrd World Petrol. Cong., 1950]. If this is true, how are we to understand the occasional formation of metallic tin and of stannic oxide? A partial answer to this question may be sought in the thermodynamic data for bulk phases of the several tin compounds of interest. These are $SnCl_2$, SnS, and SnO_2.

As an example, we may consider the reaction $SnCl_2(\ell) + H_2(g) = Sn(\ell) + 2HCl(g)$. In $SnCl_2$ and Sn are immiscible condensed phases and if gas nonideality is neglected, then the equilibrium constant is

$$K(T) = \left.\frac{p^2_{HCl}}{p_{H_2}}\right|_{equil.}$$

Under actual reactor conditions, p_{HCl} and p_{H_2} have some actual values which are not dictated by equilibrium considerations. If the ratio of actual partial pressures is defined as a quantity R_{act}, where

$$R_{act} \equiv \left.\frac{p^2_{HCl}}{p_{H_2}}\right|_{actual},$$

then the reduction by H_2 of $SnCl_2(\ell)$ to $Sn(\ell)$ will be thermodynamically (not necessarily kinetically) favored provided the condition $R_{act} < K(T)$ is satisfied. If $R_{act} > K(T)$, the reduction will not occur.

Similar calculations may be made for other reactions, which lead to the formation of SnS(c) or SnO_2(c). As will be discussed below, the calculations are subject to major uncertainties of two kinds: estimation of the actual partial pressures of HCl, H_2O, and H_2S; and disparity in the tabulated values of free energies of formation, particularly for $SnCl_2$ and SnS.

Table 1 summarizes the results of such calculations for five reactions. The values of K correspond to the best estimates of $\Delta G°$ for the several reactions at 400°C. The definition of R_{act} in each case corresponds to the same ratio of partial pressures as appears in the equilibrium expressions (for the K's), but with estimates of the actual values of partial pressures in the autoclave. As plausible, but arbitrary, values of the actual pressures, we employed p_{H_2} = 100 atm, p_{H_2S} = 0.2 atm, p_{HCl} = 0.02 atm, and p_{H_2O} = 10 atm.

The listed reactions were chosen to answer, serially, the questions:

1. Should $SnCl_2$ be reduced by H_2 to Sn under autoclave conditions?
2. Should Sn be sulfided by H_2S?
3. Should $SnCl_2$ be converted to SnS?
4. Should $SnCl_2$ be oxidized by H_2O to form SnO_2?
5. Should SnS be oxidized by H_2O to form SnO_2?

TABLE 1

Thermodynamic Considerations

No.	Reaction	K(400°C)	R^*_{act}
(1)	$SnCl_2(\ell) + H_2(g) = Sn(\ell) + 2HCl(g)$	3×10^{-5}	4×10^{-6}
(2)	$Sn(\ell) + H_2S(g) = SnS(c) + H_2(g)$	10^4	5×10^2
(3)	$SnCl_2(\ell) + H_2S(g) = SnS(c) + 2HCl(g)$	0.3	2×10^{-3}
(4)	$SnCl_2(\ell) + 2H_2O(g) = SnO_2(c) +]HCl(g) + H_2(g)$	2×10^{-3}	4×10^{-4}
(5)	$SnS(c) + 2H_2O(g) = SnO_2(c) + H_2S(g) + H_2(g)$	5×10^{-3}	0.2

*Assumed: $p_{H_2} = 100$, $p_{H_2S} = 0.2$, $p_{HCl} = 0.02$, $p_{H_2O} = 10$ [atm]

Inspection of the tabulated values for K and R_{act} shows that for the first four questions, the answer is, "Yes." This comparison of K and R_{act} says nothing about reaction kinetics, of course, but only that the reaction is thermodynamically feasible. For reaction (5) the answer is, "No." In fact, for all cases listed SnS(c) appears to be the thermodynamically stable phase, in agreement with the conclusions reached some 30 years ago. On the other hand, the production of metallic Sn and of SnO_2, by reaction of $SnCl_2$ with H_2 or H_2O, are feasible; it will be a matter of relative reaction rates whether or not these phases will actually be produced. These calculations at least rationalize the observations of Shibaoka et al.

The comparison of R and K values in Table 1 requires two caveats. First, the assumed values of actual partial pressures may be plausible, but they will differ in different experiments. Second, the free energies (and even heats) of formation are still uncertain for $SnCl_2$ and SnS. The chemical conclusions reached depend on the comparison of R and K, and in two cases, reactions (1) and (4), R and K differ by less than a factor of 10.

The uncertainty in thermodynamic data may be illustrated for $SnCl_2$ and SnS, key compounds in these calculations. Three recent compilations of thermodynamic data are (1) Bureau of Mines Bull. 605, 1963 [BM]; (2) NBS Tech. Note 270-3, 1968 [NBS]; and (3) Kubaschewski and Alcock, "Metallurgical Thermochemistry," 5th Ed., 1979 [K-A]. Table 2 shows the data for $\Delta H_f^\circ(298)$ and $\Delta G_f^\circ(298)$ from these sources for $SnCl_2(c)$ and SnS(c). The situation for $SnCl_2$ is astonishingly poor.

The calculated values of K(400°C) in Table 1 are uncertain to the extent that the free energies of reaction (ΔG_r°) are uncertain. The following tabulation shows the hazard of drawing rigorous conclusions from Table 1:

Uncertainty in $\Delta G_r^\circ(400°C)$	Uncertainty in K(400°C), factor of:
± 1 k cal	2.1
± 1.5	3.1
± 2	4.5
± 3	9.4

Table 2

Thermodynamic Data

Compound	$\Delta H_f^\circ(298)$	$\Delta G_f^\circ(298)$	S°(298)	Source
$SnCl_2(c)$	-81	(-71.6 est)	(34 est)	BM
	-77.7	--	--	NBS
	-79.1	--	(31.5 ± 1.5)	K-A
SnS(c)	-24	-23.5	18.4	NBS
	-25.9	-25.5	18.4	K-A

Thermodynamic calculations aside, autoclave tests have been carried out to examine the effects of $SnCl_2$, SnS, or SnS + NH_4Cl on the liquefaction of coal (West Virginia) in the presence of solvent and H_2. The initial charge was always 40 g coal, 161 g tetralin, 29.4 g naphthalene, and 1000 psia H_2; Sn compounds, where used, were kept at a constant loading of 5.3 wt% Sn based on coal. The mixed solvent was made up to minimize the extent of the reaction,

$$\text{Tetralin} = \text{Naphthalene} + 2H_2,$$

by starting with a T/N mixture close to that calculated for equilibrium under reaction conditions.

These autoclave tests were carried out for 50 minutes at 405 ± 2°C. Table 3 summarizes the principal results.

Table 3

Effect of Sn Catalysts at Coal Liquefaction Conditions
(Molecular Hydrogen Present)

	Run Number	16	14	19	21
	Catalyst Type	None	$SnCl_2$	SnS	SnS + NH_4Cl
(a)	Oil Production (wt% of maf coal)	37%	63%	37%	63%
	Coal Conversion (wt% of maf coal)	79%	71%	76%	82%
(b)	Hydrogen Atoms from $T \rightarrow N + 4[H]$	0.27g	0.18g	0.20g	0.31 g
(c)	$H_2(g)$ Consumption	0.44 g	0.82 g	0.56 g	0.70 g
(d)	Total Hydrogen Transfer (wt% of feed coal)	1.8%	2.5%	1.9%	2.5%

(a) $\frac{\text{wt. of oil in the solvent}}{\text{wt. of maf coal (35 g)}}$

(b) (Moles of T reacted) x 4

(c) (H_2 charged) - (H_2 discharged)

(d) $$\frac{\text{Hydrogen Atoms from } T \rightarrow N + 4[H] + H_2(g) \text{ Consumption}}{\text{wt. of feed coal (40 g)}}$$

In these experiments, "oil production" (Table 3) was based on a mass balance for the vehicle, which in turn was based on an HPLC analysis of tetralin, naphthalene, and fluorene (added as an internal standard). The "coal conversion" (of the organic matter in the coal to toluene solubles and gases) was calculated from an ash balance by the (previously used) formula,

$$x = 10^4 \, \frac{(1 - c/100)A - (a - b)}{A(100 - a)}$$

where

A = % ash in toluene insoluble (T.I.)

a = % ash in dry coal

b = weight of ash due to added catalyst per 100 g dry coal

c = weight of added catalyst in T.I. per 100 g dry coal

In the case of Sn catalysts, "coal conversion" was calculated under the assumption that the catalyst remaining in T.I. was in the form of SnS, and that subsequent ignition of the T.I. sample converted the sulfide to SnO_2. The ash from catalyst is 2.67 g based on 40 g of feed coal (containing 3 wt% moisture). Thus, on a basis of 100 g dry feed coal, the values are $b = c = 6.9 \; \frac{2.67}{40 \times (1 - 0.03)} \times 100$ for all catalytic runs. The "hydrogen atoms from T → N + 4[H]" was calculated from the HPLC analysis of tetralin (T) and naphthalene (N) in the reaction product and the amounts of T and N initially charged. The "H_2(g) consumption" was calculated from the G.C. analysis of H_2 in the gas product and the amount of H_2 initially charged. Finally, the "total hydrogen transfer" (wt% of feed coal) was derived from the sum of "hydrogen atoms from T → N + 4[H]" and "H_2 gas consumption."

Of particular interest in Table 3 are the catalyst effects on oil production and on total hydrogen transferred to coal, both from tetralin and from hydrogen gas. [Note: The total coal conversion values are high in all cases and somewhat erratic, possibly because the values are deduced from an ash balance.] The addition of SnS alone (Run 19) gives essentially the same results as no catalyst at all (Run 16). $SnCl_2$ (Run 14) produces a dramatic increase in oil, 63% of maf coal as compared with 37%, with an accompanying increase in total hydrogen transferred to coal, 2.5% vs. 1.8%. The combination of SnS + NH_4Cl (Run 21) is synergistic; the combination is equivalent to $SnCl_2$.

Two points may be noted:

1. The synergism exhibited here for SnS and NH_4Cl, in the presence of tetralin, qualitatively duplicates the same effect reported some decades ago (Weller, Pelipetz, Friedman, and Storch, Ind. Eng. Chem. 42, 330 (1950)), in experiments performed in the absence of added solvent.

2. The puzzle in understanding this result is as troubling today as it was in 1950. If, as indicated above in the discussion of thermodynamics, SnS is the stable phase under liquefaction conditions, how is one to interpret both the inactivity of SnS alone and the excellent results with SnS + NH_4Cl? When SnS is added as catalyst, one does not expect transient reduction to Sn metal (as Shibaoka has found for $SnCl_2$). In that case, the hydrogenating role postulated for Sn in the Sn - HCl combination (Weller, Clark, and Pelipetz, Ind. Eng. Chem. 42, 334 (1950)) has also to be attributed to SnS, which is certainly not known as a hydrogenation catalyst. This kind of question about the role of Sn catalysts in coal liquefaction remains unresolved.

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V. Task No. 4: Multifunctional Screening Tests

Methyl naphthalenes are major components of recycle process vehicles in coal liquefaction processes. It is important to understand their fate, especially in processes, like H-Coal, which employ a catalyst in the primary reactor. The claim is occasionally made that the primary function of such catalysts is simply to re-hydrogenate a depleted hydrogen donor solvent, i.e., to catalyze the ring hydrogenation of naphthalenic constitutes. This reaction is catalyzed, but others may be also.

The catalytic hydrotreating of methyl naphthalenes was reported by Ipatiev and Orlov in 1929 [1]. Preliminary results on the hydrotreating of 1-methylnaphthalene (1-MN) as a screening test for Co/Mo/Al_2O_3 coal liquefaction catalysts were published in 1979 by Brammer and Weller [2]. A single commercial catalyst was tested in a batch autoclave at 450° and 500°C. for three catalytic functions: ring hydrogenation (RHG), hydrodemethylation (HDM), and ring hydrocracking (RHC). At about the same time Patzer et al. at Gulf reported the use of 1-MN as a model compound for characterization of Co/Mo/Al_2O_3 catalyst in coal liquefaction [3]. Patzer et al. employed a steady-state flow trickle bed reactor for their studies.

This report presents batch autoclave results obtained with samples of eight Co/Mo/Al_2O_3 catalysts obtained from five catalyst manufacturers. For comparison, tests were also made with no catalyst and with stannous chloride, known to be an excellent coal liquefaction catalyst. Catalysts were tested at low concentration, 0.5 wt% based on 1-MN charge. Interpretation of the results is based on (1) analysis of the liquid product, (2) final pressure in the autoclave after cooling, and (3) analysis of the autoclave.

EXPERIMENTAL

The reaction was carried out in a one-liter stirred autoclave equipped with a glass liner. Runs 1 to 15 (Table 2) were made for 1 hour at 450°C. Runs 16 to 27 (Table 3) were made for 30 minutes at 500°C. The initial charge to the autoclave was 200g of 1-MN (1.43 moles), 1 g. of ground catalyst, and 1000 psi H_2 (cold). In the 450°C runs, all of the Co/Mo/Al_2O_3 catalysts were tested both in the as-received condition (oxide form) and after presulfiding with 15% H_2S - 85% H_2 for 2 hours at 450°C. The catalysts used in the 500°C runs were tested only after presulfiding. 1-MN was obtained from two sources, Eastman Kodak and Fisher Scientific; these differed somewhat in purity.

Table 1 summarizes the properties of the as-received Co/Mo/Al_2O_3 catalyst samples. The two Akzo Chemie catalysts (PA-23924 and 77-RAM-3) were experimental samples, specially made on Al_2O_3 supports differing in specific area by about a factor of two, but with the MoO_3 and CoO contents adjusted so the surface loadings (g MoO_3/m^2 of catalyst surface) were somewhat comparable.

At total of 15 runs was made at 450°C; 5 runs with as-received catalysts (oxide form), 6 with presulfided catalysts, 2 with reduced-only catalysts (oxide form), 1 with $SnCl_2$, and 1 with no catalyst. There were 11 runs at 500°C; 9 with presulfided catalysts, 1 with $SnCl_2$, and 1 with no catalyst.

The G. C. column used to analyze the liquid product was 1.5% OV-101 for runs 1-15, and 3% Dexsil 300 for runs 16-26.

RESULTS AND DISCUSSION

The runs are listed in Tables 2 and 3. Also listed for each run are the final (cold) pressure and the moles of CH_4 produced per 200 g 1-MN. Runs 14 and 15 differ in the time of pre-reduction in flowing H_2 at 500°C. Runs 17 and 18, runs 19 and 20, and Runs 21 and 22 differ in the purity of reactant, 1-MN (see below). Gas analyses are not presented, except for the CH_4 contents listed in Tables 2 and 3. Although C_2H_6 was detected in runs at 500°C, its amount was negligible, always below 0.02 mole. C_3H_8 or higher hydrocarbons were not present in measurable quantity in these runs.

The analyses of the liquid products are listed in Table 4.

Table 1

Properties of As-Received Catalysts

	Harshaw 0402T	Akzo PA-23924	Akzo 77-RAM-3	Cyanamid HDS-1442B	Cyanamid HDS-1441A	Ketjenfine 22434	Amocat 1A	Amocat 1B
%CoO	3.0	4.0	2.5	3.2	3.5	3.9	3.2	--
%MoO_3	15.0	11.5	8.1	16.0	14.5	11.8	16.2	14.9
%SiO_2	5.0	--	--	0.2	3.5	1.2	--	--
Surf. area, m^2/g	200	150	86	330	290	2 51	154	167
Pore vol., cc/g	0.4	0.5	0.55	0.8	0.61	0.52	0.47	0.51

Table 2 Summary of Runs, 450°C

Run No.	Catalyst	Pretreatment	P_f(psia)	CH_{4}(mole)
1	Akzo Chemie PA-23924	As-Received	635	0.09
2	Akzo Chemie 77-RAM-3	As-Received	700	0.08
3	Harshaw 0402T	As-Received	645	0.05
4	Cyanamid HDS-1441A	As-Received	675	0.06
5	Cyanamid HDS-1442B	As-Received	710	0.06
6	$SnCl_2$		925	0.17
7	None (Blank)		965	0.06
8	Harshaw 0402T	Presulfided	580	0.04
9	Akzo Chemie 77-RAM-3	Presulfided	545	0.05
10	Akzo-Chemie PA-23924	Presulfided	490	0.04
11	Cyanamid HDS-1442B	Presulfided	465	0.04
12	Cyanamid HDS-1441A	Presulfided	525	0.04
13	Ketjenfine 22434	Presulfided	490	0.06
14	Akzo Chemie PA-23924	H_2, 500°C, 2Hr.	645	0.06
15	Akzo Chemie PA-23924	H_2, 500°C, 6Hr.	505	0.05

Table 3 Summary of Runs, 500°C

Run No.	Catalyst	Pretreatment	P_f(psia)	CH_4(mole)
16	None (blank		955	0.31
17[a]	Harshaw 0402T	Presulfided	697	0.30
18	Harshaw 0402T	Presulfided	708	0.30
19[a]	Akzo Chemie 77-RAM-3	Presulfided	731	0.30
20	Akzo Chemie 77-RAM-3	Presulfided	749	0.32
21[a]	Akzo-Chemie PA-23924	Presulfided	728	0.31
22	Akzo-Chemie PA-23924	Presulfided	715	0.31
23	Amocat 1A	Presulfided	648	0.33
24	Amocat 1B	Presulfided	715	0.32
25	Cyanamid HDS-1442B	Presulfided	671	0.34
26	$SnCl_2$		900	0.37

a. 0.8% of unknown impurity in reactant 1-MN.

Table 4

Analyses of Liquid Product (Area %)

Run No.	Alkyl Benzenes	T	N	1-MT	5-MT	1-MN	X
1	1.0	1.2	3.9	7.9	11.0	75.0	--
2	0.9	1.0	4.0	6.7	8.5	78.9	--
3	0.7	1.1	3.7	7.8	11.6	75.1	
4	0.6	1.1	3.8	7.1	10.5	76.9	
5	0.4	1.0	4.1	6.3	9.3	78.9	
6	0.8	0.2	6.7	1.3	--	91.0	
7	0.2	--	4.9	--	--	94.9	
8	0.6	1.5	4.0	9.6	14.9	69.3	
9	0.5	1.4	4.6	8.7	13.4	71.4	
10	0.5	1.9	4.8	10.5	17.8	65.5	
11	0.8	2.2	4.5	10.8	19.2	62.5	
12	0.5	1.6	4.1	10.0	16.7	67.1	
13	0.5	1.9	5.7	10.2	17.7	64.0	
14	0.4	1.3	5.5	7.3	10.8	74.7	
15	0.9	1.9	4.6	10.6	16.1	65.9	
16	0.7	0.1	19.2	0.6	0.1	78.1	1.2
17	5.0	2.3	20.1	1.7	2.4	66.1	2.4
18	3.4	2.0	18.6	2.4	2.7	69.0	1.9
19	4.6	2.0	18.0	1.4	2.0	69.2	2.8
20	2.9	1.8	19.4	1.9	2.2	69.7	2.1
21	4.5	1.7	18.4	1.8	2.4	68.7	2.5
22	3.9	2.0	19.6	2.1	2.8	68.2	1.4
23	4.3	2.7	18.9	2.4	3.4	66.0	2.3
24	4.2	1.8	19.4	1.8	3.0	68.3	1.5

Table 4 - (con't)

Analyses of Liquid Product (Area %)

Run No.	Alkyl Benzenes	T	N	1-MT	5-MT	1-MN	X
25	2.7	3.2	18.8	3.6	2.6	66.8	2.3
26	0.3	0.2	23.4	2.3	0.2	73.4	0.2

KeyL T = tetralin, N = Naphthalene

1-MT = 1 methyltetralin   5-MT = 5 methyltetralin

X = 2 methylnaphthalene and compounds with retention time greater than that of l-MN

For simplicity, the contents of alkyl benzenes are lumped in the table. Minor constituents--l-methylindan, l-methyldecalin and 6-methyltetralin--were in the range 0-0.3% and are included with 5-methyltetralin.

The results shown in Table 4 have been summarized in Table 5 in order to bring out more clearly the extent to which three types of reaction were occurring: these are hydrodemethylation (HDM), ring hydrocracking (RHC), and ring hydrogenation (RHG). The sum of naphthalene and tetralin is taken as the measure of HDM; lumped alkyl benzenes are the measure of RHC; and the sum of tetralin and methyltetralins (principally 1- and 5-MT) is the measure of RHG.

In these autoclave experiments, which test only the initial activities of catalysts, differences were observed to be minor for all the $Co/Mo/Al_2O_3$ catalysts tested, provided that comparison was made at the same temperature (450° or 500°C) and for catalysts in the same form (oxide or sulfide). The values shown in Table 5 for HDM, RHG, and RHC are averages, therefore, for the group of $Co/Mo/Al_2O_3$ catalysts tested under comparable conditions.

The extent of HDM is small at 450°C and is very little affected by the presence of $Co/Mo/Al_2O_3$ catalysts. However, when the reaction temperature is raised to 500°C, the extent of HDM is increased by a factor of 3 to 4, although it is still not affected by the presence of $Co/Mo/Al_2O_3$ catalysts. Apparently the activation energy for splitting the methyl-aromatic bond is relatively large.

$SnCl_2$ was studied at both 450° (Run 6) and 500°C (Run 26), for comparison with $Co/Mo/Al_2O_3$. Although $SnCl_2$ is known to be a remarkably good catalyst for coal liquefaction, it is an extremely poor catalyst for the RHG of 1-MN at both temperatures. Whatever the chemical role of $SnCl_2$ may be in liquefaction, clearly it is not simply to re-constitute a depleted hydrogen donor solvent.

The extent of RHC to yield alkyl benzenes is small at 450° for all $Co/Mo/Al_2O_3$ catalysts. At 500°C the extent of HDM is about five times higher and the extent of RHC almost 7 times higher than at 450°C. This may reflect

Table 5

Reaction Summary

Run Nos.	T,°C	Catalyst	HDM	RHG	RHC
1-5	450	$Co/Mo/Al_2O_3$ (oxide)	5.0 ± 0.1	18.4 ± 2.0	0.7 ± 0.2
6	450	$SnCl_2$	6.9	1.5	0.8
7	450	None	4.9	--	0.2
8-15	450	$Co/Mo/Al_2O_3$ (sulfided)	6.2 ± 0.5	27.3 ± 4.1	0.6 ± 0.2
16	500	None	19.3	0.8	0.7
17-25	500	$Co/Mo/Al_2O_3$ (sulfided)	21.2 ± 0.8	6.9 ± 1.3	3.9 ± 0.8
26	500	$SnCl_2$	23.6	2.7	0.3

Key: HDM = hydrodemethylation = naphthalene + tetralin
RHG = ring hydrogenation = tetralin + methyltetralins
RHC = ring hydrocracking = lumped alkylbenzenes

the less favorable thermodynamics for hydrogenation of aromatics at the higher temperature, although the RHG is still far from bein equilibrium-limited [4].

The principal reaction at 450°C is ring hydrogenation of 1-MN to 1- and 5-methyl tetralin and of N to T. As a class, the sulfided catalysts are much more active for RHG than the oxides. This is shown in Table 5, by a comparison of the averages for Runs 8-15 with those for Runs 1-5. The RHG activity of the sulfided catalysts is, of course, important for the use of $Co/Mo/Al_2O_3$ catalysts in coal liquefaction processes.

An interesting difference exists in the ratio 5-MT/1-MT (in the liquid product) between catalysts tested at 450°C in the as-received, presulfided, or reduced-only condition. Tale 6 lists this ratio for the averages of all catalysts and for Akzo Chemie PA-23924, which was tested in all conditions. The ratio is related to the detailed stereochemistry of the catalyzed RHG reaction, about which too little is known to permit interpretation of such differences.

Table 6. Comparison of 5-MT/1-MT Ratio for
As-Received, Presulfided, and Reduced Runs (450°C)

	Average Ratio for Set of Runs	Ratio for Azko Chemie PA-23924
As-Received	1.38	1.34
Presulfided	1.66	1.69
Reduced	--	1.51

The effect of catalyst state on activity for ring hydrogenation is also well illustrated by the 450°C results with Akzo Chemie PA-23924. In the as-received oxide condition (Run 1), the extent of RHG was 20.1%. After presulfiding (Run 10), RHG was greatly increased to 30.2%. After H_2 reduction for the standard 2 hours at 500°C (Run 14), RHG was 19.4%, almost the same as the as-received sample. However, prereduction for 6 hours (Run 15) resulted in 28.6% RHG, approaching the value of the presulfided material.

Of the three catalytic functions studied, HDM does not result in a net pressure change (one CH_4 molecule produced per H_2 molecule consumed). RHG consumes 2 molecules of H_2 per molecule of methyl napthalene (or naphthalene) hydrogenated to methyl tetralin (or tetralin). RHC is more complex to interpret. Typical stoichiometry would be:

$$\text{1-MN} + 5H_2 \rightarrow \text{o-Xylene} + CH_4 + C_2H_6 \tag{1}$$

which results in a net consumption of 3 molecules of gas per molecule of 1-MN cracked.

It is plausible, therefore, to attempt to correlate pressure drop (or final cold pressure) with the sum of RHG + 3/2 RHC. Such a plot is shown in Figure 1 for the runs at 450°C and 500°C. The extrapolated intercept of both lines is ca. 1000 psia. The slope is about 15 psi/1% 1-MN converted by RHG and RHC at 450°C, and about 23 psi/1% 1-MN converted at 500°C.

The interpretation of the slope may be checked by an a priori calculation. The net gas volume of the autoclave, with glass-liner and 1-MN in place is ca. 700 cc. At the initial pressure of 1000 psia, the initial charge of H_2 is 1.98 moles. If 1% of the initial charge of 1-MN (1.43 moles) undergoes RHG, the theoretical pressure drop should be $\frac{(0.01 \times 1.43 \times 2)}{1.98} \times 1000 = 14.4$ psi. This value is in good agreement with the observed value, 15 psi/% 1-MN, for the runs at 450°C where RHG is the predominant reaction. However, the observed slope is higher at 500°C, in spite of the attempted correction for RHC. Two possible sources may be suggested for the discrepancy. One is the use of area percent instead of mole percent in the G.C. analysis of mixed alkyl benzenes and unknown peak (see Table 4); the other is that the stoichiometry for RHC may be more complex than that indicated by Equation (1).

Comparison of these batch autoclave results with those of Patzer et. al. [3] for a trickle bed reactor is interesting. Patzer et al. employed lower temperatures (316° - 399°C) and much longer equivalent contact times (space velocity roughly 100 times lower, in units of mass of feed per mass of catalyst per unit time) than those used in the autoclave experiments. In the trickle bed reactor HDM was the primary reaction, with sequential hydrogenation of the product naphthalene to tetralin and then to decalin; no methyl tetralins were observed. It is not known to what extent HDM was uncatalyzed in the flow reactor, since a control run without catalyst was not reported. The autoclave experiments indicate that $Co/Mo/Al_2O_3$ has little effect on HDM; it is possible that the combination of low temperature and low space velocity in the trickle bed study may account for the relatively rapid (possibly uncatalyzed) HDM and relatively slow (catalyzed) RHG that were observed. Patzer et al. also reported that within the temperature range studied, tetralin production decreased with increasing temperature above about 340°C. This is qualitatively consistent with the autoclave results showing less RHG at 500°C than at 450°C.

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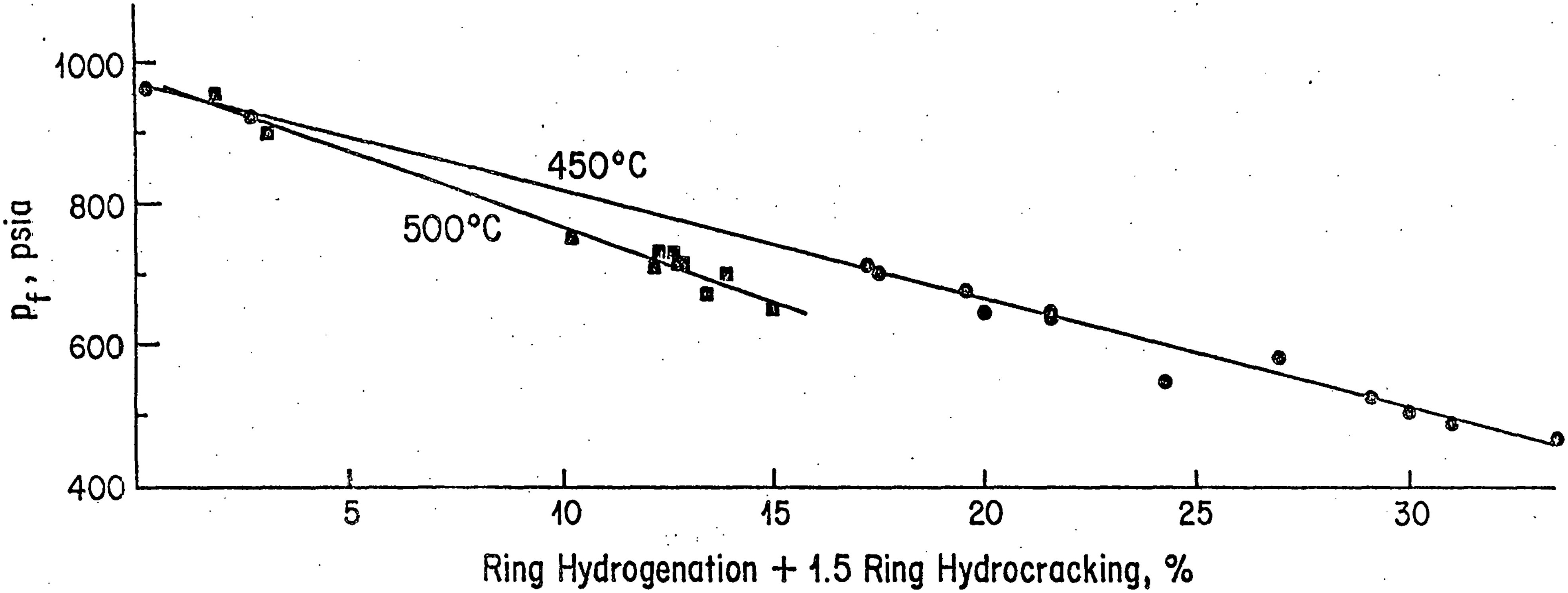

Figure 1.

Correlation of Autoclave Pressure with Conversion of 1-Methylnaphthalene