



The role of the support in catalytic hydrodesulfurization of diesel fuel  
by Carlton Dencker Grimm

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
DOCTOR OF PHILOSOPHY in Chemical Engineering  
Montana State University  
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**Abstract:**

Promoted alumina silica catalyst supports were studied for their hydrodesulfurization properties. Two support classes were used in this investigation—molecular sieves with their uniform crystalline structure and low pore diameter of 10 Å and the noncrystalline silica alumina supports whose pore diameters ranged from 50 Å upward to 180 Å.

Cobalt and molybdenum were deposited on the molecular sieves near two target figures: 3% Co 15% Mo and 5% Co 10% Mo. An ammonium ion molecular sieve was used to ion exchange cobalt or nickel onto the support with the deposited cobalt and molybdenum. Nickel and tungsten promoted molecular sieves were near 3% Ni 15% W. The noncrystalline supports were promoted near 3% Co 15% Mo.

The influence of pore size, pore volume, alumina and silica content, surface area, and density were noted for each promoted base material.

Gas oils near 31 °API gravity with 1.5 to 2.0 weight percent sulfur were used for the hydrodesulfurization runs. Temperatures 650, 725, and 800 °F were checked and the liquid hourly space velocities 1.5, 4.0, and 7.0 were run at each temperature. The plug flow reactor was pressurized to 300 psig. Sulfur analyses were made on samples taken at each flow and temperature condition and a ASTM distillation was made of the product from the LHSV 1.5, 800 °F condition.

An increase in pore volume brought increased desulfurization in similarly promoted molecular sieves. The high surface area molecular sieves did not compete with the large pore diameter noncrystalline supports, but gave 20 to 30 percent less desulfurization.

Promoted noncrystalline bases that had pore volumes between 0.30 and 0.48 cc./gm. gave the same desulfurization as bases with pore volumes between 0.78 and 1.22 cc./gm. at LHSV 1.5, but the smaller pore volume supports' performance dropped behind the larger pore volume bases at LHSV 4.0 and 7.0.

The promotion amount and support surface areas did not affect desulfurization results as did pore size and pore volume.

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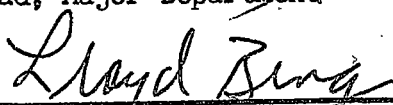
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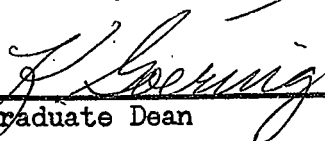
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Chemical Engineering

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## ABSTRACT

Promoted alumina silica catalyst supports were studied for their hydrodesulfurization properties. Two support classes were used in this investigation--molecular sieves with their uniform crystalline structure and low pore diameter of 10 Å, and the noncrystalline silica alumina supports whose pore diameters ranged from 50 Å upward to 180 Å.

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The influence of pore size, pore volume, alumina and silica content, surface area, and density were noted for each promoted base material.

Gas oils near 31 °API gravity with 1.5 to 2.0 weight percent sulfur were used for the hydrodesulfurization runs. Temperatures 650, 725, and 800 °F were checked and the liquid hourly space velocities 1.5, 4.0, and 7.0 were run at each temperature. The plug flow reactor was pressurized to 300 psig. Sulfur analyses were made on samples taken at each flow and temperature condition and a ASTM distillation was made of the product from the LHSV 1.5, 800 °F condition.

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The promotion amount and support surface areas did not affect desulfurization results as did pore size and pore volume.

## I. INTRODUCTION

Environmental control and ecology are terms used today to arouse the American public's interest in conserving resources, protecting his habitat, and providing a guarantee for the specie's survival. Attention is focused on all types of industry and what it does or should do to limit the fouling of man's world by the manufacturing processes or the use of industry's end production. Resources must be used and processed efficiently and possible pollution sources must be eliminated. These two goals do not follow each other, so there is a difficult optimization problem to find the best solution which is sometimes the more costly alternative. Moral, political, economic, and technological forces all play a part and these forces cannot be separated for analysis one by one.

Hydrodesulfurization is a term used by industry to indicate the sulfur removal from petroleum fractions by hydrogen treatment of the fraction. The resulting desulfurized hydrocarbon and hydrogen sulfide can be easily separated with the hydrocarbon sent on to some end product use while the hydrogen sulfide is additionally treated to obtain elemental sulfur which can be safely stored with little pollution danger to the environment until its subsequent use as a building block by industry is required.

Pollution laws enacted during the latter 1960's provide the stimulus to lower the sulfur content in heating and diesel fuels.

State and federal legislation set the upper sulfur limits and these limits are being reduced as time passes. New York City has a target of 0.5 weight percent sulfur in heating oils for May 1, 1971 after meeting the one percent sulfur target May 1970. The ultimate sulfur content goal is 0.3 weight percent<sup>1</sup>. Most crude oils found throughout the world contain sulfur in considerable amounts. The existence of low or no sulfur content in crudes is the exception and a premium price is paid for these crudes. Venezuela, Kuwait and the Middle East, and most U.S. crude oils contain sulfur with figures ranging between three and five percent. Oil is available from other sources too, but contaminants are present in them also. Tar sands contain sulfur and sulfur compounds, while oil shales contain oxygen, nitrogen, and sulfur compounds. These elements must be removed to provide an acceptable fuel for our society.

Some form of hydrotreating is needed to bring the sulfur down to the legal limits and if possible reduce the sulfur content to trace amounts. Extraction, chemical processing, and non-catalytic methods have been and are being used to remove some sulfur compounds, but the only way to reduce all sulfur compounds in a crude oil or partially refined fraction is to catalytically hydrodesulfurize the sulfur containing hydrocarbons<sup>2</sup>. Hydrogenation is effective in simultaneously removing oxygen, sulfur, and nitrogen.

Hydrogenation which forms the basis for hydrodesulfurization is not new, rather than being a product of the 50's or the 60's, its history goes back 50 or 60 years to Bergius who recognized the possibilities of non-catalytic high pressure hydrogenation<sup>3</sup>. Commercial development was slow; the first patents issued were in the late 1920's. The demand for lower sulfur content in hydrocarbons was spurred by the realization that corrosion damage occurred to equipment in which the fuel was burned. Not until a cheap hydrogen source became available with hydroreforming just prior and during World War II did the commercial hydrodesulfurization processes develop.

Catalytic hydrodesulfurization involves passing a hydrocarbon and hydrogen stream over a catalyst bed at elevated temperatures and pressures. The catalyst as described in some patents may be composed of oxides or sulfides of Group II to VII in the chemical periodic table and in conjunction with Group VIII or Groups I and II<sup>2</sup>. This covers a very wide range of chemical possibilities. Usually a catalyst carrier such as silica gel or alumina gel is employed for the base upon which the Group metal is deposited or admixed. The broad promotion classification can be narrowed down to several metal compounds. The cobalt and molybdenum oxides and sulfides and the nickel and tungsten oxides and sulfides are the catalyst promoters most employed. The role of the metal is thought to keep acidic sites

active during hydrogenation while the metal crystallite size controls the support area that can be kept free from coke and made available for cracking<sup>4</sup>. In cobalt molybdate catalyst, the cobalt is thought to provide hydrogenation and isomerization of the olefinic products from the desulfurization that the molybdenum sites provide<sup>5,6</sup>.

Elemental sulfur, mercaptans, hydrogen sulfide, open chain sulfides, disulfides, saturated cyclic sulfides, and thiophenes are all sulfur compounds found in crude oil. The following reactions taken from McKinley<sup>2</sup> are indicative of typical desulfurization reactions:

- "1. Hydrogenation of various type compounds to yield saturated hydrocarbons and hydrogen sulfide.
2. Decomposition of various type compounds to yield unsaturated hydrocarbons and hydrogen sulfide.
3. Splitting of alkane sulfides to yield thiols and alkanes.
4. Condensation of thiols to yield alkane sulfides and hydrogen sulfide.
5. Hydrogenation of disulfides to yield thiols."

Thermodynamics predicts these reactions will go essentially to completion at temperatures less than 900°F. Usually the maximum desulfurization temperature condition used is 800°F. The presence of a catalyst of course does not change the possible equilibrium conversion calculated by thermodynamics unless the catalyst is part of the reaction, but the catalyst can change the time required for

equilibrium to be reached.

Some references<sup>3</sup> state a 2:1 molybdenum to cobalt ratio is preferred for hydrodesulfurization catalyst promotion while others give lower figures for the cobalt content such as 5:1<sup>7</sup>. Andrews<sup>3</sup> also says cobalt and molybdenum content on a carrier may be built up to an amount where a maximum desulfurization is obtained, then additional cobalt and molybdenum amounts will give little additional increase in performance and possibly even a slight decrease. Nickel tungsten catalysts have a 3:1  $WO_3$  to NiO weight ratio.

The catalyst may be formed several different ways. The cobalt and molybdenum (as possible promoting metals for hydrodesulfurization catalysts) may be mixed with a slurry of the base material, then the slurry compressed by extrusion and dried; the metals may be coprecipitated on the catalyst carrier; the metals may be added separately to support pellets or a fine support powder; or the metals may be added to a alumina slurry, then hot digested and the slurry spray dried. The individual metal deposition is most satisfactory as with other methods the support strength is sacrificed in comparison to the preformed pellets which are promoted by separate metal addition and have excellent mechanical properties. Research projects at MSU have tended to favor the separate metal promotions on the preformed pellets<sup>8,9,10</sup>.

The catalyst support is vital to catalytic hydrodesulfurization



as it holds the active transition series metals in place. Ashley and Mitchell<sup>5,6</sup> published their findings on the possible coordination structure of the metals in fresh, unused catalyst and proposed the metals actually entered the support lattice when promoted. The cobalt and molybdenum are closely associated on the alumina surface of the Co-Mo-Al<sub>2</sub>O<sub>3</sub> samples. The cobalt II ion will enter octahedral cation vacancies in gamma alumina which contains random octahedral and tetrahedral vacancies.

Support materials contain alumina, silica, and some disodium oxide. Each of these three chemical compounds influences the catalyst behavior. Cracking catalyst contains 13 to 25 weight percent alumina, with the major component being silica<sup>11,12</sup>. Hydrodesulfurization catalysts usually contain activated alumina as their major component. Silica in hydrodesulfurization catalyst improves the stability and the disodium oxide is responsible for a negative effect--catalyst sintering during the catalyst life. It is an impurity present during the silica alumina support preparation. The disodium oxide content is kept below 0.2 weight percent because of the sintering effect. Also it does not affect catalyst activity early in the catalyst use, but over a long time may cause deactivation because of sintering. The most active alumina is the gamma variety and this is used in the support materials rather than bauxite.

Many commercial supports contain the silica and alumina in a

random, noncrystalline structure. The silica and alumina particles are arranged so there are spaces between them, but these spaces, openings, or tunnels do not fit any orderly layout. They are formed by the uneven joining of the alumina and silica molecules. A pore size distribution which tells the most probable pore size or spacing between the particles can be obtained and the pore volume measured by mercury or kerosene porosimetry methods. The available surface area for the supports which counts the surface of the passages and cavities within the support may be measured by the Brunauer-Emmett-Teller method.

Crystalline materials that have definite crystalline lattices are found in nature and may be made synthetically. These materials, often called zeolites, are composed of "building blocks". The zeolite crystal is formed from four oxygen ions that surround the smaller size silicon or aluminum ion. Since the ionic charge is not balanced, each of these fundamental blocks combines with other silica or aluminum ions and extends the crystal lattice in all directions. Charge deficits for oxygen in combination with the alumina lend the structure the ability to accept positively charged ions to stabilize it. Thus exchangeable ions as sodium and potassium can make up the charge deficit and are loosely connected to the oxygen tetrahedra that surround the aluminum ion. The sodium or potassium ion may be exchanged for hydrogen or ammonium ion and then in turn exchanged for

other ions<sup>13</sup>. If natural mordanite, a molecular sieve material, is used for catalysts the sodium ion appears to block the pore entrances. The molecular sieve pore size is determined by the silicon-oxygen and aluminum-oxygen tetrahedra. Cavities are present behind the building blocks and their size depends on the zeolite variety.

A British patent<sup>14</sup> states that molecular sieves may be used for catalysts. These crystalline materials with their inherent uniform pore diameters and with the proper choice of the particular sieve size and type may be selective to the molecules they admit to their inner cavities. This selective characteristic plus the large surface area they possess lends them to catalyst applications. The series with the largest pores allows benzene to enter it and this type should first be considered for the hydrotreating of the complex molecules found in petroleum fractions.

Surface area is another important consideration in support selection. Most silica alumina supports of the noncrystalline variety have surface areas greater than 200 m<sup>2</sup>/gm. Molecular sieves that have relatively small pore diameters when compared to noncrystalline materials (3 to 15 Å vs. 50 Å and greater for the respective molecular sieve and noncrystalline supports) have surface areas exceeding 400 m<sup>2</sup>/gm. The surface area must be made available for efficient catalyst use so the active sites provide the place for the reaction to occur. Problems with film and pore diffusion can

result from the wrong choice of reactor flow rate and catalyst size. A 1/16 inch diameter catalyst pellet has 95 percent of its available surface area on its exposed outside surface, while a 1/8 inch pellet exposes 55 to 60 percent. Thus if different size pellets and pellet shapes are available for a base with a given surface area per unit weight, pore diameter, and pore volume the changes in desulfurization can be attributed to pore diffusion. Film diffusion effects can be analyzed by taking different size samples and exposing them to feed flow conditions that vary proportionally with catalyst charge, i.e. maintain the same liquid fuel-solid catalyst ratio as the catalyst weight is increased for successive runs<sup>15</sup>. Also up to a point, the smaller the catalyst pellet size, the greater the activity will be without serious disadvantages arising from increased resistance to fluid flow in the reactor<sup>3</sup>.

The void volume is important in catalyst supports and the accessibility of that void volume is the governing factor. As a catalyst support porosity increases, as measured by pore volume, the optimum metal amount for maximum catalyst activity increases<sup>7</sup>. The increase in pore volume will increase the activity to a certain point, but coupled with the increase a large amount of promoting material is required to maintain the activity.

Van Zoonen in Journal of the Institute of Petroleum<sup>16</sup> states there are three methods the internal catalyst surface areas may be

best utilized. First the distance between pellet center and surface is reduced. Second, the increasing of the diffusion coefficient of the sulfur bearing compounds in the oil is another method. Finally pellets should have wide pore diameter structure. The molecules then have fewer collisions with the walls, but also possible less chance for reaction as the reactions occur at active sites on the walls.

Desulfurization reactions with most heterogeneous catalysts are thought to be diffusion rate limited<sup>4,16</sup>. The reaction rate is so swift that the sulfur containing molecules do not reach the pelleted catalyst center before the sulfur is removed. Thus reaction products reach the inner volume of the support and possible additional reaction takes place other than the completed desulfurization reactions. This contention then opposes the need for a monomolecular film of metal promotion throughout the entire catalyst support space<sup>3</sup>.

The diffusion can be either molecular diffusion where the molecules influence their nearest neighbors and happens if the mean free path of the molecules is less than the pellet pore size. A second diffusion type is Knudsen diffusion which postulates the molecular mean free path is larger than the pore diameter and the molecule collides only with the pore walls. This occurs at low pressures and in the vapor phase. Hydrodesulfurization catalyst pores may be filled with liquid even at high hydrogen to oil ratios<sup>16</sup>. Also in preparing a promoted catalyst the problem of depositing most

of the promotion on the outside surface arises. For small sized pellets, 1/16 inch diameter, this is where most of the active desulfurization sites are, as this is the greatest area available. In larger pellets, 1/4 inch diameter, more of the surface area is contained within the pellet itself rather than the outside surface. A buildup of promoted metal can obstruct diffusion from the surface to the catalyst inner spaces.

Catalyst poisoning occurs from trace metals and nitrogen compounds found in crude oil fractions. Nitrogen deactivation has more effect on the catalyst such as cobalt molybdate when low °API gravity feeds containing nitrogen are used<sup>17</sup>. Another poisoning source appears when the high molecular weight hydrocarbon compounds adsorb and coat catalytic surfaces<sup>18</sup>. Then high temperatures crack the high molecular weight compounds and coke laydown and polymer formation occur. The coke laydown on the active sites reduces the catalyst activity. Catalysts may be regenerated by burning the coke off the surface. Temperature must be monitored to prevent catalyst sintering during the "decoking" step or else sintering occurs and catalyst area and subsequent catalyst activity will be reduced.

Hydrodesulfurization operating conditions depend on the feed used. Temperatures from 300 to 400°C, pressures from 50 to 2000 psig, liquid hourly space velocities 0.5 to 20, and hydrogen flow rates

50 to 10,000 scf./bbl. are listed in one U.S. patent for a cobalt molybdate catalyst<sup>19</sup>. Other references list optimum temperatures between 700 and 800°F, pressures 200 to 1000 psig, and hydrogen flow rates below 10,000 scf./bbl.<sup>6,20,21,22</sup> Research at MSU has settled on hydrogen flow rate of 5000 scf./bbl. and pressure of 300 psig for the 30 to 32 °API gravity gas oils<sup>8</sup>.

The catalysts are most active when the promoting metals are in the sulfided form. Presulfided catalysts are available, but with a H<sub>2</sub>S--H<sub>2</sub> source, the catalyst may be sulfided in place. McKinley reports that with just a fraction of one percent hydrogen sulfide in a hydrogen stream the catalyst may be adequately sulfided<sup>2</sup>. The sulfided promotion metals are in the Co<sub>9</sub>S<sub>8</sub> and MoS<sub>2</sub> or Ni<sub>3</sub>S<sub>2</sub> and WS<sub>2</sub> forms. Sulfiding may be successfully accomplished at temperatures greater than 600°F and the only requirement is that adsorbed water be removed from the catalyst pores prior to sulfiding<sup>20</sup>. If the catalyst is to maintain its activity a hydrogen sulfide partial pressure must be maintained. This requirement is met during hydrodesulfurization by the formation of hydrogen sulfide from the reactions.

## II. PROJECT OBJECTIVES

Hydrodesulfurization of a No. 2 diesel fuel (30 °API gravity) that contains between 1.5 and 2.0 weight percent sulfur is to be attempted with transition metal promoted molecular sieves and with promoted noncrystalline alumina silica supports. The effectiveness of the two support types is to be compared.

The pore volume, pore size, surface area, and silica to alumina ratios of the molecular sieves and noncrystalline supports are to be investigated for their desulfurization effects.

The catalyst support physical and chemical compositions are to be used to predict successful hydrodesulfurization results on gas oils. The cracking ability of each catalyst preparation is to be noted.



### III. EQUIPMENT AND EXPERIMENTAL PROCEDURE

#### A. Equipment

Desulfurization is accomplished in a plug flow, heated reactor fed by a pulse feed pump. FIGURE 1 shows the equipment schematic for all the apparatus used for the hydrodesulfurization on this project, while FIGURE 2 is a cutaway drawing of the reactor and its associated heating equipment.

The reactor was made from type 304 stainless steel and was from one inch schedule 80 pipe with a total length of three feet. This reactor fitted into a hole drilled in a solid aluminum block. Nichrome resistance wire in three series of coils was wrapped around the aluminum block and served as the heating source. Power supply was regulated by three variacs on 120 volts AC and currents of 4.5 to 5.5 amperes were drawn for each of the heating elements over the temperature range studied. The fuel oil was metered from a large glass reservoir and a smaller burette. The burette was used to obtain accurate liquid flow rates throughout equipment operation. A Lapp pump which had a variable stroke provided the desired liquid flow rate.

A manifold for hydrogen, nitrogen, and hydrogen sulfide--hydrogen compressed gas let a a rotameter. A precision valve allowed gas velocities to be varied through the rotameter and then through the reactor. The rotameter was calibrated with a wet test

meter and the flow rates were checked periodically during the runs.

A condenser was built into the line just after the reactor tube left the heating block. Water was used for cooling. Next downstream from the condenser was a back pressure valve used to maintain the required operating pressure.

Sample collection was done following the back pressure valve. A series of solenoid operated valves could be used to take samples at desired intervals if needed; however during actual operation these solenoid valves were susceptible to plugging and thus rarely used.

The gas streams containing the unused hydrogen and the resulting hydrogen sulfide from the hydrodesulfurization reactions were passed through scrubbing solutions and then vented to the atmosphere. There was no recycle of the gas stream.

A thermowell ran two-thirds the reactor length and contained three chromel alumel thermocouples connected to a Leeds and Northrup temperature recorder; one iron constantan thermocouple was also present in the thermowell and its temperature indication was read directly with a potentiometer.

The reactor was packed with inert alundum pellets one quarter inch in diameter for 18 inches of the reactor length. Then three to four inches of one eighth inch alundum pellets followed. The actual catalyst bed contained 30 cc. of experimental catalyst plus 30 cc. of the one eighth inch alundum pellets. This 60 cc. total charge was

well mixed so the alundum pellets would eliminate or reduce hot spots during the exothermic hydrodesulfurization reaction. After the catalyst bed, three more inches of one eighth inch alundum pellets were packed and the remaining reactor volume was filled with one quarter inch pellets. A stainless steel screen was placed prior to the reactor exit.

#### B. Experimental Procedure

The reactor operating pressure was 300 psig; hydrogen flow rate was 5000 scf./bbl.; the temperatures checked were 650, 725, and 800 degrees Fahrenheit; liquid hourly space velocities (LHSV) of 1.5, 4.0, and 7.0 were run. The gas oil obtained from the Husky Oil Company, Cody, Wyoming was from the Oregon basin. The 31.1 °API gravity feed contained 1.62 weight percent sulfur. This feed was used for the early runs of the test series (1 through 16) and then a feedstock of the same origin, but having 30.4 °API gravity and 1.82 weight percent sulfur was used on the remaining runs (17 through 57). Fuel properties including distillation data and sulfur content of six distillation fractions of the feed are contained in TABLE I. A run recapitulation is given in TABLE II.

A typical catalyst evaluation run took four to five days with each of the three flow rates checked at each of the three temperatures. One day was required for equipment startup and sulfiding;

then on successive days one temperature was checked per day.

A run started with the equipment being brought up to the operating temperature with the hydrogen flow rate at 0.5 scf./hr. After 650°F had been reached the system was purged with dry nitrogen for several hours at 0.5 scf./hr. This step was necessary to remove water from the catalyst and alundum pellets prior to sulfiding and fuel injection. Operating pressure was set by the back pressure valve and 50 psi pressure drop was allowed through the catalyst bed.

The system was checked for leaks while on the nitrogen purge, then sulfiding with a 20 percent hydrogen sulfide--80 percent hydrogen mixture took place at 650°F, gas flow rate 0.5 scf./hr. The catalyst for most runs was sulfided at 650°F and 300 psig; however some catalysts were sulfided between 650 and 725°F and from 100 to 300 psig with no change in effectiveness. Sulfiding lasted from five to seven hours.

The gas oil and hydrogen feed were introduced to the reactor after the catalyst had been sulfided. The lowest temperature 650°F was checked first at the lowest flow rate of 1.5. The 4.0 and 7.0 LHSV's were checked next in sequence. As stated before, one temperature was checked per day, with the reactor being heated to the next highest temperature the following night. At 800°F the sequence of flow rates was changed during the catalyst evaluation. The highest LHSV--7.0 was checked first, then followed by 4.0 and finally LHSV

1.5, the lowest liquid hourly flow rate.

Liquid samples were of course taken at each flow rate for each temperature. Actually three samples spread over a three hour period were taken for each flow and temperature condition. Also the reactor was allowed to stabilize from one to three hours prior to sample collection. With three samples taken at each condition, a comparison between the three easily showed if the reactor had stabilized and steady state flow and reaction conditions had been achieved.

Sulfur analysis was done by the lamp method (ASTM D-1266-647)<sup>24</sup>. A known fuel sample weight was burned, the combustion gases passed through a hydrogen peroxide solution, then sodium hydroxide titration provided data from which the percent sulfur was calculated.

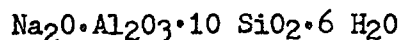
A distillation of the sample taken at the most severe operating conditions (800°F LHSV 1.5) was done according to ASTM D 86-IP 123<sup>25</sup>. A second distillation was made on the same sample with six separate volume fractions collected at specified temperatures. Sulfur analyses of these fractions were compared with similar fractions in the feed. The specific gravity in terms of °API was determined for the sample taken at 800°F and LHSV 1.5.

TABLE II lists those deviations from the operating procedures specified here. It also contains some reasons for making various runs.

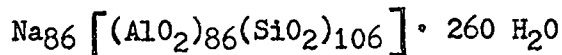
#### IV. CATALYST SUPPORT MATERIALS

##### A. Molecular Sieves

Six different molecular sieve base materials, six commercially available noncrystalline catalyst supports, and two commercially promoted catalysts were tested. Five molecular sieve supports were supplied by Norton Company and these were mordanite crystal structure types. The mordanite has the chemical formula:



Linde's 13-X faujasite molecular sieve has the general formula:



and contained 20 percent natural clay as binder.

Norton's molecular sieves ranged from pure mordanite in sample 0081, 93.8 percent in 20072, 90 percent in 0255, to 60 percent in sample 0256. Sample 44001 was a bonded high silica powder. Those bases containing less than pure mordanite had amorphous aluminum silicate as binder. A summary of the molecular sieves or crystalline structure catalyst supports is found in TABLE III. The sieve pore diameters were 10 Å and smaller, while the pore volumes went from 0.67 cc./gm. for Linde 13-X to 0.33 cc./gm. for the five Norton samples. Surface areas were high--above 450 m<sup>2</sup>./gm. Norton's personnel said the molecular sieve surface areas were difficult to measure, so the data comes from the mercury porosimetry readings rather than the BET methods used for the noncrystalline materials.

One of Norton's base materials was in the ammonium ion form and this led to ion exchange with promoting metals plus the deposition of the hydrodesulfurization catalyst promoters. All the crystalline bases contained  $\text{SiO}_2$  as the major chemical component. One of Norton's materials had a silica to alumina ratio of 44 to 1. Norton's other materials contained silica to alumina ratios of 10 to 1.

B. Noncrystalline Supports

TABLE IV lists the noncrystalline support material compositions and physical data. The six base materials went from the high silica Nalcat 2910-A with the large pore diameter 180 Å, pore volume 1.22 cc./gm. to the high alumina Alcoa H-151 which possessed a pore diameter of 50 Å, pore volume 0.30 cc./gm. The pore volumes were known for all the supports presented, but the minimum pore diameters were unobtainable for the two samples Harshaw 1602 and 1802. In some cases the  $\text{SiO}_2$  or the  $\text{Al}_2\text{O}_3$  contents were known, but not both figures, then the known amount was reported and the difference could be assumed to be the missing figure. Disodium oxide content was low for all the base materials studied.

Two commercially made catalysts were evaluated. These (Houdry C and Harshaw 4401-E) were relatively low minimum pore diameter, noncrystalline supports. Alumina content of Houdry C exceeded 90 percent before promotion while 4401-E contained 50 percent silica. The Houdry

C contained 3.2 weight percent CoO and 14.6 weight percent MoO<sub>3</sub>. All catalysts made by this author were reported in weight percent cobalt and weight percent molybdenum. Harshaw 4401-E was a presulfided 6.0 percent nickel 19.0 percent tungsten catalyst. These two catalysts were used to test operating procedures and to give data from which to compare the performance of the catalysts made by the author.



## V. CATALYST PREPARATION

Twelve distinct catalyst support materials were promoted with various combinations of cobalt and molybdenum or nickel and tungsten. These transition metal catalyst promoters were deposited on the supports by soaking the support in solutions of the metal salts. Some catalyst samples were made with ion exchanged cobalt and molybdenum in addition to the standard deposition type catalysts.

Two promotion targets were set for the molecular sieve supports-- 3.0 % Co 15.0 % Mo and 5.0% Co 10.0% Mo. The noncrystalline material was targeted for the 3.0% Co 15.0% Mo promotion. At least three cobalt molybdenum promotion combinations were made on each base material with the exception of Norton 0255 and 0256 where only two promoted catalysts were run in the reactor. All of the molecular sieves and one noncrystalline support were tested as hydrodesulfurization catalysts without any promoting metal. Their performance and the promoted catalyst performance will be discussed in a later section.

All promotions of the crystalline and the noncrystalline base materials are given in TABLES V and VI. Their best performance and the conditions where this was achieved along with the specific run number are summarized there. FIGURES 3 and 4 give a graphical representation of the same data with FIGURE 3 showing the Co Mo promotions of molecular sieves and FIGURE 4 the Co Mo promotions of

noncrystalline supports.

The desired catalyst base material was calcined at 500 to 700°F prior to initial weighing. Usually a 70 to 80 gram sample was used for promotion. The cooled support was then immersed in a concentrated solution of molybdenum trioxide in ammonia hydroxide. The molybdenum trioxide concentration was kept around 0.2 gm./ml.  $\text{NH}_4\text{OH}$ . The heat of absorption was removed from the support and its surrounding solution by an ice or cold water bath. The support was allowed to soak for 24 hours in the  $\text{MoO}_3$ -- $\text{NH}_4\text{OH}$  solution. A pressure tight seal was maintained to prevent ammonia breakout and the possible surface deposition on the support. Then the remaining solution was drained off and the support was air dried. Subsequent drying was at 160°F in a tray drier, followed by calcination with the maximum temperature of 900°F reached after six hours, then temperature maintenance for twelve hours. The  $\text{MoO}_3$  promoted base was weighed and the whole procedure could be repeated to bring the  $\text{MoO}_3$  content to the required amount.

Cobalt promotion was done similarly to the molybdenum deposition.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was used in a 0.2 gm./ml.  $\text{H}_2\text{O}$  concentration. After several hours of catalyst support material soaking in the cobalt solution, a vacuum was drawn on the enclosure and air was withdrawn from the catalyst support so the cobalt could penetrate the support easier. The maximum calcination temperature for the cobalt promoted base was 500°F. The temperature was maintained for six to

twelve hours after initial slow heating to the 500<sup>0</sup>F temperature.

Both molecular sieves and the noncrystalline materials were promoted in this manner. Norton's molecular sieve series tended to crumble after successive promotions so several attempts were made on each distinct cobalt molybdenum promotion target to obtain a useable catalyst. The Alcoa H-151 noncrystalline support was very difficult to promote as thermal fracture from the absorption heat resulted in "egg shells" breaking off the spherical support. The nickel and tungsten catalysts were prepared with the same method as the cobalt and molybdenum catalysts. Tungsten was promoted first from a tungstic acid solution, then the nickel from a nickel nitrate solution. After calcination the tungsten was taken to be in the WO<sub>3</sub> form and the nickel as NiO.

Both cobalt and nickel were ion exchanged onto Norton's base 20072. Support 20072 was in the NH<sub>4</sub><sup>+</sup> form and 8.7 percent of its weight could be ion exchanged. Either a cobalt or nickel salt solution was made up for the ion exchange. The weighed crystalline sample was added and allowed to soak in the solution. The ion exchanged sample was washed several times and dried. After washing the ion exchanged support was calcined at 1100<sup>0</sup>F to remove residual ammonia. Then cobalt and molybdenum were deposited on the samples as described in prior paragraphs.

While commercially prepared catalysts such as Houdry C reported their cobalt as percent CoO and molybdenum as percent MoO<sub>3</sub>, this author gives all promotion amounts as percent cobalt (or nickel) percent molybdenum (or tungsten). Ion exchanged cobalt or nickel is reported just before the cobalt (nickel) and molybdenum (tungsten) deposition figures.

One molecular sieve sample is promoted with nickel as the sole promoter and is in the promoted molecular sieve catalyst class. A comprehensive listing of Co Mo, Ni W, and the ion exchanged catalysts for both the crystalline and the noncrystalline supports is given in TABLES V and VI and also FIGURES 3 and 4.

Physical examination of the catalysts between promotion steps and after the catalyst was finished showed the promotion appeared uniform throughout the support for the noncrystalline materials while for Norton's molecular sieves the very center of the support received little of the promoting metals. The promotion then decreased as the support center was approached in the crystalline materials. After the catalysts had been evaluated in the reactor, the promoted and sulfided support was examined, and for both the noncrystalline and molecular sieve supports a uniform black color pervaded the entire pellet cross section.

## VI. DISCUSSION

### A. Organization of Data and Interpretations

Two catalyst support types are studied in this project. The crystalline, molecular sieve supports and the noncrystalline materials are promoted with cobalt and molybdenum or nickel and tungsten and the results compared. The body of this discussion is divided into two distinct divisions: one section dealing with molecular sieves and their desulfurization characteristics and the other section is concerned with the noncrystalline supports and their promotions. In these two divisions the supports are listed by their sample number (see TABLES III and IV). For each sample support two, and usually three or more, promotions with the transition metals are given. Percent desulfurization is plotted versus the reciprocal liquid hourly space velocity at a given temperature. Thus for each sample and its promotions, three temperature plots are presented.

The molecular sieves and noncrystalline supports are compared as desulfurization catalysts without any promotion on three plots, one for each temperature. Both support types are also compared at the three percent cobalt fifteen percent molybdenum and five percent cobalt and ten percent molybdenum targets. The best catalyst of each sample class (examples: Norton 0081 with 3.5% Co 10.0% Mo, Norton 20072 with 5.1% Co 19.3% Mo, and Norton 0255 with 2.3% Co 12.3% Mo) are compared for each of the two support classifications.













































































































































































































































































































































