

Evaluation of Catalysts for Hydrodesulfurization and Liquefaction of Coal

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INTRODUCTION

A novel process called the Synthoil process is being developed by the Bureau of Mines for converting coals into low-sulfur nonpolluting fuel oil by hydrodesulfurization (HDS). Development of the process to commercial scale would provide electric power plants with clean fuel derived from abundant high-sulfur coals presently unacceptable as fuels because of air quality standards.

In the Synthoil process, coal slurried in recycle oil is transported by a high-velocity, turbulent-flow of hydrogen through a reactor containing a fixed-bed of pelleted catalyst (1).¹ The coal reacts with hydrogen and probably with hydrogen donor compounds and is rapidly liquefied and desulfurized in a single stage. Reactions occur in the liquid phase, but the mixture also includes a gas phase and both organic and inorganic solid phases. High turbulence in the reactor serves to minimize the influence of interparticle mass transfer on reaction rates, while short reaction times and the moderate temperatures used tend to keep hydrogen consumption at a minimum.

Much work has been done recently on catalysts for coal hydroliquefaction and desulfurization, particularly on catalysts used in an ebullated or highly fluidized state. However, most of the work has been proprietary and there are no published data that would assist researchers in the selection of the best existing catalysts or guide the way to the design of new catalysts. This study was undertaken to provide a basis for selecting the best catalyst for use in the Synthoil process. Catalysts were prepared by impregnating commercial supports with compounds of metals known to be active in coal hydrogenation. These and a number of commercial HDS catalysts were then tested in a batch nonflow reactor to evaluate compositions and physical properties with regard to activities for coal conversion to oil and sulfur removal.

EXPERIMENTAL

Hydrogenation Feed Stocks

Pittsburgh-seam high-volatile A bituminous (hvab) coal from the Bureau's experimental mine at Bruceton, Pennsylvania was used in most hydrogenation tests of catalyst activities. One test was made with Indiana #5 hvbb coal. Both coals were pulverized to minus 60 mesh, and the hvab coal was dried in air at 70° C for 20 hours prior to use. As shown in table 1, sulfur contents of the coals were 1.1 and 3.5 percent by weight for the hvab and hvbb coals, respectively. About 60 percent of the sulfur in both coals was organic.

Also shown in table 1 are analyses of topped high-temperature coal tar used as a vehicle oil in hydrogenation experiments. The tar was produced in a commercial slot-type coke oven and consisted of about 15 percent by weight of material insoluble in benzene and 85 percent of benzene-soluble oil (asphaltene plus pentane-soluble oil).

¹ Underlined numbers in parentheses refer to the list of references at the end of this report.

Catalyst Descriptions and Preparation

Screening tests were made with five commercial catalysts and with 74 catalysts prepared by impregnating 17 commercial supports with compounds of Mo, Sn, Ni, Co, and Fe both singly and in combination. In addition, one catalyst was prepared by impregnating Sn on a commercial Co-Mo catalyst.

Descriptions of all catalysts used are given in table 2. Most of the support analyses are manufacturer's data whereas most of the surface areas and pore volumes listed were determined at this laboratory. Surface areas were measured by the BET method using low-temperature nitrogen. Pore volumes of supports were determined by a water retention method, and pore volumes of commercial catalysts were determined by low-temperature adsorption of nitrogen. Pores measured by these methods have diameters above 10 to 14 Å. Average pore diameters were calculated from pore volume and surface area data by determining the diameter of a cylinder having the indicated volume and area. Physical properties of impregnated catalysts listed in table 2 are values for supports before addition of metallic hydrogenation components.

Commercial catalysts tested included two Co-Mo and two Ni-Mo catalysts on alumina supports. A fifth commercial catalyst consisted of Fe on alumina. All had high surface areas and relatively small pores.

Support materials were selected so as to cover wide ranges of compositions, areas, and pore volumes in order to evaluate these properties. Alumina contents were 3.1 to 99.3 percent and silica contents were 0.1 to 96.0 percent. Three contained silicon carbide as the principal component. The supports could be classified as either high-surface area (55 to 425 m²/g) or low-surface area (0.04 to 1.23 m²/g) materials.

Metal compounds used in impregnations were (NH₄Mo₇O₂₄·4H₂O, SnCl₂·2H₂O, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, and FeSO₄·7H₂O. When impregnating a single component, the required amount of metal compound was dissolved in a solvent, and the solution was added dropwise to 200 to 300 g of predried support while stirring constantly under a nitrogen atmosphere. Mo, Ni, Co, and Fe compounds were dissolved in water while stannous chloride was dissolved in aqueous ethanol. Solution volumes equalled support pore volumes plus a several percent excess to allow for handling losses. An impregnation was completed by drying the catalyst to constant weight at 70° C under nitrogen.

Co-Mo catalysts 78, 79, 80, 81, and 82 were prepared by the same single impregnation method using a solution containing both Co and Mo. Following impregnation, catalysts 79 and 81 were calcined in air at 600° C for about 8 hours.

Sn and Mo in catalysts 83 and 84 were impregnated stepwise. In preparing 83, the procedure consisted of adding ammonium molybdate and drying, then adding stannous chloride in aqueous ethanol and re-drying. Catalyst 84 was prepared by a three-step procedure. One-third of the Sn in dilute aqueous HCl and one-third of the Mo in water were combined and added to the support. After drying, the procedure was repeated two more times.

All catalysts except 2 and 10 were presulfided in the batch hydrogenation reactor (before charging with coal and vehicle oil) for 4 hours at 260° C with a gaseous mixture that initially was composed of 15 percent H₂S and 85 percent H₂. Sulfiding of single component catalysts averaged more than 90 percent of amounts needed to form MoS₂, SnS, NiS, CoS, and FeS. The average for multi-component catalysts was more than 75 percent. Actual forms of metal sulfides were not determined.

Hydrogenation Equipment and Procedures

The hydrogenation reactor was a 1.2-liter batch autoclave that was placed in a horizontal position and rotated during an experiment. A detailed description of the vessel and accessory equipment has been published (2).

Charges were contained in a glass liner that fitted closely to the autoclave wall. The charge in most experiments was 50 g of coal, 75 g of tar, and 50 cc of catalyst. A constant catalyst volume was used so that the fluidity of the catalyst-reactant mixture and, hence, the degree of mixing would be nearly the same in all experiments. In addition, catalyst external surface areas would not differ greatly. The amount of catalyst 2 charged was 25 cc, and in experiments with catalysts 79 and 81, charges consisted of 25 g of coal, 37.5 g of tar and 25 cc of catalyst.

After charging, the autoclave was purged of air and pressurized to about 1,900 psi with electrolytic hydrogen from commercial cylinders. Hydrogen charge weights which averaged 9.8 g were determined from prior calibrations of hydrogen weight vs charge pressure for the autoclaves used. Rotation was started and the autoclave was heated to 400° C in about 55 minutes. Pressure increased to about 4,000 psi. After 30 minutes at 400° C, the autoclave was cooled to room temperature at a somewhat slower rate.

Gases were depressurized, scrubbed to remove CO₂ and H₂S, metered and analyzed. Light oil and water were then removed by vacuum distillation to about 110° C and 2 to 3 mm of Hg. Solids and higher-boiling liquids remaining in the autoclave were washed out with benzene and separated by hot benzene extraction into insoluble and soluble fractions. Insolubles were further separated by screening into a fraction of fines consisting mostly of coal- and tar-derived solids and a fraction consisting of pellets of used catalyst. Fines included small but undetermined amounts of catalyst, while the pellets contained coal- and tar-derived solids in their pores in amounts up to about 15 percent depending on the porosity of the catalyst. Benzene solubles were separated into fractions insoluble and soluble in n-pentane. Both fractions of solids and all organic liquid fractions were analyzed for sulfur. The weight of organic benzene insolubles in the fines was calculated as the difference between the weights of the fines and ash in the fines. An estimate of the weight of organic benzene insolubles in used catalyst pellets was made on the basis of the carbon and hydrogen content of the pellets.

An autoclave was weighed on a bullion balance to within + 0.1 g before charging with hydrogen, after depressurizing, and after vacuum distilling. From these weighings and known weights of all materials charged, accurate weights for groups of products were determined as follows: (1) Gases and vapors depressurized, (2) vacuum distillate, and (3) solids and heavy liquids. Actual recoveries were adjusted (normalized) to correspond to the weights of these groups of products by assuming that losses (or gains) in each group of products were distributed among the components of that group in the same proportions as actual recoveries. Adjustments made to normalize recoveries averaged about 2 percent of the total charge.

In the hydrogenation data shown in table 3, product distributions are expressed as weight-percent of moisture- and ash-free (maf) charge. Organic benzene insolubles are the sum of organic insolubles in the fines and in the used catalyst. Asphaltene is oil soluble in benzene but insoluble in pentane. The pentane-soluble oil in table 3 includes pentane-soluble oil recovered in the benzene extraction step and light oil recovered by vacuum distillation, while benzene-soluble oil is the sum of asphaltene and pentane-soluble oil. Conversion of organic benzene insolubles is the difference between organic benzene insolubles charged (maf coal plus insolubles in the tar) and organic benzene insolubles recovered expressed as percent of organic benzene insolubles charged.

Results for seven of the experiments listed in table 3 are average values of duplicate tests. Average differences in yields of benzene-soluble oil in these duplicates was 2.3 percent and the sulfur contents of the oils differed by an average of 0.04 percent.

RESULTS AND DISCUSSION

Of primary interest in hydrogenation tests were catalyst activities for coal liquefaction as measured by oil production and for desulfurization as indicated by the sulfur content of the product oil. The total amount of sulfur removed was the preferred indicator of desulfurization activity but total sulfur removal from coal and tar could not be determined accurately. Coal- and tar-derived solids and the used catalyst both contained sulfur and it was not possible to clearly distinguish between the two. Coal conversions were not reported but can be estimated from the hydrogenation results shown in table 3 by assuming there was no conversion of insolubles in the tar. This assumption is probably justifiable for most experiments by results of batch experiments made with tar and an active Co-Mo catalyst in the absence of coal at 4,000 psi and 425° C. Conversions of insolubles were negligible.

The mild conditions used in this study (30 minutes at 400° C) were chosen so that moderate levels of liquefaction and desulfurization would be obtained with good catalysts, and consequently higher as well as lower activities of other catalysts could be readily discerned.

The feed composition provided one of the base comparison points needed for evaluation of hydrogenation results. When Pittsburgh coal was used, the maf feed contained 52 percent benzene-soluble oil (hereafter called oil) that originated with the tar used as vehicle oil. This oil contained 0.56 percent sulfur, while the total maf feed contained 0.64 percent sulfur.

As shown by the hydrogenation results of the first experiment in table 3, some HDS occurs without an added catalyst. The oil yield of 60 percent represented a net production of 8 percent, and the oil contained 0.06 percent less sulfur than oil in the feed. Total sulfur removal was 24 percent. These results provided a second set of base data for comparison purposes.

Commercial Catalysts

The most effective pelleted catalyst tested based on activities for both oil production and desulfurization was catalyst No. 1, a silica-promoted Co-Mo on alumina (Harschaw 0402T).² Oil containing 0.15 percent sulfur was produced in a yield of 80 percent. Estimated coal conversion was 78 percent. After these results were obtained, the objective in developing new catalysts became one of trying to get results superior to those obtained with 0402T. Catalyst 0402T has been used in all recent Synthoil pilot plant experiments. Catalyst 2 consisted of 25 cc of 0402T or half the standard charge. The experiment with catalyst 2 showed that there was a response to a change in catalyst concentration between 25 and 50 cc and indicates that 50 cc probably does not constitute an excess of catalyst.

The effect of presulfiding 0402T can be seen by comparing results with catalyst 1 and catalyst 3 which was not presulfided. Catalyst 3 was considerably less effective and, hence, presulfiding is clearly desirable in batch tests. Apparently in-situ activation does not occur quickly enough to reach maximum activity in a batch reactor where only the initial activity can be tested. In continuous flow experiments with a fixed bed of catalyst, presulfiding was found to be detrimental to steady state catalyst activity (3).

² Reference to specific brands of materials is made for identification only and does not imply endorsement by the Bureau of Mines.

Catalyst 4 consisted of Co-Mo 0402T pulverized to minus 200 mesh before presulfiding. The use of smaller catalyst particles resulted in increased sulfur removal and a small but possibly insignificant increase in oil production. This effect of a decrease in catalyst particle size indicates the desulfurization reaction is retarded or possibly controlled by intraparticle diffusion. This result is entirely reasonable in view of the numerous instances of diffusion retardation reported in HDS studies of high-molecular weight petroleum fractions (4). It was found, for example, that in the HDS of residual oils in an ebullating bed reactor, decreasing the size of catalyst particles increased the rate of desulfurization (5). However, the use of small catalyst particles to lessen diffusion retardation in a fixed-bed reactor such as is used in the Synthoil process would be impractical because of the resultant higher pressure drop across the bed and the increased risk of flow and temperature control problems.

An experiment was made with catalyst 0402T (No. 5 in table 3) to determine its effectiveness for HDS of a high-sulfur coal--Indiana #5 hvbb coal containing 3.4 percent sulfur. The catalyst proved to be highly effective for liquefaction and desulfurization in the batch reactor, and later was found to be very effective in the HDS of the same coal in a continuous-flow fixed-bed reactor (6).

Commercial HDS catalysts 6 (Co-Mo), 7 (Ni-Mo), and 8 (Ni-Mo) were as effective as catalyst 0402T for desulfurization, but catalyst 0402T produced 12 percent more oil than catalyst 6, and 3 percent more than the Ni-Mo catalysts. Even though the Ni-Mo catalysts were somewhat less effective than catalyst 0402T in these batch tests, final selection of one for use in a large scale Synthoil plant would depend on their aging and regeneration characteristics. Catalyst 9 (Fe on alumina) was moderately active for oil production but ineffective for sulfur removal.

High-Surface Area Impregnated Catalysts

Supports for catalysts 10 through 30 were three high-surface area aluminas containing small amounts of silica. The test with catalyst 10, which consisted of UOP alumina without an added hydrogenation component, showed that high-surface area alumina has no activity. Results were virtually the same as in the experiment with coal and tar alone (first experiment in table 3). In experiments with 5 percent Mo, Sn, Ni, Co, or Fe impregnated on these aluminas, there were no differences in results that were clearly attributable to the support properties shown in table 2. The results did show that when these metals are used as single components on high area aluminas, Mo is the best catalyst for sulfur removal and Sn is the best catalyst for the conversion of coal to oil. Fairly high oil yields were also obtained with Mo and Ni.

Mo and Sn concentrations were investigated with catalysts 11-16, 20, and 21 using 1, 5, and 10 percent on UOP and ALCOA H-151 aluminas. As the Mo concentration was increased, the desulfurization activity also increased but did not approach the activity of catalyst 0402T. Higher levels of desulfurization could probably be obtained with higher concentrations, but with 14 percent or more of Mo, complete coverage of the support surface with a monolayer of MoS_2 could occur with consequent loss of any catalytic contribution of the surface toward sulfur removal. Oil production increased with increasing Mo concentration to 5 percent, but a further increase was of no benefit. Sn catalysts were highly effective for oil production at all concentrations used, but desulfurization activities were poor and decreased as the Sn concentration increased. Supported Mo or Sn used as single components do not appear to be promising coal HDS catalyst candidates.

Catalysts 31 and 32 contained 5 percent Mo on silica-alumina supports that had the same composition but wide differences in surface areas (80 and 425 M^2/g) and some differences in pore volumes and average pore diameters. Hydrogenation results with

these catalysts were similar indicating little or no effect of their differences in physical properties. However, desulfurization activities of these silica-alumina-supported catalysts were lower than activities of alumina-supported catalysts containing 5 percent Mo.

Low-Surface Area Catalysts

Supports for catalysts 33-77 all had low surface areas. They had widely different compositions, pore volumes that ranged from 0.07 to 0.56 cc/g, and average pore diameters that were two to three orders of magnitude larger than those of the high-surface area supports. Whereas all high-surface area catalysts contained less than the amounts of metals needed for a monomolecular layer after sulfiding, the low-surface area catalysts (except for No. 42) contained metals in amounts that could provide from 50 to 1500 layers of metal sulfides. It is therefore likely that in experiments with the low-surface area catalysts, support surfaces were completely covered and had no catalytic or promotional effect on reactions.

Catalysts 33-41 contained 5 percent of impregnated metals. Although their desulfurization activities were very poor (catalyst 34 may be an exception), high oil yields of 80 to 84 percent were obtained with three of the catalysts. This is evidence that a high level of activity for oil production requires neither a high-surface area catalyst nor the availability of a support surface. On the other hand, the low levels of sulfur removal indicate that a high activity for desulfurization may require (in addition to the metal component surface) access to the support surface or a high area or both.

Catalysts 43-77 were impregnated with 1 percent of the metal components. Support combinations AELT-AEHT, SELT-SEHT, and CELT-CEHT were pairs having identical compositions but differing in areas and porosities. Comparisons of hydrogenation results with supports having the same compositions showed no consistent trends attributable to differences in areas or porosities. The most significant features of the experiments were the consistently high yields of oil obtained with Sn catalysts and the low average level of desulfurization with all metal components. Oil yields of 80 percent were obtained in two experiments with Sn catalysts. Thus, in addition to not requiring high surface areas, high metal concentrations are also not required for high coal conversions when Sn is used.

To determine whether the desulfurization activity of a low-surface area catalyst would increase if the support surface was not completely covered, catalyst 42 was prepared using less than 0.002 percent Mo. Fractional coverage of the surface of catalyst 42 was approximately equal to that of catalyst 12 containing 5 percent Mo on UOP alumina. Catalyst 42 was ineffective for oil production but was apparently more active for sulfur removal than catalyst 43 which contained 1 percent Mo on the same support. In fact the 0.36 percent sulfur in the oil was lower than the sulfur content of oil obtained with any low-surface area catalyst containing 1 percent of metal. This result strongly suggests that Mo-catalyzed desulfurization reactions of coal are promoted by the surface of an acidic support. The result is consistent with findings in several recent studies of the mechanism of HDS of thiophene compounds wherein it was reported that the reactions include steps occurring at acid sites on catalyst surfaces (4).

Multicomponent Catalysts

The effectiveness of UOP and H-151 aluminas as supports for Co-Mo catalysts was investigated with catalysts 78-81. These contained Co and Mo in the same percentages as catalyst No. 1 (0402T). Catalysts 78 and 80 were not calcined before sulfiding and were less active than catalyst 1. Catalysts 79 and 81 were calcined

before sulfiding but were otherwise identical to 78 and 80, respectively. Both of the calcined catalysts showed higher activities for oil production but only 79 showed improved desulfurization activity. Activities of 79 were virtually equal to those of catalyst 1 indicating that the UOP alumina is highly suitable as a support. Calcination is widely recognized as a beneficial activation step for HDS catalysts and is generally a part of commercial preparation procedures. Activity increases presumably are the results of improved dispersions of Co and Mo and interactions of Co, Mo, and the support that occur during calcination. Structural studies have indicated that Mo becomes distributed in a monolayer and that part of the Co is converted to a form comparable to that in CoAl_2O_4 . In a recent investigation using electron spin resonance spectra, it was reported that this form of Co persists even after sulfiding (7).

Catalyst 82, containing 2.4 percent Co and 10 percent Mo on a low-surface area support, was ineffective for coal liquefaction and only moderately active for desulfurization. Hydrogenation results with this catalyst showed that the amounts and proportion of Co and Mo used are not the only properties that determine the desulfurization activity of Co-Mo catalysts. The experiment provided additional evidence that a high surface area and accessibility of the support surface may also be important.

Catalysts 83 and 84 were prepared to investigate combinations of Sn and Mo, the best metal component for liquefaction and the best metal component for desulfurization when used singly. The support was a high-surface area alumina. Procedures used in preparing 83 and 84 differed but caused no significant differences in hydrogenation results. Both catalysts produced oil in the high yields obtained when Sn was used alone, but less sulfur was removed than when Mo was used alone. Catalysts 83 and 84 offered no overall advantage.

Catalyst 85 represented an attempt to increase the liquefaction activity of Co-Mo catalyst 0402T by addition of 5 percent Sn. The activity of catalyst 85 for oil production was equal to that of Sn when used alone, but the addition of Sn decreased the activity of catalyst 0402T for sulfur removal. Final assessment of the Sn-Co-Mo combination will require experimentation with other compositions and preparation procedures.

SUMMARY

Based on activities for both liquefaction and desulfurization of coal, the best catalyst tested in this batch study was a commercial high-surface area silica-promoted catalyst containing 2.4 percent Co and 10 percent Mo on an alumina support. This catalyst has been used in all recent experiments in the Bureau of Mines' Synthoil pilot plant. The increased desulfurization that resulted when this catalyst was pulverized indicated that the sulfur removal reactions were diffusion hindered.

Experiments with Mo, Sn, Ni, Co, and Fe impregnated as single components on high- and low-surface area supports showed that Mo catalysts were best for sulfur removal and Sn catalysts were best for conversion of coal to oil. Single component catalysts did not appear to be promising for combined liquefaction and desulfurization.

Maximum desulfurization activity apparently requires a high-surface area catalyst and results from a combination of the catalytic activity of supported metal components and the promotional effect of the support surface. High desulfurization activities were achieved only when less than a monolayer of metal component was deposited on the support. Even with a low-surface area support, the application of less than a monolayer increased the desulfurization activity.

A high surface area or high metal concentration is not essential for high conversions of coal to oil. High oil yields were obtained with several low-surface area catalysts, and, in the case of Sn, with only 1.0 percent of supported metal component.

Sn-Mo and Sn-Co-Mo combinations were not highly effective, but final assessment of these combinations will require further experimentation.

REFERENCES

1. Akhtar, Sayeed, Sam Friedman, and P. M. Yavorsky. Process for Hydrodesulfurization of Coal in a Turbulent-Flow Fixed-Bed Reactor. Paper presented at the 71st Nat. Meeting, AIChE, Dallas, Texas, Feb. 20-23, 1972. (Preprints available.)
2. Hawk, C. O., and R. W. Hiteshue. Hydrogenating Coal in the Batch Autoclave, BuMines Bull. 622, 1965, 42 pp.
3. Yavorsky, P. M., Sayeed Akhtar, and Sam Friedman. Process Developments: Fixed-Bed Catalysis of Coal to Fuel Oil. Paper presented at the 65th Annual Meeting, AIChE, New York, N.Y., Nov. 26-30, 1972. (Preprints available.)
4. Schuman, S. C., and Harold Shalit. Hydrodesulfurization, Catalysis Reviews, v. 4, No. 2, 1970, pp. 245-318.
5. Mounce, William, and R. S. Rubin. H-Oil Desulfurization of Residual Oil, 68th Nat. Meeting, AIChE, Houston, Texas, Feb. 28-March 4, 1971, Preprint 20a.
6. Akhtar, Sayeed, Sam Friedman, and P. M. Yavorsky. Low-Sulfur Fuel Oil From Coal, BuMines TPR #35, 1971, 11 pp.
7. Lo Jacono, M., J. L. Verbeek, and G. C. A. Schuit. Magnetic and Spectroscopic Investigations on Cobalt-Alumina and Cobalt-Molybdenum-Alumina, J. of Catalysis, v. 29, No. 3, June 1973, pp. 463-474.

TABLE 1.- Analyses of feed materials
Basis: percent by weight

Material	Pittsburgh- seam hvab coal	Indiana #5 hvbb coal	High- temp. coal tar
Proximate analysis, as received			
Moisture	0.5	6.1	0.0
Ash	6.0	8.9	0.04
Volatile matter	35.8	38.6	-
Fixed carbon	57.7	46.4	-
Ultimate analysis, moisture-free			
Ash	6.0	9.5	0.04
Hydrogen	5.2	4.9	4.9
Carbon	78.2	71.4	92.8
Nitrogen	1.5	1.5	1.1
Oxygen (by difference)	8.0	9.2	0.56
Sulfur	1.1	3.5	0.6
as sulfate	0.04	0.38	-
as pyrite	0.39	1.00	-
as organic	0.67	2.12	0.6
Solvent analysis			
Benzene insolubles			15.1
Asphaltene			39.8
Oil, n-pentane-soluble			45.1

TABLE 2.- Catalysts used in coal hydrogenation tests

Cat. No.	Catalyst or support supplier and supplier's identification	Particle description	Pore vol., cc/g	Sur-face area, m ² /g	AVG pore dia., Å	Support composition, wt pct			Wt of metal com-pound + support, wt%	Wt. of catalyst charged, g
						Al ₂ O ₃	SiO ₂	Other		
<u>Commercial Catalysts</u>										
1	Harshaw 0402T	1/8-in. tablet	0.40	200	80	Major	5.0	-	2.4 Co, 10.0 Mo	57.7
2	do.	do.	do.	do.	do.	do.	do.	do.	do.	27.0
3	do.	do.	do.	do.	do.	do.	do.	do.	do.	52.1
4	do.	-200 mesh	do.	do.	do.	do.	do.	do.	do.	57.7
5	do.	1/8-in. tablet	do.	do.	do.	do.	do.	do.	do.	56.2
6	Grace-Davison SMR 7-3776	1/16-in. extrudate	0.53	310	68	Major	-	-	3.2 Co, 10.8 Mo	33.6
7	American Cyanamid AERO HDS-3A	1/8-in. extrudate	0.57	170	135	Major	-	-	2.5 Ni, 10.0 Mo	41.5
8	American Cyanamid AERO HDS-9A	1/8-in. extrudate	0.49	130	150	Major	-	-	3.0 Ni, 12.0 Mo	40.5
9	Strem Chemical 26-272	1/8-in. tablet	0.21	55	155	Major	-	-	12.4 Fe	64.7
<u>Bureau-Prepared Impregnated Catalysts</u>										
10	DOP	1/16-in. sphere	1.15	170	270	91.2	0.7	-	None	25.7
11	do.	do.	do.	do.	do.	do.	do.	do.	1 Mo	27.8
12	do.	do.	do.	do.	do.	do.	do.	do.	5 Mo	30.5
13	do.	do.	do.	do.	do.	do.	do.	do.	10 Mo	32.8
14	do.	do.	do.	do.	do.	do.	do.	do.	1 Sn	28.0
15	do.	do.	do.	do.	do.	do.	do.	do.	5 Sn	29.6
16	do.	do.	do.	do.	do.	do.	do.	do.	10 Sn	35.1
17	do.	do.	do.	do.	do.	do.	do.	do.	5 Ni	30.4
18	do.	do.	do.	do.	do.	do.	do.	do.	5 Co	33.5
19	do.	do.	do.	do.	do.	do.	do.	do.	5 Fe	31.4

1 Charged 25 cc.

2 Not presulfided.

3 Indiana #5 hvbb coal.

TABLE 2.- Catalysts used in coal hydrogenation tests (Cont.)

Cat. No.	Catalyst or support supplier and supplier's identification	Particle description	Pore vol., cc/g	Sur-face area, m ² /g	Avg pore dia., A	Support composition, wt pct			Wt of metal compound + support, wt% g	Wt of catalyst charged, g
						Al ₂ O ₃	SiO ₂	Other		
20	ALCOA H-151	1/8-in. sphere	0.46	290	63	90.0	1.7	-	1 Mo	45.7
21	-----	do.	do.	do.	do.	do.	do.	do.	5 Mo	50.6
22	-----	do.	do.	do.	do.	do.	do.	do.	5 Sn	48.4
23	-----	do.	do.	do.	do.	do.	do.	do.	5 Ni	56.4
24	-----	do.	do.	do.	do.	do.	do.	do.	5 Co	58.6
25	-----	do.	do.	do.	do.	do.	do.	do.	5 Fe	53.6
26	ALCOA F-1	8 x 12 mesh	0.52	230	90	92.0	0.1	-	5 Mo	57.2
27	-----	do.	do.	do.	do.	do.	do.	do.	5 Sn	56.8
28	-----	do.	do.	do.	do.	do.	do.	do.	5 Ni	62.0
29	-----	do.	do.	do.	do.	do.	do.	do.	5 Co	60.9
30	-----	do.	do.	do.	do.	do.	do.	do.	5 Fe	60.0
31	Houdry 511 CP	4-mm tablet	0.60	80	300	12.4	87.3	0.25 Na ₂ O	5 Mo	38.6
32	Houdry 24 CP	4-mm tablet	0.88	425	83	12.4	87.3	do.	5 Mo	32.7
33	Norton SA 101	1/8-in. tablet	0.27	0.13	8.3 x 10 ⁴	90.4	8.5	-	5 Mo	77.5
34	-----	do.	do.	do.	do.	do.	do.	do.	5 Sn	79.9
35	-----	do.	do.	do.	do.	do.	do.	do.	5 Ni	71.8
36	-----	do.	do.	do.	do.	do.	do.	do.	5 Co	66.3
37	-----	do.	do.	do.	do.	do.	do.	do.	5 Fe	69.5
38	Norton BC 132	1/8-in. tablet	0.31	0.04	31 x 10 ⁴	4.7	28.5	65.8 SiC	5 Mo	58.9
39	Norton LA 956	1/8-in. tablet	0.22	0.04	22 x 10 ⁴	99.3	0.4	-	5 Mo	72.3
40	Norton SA 5209	3/17-in. sphere	0.32	0.37	3.5 x 10 ⁴	87.0	11.7	-	5 Mo	54.7
41	Norton BS 131	1/8-in. tablet	0.28	1.23	0.9 x 10 ⁴	3.1	96.0	-	5 Mo	56.8
42	Carborundum AELT	1/8-in. tablet	0.17	0.11	6.2 x 10 ⁴	72.0	21.8	-	0.002 Mo	72.5
43	-----	do.	do.	do.	do.	do.	do.	do.	1 Mo	72.8
44	-----	do.	do.	do.	do.	do.	do.	do.	1 Sn	77.9
45	-----	do.	do.	do.	do.	do.	do.	do.	1 Ni	76.8
46	-----	do.	do.	do.	do.	do.	do.	do.	1 Co	76.9
47	-----	do.	do.	do.	do.	do.	do.	do.	1 Fe	73.7
48	Carborundum AEHT	1/8-in. tablet	0.41	0.08	21 x 10 ⁴	72.0	21.8	-	1 Mo	48.6
49	-----	do.	do.	do.	do.	do.	do.	do.	1 Sn	52.1
50	-----	do.	do.	do.	do.	do.	do.	do.	1 Ni	49.3
51	-----	do.	do.	do.	do.	do.	do.	do.	1 Co	50.4
52	-----	do.	do.	do.	do.	do.	do.	do.	1 Fe	51.0

TABLE 2.- Catalysts used in coal hydrogenation tests (Cont.)

Cat. No.	Catalyst or support supplier and supplier's identification	Particle description	Pore vol., cc/g	Sur-face area, m ² /g	Avg pore dia., Å	Support composition, wt pct			Wt of Metal compound + support, wt%		Wt of catalyst charged, g
						Al ₂ O ₃	SiO ₂	Other	wt support	wt%	
53	Carborundum SELT	1/8-in. tablet	0.37	0.23	6.4 x 10 ⁴	5.8	93.1	-	1 Mo		47.4
54	-----	-----	-----	-----	-----	-----	-----	-----	1 Sn		49.0
55	-----	-----	-----	-----	-----	-----	-----	-----	1 Ni		47.9
56	-----	-----	-----	-----	-----	-----	-----	-----	1 Co		46.2
57	-----	-----	-----	-----	-----	-----	-----	-----	1 Fe		48.2
58	Carborundum SEHT	1/8-in. tablet	0.56	0.70	3.2 x 10 ⁴	5.8	93.1	-	1 Mo		37.7
59	-----	-----	-----	-----	-----	-----	-----	-----	1 Sn		40.2
60	-----	-----	-----	-----	-----	-----	-----	-----	1 Ni		39.7
61	-----	-----	-----	-----	-----	-----	-----	-----	1 Co		40.2
62	-----	-----	-----	-----	-----	-----	-----	-----	1 Fe		38.4
63	Carborundum CELT	1/8-in. tablet	0.21	0.04	21 x 10 ⁴	11.2	26.9	58.6 SiC	1 Mo		64.0
64	-----	-----	-----	-----	-----	-----	-----	-----	1 Sn		61.0
65	-----	-----	-----	-----	-----	-----	-----	-----	1 Ni		61.8
66	-----	-----	-----	-----	-----	-----	-----	-----	1 Co		60.7
67	-----	-----	-----	-----	-----	-----	-----	-----	1 Fe		61.8
68	Carborundum CEHT	1/8-in. tablet	0.30	0.13	9.2 x 10 ⁴	11.2	26.9	58.6 SiC	1 Mo		54.6
69	-----	-----	-----	-----	-----	-----	-----	-----	1 Sn		56.0
70	-----	-----	-----	-----	-----	-----	-----	-----	1 Ni		54.2
71	-----	-----	-----	-----	-----	-----	-----	-----	1 Co		55.6
72	-----	-----	-----	-----	-----	-----	-----	-----	1 Fe		52.8
73	Norton BA 307	3/16-in. sphere	0.07	0.06	4.7 x 10 ⁴	92.7	6.0	-	1 Mo		89.0
74	-----	-----	-----	-----	-----	-----	-----	-----	1 Sn		91.8
75	-----	-----	-----	-----	-----	-----	-----	-----	1 Ni		93.5
76	-----	-----	-----	-----	-----	-----	-----	-----	1 Co		94.9
77	-----	-----	-----	-----	-----	-----	-----	-----	1 Fe		91.7
78	UOP	1/16-in. sphere	1.15	170	270	91.2	0.7	-	2.4 Co, 10 Mo		35.6
79	Same as catalyst 78 except catalyst calcined before sulfiding and 25 cc charged										17.8
80	ALCOA H-151	1/8-in. sphere	0.46	290	63	90.0	1.7	-	2.4 Co, 10 Mo		56.8
81	Same as catalyst 80 except catalyst calcined before sulfiding and 25 cc charged										28.4
82	Carborundum SELT	1/8-in. tablet	0.37	0.23	6.4 x 10 ⁴	5.8	93.1	-	2.4 Co, 10 Mo		47.4
83	UOP	1/16-in. sphere	1.15	170	270	91.2	0.7	-	5 Sn, 10 Mo		36.8
84	-----	-----	-----	-----	-----	-----	-----	-----			41.0
85	Harshaw 0402T	1/8-in. tablet	0.40	200	80	Major	5.0	-	5 Sn, 2.4 Co, 10 Mo		62.0

⁴ Impregnated in 2 steps.⁵ Impregnated in 3 steps.⁶ Sn impregnated on Harshaw Co-Mo 0402T.

TABLE 3.- Hydrogenation results
 Charge: 50 g coal, 75 g vehicle oil, 50 cc catalyst
 Conditions: 4,000 psi, 400° C, 30 minutes at temperature

Hydro- genation components and conc., Cat. No.	wt pct	Conv. of organic benzene insols. charged, wt pct	Distribution of products, wt pct of moisture- and ash-free charge					Sulfur content of products, wt pct				
			Organic benzene insols.	Total oil, benzene soluble	As- phal- tene	Pentane soluble oil	Hydro- carbon gases	Benzene soluble oil	As- phal- tene	Pentane soluble oil	Benzene insols.	
No catalyst used		25	36	60	36	24	0.6	0.50	0.53	0.46	0.88	
1 2.4 Co, 10 Mo		63	18	80	27	53	1.8	0.15	0.21	0.13	2.01	
2 do.		52	23	74	34	40	2.2	0.25	0.34	0.18	1.66	
23 do.		39	29	68	31	37	1.4	0.28	0.33	0.24	1.14	
4 do.		73	13	82	30	52	2.2	0.11	0.13	0.10	-	
35 do.		74	12	81	28	53	2.8	0.24	0.32	0.20	4.2	
6 3.2 Co, 10.8 Mo		44	27	69	22	47	1.1	0.16	0.34	0.07	-	
7 2.5 Ni, 10 Mo		57	20	77	23	54	1.4	0.16	0.26	0.12	2.3	
8 3.0 Ni, 12 Mo		57	21	77	24	53	1.8	0.14	0.28	0.08	1.6	
9 12.4 Fe		49	25	72	40	32	1.4	0.45	0.51	0.37	1.34	
10 None		20	38	58	30	28	1.0	0.49	0.53	0.45	0.86	
11 1 Mo		50	24	73	27	46	2.1	0.35	0.43	0.31	-	
12 5 Mo		64	17	79	34	45	1.0	0.32	0.34	0.30	1.93	
13 10 Mo		64	17	80	30	50	1.1	0.27	0.33	0.24	-	
14 1 Sn		77	11	84	36	48	1.7	0.36	0.43	0.30	-	
15 5 Sn		80	9	88	36	52	2.4	0.39	0.43	0.36	-	
16 10 Sn		71	14	84	29	55	1.9	0.45	0.55	0.34	-	
17 5 Ni		68	15	80	36	44	1.4	0.35	0.36	0.34	2.03	
18 5 Co		56	21	75	35	40	0.7	0.40	0.48	0.32	1.70	
19 5 Fe		49	24	73	39	34	1.6	0.41	0.48	0.32	1.85	

1 Charged 25 cc of catalyst.

2 Catalyst was not preulfidated.

3

Experiment made with Indiana #5 hvbb coal.

TABLE 3.- Hydrogenation results (Cont.)

Cat. and conc., wt pct	Hydro- genation components	Conv. of organic benzene insols. charged, wt pct	Distribution of products,					Sulfur content of products, wt pct				
			wt pct of moisture- and ash-free charge	Total oil, benzene soluble	As- phal- tene	Pentane soluble oil	Hydro- carbon gases	Benzene soluble oil	As- phal- tene	Pentane soluble oil	Benzene insols.	
53	1 Mo	60	19	78	39	39	1.2	0.43	0.45	0.40	1.04	
54	1 Sn	52	23	75	41	34	1.2	0.46	0.52	0.40	1.41	
55	1 Ni	50	24	72	41	31	1.2	0.42	0.49	0.34	1.41	
56	1 Co	55	22	76	45	31	1.3	0.43	0.47	0.36	1.44	
57	1 Fe	26	35	62	31	31	0.5	0.51	0.53	0.48	1.02	
58	1 Mo	46	26	72	39	33	1.2	0.44	0.51	0.36	1.09	
59	1 Sn	54	22	75	36	39	1.0	0.38	0.50	0.28	-	
60	1 Ni	54	22	75	47	28	1.4	0.42	0.45	0.36	1.11	
61	1 Co	56	21	75	38	37	1.2	0.43	0.49	0.36	-	
62	1 Fe	46	26	72	35	37	1.3	0.44	0.48	0.40	1.29	
63	1 Mo	33	32	65	35	30	0.7	0.51	0.58	0.44	1.22	
64	1 Sn	49	24	74	36	38	1.4	0.51	0.59	0.44	1.37	
65	1 Ni	42	28	71	40	31	1.8	0.41	0.45	0.36	1.16	
66	1 Co	42	28	69	39	30	1.2	0.47	0.53	0.39	1.23	
67	1 Fe	37	30	70	40	30	0.5	0.48	0.56	0.38	1.23	
68	1 Mo	47	25	72	38	34	1.3	0.44	0.48	0.39	1.19	
69	1 Sn	51	23	74	37	37	1.2	0.50	0.59	0.41	1.40	
70	1 Ni	32	33	64	33	31	1.3	0.46	0.50	0.42	1.18	
71	1 Co	25	36	62	36	26	0.7	0.53	0.59	0.44	0.94	
72	1 Fe	41	28	69	39	30	1.4	0.48	0.53	0.41	1.14	
73	1 Mo	47	25	71	33	38	0.9	0.38	0.48	0.29	1.51	
74	1 Sn	54	22	76	34	42	1.6	0.48	0.58	0.40	1.40	
75	1 Ni	29	34	62	35	27	1.4	0.48	0.55	0.40	1.35	
76	1 Co	38	29	67	32	35	0.8	0.47	0.54	0.41	1.66	
77	1 Fe	44	27	71	40	31	1.0	0.43	0.50	0.34	1.75	
78	2.4 Co, 10 Mo	42	28	68	33	35	1.6	0.23	0.28	0.18	-	
79	do.	69	15	79	35	44	1.4	0.18	0.26	0.12	2.5	
80	do.	58	20	76	27	49	1.5	0.22	0.37	0.13	-	
81	do.	63	18	78	34	44	1.6	0.24	0.31	0.18	3.1	
82	do.	37	30	65	33	32	0.9	0.35	0.38	0.31	3.3	
83	5 Sn, 10 Mo	78	11	85	33	52	1.5	0.33	0.39	0.29	-	
84	5 Sn, 10 Mo.	77	11	86	25	61	1.8	0.31	0.37	0.29	-	
85	5 Sn, 2.4 Co, 10 Mo	67	16	83	31	52	1.8	0.36	0.24	0.29	3.3	