



Catalytic hydrotreating of solvent refined coal (SPC-II) : the effect of metal combinations, impregnation technique and water addition on catalyst activity
by Turgut Sahin

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering
Montana State University
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Abstract:

Solvent refined coal (SRC-II) must be catalytically hydrotreated at elevated temperatures and pressures to improve its stability and meet the feedstock requirements of conventional petroleum refineries and boilers. Once the operating conditions are set, the development of catalysts is the primary problem.

Four transition metals, cobalt (Co), nickel (Ni), molybdenum (Mo) and tungsten (W), were selected as the catalytic agents and impregnated on a γ -alumina support having large surface area and pore size. In the first stage, seven different combinations of the metals were impregnated by a stepwise impregnation technique to test their hydrotreating activity. In the second stage, the most active metal combinations, Ni-Mo and Co-Mo, were subjected to three different impregnation techniques to test the effect of impregnation method on catalytic activity. The effect of the presence of 2 % water in the feed on the catalytic activity was tested for every catalyst.

The most active metal combinations among the seven were Ni-Mo for hydrodenitrogenation (HDN) and hydrogenation (HYD), and Co-Mo for hydrocracking (HYC). Water enhanced HDN activity of the catalysts containing Ni-Mo and Co-W combinations, but inhibited activity of the catalysts containing Co-Mo and Ni-W combinations. In general, HYC activities of the catalysts prepared by stepwise impregnation were improved by water addition.

Batchwise impregnation of Co after batchwise Mo impregnation reduced the interaction of Mo with the support giving more surface CoMoO₃ type phase and produced the most active catalyst. HDN and HYD activities of Ni-Mo catalysts were not greatly affected by the impregnation technique. In general, batchwise impregnation of Mo reduced Mo-support interaction and improved HYC activity of both Ni-Mo and Co-Mo catalysts. When both step size and order of metal impregnation were changed, the enhancing effect of water on HDN and HYC activities of the Ni-Mo catalysts disappeared and the inhibiting effect on HDN activities of the Co-Mo catalysts became more inhibiting.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and it is ready for submission to the College of Graduate Studies.

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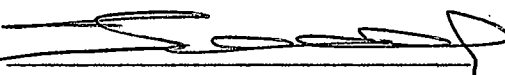
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This thesis is dedicated to my son, Koray, and my wife, Hatice

VITA

The author, Turgut Sahin, was born in Hisarardi, a small mountain village in a south-western province (Mugla) of Turkey, on March 1954 to Mr. Mustafa and Mrs. Gullu Sahin.

His elementary education was acquired in the same village: He attended the Middle School in the nearby town of Cine. He was graduated from Mugla Turgutreis Lysee (high school) in September 1972. In July 1979, he received his Bachelor of Science Degree in Chemical Engineering from Middle East Technical University in Ankara, Turkey.

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He was married to the former Hatice Aslan in May 1979 and they have a son, Koray.

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ABSTRACT

Solvent refined coal (SRC-II) must be catalytically hydrotreated at elevated temperatures and pressures to improve its stability and meet the feedstock requirements of conventional petroleum refineries and boilers. Once the operating conditions are set, the development of catalysts is the primary problem.

Four transition metals, cobalt (Co), nickel (Ni), molybdenum (Mo) and tungsten (W), were selected as the catalytic agents and impregnated on a γ -alumina support having large surface area and pore size. In the first stage, seven different combinations of the metals were impregnated by a stepwise impregnation technique to test their hydrotreating activity. In the second stage, the most active metal combinations, Ni-Mo and Co-Mo, were subjected to three different impregnation techniques to test the effect of impregnation method on catalytic activity. The effect of the presence of 2 % water in the feed on the catalytic activity was tested for every catalyst.

The most active metal combinations among the seven were Ni-Mo for hydrodenitrogenation (HDN) and hydrogenation (HYD), and Co-Mo for hydrocracking (HYC). Water enhanced HDN activity of the catalysts containing Ni-Mo and Co-W combinations, but inhibited activity of the catalysts containing Co-Mo and Ni-W combinations. In general, HYC activities of the catalysts prepared by stepwise impregnation were improved by water addition.

Batchwise impregnation of Co after batchwise Mo impregnation reduced the interaction of Mo with the support giving more surface CoMoO_4 type phase and produced the most active catalyst. HDN and HYD activities of Ni-Mo catalysts were not greatly affected by the impregnation technique. In general, batchwise impregnation of Mo reduced Mo-support interaction and improved HYC activity of both Ni-Mo and Co-Mo catalysts. When both step size and order of metal impregnation were changed, the enhancing effect of water on HDN and HYC activities of the Ni-Mo catalysts disappeared and the inhibiting effect on HDN activities of the Co-Mo catalysts became more inhibiting.

CHAPTER 1

INTRODUCTION

When the world oil crisis started in the early seventies, many nations around the world seriously started looking for alternative energy resources.

Among the several alternatives, coal is the most important one to the countries which have abundant coal reserves such as the United States. The United States has 3,600 billion metric tons of coal reserves and 200 billion metric tons of it is estimated to be currently economically recoverable [1]. According to the forecasts, it will be enough to supply the nation's liquid-fuel needs more than a century [2] if it is used only for liquefaction.

Coal as a solid fuel is not convenient to substitute for petroleum or natural gas, because the transportation sector exclusively depends on liquid fuels, the residential and commercial sectors depend heavily on gaseous fuels, and industry requires three quarters of its needs as liquid and gaseous fuels [3, 4]. Consequently, the conversion of coal to conventional forms (liquid or gas) is necessary.

The first gasification and liquefaction processes were developed in Germany during the 1900s and 1930s. They constitute the basis of the today's technology. Today, there are four basic coal liquefaction processes in the U.S., Solvent Refined Coal (SRC), Exxon Doner Solvent

(EDS), H-Coal, and Synthoil. They convert high sulfur coal to distillate liquids. The chemical composition and the physical properties of the coal liquids are considerably different from those of petroleum. They have a higher carbon-to-hydrogen ratio and higher heteroatom (S, N, O) concentrations.

Raw coal-derived liquids, as received from liquefaction units, must be further hydrotreated before being used either as a boiler fuel or refinery feed stock because of their high heteroatom content. Nitrogen, sulfur, and oxygen cause storage problems [5]. Sulfur and nitrogen content must meet the EPA emission standards [6]. In addition, basic nitrogen content must be minimized for refining processes to prevent catalyst poisoning.

The maximum requirement for nitrogen in refineries varies from process to process, but should not be more than 0.3 wt% in order to be processed in the existing refineries [7]. In this study, 0.3 wt% nitrogen in the product was taken as the minimum requirement.

The objective of this study was to develop catalysts which would be able to upgrade SRC-II Light Ends Column Feed (LECF) to a feed stock acceptable to present petroleum refineries.

CHAPTER 2

BACKGROUND

COAL AND COAL CONVERSION

Coal: Coal is a generic term applied to widespread and widely differing natural rocks that consists primarily of organic material admixed with smaller quantities of mineral matter [8].

Coal deposits were formed from plant materials by the action of heat and pressure for long periods of time. The first stage of coalification involves the hierarchical formation of peat, lignite, followed by subbituminous coal, bituminous coal, and finally anthracite. Coal is ranked differently in different countries and the classification method currently being used in the U.S. is shown in Table 1 [9].

Despite the years of research in this field, the chemical structure and chemical properties of coal are still not well understood today. The basic reason is the complexity of coal and dependence of chemical properties and structure on the geographical origin and rank [10]. The major elemental components of coal are carbon, hydrogen and oxygen; the minor elements include sulfur, silicon, nitrogen, aluminum, iron, calcium, magnesium, potassium, sodium, and titanium. Carbon is the most abundant element, and its molecular form in combination with small amounts of hydrogen and oxygen provides the structural integrity of coal. The organic compounds shown in Fig. 1 are thought to be among the important components in the organic portion of coal structure.

Table 1. Classification of Coals by Rank [9].

Class	ASTM classification method			Ultimate analysis ratio ^b	
	Limits of fixed carbon ^a (% w/w)	Limits of heat content (Btu/lb)		Hydro-Carbon gen	Oxygen
I. Anthracite	86-98	-		90-97	3-5 1-3
II. Bituminous				85-90	4-5 5-10
low-volatile	68-86	-			
medium-volatile	69-78	-			
high-volatile A	<69	≤14,000			
high-volatile B		13-14,000			
high volatile C		11,500-13,000			
III. Subbituminous		8,300-11,500		75-85	5 10-20
IV. Lignitic		6,300-8,300		70-75	4-5 20-25
(plants and trees)	25-30	4,000-5,000		50-60	5-6 35-40

a Mineral-matter-free (mmf) basis. To convert to MJ/kg, multiply by 0.00232.

b Dry-mineral-matter-free (dmmf) basis, normalized for exclusion of sulfur and nitrogen.

These organic structures are bonded together to form cross-linked polymers. These polymeric chains represent the molecule of coal. However, there is no unique structure found to represent a coal molecule. Among many proposed representative coal structures [13, 14, 15, 16], the one proposed by Solomon [17] is shown in Fig.

2.

Coal Utilization and Conversion: Commercial utilization of coal is directly linked to industrialization. When the British were faced with deforestation, they substituted coke from coal for wood charcoal [18]. Coal was used extensively in steam generation for steam engines and electricity production, as well as home heating, until the liquid distillate fuels from petroleum became more efficient for

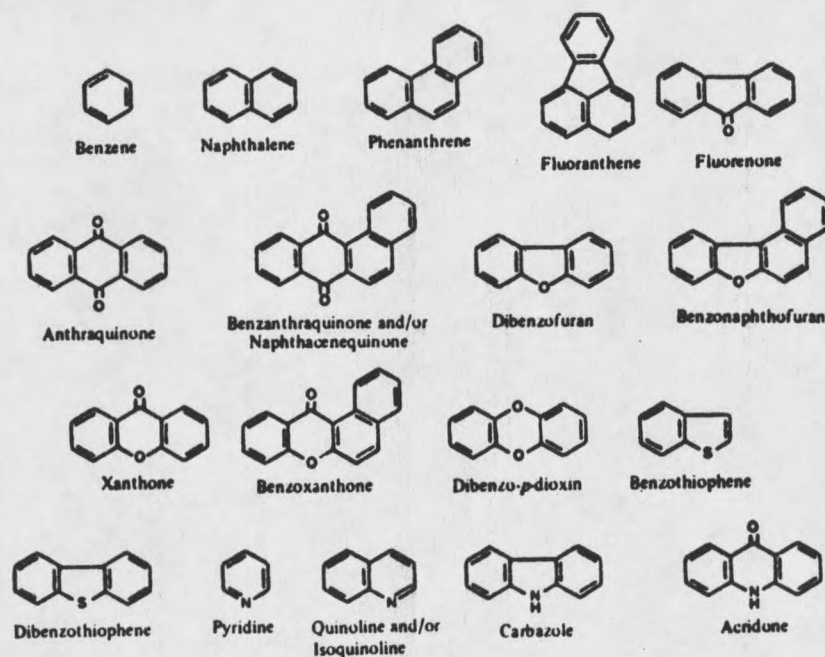
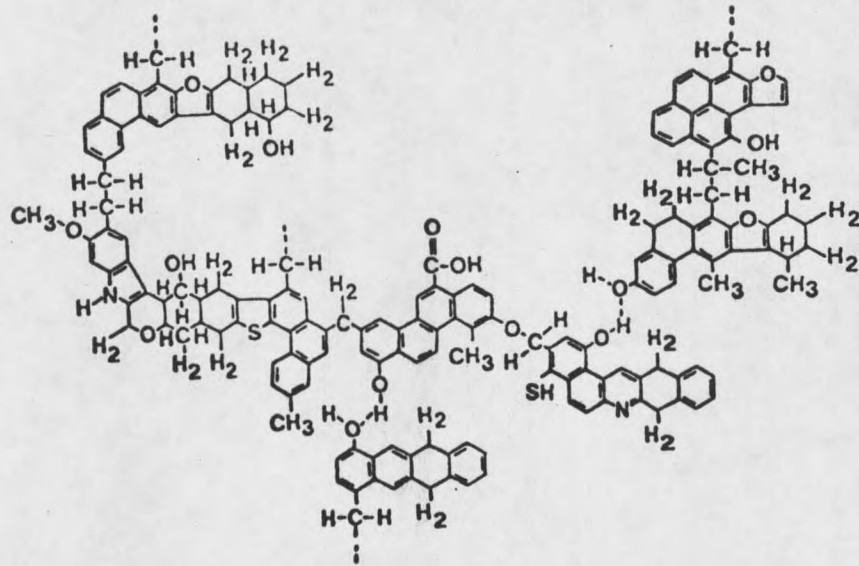
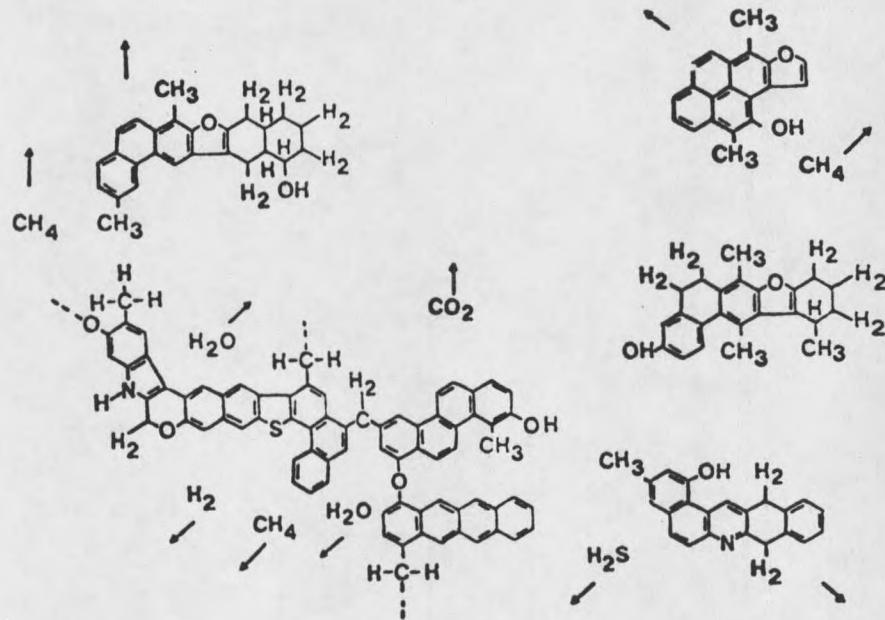


Figure 1. Aromatic Units Present in Coal Structure (adapted from the reference 12)



Proposed coal structure



Possible racking of a coal molecule

Figure 2. Representative Structure of Coal Molecule

transportation, home heating and other forms of energy production. A factor in the decline of coal utilization was the extensive usage of natural gas in utilities after World War II [3].

The reasons behind these shifts include both convenience and cost. One measure of convenience is the concentration of energy per unit of fuel product. Approximately, wood contains 16 million Btu/ton, coal contains 26 million Btu/ton, and petroleum contains 40 million Btu/ton. This represents efficiency in transportation, storage and usage. The cost of crude oil was very low until 1973, and the natural gas prices were held at artificially low levels [3].

At present, the most common utilization of coal is metallurgical usage and combustion for energy production. For more extensive utilization of coal in today's technology, its conversion into gaseous or liquid fuels is required because of the dependence of users on these forms [3].

Conversion of coal is not a new idea. It extends far back to the early 18th century. When coke from coal was produced, the by-products were gaseous and liquid fuels from the pyrolysis ovens. However, only the gaseous products were used as fuel. The liquid products were utilized as chemicals.

After this initial stage, technological improvements were made for gasification of coal. Even though synthetic gas is not popular in the U.S., there are many commercial gasifiers around the world, especially in Europe. It is, however, reemerging in the U.S. today. There are about six major coal gasification processes; Descending

Bed, Fluidized Bed, Entrained Flow, Molten Bath, Tumbling Bed, and Underground Gasification.

In contrast to the gasification technology, the development of liquefaction technology waited until this century. Processes were pioneered in Germany during the 1920s and 1930s. Development of synthetic liquid fuels from coal followed two separate routes. First, the direct hydrogenation of coal was initiated by Bergius in 1913; and secondly, the production of liquids by the reaction of CO and H₂ was reported by Fischer and Tropsch in 1923 [19].

There were several commercial plants producing liquid fuels by using these two processes before and during the World War II. German capacity of the Bergius process was 70,000 bbl/day and that of Fischer-Tropsch process was 15,000 bbl/day [19]. Today, South Africa's SASOL process, based on the Fischer-Tropsch process, is the only commercial one producing liquid fuels from coal.

Coal liquefaction processes are usually classified as shown below [19];

<u>Classification</u>	<u>Example</u>
Pyrolysis	Coal-Oil-Energy-Development (COED) Lurgi-Ruhr gas
Direct Liquefaction	H-Coal and Bergius
Solvent Extraction	Solvent Refined Coal (SRC) Exxon Doner Solvent (EDS) Consolidation Synthetic Fuel (CSF)
Indirect Liquefaction	Fischer-Tropsch, Methanol

In the Pyrolysis Process, coal is heated in the absence of oxygen. This heating breaks down the coal molecules to form hydrogen rich gas, tar, and a hydrogen deficient char. The tar products are primarily aromatic in nature. This has been practiced industrially for decades.

In Direct Hydrogenation, a high purity hydrogen is used to react with coal at elevated temperatures and pressures in the presence of a catalyst. The products are primarily aromatic.

The Solvent Extraction Processes involve slurring the pulverized feed coal in a coal-derived liquid and reacting at elevated temperatures and pressures. Hydrogen is added to the SRC and EDS processes. The products are primarily aromatic.

In Indirect Liquefaction, the feed coal is completely gasified to produce a synthesis gas consisting primarily of hydrogen and carbon monoxide. After purification, hydrogen and carbon monoxide are reacted at elevated temperatures and pressures in the presence of a catalyst. The products are aliphatic and olefinic in nature.

Thermal efficiency of these processes differ considerably from each other. In general the efficiencies of hydroliquefaction processes such as extraction, donor solvent, and direct hydrogenation are higher than those of complete pyrolysis and indirect liquefaction processes such as Fischer-Tropsch and methanol. Estimated efficiency of SRC-II is in the 63-77% range [19].

SRC Process: The SRC project was begun in 1962 when Spencer Chemical Company was awarded a research contract by the Office of Coal Research (OCR, subsequently a part of DOE) to study the technical feasibility of a coal deashing process (now called SRC process). In

1965, the process was successfully demonstrated with a 50-pound-per-hour continuous flow unit. During the term of contract, Gulf Oil Corporation acquired Spencer Chemical Company. After reorganization, the contract was assigned to the research department of Pittsburgh and Midway Coal Mining Company (P&M) [20].

Construction of a 50-ton-per-day pilot plant at Fort Lewis (Tacoma), Washington, was begun in 1972 and became fully operational in 1974. This early process is called SRC-I and produced a solid product. Later in 1977, the SRC-I process was modified to the SRC-II process to produce liquid products [20]. The SRC-II process flow diagram is shown in Fig. 3 [19].

In the SRC-II process, dried and pulverized coal is fed to the slurry mixing vessel where it is mixed with a slurry recycle stream and a filtered process solvent recycle. The entire slurry is pumped from the mixing vessel and the recycle plus make up hydrogen is injected in the stream ahead of the slurry heater. The mixture is heated to about 370°C in the slurry heater and then enters the dissolver at a pressure of about 13.8 MPa. The products come out of the reactor at about 425°C and are let down in pressure and cooled in several flash separations in the vapor/liquid separation section. The gases are sent to the acid gas removal unit to remove carbon dioxide and hydrogen sulfide to purify hydrogen. Part of the slurry stream is recycled back to the slurry mixing vessel; the rest is filtered to remove mineral residue and recover liquid products. The filtrate is vacuum distilled to produce distillate fuels overhead and SRC bottoms. The distillates are fractionated into light oil, light

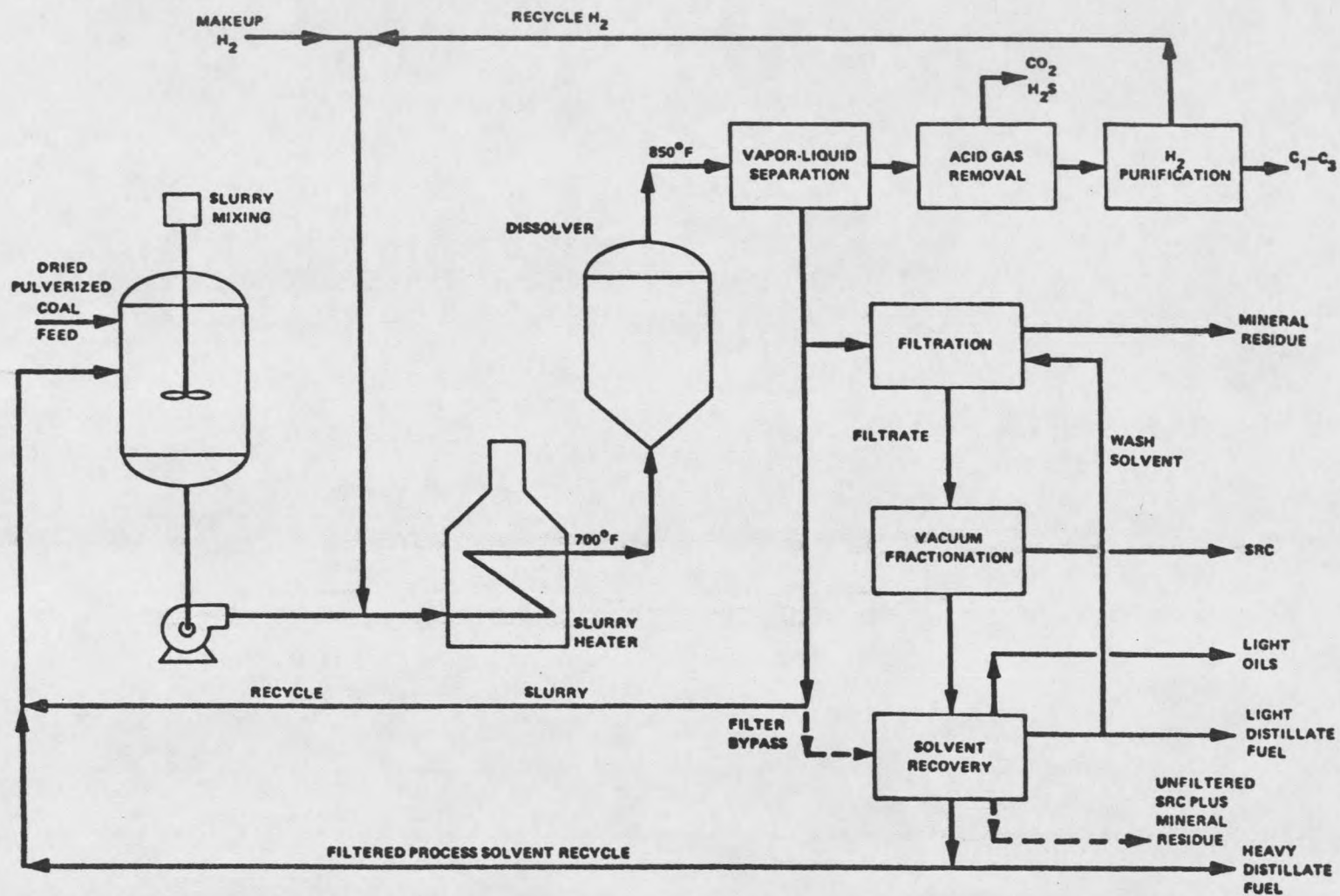


Figure 3. SRC-II Process Flow Diagram

distillate, and heavy distillate streams, including the wash solvent (part of the light distillate) and the filtered process solvent (part of the heavy distillate).

The feedstock used in this research, the Light Ends Column Feed (LECF), was distillate fuels obtained from the vacuum distillation overhead. The physical properties of LECF is shown in Table 2. It contains about 24 wt% light oil (naphtha), 65 wt% middle distillate and 11 wt% heavy oil. Hydrogen/Carbon atomic ratio is about 1.23. The heteroatom content is 1.21 wt% sulfur, and 0.67 wt% nitrogen. For the detailed analysis of the SRC-II product see Appendix A.

CATALYTIC UPGRADING OF COAL LIQUIDS

Coal liquids, as received from the liquefaction plants, are not suitable for conventional use. They contain very high concentrations of heteroatoms such as nitrogen, sulfur and oxygen, and H/C atomic ratio (see Fig. 4) is too low to meet the standards. The low H/C ratio is caused primarily by high percentage of condensed ring aromatic compounds present in the coal liquids. H/C ratio is a rough measure of aromaticity. In general aromatic compounds have lower H/C ratios than their aliphatic or olefinic counterparts.

Table 2. Properties of SRC-II Light Ends Column Feed

Elemental Analysis (wt %)		Distillation Fractions (wt%)	
Carbon	87.80	Light Oil (40-205°C)	24.09
Hydrogen	8.97	Middle Oil (205-298°C)	64.77
Sulfur	1.21	Heavy Oil (298+)	11.14
Nitrogen	0.67		
Oxygen*	2.25		
Ash	0.02		
Specific Gravity, 60/60°F = 0.96			

* By difference.

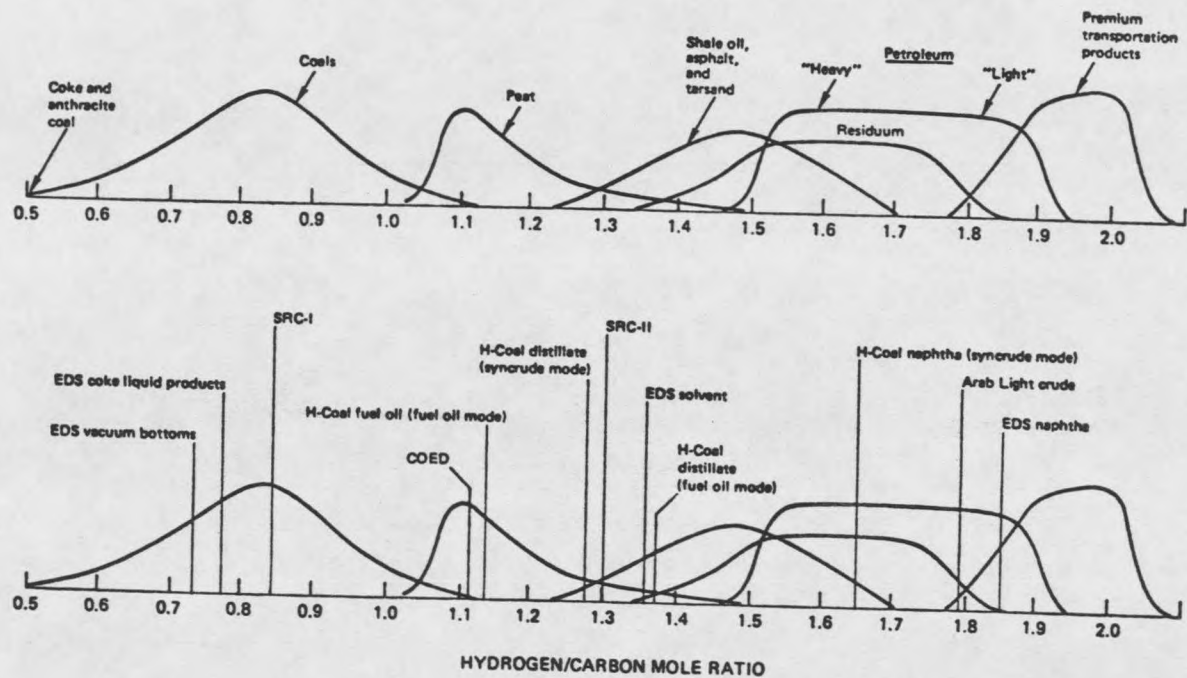


Figure 4. H/C Ratios for Various Hydrocarbon Sources and End Products

Heteroatoms, in general, reduce the stability of the coal liquids and cause storage problems [5]. Sulfur and nitrogen are very severe pollutants and must meet the current EPA standards. Basic nitrogen and sulfur compounds cause catalyst poisoning in the downstream refining processes such as catalytic cracking, hydrocracking and reforming. The tolerable nitrogen content varies from process to process. The maximum allowable nitrogen content in the existing petroleum refineries is 0.3 wt% [7].

Another problem with coal liquids is the presence of polycyclic organic compounds in high percentages. These compounds produce smoke upon burning and can not be cracked without hydrogenation. Hydrogenation of these polycyclic organic compounds reduces smoke production and eases cracking. However, hydrogenation is a very expensive process. If these compounds are entrained during combustion, they cause environmental and health problems. Some carcinogens have been identified among these products [21]. They also dissolve in the process water and cause cleaning problems [22]. Therefore, catalytic hydrotreating is a necessary step.

Catalysts:

The role of a catalyst, in general, is to control the rate and direction of a reaction. A catalyst increases the rate of a reaction by lowering the activation energy of a reaction by creating an alternative path or mechanism for the reaction.

In a multicomponent chemical environment such as coal liquids, the number of possible reactions are many. In this case a catalyst must selectively catalyze the desired reactions. Therefore, the

hydrotreating catalysts for coal liquids must be selective as well as active on certain desired reactions like Hydrodenitrogenation (HDN), Hydrodesulfurization (HDS), Hydrodeoxygenation (HDO), Hydrogenation (HYD), and Hydrocracking (HYC). An excessive hydrogenation is not desired because hydrogen is very costly; however, a certain level of hydrogenation activity is necessary to assure heteroatom removal and to minimize aromaticity and coking.

In both petroleum hydrotreating and coal-liquids hydrotreating, supported metal catalysts are usually used. The metals are transition metals, usually Co, Mo, Ni and W. Supported metal catalysts are prepared by impregnating the water soluble salts of the metals on a high surface area support. A gamma-alumina or gamma-alumina-silica are the supports most widely used.

Characteristics of the supported metal catalysts are not well understood today. Most technological patents and know-how are usually only accidental findings rather than a result of a scientific prediction [23]. This is due to the complexity of the processes of catalyst synthesis and testing. The most important of these is the catalyst synthesis, or in other words, catalyst preparation.

Catalyst preparation starts with selection of a proper support for the specific reactions involved. It must ensure [23] (1) a large enough pore diameter for the free passage of molecules involved in the reaction, (2) high dispersion of an active component (high surface area), (3) the required type of macro distribution of an active component along the radius and micro distribution on the surface, (4) absence of an unwanted interaction of the active component with the

support affecting the catalyst activity, (5) high mechanical and thermal stability of the catalyst under working conditions, (6) minimum heat and mass transfer resistance in the pellets and between them, and (7) absence of impurities or additives which reduce activity and selectivity of the catalyst for the desired reactions.

The pore diameter and pore size distribution is a very important physical property. Because of the very large molecules present in the coal liquids, a majority of the pores must be larger than the largest molecule. It must also be assured that the number of bottlenecks between the pores is minimum. This can be checked by the hysteresis in the adsorption-desorption curves.

The macro distribution of active components are dictated by the process, type of reaction, diffusion problems and the cost of the active components. It can be controlled by controlling the duration of the support in the solution, the rate and type of drying, and the type of impregnation (sorption, capillary and ion exchange). Details are given in references [23, 24, 25, 26, 27].

Once a proper support is selected, the impregnation technique becomes the most important step. The solution concentration, the pH of the solution [28], the sequence of metal impregnation [29, 30, 31, 32, 33, 34], the duration of the support in the solution, the percent metal load on the support, and the drying and calcining conditions are among the most important factors which must be carefully controlled to assure the desired activity and selectivity. The basic reason of the appearance of so many papers contradicting with each other is the complexity of controlling these factors.

Co-Mo/Al₂O₃ Catalysts: Chung and Massoth [29, 30] and Okamoto et al. [31] studied the effect of impregnation technique on the surface structure of Co-Mo/Al₂O₃ catalysts. The former investigators studied the effect of the sequence of metal loading, the calcining temperature and the solution concentration (in other words, stepwise and batchwise impregnation). The latter investigators studied the effect of the sequence of loading and the calcining temperature.

For Co+Mo (Mo impregnated after Co), the chemical state of Co depends on the method of Co impregnation. When Co is impregnated stepwise (1% each time), Co is present in the Al₂O₃ lattice. It is mostly CoAl₂O₄ (non-reducible, non-sulfidable) and with some octahedral CoO tightly bound to CoAl₂O₄ phase (non-reducible but sulfidable). The percent of the both phases increases with increasing Co concentration. No Co₃O₄ phase is detected up to 3.5 wt% Co, but no data was taken above this concentration. When Co is added batchwise, no Co₃O₄ phase is detected up to 1.5 wt% Co, and the phases present are the same as the Co-step catalyst. However, when the concentration of Co is more than 2 wt%, the octahedral Co₃O₄ (both reducible and sulfidable) starts to appear and increases linearly with increasing Co concentration. The concentrations of CoAl₂O₄ and CoO decreases with Co concentration after reaching a maximum at around 2 wt% Co. When the Co-batch catalyst is calcined at 750°C instead of 500°C, the phases present are similar to that of the Co-step catalyst. Calcining at high temperatures causes the migration of Co into the Al₂O₃ lattice. In this particular catalyst system (Co+Mo), Mo does not interact with the Co phase present on the support, and preexistence of Co limits

the Mo-Al₂O₃ interaction since most of the Al₂O₃ sites are occupied by Co. Usually, in all Co-Mo catalysts, Co limits the Mo-Al₂O₃ interaction and this is interpreted as the stabilizing action of Co by some investigators [31, 35, 36] since it also limits the formation of a separate crystalline MoS₂ phase upon sulfiding.

In the case of Mo+Co catalyst (Co added after Mo), the chemical state of Co and Mo is different from the previous case. When Co is added stepwise on Mo, Co is present at tetrahedral sites resembling CoAl₂O₄ type structure (non-reducible but sulfidable to a certain extent), and there is no Co₃O₄ formed. Since the tetrahedral Co phase is sulfidable, it is not totally CoAl₂O₄, but probably a surface Co-Mo interaction where Co is strongly attached to the Al₂O₃ surface. This could be caused either by altering the surface acidity of Al₂O₃ [37] or Mo blocking Co-diffusion paths through the Al₂O₃ matrix [38]. However, when Co is added batchwise on Mo/Al₂O₃ (Mo+Co/Al₂O₃ catalyst), the less amount of the CoAl₂O₄ (T) phase is present than that is present in the Co+Mo/Al₂O₃ catalyst [29, 30, 39], and no Co₃O₄ is detected. The majority of Co is present in a surface CoMo complex (precursor to CoMoO₄) where Co occupies tetrahedral sites [29, 30, 40-42]. The rest of Co is present as CoO tetrahedral attached to the Al₂O₃ surface. Calcination of this catalyst above 650°C gives more CoAl₂O₄ by moving Co into the Al₂O₃ matrix. This shows the importance of the calcining temperature. Nevertheless, there are some disagreements on the presence of Co₃O₄ [31] and the sites occupied by Co in the surface CoMo complex [43], probably because of differences

in the preparation procedures other than the sequence of metal impregnation. Even though it is believed that the surface structure of the sulfided catalysts are similar to the oxidic precursors [31], the phases present are not certainly understood [30]. Upon sulfiding, CoO (0) and CoMo surface complex is sulfided to CoS, Co_9S_8 and MoS_2 respectively. Some MoS_2 may crystallize, but it has not been determined to be significant for the Mo concentrations less than 10 wt% [30].

When Co and Mo are coimpregnated, (Co-Mo)/ Al_2O_3 catalyst, a discrete CoMoO_4 phase is observed when Co concentration is greater than 2 wt% [30, 44-48]. However, some investigators disagree with this finding [31, 36, 69, 43, 49-53]. Disagreement appears to be due to the differences in preparation technique. The major factor is the calcining temperature. When the catalysts containing CoMoO_4 are heated up to 750°C , the amount of CoMoO_4 decreases with increasing temperature [29, 41, 50]. The presence of other phases like Co_3O_4 are not known. Sulfiding gives some Co_9S_8 , but a substantial fraction of Co remains unsulfided. Some investigators [54] give evidence for the presence of a two dimensional Co: MoS_2 structure.

Ni-Mo/ Al_2O_3 Catalysts: It is interesting to note that there is no other supported metal catalyst that has received as much attention as Co-Mo, probably because of its extensive usage in petroleum hydro-treating. The Ni-Mo catalysts are one of the least studied catalysts. Only a few recent studies are concerned with the surface structure of the Ni-Mo catalysts [33, 55-59].

Even though some similarities with the Co-Mo catalysts can be devised it has a considerably different surface structure. Since Mo+Ni/Al₂O₃ (Ni added after Mo) is the only Ni-Mo catalyst studied, it will be given here.

For the concentrations up to 6 wt% Ni, no NiO phase is detected [58]. For low Ni content (Ni less than 3 wt% and Mo 14 wt%), the Ni and Mo species are well dispersed on the support as two independent two-dimensional layers, "NiAl₂O₄" and polymolybdate. They do not have any mutual interactions. The presence of this structure is very sensitive to the preparation technique [33, 55, 56, 60]. In this structure, the Mo and Ni species which are incorporated in the surface polymolybdate occupy octahedral sites and resemble a distorted octahedra [56]. As the Ni content increases (Ni > 3 wt%), formation of a new phase, a combination between the polymolybdate and [a] NiMoO₄ as an intermediate phase (not very well defined), takes place which results from interaction between the Ni and polymolybdate species. When the molar ratio Ni/Mo = 1/1, the [a] NiMoO₄ phase is distinctive [55]. Calcination temperatures between 350-550°C do not have any effect on the basic structure. However, when temperature is higher than 550°C, the Ni species migrate into the bulk of the Al₂O₃ lattice where a surface spinel with Ni in octahedral and tetrahedral positions is formed [41, 55, 56, 61]. This treatment leads to less distorted, two-dimensional monolayer of edge-sharing MoO₆ octahedra.

Ni-W/Al₂O₃ Catalysts: Even though Ni-W is a good hydrogenation and hydrocracking catalyst, it was not a subject of more than a few studies [62, 63]. Similarly to the Ni-Mo catalysts, there is no NiO

detected on the catalyst. Nevertheless, Ni is present on the catalyst as Ni_2O_3 and NiAl_2O_4 , where Ni_2O_3 is not detected on Ni-Mo catalysts. Ni_2O_3 species are dispersed on top of the W monolayer. Separate WO_3 , NiWO_4 and $\text{Al}_2(\text{WO}_4)_3$ phases are absent. However, in contrast to Mo, W interacts with Al_2O_3 support to form a monolayer of interaction complex which is not reducible but sulfidable. Upon sulfiding with H_2S , NiS , Ni_3S_2 and WS_2 are formed. If sulfiding is not complete, a W-surface complex intermediate is formed which has both a terminal oxygen and a terminal sulfur.

At this point a question may arise; what is the importance of knowing the surface structure to the catalyst performance? Since all of the reactions take place on the catalyst surface, the first few atomic layers of the catalyst surface determines activity and selectivity of a catalyst. That is why some catalysts are superior to the others even though they contain the same metals on the same support. The difference in the sequence of metal impregnation, the calcining temperature or other procedural changes make the activity and selectivity of a catalyst different, as in the case of Co-Mo [39, 64] and Ni-Mo [34, 60] catalysts. It is well known that Co or Ni added on Mo catalysts are more active for HDS than the others. Another finding is that, when Ni-Mo is calcined at high temperatures, it has low HDS activity. As discussed above, such a treatment causes the migration of Ni into the Al_2O_3 lattice.

Activity and Selectivity of Ni-Mo, Ni-W and Co-Mo Catalysts:

In general, the Co-Mo catalysts possess a lower hydrogenation activity than the Ni-Mo or Ni-W catalysts at the same or higher

degree of HDS [65, 66]. That is why the Co-Mo catalysts are preferred in the petroleum industry for HDS. The Ni-Mo catalysts possess a higher HYD activity and HDN activity than the Co-Mo and Ni-W catalysts [65, 66, 67]. If the primary objective is removal of nitrogen and hydrogenation of aromatic compounds in addition to HDS, as in the case of coal liquids upgrading, the Ni-Mo catalysts are preferred. The Ni-W catalysts are active for hydrocracking in addition to HDS and HYD [66, 68]. However, Ni-W is poorer for HDN reactions than the other two [69], even though there is some disagreement [66, 70, 71] (see discussion later). Catalyst activity or selectivity can be altered by some additives to the major metal lattice [65]. When phosphoric acid is added to the Ni-Mo catalysts with low metal content and medium phosphorus content (Ni < 3 wt%, Mo < 10 wt% and P < 3 wt%), HDS activity is increased: with high metals/high phosphorus catalyst the best HDN with the lowest hydrogenation and coke formation is obtained [55]. In the latter case, HDS is decreased.

Transport Phenomena in the Catalyst Pores:

Mass Transfer Effects: Mass transfer resistance within the catalyst pores has a significant role on the effectiveness of a catalyst and its life. Sometimes diffusion of reactants may control the global rate of a reaction if the pores are small compared to the size of reactant molecules involved. Therefore, during selection of a catalyst support or a commercial catalyst, this point must be considered as has been discussed above. For example, Cecil et al. [73] found that when the average pore diameter was increased from 7.8 to 10.3 nm, the effectiveness factor of a 1.6 mm cylindrical pellet was

increased from 0.4 to 0.8 in HDS of Middle Eastern residua. In addition to the average pore diameter, the critical pore diameter, diameter at the narrowest point, is important in diffusion effects as pointed out by Berg and Kim [74]. This effect is relatively easy to establish for simple molecules, but the importance of molecular configuration becomes increasingly important for higher molecular weight substances and complicates the study [75].

Heat Transfer Effects: Intraparticle heat transfer can have a significant effect on the reaction rate, activity and selectivity. If a reaction takes place in completely liquid filled pores, the temperature difference between the pellet center and the periphery will not be significant. However, if the pores are filled with vapor, a case which arises quite often for fast reactions with low flow rates, an exothermic reaction causes a large temperature difference [75]. As a result, catalyst performance is affected by transport phenomena. Therefore, selection of a catalyst support or a commercial catalyst and operating conditions must be made after carefully studying the specific reactions and reactants involved. This is another source of contradictory results reported in the literature.

Catalyst Aging: The catalyst aging is one of the most serious problems in all catalytic processes. Some catalysts last for years, some only a few months or days, and sometimes even a few hours, depending on the feed composition and reaction conditions. There are two general types of aging (or deactivation); permanent and temporary.

The permanent deactivation is usually caused by sintering of a catalyst or changing the surface structure (e.g. Ni-Mo and Co-Mo as

discussed above) because of excessive heat treatment or formation of volatile metal salts from the impurities in the feed (e.g. Chlorine ions) [76], deposition of metals (Ni, V, As, etc.) on the surface from demetallization reactions of organometallic compounds and deposition of solids (like iron and scale) [77, 78, 79]. These deposits cause pore blocking and restrict diffusion of reactants.

The temporary deactivation is caused mainly by coke deposition and other chemisorbed compounds depending on the feed composition and catalyst composition [77, 80]. Of these, coke deposition is the most serious problem. Its formation can be minimized by increasing the selectivity of the catalyst (e.g. phosphorus addition to Ni-Mo) or increasing H_2 pressure, but cannot be prevented in hydrocarbon processes. Coke deposition causes pore blocking. The chemisorbed compounds originate either from the feed or reaction products. Therefore, chemisorption can be minimized by purifying the feed or by altering the selectivity if the chemisorbed compounds are from the side reactions.

Coke is usually removed by air burnoff under strict temperature control. If temperature is not controlled very well, it may cause permanent loss of catalyst activity by sintering [76, 77] or changing the surface structure of the metals on the catalyst surface as discussed above [33, 56].

Catalysts for Petroleum and Coal Liquids Upgrading:

The types of catalysts to be used in both petroleum and coal liquids upgrading largely depend on the physical and chemical properties of the feedstock to be treated. In hydrotreating light

petroleum fractions, usually Co-Mo catalysts are the best because they have higher selectivity for HDS over HYD. However, if HDN and saturation of condensed ring aromatic compounds are desired prior to hydrocracking and where unsaturated aromatic compounds pass through without cracking and nitrogen compounds poison the noble metal molecular sieve catalysts, the desired catalyst is Ni-Mo [76] or Ni-W [21]. The composition of metals are in the range of 3-6 wt% for Co or Ni and 12-18 wt% for Mo or W. All catalysts are sulfided prior to use. As discussed before, the selection of support is important with respect to the feed. In general, heavier and highly aromatic feeds require larger pore diameters and pore volume, which is a compromise over larger surface area.

Similar catalysts will probably serve for the coal-liquids upgrading. However, the severity of conditions and composition and physical properties of the catalysts may be different since the chemical and physical composition of coal liquids are different from that of petroleum [81]. Coal liquids are more aromatic in nature and contain high molecular-weight condensed-ring aromatic compounds as well as insoluble organic and inorganic materials in varying concentrations, depending largely on the source of the coal liquids. They contain fairly large concentrations of heterocyclic nitrogen, sulfur and oxygen compounds. The reactivity of these compounds are relatively less than their counterparts in petroleum [21]. In practice, removal of nitrogen is generally more difficult than sulfur, especially in the condensed-ring compounds [21, 76, 81]. The reactions desired are HDN, HDS, HDO, HYD and HYC.

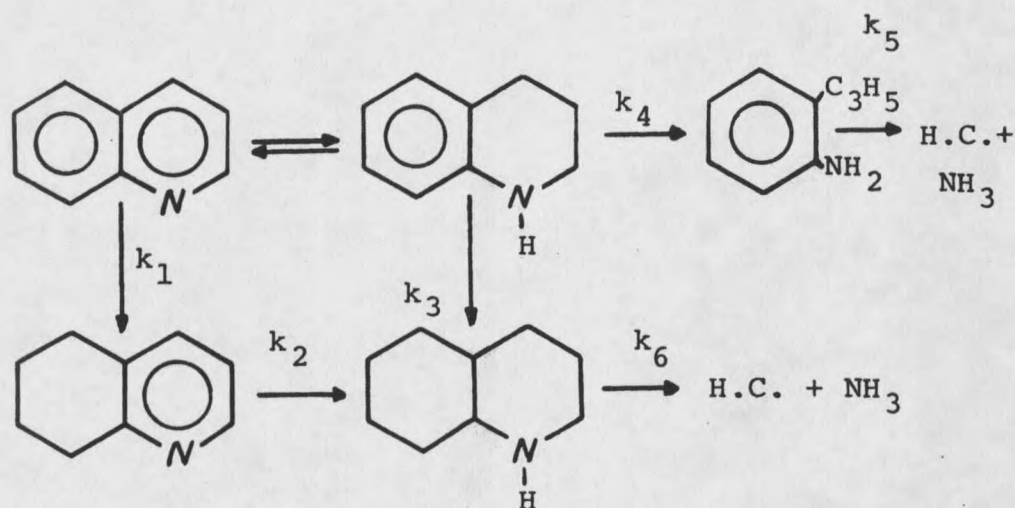
Therefore, the catalysts for coal liquids must be selective as well as active. Activity can be controlled and improved by changing the composition of metals on the support. Selectivity can be maintained or controlled by changing chemical structure or composition of the metals or by adding some promoters as discussed above. To prevent diffusion problems, physical properties of the catalysts must be very well controlled. Larger pore diameters and pore volumes are required while at the same time maintaining a large surface area [81]. As can be understood from this discussion, the catalysts should be bifunctional or multifunctional; selectively removing the heteroatoms with a minimum of hydrogen consumption.

Hydrotreating Coal Liquids and Representative Model Compounds:

Hydrotreating studies on coal liquids followed two different routes; (1) studies on model compounds to determine the mechanism of HDN, HDS, HDO, HYD and HYC, and (2) studies on actual coal liquids to determine the process variables, catalysts and operating conditions. The model compound studies are important to understand the intrinsic mechanisms involved. However, they possess a drawback and can be misleading sometimes since they do not consider the complex interaction of different compounds, functional groups and competing reactions that are present in actual coal liquids.

Chemistry of Hydrodenitrogenation (HDN): To understand the mechanism of HDN, the most studied compounds are pyridine [82-99], quinoline [66, 91, 100-103], acridine [66] and indole [85, 104]. Some of these studies considered the gas phase reactions and the others liquid phase reactions [67]. Since the reactions of coal liquids will

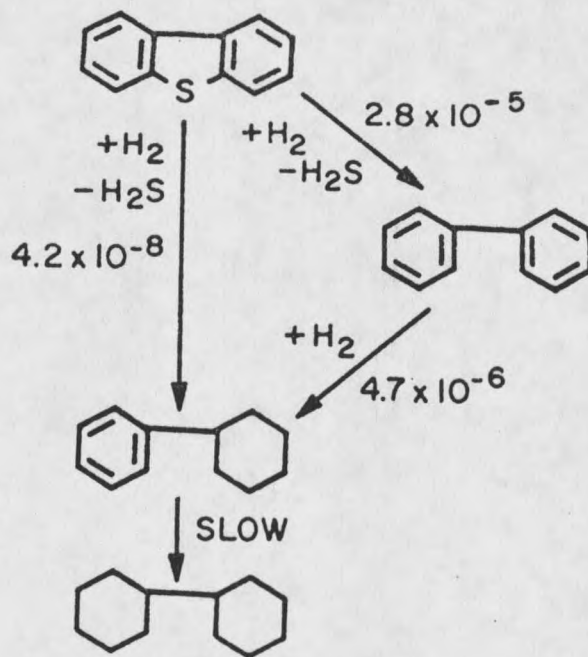
take place in liquid phase, the mechanisms derived from the liquid phase reactions will be closer to the coal liquids. The mechanism of quinoline HDN proposed by Shih et al. [66] is given below as an example.



The most favored path is the lower one with every catalyst (Ni-Mo, Ni-W or Co-Mo). The rate constant k_4 is the smallest for every catalyst. Ni containing catalysts favor hydrogenation of benzenoid ring (k_1 and k_3), but Mo containing catalysts favor hydrogenation of the heteroaromatic ring (k_2). The cracking steps (k_4 and k_6) are more dependent on the source of the alumina than on the metals present which is reasonable since cracking requires acidic sites. Presulfiding has a marked influence on the rate of hydrogenation steps, increasing them several times. The cracking reactions are

not affected. Addition of H_2S to the system increases the C-N bond breaking rate constants (k_4 and k_6). This fact is true for most of the HDN reactions. Severe conditions make Ni-Mo catalysts more active compared to Co-Mo catalysts, probably because of excessive hydrogenation since high pressures make thermodynamic equilibrium favorable towards more hydrogenation for this system. Even though Co-Mo is less active than Ni-Mo, it is more selective in hydrogenating heteroatom rings which are required prior to C-N bond breaking [101]. The activity of each catalyst also depends on the heterocyclic nitrogen compounds studied [104]. For example, Co-Mo is more active for Pyrole and Carbozole HDN than Ni-Mo.

Chemistry of Hydrodesulfurization (HDS): This is the most studied reaction among hydrotreating reactions because of its importance in the petroleum industry. The most studied cyclic sulfur compound is thiophene [68, 77, 98, 105-115]. The other polycyclic thiophenes received attention in the recent years [116-123]. HDS of heterocyclic sulfur compounds differ with their molecular structure. From the easiest to the most difficult: thiophene > benzothiophene > benzo[b]naphtho[2,3-d]-thiophene > 7,8,9,10-tetrahydro-benzo[b]naphtho[2,3-d]-thiophene > dibenzothiophene > methyl substituted benzothiophenes [76, 118]. As an example, HDS mechanism of dibenzothiophene is given [116, 120],



The lower path is favored with sulfided Co-Mo catalysts, and the fastest reaction is the removal of sulfur without any hydrogenation of benzene rings. This is the advantage of the Co-Mo catalysts over the Ni-Mo or Ni-W catalysts. Co-Mo is very selective for removing sulfur without spending any hydrogen other than necessary to remove sulfur. With Ni-Mo catalysts, the activity is about two times higher than Co-Mo, but the yield of cyclohexylbenzene is three times higher. This shows how poorly selective is the Ni-Mo catalysts even though it is very active. Ni-W gives similar results to Ni-Mo, but stays intermediate between Ni-Mo and Co-Mo. Addition of H_2S suppresses HDS but

enhances hydrogenation of benzene ring. These results are true for the most of the HDS reactions of heterocyclic sulfur compounds.

Hydrogenation and hydrocracking also takes place on these catalysts at the same time because of their bifunctional character, and they follow similar mechanisms in both HDS and HDN. Cracking activity of catalysts depends more on the support than on metals. Silica containing gamma-alumina supports are more active [124]. Ni-W catalysts are more active for cracking than Co-Mo and Ni-Mo [124]. Studies with model compounds showed that HYD, HDN and HDS take place on different sites of the surface [124, 125]. Presence of heterocyclic nitrogen compounds hinders the HDS and HYD activity of Co-Mo catalysts. HDS is in general not sensitive to the basicity of a compound, but HYD is very sensitive to the basicity of the compounds. However, HDS deactivates more than HYD [124].

The first papers concerning coal-liquids upgrading appeared in the literature in the late seventies [126-135] and in the early eighties [67, 69, 136-159]. Their primary objective was to remove heteroatoms in the syncrude. They covered various operating conditions, tested almost every commercially known hydrotreating catalyst and developed new catalysts to achieve their objective. The common conclusion was the difficulty of removing nitrogen, especially from heavy syncrudes or syncrude fractions, and the necessity for continued research to develop new highly selective HDN catalysts.

It appears from some of these studies [69, 130-132, 140, 142] that the catalyst-support physical properties have a significant effect on the activity of the catalysts for HDN, HDS and HDO. The

catalyst with larger surface area and pore size distribution in the larger pore diameter range gave better HDN. HDS and HDO are less sensitive to pore size distribution [69]. One reason for poor performance of some good commercial hydrotreating catalysts for heavy coal liquid fractions is their pore size distribution even though they have large surface area [131, 132, 142]. The commercial catalysts have been developed for petroleum hydrotreating and their pore volume distribution is usually in the small pore diameter range.

The catalytic factor comes from the metals present. Metal content and composition have a pronounced effect on the catalyst activity and selectivity. However, if a right catalyst support is not selected, the effect of metals appears to be negligible. There is some disagreement about which metal combinations are most active; Ni-Mo, Co-Mo or Ni-W. The common conclusion is, however, that the Ni-Mo catalysts are more active for HDN and HYD than either Co-Mo or Ni-W [67, 79, 128, 132, 140]. The reasons for the disagreement appear to be originating either in the physical properties [131, 150] or in the impregnation methods [144, 132, 153]. Increasing the concentration of Mo on the catalyst increases the HDN activity [131, 132, 152]. Increasing Ni or Co at fixed Mo concentration (12-16%) increases the HDN activity [69]. Adding phosphorus as a promoter increases the HDN activity of Ni-Mo [69, 128]. Ni-Mo catalysts produce more saturated hydrocarbons, alicyclics or naphthenes, but Co-Mo produces more aromatics. The operating conditions have a marked effect on HDN, HDS, HDO and HYD. HDN, HDS and HDO are improved by increasing temperature [67, 127, 128, 130, 131, 138, 141, 146, 150, 153, 155, 157, 159]. However the

effect of temperature on HDS is not great [67, 138, 154]. The effect of temperature on hydrogenation depends on pressure, and sometimes high temperatures decrease hydrogenation because of thermodynamic equilibrium [127]. Low space velocities or short residence times give better HDN, HDS, HDO and HYD [128, 131, 138, 141, 146, 155, 159]. Nevertheless, selectivity is best at a low residence time and high temperature [141]. Generally, higher pressures and temperatures and lower space velocities (high severity conditions) are required for heavier feeds. Light fractions of coal liquids can easily be hydro-treated under mild operating conditions. The operating conditions will be, however, more severe than petroleum hydrotreating [67]. High severity conditions produce more gaseous and hydrogenated products, but less coke [67, 148, 150]. Usually, most of nitrogen is left in the heavy fractions indicating the difficulty of removing these heavy molecular weight nitrogen compounds [143].

One of the most serious problems in coal liquids upgrading is the very short catalyst life. Catalyst deactivation is very fast compared with petroleum processes. Deactivation rate depends largely on the composition of the feed, the operating conditions, the catalyst physical properties and the reactor type. Heavier feedstocks cause more rapid catalyst deactivation than the lighter feedstocks [145-147, 153, 154]. Heavy feedstocks tend to form more coke. Stability of the feed under high temperatures is also an important factor [147, 148]. Feeds containing mineral and particulate matter cause severe catalyst aging [139, 146]. Mineral matter deposits on the outer surface and combines with the metals. It also causes more coke formation [139].

Catalysts with pore volume distribution in the smaller pore-diameter range tend to deactivate faster because coke blocks the small pores [69]. The type of reactors plays a role in catalyst deactivation. For example, catalysts in upper portions of a trickle bed reactor start to deactivate first and most of the metal deposition and coke formation take place in this section [146, 147]. In the other reactor types, deactivation is more homogeneous.

The type of reactor to be used is usually determined by the feed composition and properties. Heavy and high boiling point feeds, and feeds causing operational problems in the trickle bed reactors are usually tested or processed in a batch, a slurry or a fluidized bed reactor [147, 151]. However, the batch reactors are not suitable for bench scale or pilot plant operations. Data evaluation is also difficult for these because of difficulty in controlling residence time. Using trickle bed reactors for liquid feeds is common. Handling and data interpretation is easier for trickle bed reactors.

Trickle Bed Reactors:

In a trickle bed reactor, a liquid phase and a gas phase flow concurrently downward through a fixed bed of catalyst particles while reaction takes place. The first commercial trickle bed reactors were developed by the Shell Companies and the British Petroleum Company. They are extensively used in the petroleum industry for hydrotreating, hydrocracking and hydrogenating units [75, 160].

Hydrodynamics: The two most important hydrodynamic factors in the lab-scale trickle-bed reactors are liquid distribution and pressure drop. A poor liquid distribution causes low conversions. Usually,

liquid tends to flow along the wall and the catalysts are left poorly wetted. Higher ratio of reactor-to-particle diameter is required to assure a good liquid distribution. Particle shape also affects good liquid distribution. They are from the best to the worst: granular, spherical and cylindrical [75, 161]. That is why the upper sections of reactors are sometimes packed with inert spherical or granular particles. Therefore, for a good liquid distribution, small catalyst particles are needed in small size lab reactors. However, small particles cause excessive pressure drop through the bed. When there is a problem with coking in the upper sections of the catalyst bed, this causes serious pressure drops, even reactor plug ups [147, 148].

Mass Transfer: External mass transfer limitations to hydrogen will not be significant since the limiting reactant is in the liquid phase in hydrotreating reactions [162].

Contacting Effectiveness: In most practical laboratory-scale trickle-bed reactors, the total external area of the catalyst is not wetted. The wetted fraction increases with increasing liquid velocity [163, 164]. The effect of gas velocity is negligible [165]. However, measurements are extremely difficult. One way of overcoming this problem is catalyst dilution [165]. By catalyst dilution with inert particles, axial dispersion is reduced, and plug flow is approached, catalyst wetting and heat transfer is improved.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) IN CATALYST CHARACTERIZATION

Surface analysis by x-ray photoelectron spectroscopy (XPS), more commonly known as electron spectroscopy for chemical analysis (ESCA),

is accomplished by irradiating a sample with monoenergetic soft x-rays and energy analyzing the electrons emitted. MgK α x-rays (1253.6 ev) or AlK α x-rays (1486.6 ev) are used. The penetrating power of these photons in a solid is in the order of 1-10 micrometers. They interact with atoms in this surface region by photoelectric effect, causing electrons to be emitted. The emitted electrons have kinetic energies given by:

$$KE = hv - BE - Q$$

where hv is the energy of a photon, BE is the binding energy of the atomic orbital from which the electron originates, and Q is the spectrometer work function.

The binding energy can be regarded as an ionization energy of the atom for the particular shell involved. Therefore, every shell of an atom or different atoms will emit at different energy levels depending on the energy level of the shell.

Even though the photons can penetrate to a depth of a few micrometers, only those electrons that originate within tens of Angstroms below the solid surface can leave the surface without energy loss. It is these electrons which produce peaks in spectra. A more detailed theory and uses of ESCA is given in the references [167-171].

The electrons leaving the sample are detected by an electron spectrometer according to their kinetic energy. The analyzer operated as an energy "window", accepting only those electrons having an energy within the range of this fixed window, referred to as the pass

energy. Scanning for different energies is accomplished by applying a variable electrostatic field before the analyzer is reached.

Application of ESCA to catalyst characterization is new, and has been applied only for a decade. The basic applications to determine the chemical state of catalytic compounds, for example, transition metal oxides and sulfides, started in the early seventies [172-183].

When it was understood that ESCA had great potential applications in determining the chemical state of the metals on the catalyst, it found an extensive application in this field. Most of the applications were done on the Co-Mo catalysts since this catalyst was very important to the petroleum industry [31, 35, 40, 42, 52, 56, 181, 184-192].

Recently some nickel-containing catalysts, such as Ni-Mo, Ni-W, Ni or some tungsten catalysts, were studied by ESCA [55, 62, 193-197].

From the shifts in the BE of an element on the catalyst surface, its chemical environment can be qualitatively obtained. Usually the BE shifts range from 0.2 to 5 eV. See Fig. 5 for example.

It is also possible to obtain quantitative results on the quantities of metal ions present, dispersion of metals on the surface, etc. [198-200].

RESEARCH OBJECTIVE AND PLAN

The objective of this research was to develop catalysts which would be able to upgrade the SRC-II Light Ends Column Feed to a feedstock acceptable to the conventional petroleum refineries or a boiler fuel.

To achieve this objective the following research plan was proposed.

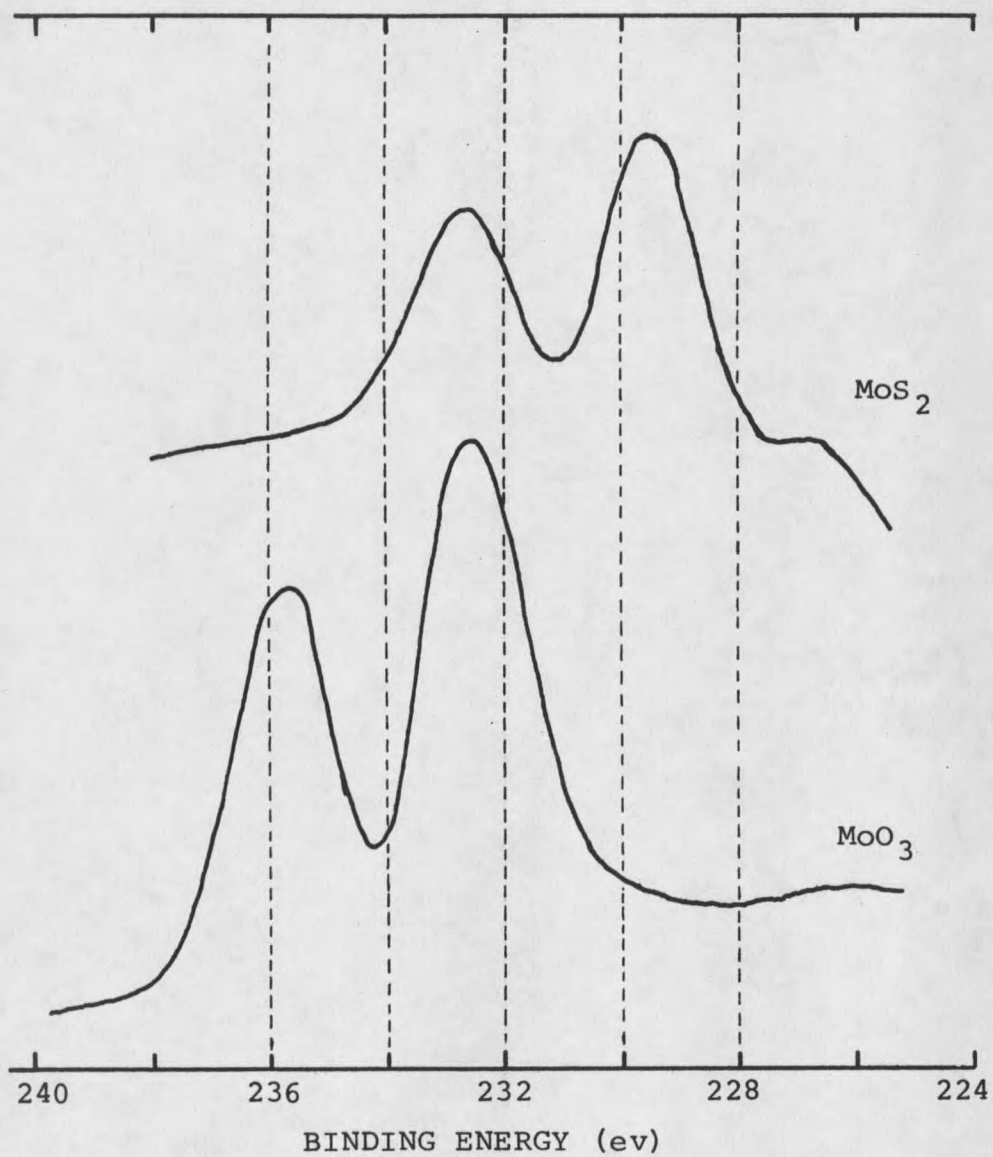


Figure 5. An example of XPS (ESCA) Binding Energy Shifts

Phase I:

- a) Selection of a proper catalyst support (a large surface area and a pore volume distribution in the large pore diameter range),
- b) Determining the effect of metal combinations on the catalyst activity and selectivity,
- c) Determining the effect of water addition to the feed on activity and selectivity of the metals on certain reactions involved,

Phase II: A further study of the two best metal combinations in phase I.

- a) Determining the effect of impregnation technique on the activity and selectivity of the catalysts,
- b) Determining the effect of water on the activity and selectivity of the catalysts produced in part a.

Phase III: Consists of characterization of catalysts tested in phase I and II by ESCA, and correlation of catalyst activity and selectivity with the surface structure of the catalysts.

The effect of water on catalyst activity was also studied since water is present in coal liquids in certain amounts and it is always produced during the process from HDO reaction. Coal liquids contain approximately 3 wt% oxygen and the amount of water can reach a substantial amount in the catalyst pores to affect the activity of a catalyst. If its effect is known in advance some precautions can be taken or a catalyst resistant to the effect of water should be utilized if the effect is negative.

CHAPTER 3

EXPERIMENTAL

FEEDSTOCK AND MATERIALS USED

Solvent Refined Coal (SRC-II) Light Ends Column Feed (LECF) was used as a feed stock in this research. SRC-II LECF was obtained from the Tacoma (Washington) pilot plant of Pittsburgh & Midway Coal Mining Company. The properties of the feed are shown in Table 2.

The catalyst support was obtained from Katalco (serial no. 81-6731) which is a 0.794 mm γ -alumina extrudate. The support possesses a surface area of 223 m²/g, a pore volume of 1.1 ml/g, and a pore diameter of 169 Å. See Appendix B for the detailed analysis of the support properties. The metal salts used to impregnate the metals were;

1. Ammonium Hepta Molybdate (from Baker Analyzed, reagent grade); $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (F.W.= 1235.9 gm) with 81.4 % essay in MoO_3 (M.W.=143.94 gm).
2. Nickel Nitrate (from Baker Analyzed, reagent grade): $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (F.W.=290.82 gm) with 99.2 % essay in NiO (M.W.=74.71).
3. Cobalt Nitrate (from MCB, reagent grade): $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (F.W.= 291.55 gm) with 99.5 % purity.

4. Ammonium Meta Tungstate (from MCB, technical grade):

$(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ with 85 % assay in WO_3 (M.W. = 231.85 gm).

The reference compounds used for ESCA (XPS) analyses were;

1. Molybdenum (IV) Sulfide (from Aldrich); MoS_2 with 99+ % purity.
2. Cobalt (II,III) Oxide (from Aldrich); Co_3O_4 with 99.999 % purity.
3. Cobalt (II) Oxide (from Alfa); CoO with 95 % purity.
4. Cobalt (II) Molybdate (from Alfa); CoMoO_4 with 98 % purity.
5. Cobalt Aluminate (from Alfa); CoAl_2O_4 with 98 % purity.
6. Aluminum Molybdate (from Alfa); $\text{Al}_2(\text{MoO}_4)_3$ with 99 % purity.
7. Nickel Molybdate (from Alfa); NiMoO_4 with 98 % purity.
8. Molybdenum Trioxide (from Baker); MoO_3 with 100 % purity.
9. Nickel(ous) Oxide (from Fischer); NiO with 99.97 % purity.
10. Tungsten Oxide (from Fischer); WO_3 , pure.
11. Ni_6S_5 and Co_9S_8 were synthesized in the lab as described in reference 201.

CATALYST PREPARATION TECHNIQUES

Catalysts were prepared by impregnating metal salts on a 0.794 mm (1/32 ") alumina-extrudate catalyst support by using the incipient wetness technique. In this study, the total metal load (as oxides) was kept at 20 wt% (which is percent weight increase over the support), with promoters (Ni and/or Co) and active metals (Mo and/or W) at 4 wt% and 16 wt% respectively. This enabled us to determine the effect

of metal combination on the activity of catalysts for upgrading SRC-II.

Stepwise Impregnation: Stepwise impregnation was used to impregnate the metals because of the difficulty in impregnating Mo and also to achieve better activity. In our earlier studies, when the concentration of Mo solution exceeded 4 wt%, the solution turned milky and a sticky white precipitate covered the outer surface of the particles a few minutes after soaking the support in the solution. Catalysts prepared this way were less active than their commercial counterparts [202, 153]. It was postulated that the precipitated material was plugging up the pores and also causing poor distribution of impregnated metals. In stepwise impregnation, the following procedure was used.

1. Wash the support,
2. Dry at room temperature until the particles can move freely, then oven dry for 8 hours at 110°C,
3. Calcine in an oven for 8 hours at 500°C,
4. Cool the support in a desiccator to room temperature,
5. Prepare a solution to impregnate 1 wt% metal oxide for Ni or Co and 3 wt% for Mo or W,
6. Soak the support in the solution while mixing the contents, and continue mixing for 1 minute,
7. Drain the excess solution (no excess solution in the case of Mo and W) and dry the catalyst by spreading it on a paper towel at room temperature,
8. Repeat steps 2-7 until the desired metal loading is reached.

9. Repeat steps 2-7 until the desired metal loading for Mo or W is reached. Follow the sequence of metal impregnation and the metal composition given in Table 3.

Seven catalysts (see Table 3), containing different metal combinations and compositions, were produced this way and tested for the effect of metal combinations.

Table 3. Metal Composition of Catalysts

Name of Catalyst	Metal Load as wt% increase over support				Impregnation Sequence and type
	Co	Mo	Ni	W	
TS-11	4	16	-	-	Co(s)+Mo(s)
TS-12	4	8	-	8	Co(s)+Mo(s)+W(s)
TS-13	4	-	-	16	Co(s)+W(s)
TS-14	2	8	2	8	Co(s)+Mo(s)+Ni(s)+W(s)
TS-15	-	-	4	16	Ni(s)+W(s)
TS-16	-	8	4	8	Ni(s)+Mo(s)+W(s)
TS-17	-	16	4	-	Ni(s)+Mo(s)
TS-18	4	16	-	-	Mo(b)+Co(b)
TS-19	-	16	4	-	Mo(b)+Ni(b)
TS-20	-	16	4	-	Ni(s)+Mo(b)
TS-21	4	16	-	-	Co(s)+Mo(b)

b = batchwise impregnation

s = stepwise impregnation

Single Step Impregnation: The best metal combinations from the stepwise impregnation technique (Co-Mo and Ni-Mo) were prepared with two different impregnation techniques as described below to test the effect of impregnation technique on the catalyst activity.

First, the order of impregnation of metals was reversed. Initially Mo and then Co or Ni were impregnated with calcination between each metal impregnation. The following procedure was used.

1. Follow steps 1-4 in the stepwise impregnation,
2. Prepare a solution to impregnate 16 wt% Mo,

3. Soak the catalyst support in the solution and keep under constant mixing for an hour,
4. Drain the excess solution and dry the catalyst by spreading on a paper towel at room temperature,
5. Sift the catalyst to remove the precipitate on the outer surface of the catalyst,
6. Oven dry at 110°C for 8 hours,
7. Calcine at 500°C for 8 hours,
8. Cool the catalyst to room temperature in a desiccator,
9. Prepare a solution to impregnate 4 wt% Co or Ni,
10. Soak the catalyst in the solution while mixing the contents and continue mixing for 5 minutes,
11. Repeat steps 4, 6, 7, and 8.

Second, the order of impregnation of the metals was the same (first Co or Ni then Mo), but Co or Ni was impregnated in two steps (2 wt% each time) and Mo in a single step. The following procedure was followed.

1. Follow steps 1-4 in stepwise impregnation,
2. Prepare a solution to impregnate 2 wt% Co or Ni,
3. Soak the support in the solution and mix for five minutes,
4. Follow steps 4, 6, 7, and 8 in the previous procedure,
5. Repeat steps 2-4 once more to make 4 wt% Co or Ni,
6. Prepare a solution to impregnate 16 wt% Mo,
7. Soak the catalyst in the solution and keep under constant mixing and blowing air at room temperature until the catalyst is dry,

8. Follow the steps 5-8 in the previous procedure,
9. Wash the catalyst with distilled water to remove the precipitate on the outer surface of the catalyst,
10. Repeat step 8.

The catalysts produced in this way are listed in Table 3 and given the names; TS-18 (Mo+Co), TS-19 (Mo+Ni), TS-20 (Ni:s+Mo:b), and TS-21 (Co:s+Mo:b).

Catalyst Pretreatment: Catalysts were sulfided before being used to improve their activity and reduce surface poisoning [77]. The reactor (will be explained later) was loaded with catalyst and heated to 400°C by an electric furnace while a stream of 10% H₂S/H₂ mixture passed through the catalyst bed for 12 hours (see Fig. 6). The spent gas from the sulfiding reactor was scrubbed by a series of impingers with 20% NaOH solution.

Extreme caution was taken during this operation because exposures of 800 to 1,000 ppm H₂S may be fatal in 30 minutes [203]. The low concentrations (20 to 150 ppm) of H₂S can be identified by a distinctive odor similar to a rotten egg. However, at higher concentrations it can not be detected by its odor.

CONTINUOUS TRICKLE BED REACTOR SYSTEM

For this study, a bench scale reactor fabricated by the Chemical Engineering Department at Montana State University was used. The reactor system is shown in Fig. 7. The reactor was a 101.6 cm long 2.54 cm diameter Schedule 80 Inconel pipe. A 0.635 cm stainless steel cross was welded to the top of the reactor to serve as liquid and gas

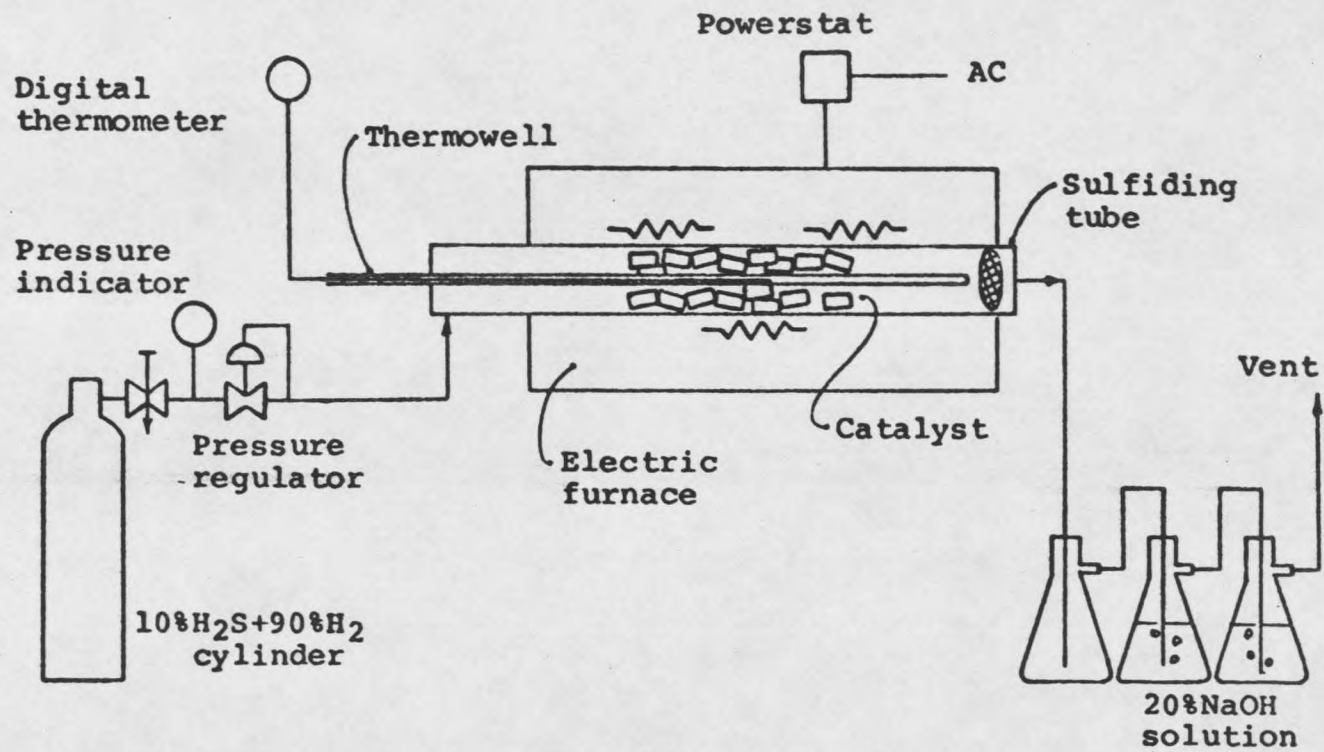


Figure 6. The Silfiding Equipment

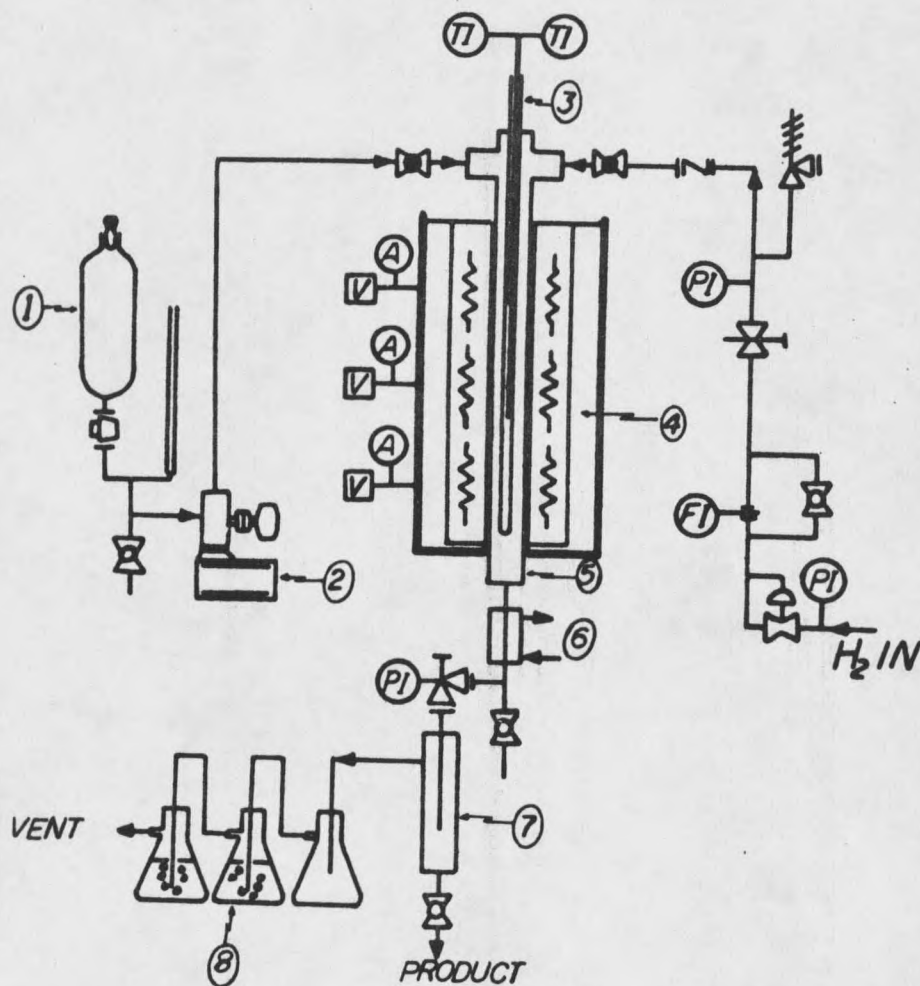


Figure 7. Trickle Bed Reactor System, (1) Feed Reservoir, (2) Milton Roy pump, (3) Thermowell, (4) Aluminum heating block and insulating material, (5) Reactor, (6) Condenser, (7) Gas-liquid separator, (8) 20% NaOH solution and gas scrubber, (A) Amperemeter, (FI) Hydrogen flow meter, (PI) Pressure gage, (TI) Digital thermometer, (V) Variac, (PR) Pressure regulator, (NHW) NiChrom heating wire, (BPR) Back pressure regulator, (PRV) Pressure relief valve, (CV) Check valve, (MV) micro-meter valve.

feed ports to the reactor, and the fitting of a 95 cm long thermowell tubing. The reactor was placed into the bore of a 15.24 cm O.D. 91.44 cm long aluminum block wrapped with three sets of ceramic bead encased NiChrome wire heating coils. Each of the three coils was connected to a Powerstat variable transformer which is manually controlled for temperature. Two chromel-alumel (type K) thermocouple wires were placed in the thermowell to monitor temperatures at the end of the preheat section and at the center of the catalyst section. The temperatures were read by Cole-Palmer digital thermometers (Model 8520-40).

The upper section of the reactor was loaded with 175 ml of 0.635 cm spherical Denstone inert support [204] and 25 ml of 0.318 cm cylindrical Denstone inert support. The function of this section is mainly to preheat and uniformly distribute the feed. 44 gm of catalyst (based on oxide form and corresponding to approximately 60 ml) diluted [164] with 60 ml of 0.318 cm cylindrical Denstone inert support was loaded below the preheat section. The remainder of the reactor was filled with 0.318 cm cylindrical Denstone inert support (see Fig. 8). Finally, a stainless steel screen was placed to support the catalyst bed above the reactor plug which was threaded into the pipe.

The SRC-II LECF was pumped into the top of the reactor by a Milton-Roy simplex piston pump (Model A MR-1-23) through a 0.318 cm stainless steel tube. The pump is equipped with a manually controlled micrometer adjustment for feed rate control. Technical grade hydrogen was fed through a pressure regulator, a 0.318 cm stainless steel tube, a micrometer valve (to adjust the flow rate), a Brooks Thermal

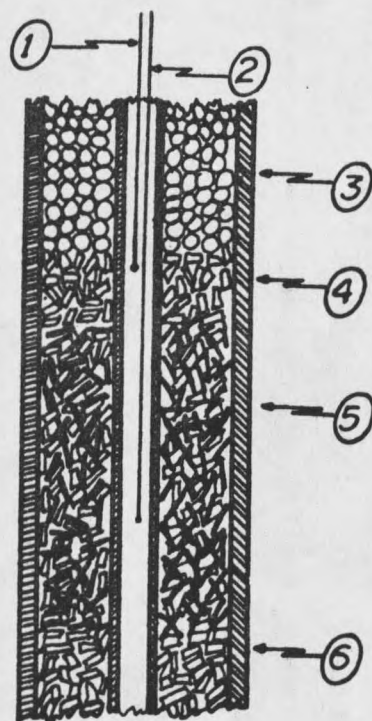


Figure 8. Cross Section of the Packed Reactor

① Thermocouple which monitors temperature at the catalyst section inlet, ② Thermocouple which monitors temperature at the catalyst section, ③ Preheat section (0.635 cm spherical inert support), ④ Inlet to the catalyst section (0.318 cm cylindrical inert support), ⑤ Catalyst section (mixture of catalyst and 0.318 cm inert support), ⑥ Inert section (0.318 cm inert support).

Mass Flowmeter [205], and a ball check valve to the top of the reactor.

Hydrogen and the SRC-II feed was passed through the pressurized and packed reactor bed concurrently, to a condenser, and then to a gas-liquid separator through a Grove back-pressure regulator equipped with a corrosion-resistant Teflon diaphragm. The exit gases were scrubbed by a 10% NaOH solution and vented. The liquid product was collected in a bottle continuously.

EXPERIMENTAL PROCEDURES AND OPERATING CONDITIONS

The loaded and sealed reactor was placed in the heating unit and connected to the feed lines and product separator. The system was pressurized to 6.9 MPa (1000 psig) with nitrogen and the all connections were checked for leaks with Snoop liquid detergent. If there were no leaks, the heaters were turned on and the reactor was flushed with nitrogen for 10 minutes to remove air. The system was kept under nitrogen pressure until the desired starting temperature of 350 C was reached.

The cooling water valve for the condenser was opened and nitrogen pressure was released before connecting the hydrogen line to the system. When the system reached the desired hydrogen pressure of 6.9 MPa, the hydrogen flow rate was adjusted to 1,900 scm/min (10,000 scf/bbl of oil) with the micrometer valve. The feed reservoirs were filled with SRC-II LECF and the pump was turned on. Feed rate was measured by timing the change in the fluid level in the buret and

adjusted by the pump micrometer. The flow rate was checked every two hours to ensure a steady flow rate.

Every run was started at 350°C, and Liquid Hourly Space Velocity (LHSV) was kept at 15.0 hr⁻¹ for the first 5 minutes to help prevent an initial rapid deactivation of the catalyst. The temperature was steadily raised to the steady state value of 400°C within 5 hours. The other operating conditions were: pressure of 6.9 MPa (1000 psig), Hydrogen flow rate of 1900 scm/min (10,000 scf/bbl of oil), and LHSV of 1 hr⁻¹ (or WHSV of 1.3) (see Table 4). Water was added to the feed as 2% of the feed for the runs which applied this technique.

Table 4. Operating Conditions

Starting Temperature,	°C	350 ± 10
Starting LHSV*,	hr ⁻¹	15 ± 1
Operating Pressure,	MPa	6.9 ± 0.6
Operating Temperature,	°C	400 ± 10
Operating LHSV,	hr ⁻¹	1.0 ± 0.1
WHSV**,	hr ⁻¹	1.3 ± 0.2
Amount of Catalyst,	ml	60 ± 2
Amount of Catalyst***,	g	44.2 ± 0.2

* Liquid Hourly Space Velocity, for only the first three minutes.

** Weight Hourly Space Velocity.

*** Based on oxidic (unsulfided) form of the catalyst.

It varies for every catalyst in sulfided form since every catalyst uptakes a different amount of sulfur.

The product was collected continuously in a bottle and the bottle was changed every 10 hours. Product samples for analysis were taken from these bottles so that every analyzed sample reflects the average value of 10 hours.

When the run was completed (either 140 or 100 hours), the pump was turned off and hydrogen was let flow for 30 minutes to make sure

that oil left in the reactor had enough time to react. Then, the hydrogen valve was closed, the heaters were turned off, and the system was depressurized.

ANALYTICAL PROCEDURES

Sample Pretreatment: After completion of a run, the amount of product in every bottle was measured and recorded. Water produced in the process was separated from the oil and the oil was washed with distilled water to remove water soluble nitrogen compounds. The oil was separated from the water again. Some samples were taken from the bottles containing the product for the periods 10-20, 50-60, 90-100, and 130-140 hours for nitrogen analysis.

Nitrogen Analysis: The nitrogen analysis for the product samples were done by Macro-Kjeldahl Method [206-208]. The percent Hydrodenitrogenation (HDN) was calculated with the following equation;

$$\% \text{ HDN} = \frac{(\text{wt}\% \text{ N in the feed}) - (\text{wt}\% \text{ N in the product})}{(\text{wt}\% \text{ N in the feed})}$$

Where N is nitrogen present in the feed or the product.

Distillation: Product distillations were done in a column with three theoretical plates and a reflux ratio of three to determine the quality of the product obtained.

Elemental Analysis: The elemental analysis of the product samples was done by Carlo Erba Elemental Analyzer (model 116). Sample containers were cleaned with acetone, dried in an oven and then weighted. About 1.0 mg of sample was injected into the containers and the container mouth was sealed by squeezing with a pair of pliers.

After recording the weight of the sample the containers was placed in a rotating disc of the analyzer. Disc contains 22 sample holes. With every batch of sample analysis a couple of blank containers and standard chemicals were also analyzed as references [209]. Every sample was analyzed three times to get a reliable result. When enough consistency is reached the result was assumed to be the correct value.

ESCA (XPS) Analysis: The ESCA analyses of the catalysts were done by Leybold-Heraeus X-ray Photoelectron Spectrometer (L-H EA11). The catalyst particles were mounted on an Indium foil and evacuated in a separate evacuation chamber at 100°C under vacuum of 10^{-5} torr. A double-stick scotch tape was used for the reference compounds, the catalysts tested for the effect of impregnation technique and sulfided catalysts. The sulfided samples and the reference samples were prepared in a glove bag under inert atmosphere to avoid contact with oxygen. Then, the samples were mounted on the sample holder of the instrument as quickly as possible to avoid adsorption of moisture. The sample holder allows a quick insertion of the sample into preparation chamber and then to the analysis chamber. When vacuum in the chamber reached 10^{-7} or 10^{-8} torr, the x-ray source was turned on. The data was recorded both with an analog and a digital recorder. The latter was done by a Tektronix computer, and stored on a magnetic tape. For low signals such as Co 2p and Ni 2p spectra, a few scans were recorded by adding signal count rates on top of each other to magnify the signal.

When the analysis of all the catalysts were completed, the data were cleaned from noise (basically caused by the digital recorder) and smoothened by a second order smoothening function (see App. C for details). A copy of every scan was taken by a Tektronix Hard Copier or an X-Y recorder which is connected to the computer. The peak binding energies and intensities were determined and all binding energies were referenced to C 1s peak binding energy of 284.6 eV to account for the charging of insulating type catalyst samples.

CHAPTER 4

RESULTS

Results will be reported in three sections. The first section covers the effect of metal combinations on HDN, HYD and HYC activities of the seven catalysts fabricated with different combinations of Ni, Co, Mo and W. The second section includes the effect of impregnation technique on HDN, HYD and HYC activities of the Co-Mo and Ni-Mo combinations. The third section explains the results of ESCA (XPS) analysis of all catalysts evaluated in the first two sections.

EFFECT OF METAL COMBINATIONS

As explained in Chapter 3, seven catalysts were fabricated by impregnating different combinations of Co, Mo, Ni and W. Co and Ni were impregnated stepwise in 4 or 5 steps, and Mo or W were impregnated stepwise to an additional 3 wt% each time until the desired metal load was reached. Each catalyst was evaluated with respect to catalytic activity twice, once with and once without water addition to the feed to test the effect of water on the catalyst performance. In addition to the seven catalysts fabricated, the blank support was tested for its capability to upgrade SRC-II LECF, both with and without water addition to the feed, as a reference to the impregnated catalysts. HDN results are plotted in Fig. 9. Overall average nitrogen content of the product oil, average HDN, H/C atomic ratio, distillation

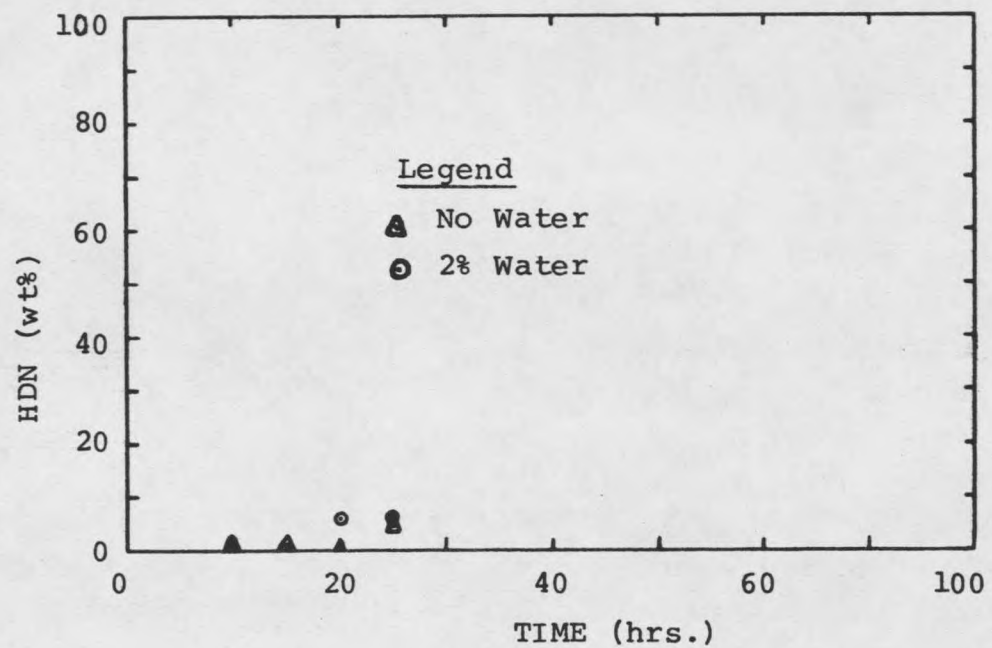


Figure 9. Hydrodenitrogenation vs. Time for the Blank Carrier (Alumina, Katalco)

fractions and percent carbonaceous material deposited on the catalyst are given in Table 5. As can be seen both from the Fig. 9 and Table 5, the blank support does not have any HDN activity and the water did not show any significant effect on HDN. Table 6 summarizes the difference between the H/C ratio and distillation fractions of the product oil and that of the feed. It also includes the relative percent change in these quantities over the feed. The effect of water on HDN, H/C ratio and distillation fractions are given in Table 7 as differences between the runs with and without water addition. Even though water did not have any effect on HDN, it enhanced the light oil production (see Table 7). In both cases, with and without water addition, the amount of light oil decreased, 2.1% and 7.1% respectively (see Table 6). The amount of middle oil increased, indicating some condensation of light hydrocarbons (see Fig. 10 and Fig. 11). Some hydrogenation occurs with the support but it is not great (Table 6 and Fig. 12).

Fig. 13 shows the HDN results of the catalyst TS-11 (4% Co, 16% Mo) as a function of time. HDN activity of the catalyst slowly decreased with time. However, the catalyst was operated for over 140 hours, and the time averaged HDN was 71 wt% and 74 wt% for the runs with and without water addition respectively. The effect of water on HDN was not significant (or may be slightly inhibiting) for this catalyst. The amount of light oil produced was 12.1 and 10.9 wt% over the feed with and without water addition respectively, and middle and heavy oil contents were reduced significantly (see Table 6 and Figures 10 and 11). This corresponds to 50% and 45% increase in light oil

Table 5. The Effect of Metal Combinations and Water on HDN, Product Quality (Distillation Fractions) and Catalyst Coking

Catalyst & Run	%N wt%	HDN wt%	H/C ^a	LO ^b wt%	MO ^c wt%	HO ^d wt%	%C ^e wt%
TS-10NW*(support)	0.71	0	1.25	22.4	66.3	11.4	10.03
TS-10W*	0.71	0	1.25	23.6	65.4	11.0	9.81
TS-11NW (Co+Mo)	0.18	74	1.38	35.0	55.7	9.4	13.06
TS-11W	0.19	71	1.38	36.2	55.0	9.1	11.61
TS-12NW (Co+Mo+W)	0.25	63	1.34	31.2	58.9	10.7	11.19
TS-12W	0.27	59	1.33	33.0	57.3	10.5	9.90
TS-13NW (Co+W)	0.35	49	1.33	33.0	56.8	10.2	9.45
TS-13W	0.25	63	1.32	35.2	57.8	6.9	12.63
TS-14NW (Co+Mo+Ni+W)	0.29	57	1.36	31.8	59.0	9.3	12.07
TS-14W	0.36	46	1.32	29.6	60.8	9.7	9.51
TS-15NW (Ni+W)	0.41	39	1.34	28.9	61.5	9.6	9.90
TS-15W	0.44	36	1.30	29.4	61.2	9.5	8.40
TS-16NW (Ni+Mo+W)	0.43	36	1.33	27.4	62.3	10.3	8.37
TS-16W	0.42	37	1.31	28.2	62.1	9.7	7.77
TS-17NW (Ni+Mo)	0.13	81	1.40	33.9	57.3	8.8	14.40
TS-17W	0.07	90	1.40	35.8	56.0	8.3	15.23

* NW = No water added, W = 2 % water added.

^a Hydrogen to carbon atomic ratio.

^b Light oil content in the boiling range 40 - 205 °C.

^c Middle oil content in the boiling range 205 - 298 °C.

^d Heavy oil content in the boiling range 298 - end point.

^e Carbonaceous material deposited on the catalyst.

Table 6. Change in H/C Ratio, Light Oil (LO), Middle Oil (MO) and Heavy Oil (HO) from the Feed

Catalyst & Run	Composition Change From the Feed				Percent Relative Change From the Feed for Each Category			
	LO	MO	HO	H/C	LO	MO	HO	H/C
TS-10NW* (support)	-1.7	1.5	0.2	0.02	-7.1	2.3	2.7	1.6
TS-10W*	-0.5	0.7	-0.1	0.02	-2.1	0.9	-0.9	1.6
TS-11NW (Co+Mo)	10.9	-9.1	-1.8	0.15	45.3	-14.0	-15.3	12.2
TS-11W	12.1	-9.8	-2.3	0.15	50.2	-15.3	-18.0	12.2
TS-12NW (Co+Mo+W)	7.1	-5.8	-1.3	0.11	29.5	-9.1	-3.6	8.9
TS-12W	8.9	-7.3	-1.6	0.10	37.0	-11.6	-5.4	8.1
TS-13NW (Co+W)	8.9	-7.8	-1.1	0.10	36.9	-12.4	-8.1	8.1
TS-13W	11.2	-7.0	-4.2	0.09	46.5	-10.8	-37.8	7.3
TS-14NW (Co+Mo+Ni+W)	7.7	-5.8	-1.9	0.13	32.0	-9.0	-16.2	10.6
TS-14W	5.5	-4.0	-1.5	0.09	22.8	-6.2	-12.6	7.3
TS-15NW (Ni+W)	4.8	-3.3	-1.6	0.11	19.9	-5.1	-13.5	8.9
TS-15W	5.3	-3.6	-1.7	0.07	22.0	-5.7	-14.4	5.7
TS-16NW (Ni+Mo+W)	3.3	-2.5	-0.8	0.09	13.7	-3.9	-7.2	7.3
TS-16W	4.1	-2.6	-1.5	0.08	17.7	-4.2	-12.7	6.5
TS-17NW (Ni+Mo)	9.8	-7.5	-2.4	0.17	40.7	-11.6	-20.7	13.8
TS-17W	11.7	-8.8	-2.9	0.17	48.6	-13.6	-25.2	13.8

* NW = No water, W = 2 % water added.

Table 7. The Effect of Water on HDN, H/C ratio, and Light Oil (LO), Middle Oil (MO) and Heavy Oil (HO) Contents

Catalyst & Run	Difference in % Composition Between Runs NW and W (W-NW)*				
	H/C	LO	MO	HO	HDN
TS-10 (Support)	0.00	1.2	-0.9	-0.4	0.0
TS-11 (Co+Mo)	0.00	1.2	-0.7	-0.5	- 3.0
TS-12 (Co+Mo+W)	-0.01	1.8	-1.5	-0.3	- 4.0
TS-13 (Co+W)	-0.01	2.4	1.0	-3.3	14.0
TS-14 (Co+Mo+Ni+W)	-0.04	-2.2	1.8	0.4	-11.0
TS-15 (Ni+W)	-0.04	0.5	-0.3	-0.1	- 3.0
TS-16 (Ni+Mo+W)	-0.01	0.8	-0.2	-0.6	1.0
TS-17 (Ni+Mo)	0.00	1.8	-1.3	-0.6	9.0

* NW = No water added, W = 2% water added.

contents over the feed for these runs. Despite the insignificant effect of water on HDN, water enhances the light oil production (see Tables 6 and 7 and Fig. 10). The H/C ratio remained the same both with and without water addition (Fig. 12). This may indicate some contribution to HYC from water.

Fig. 14 shows HDN results of the catalyst TS-12 (4% Co, 8% Mo, 8% W). This catalyst was less active than the catalyst TS-11 (Co+Mo) which gave 74 wt% HDN vs. 63 wt% HDN for the present catalyst (see Table 5). Deactivation was faster for TS-12 (Co+Mo+W) than for TS-11 (the slope of the line gives the trend of deactivation). Quality of product was not as good using TS-12 (Co+Mo+W) as with TS-11 (Co+Mo). Going from the TS-12 (Co+Mo+W) to TS-11 (Co+Mo) catalyst, light oil production was lowered from 10.9% to 7.1% without water addition and from 12.1% to 8.9% with water addition (see Table 6 and Fig. 10); the H/C ratio was also lower (less HYD activity). The effect of water on HDN appeared slightly inhibiting (although not significant), but it

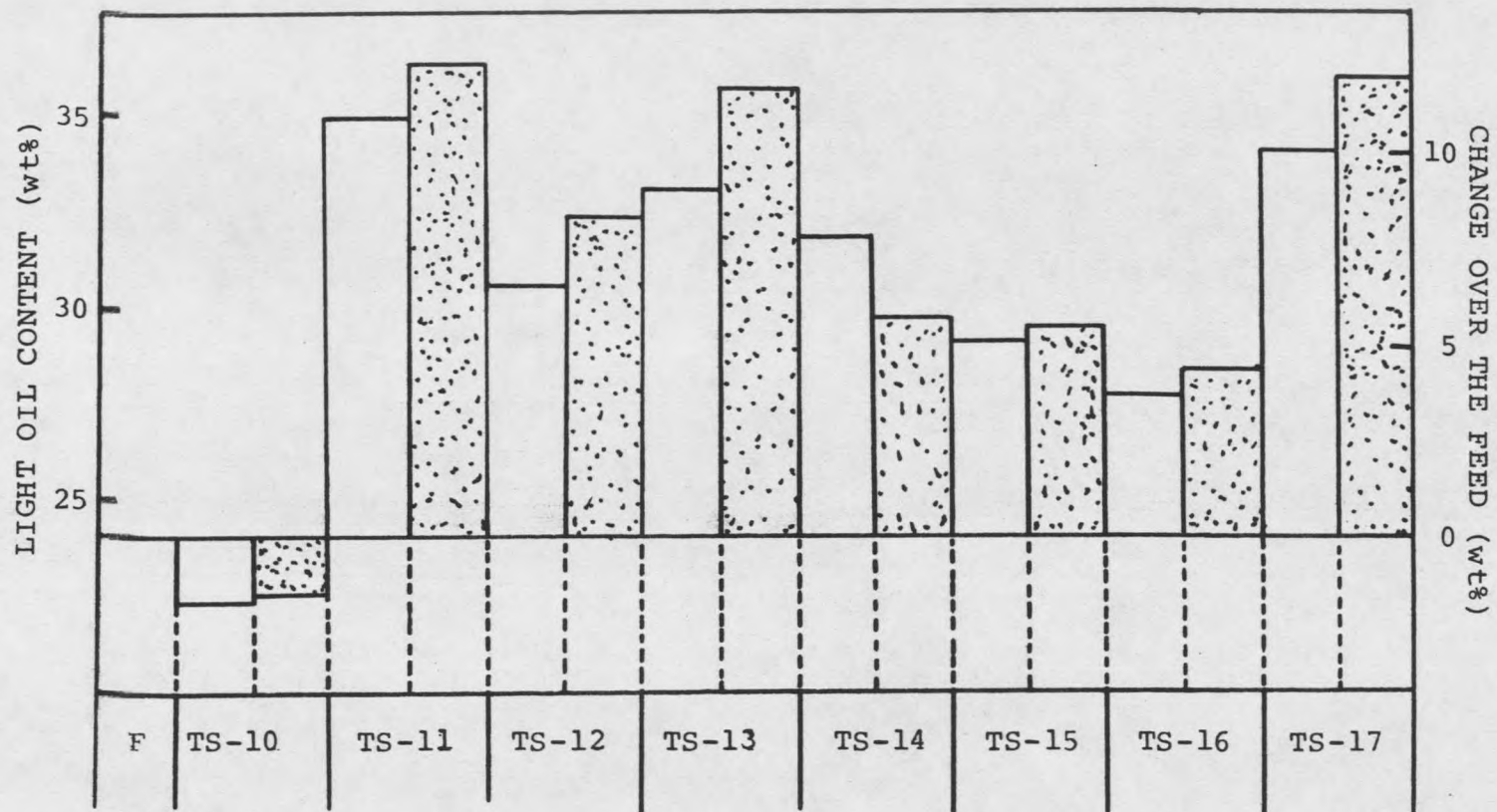


Figure 10. The Effect of Metal Combinations and Water Addition on Light Oil Yield

F = Feed, TS-10; blank carrier (alumina, Katalco), TS-11; Co+Mo, TS-12; Co+Mo+W, TS-13; Co+W, TS-14; Co+Mo+Ni+W, TS-15; Ni+W, TS-16; Ni+Mo+W, TS-17; Ni+Mo.

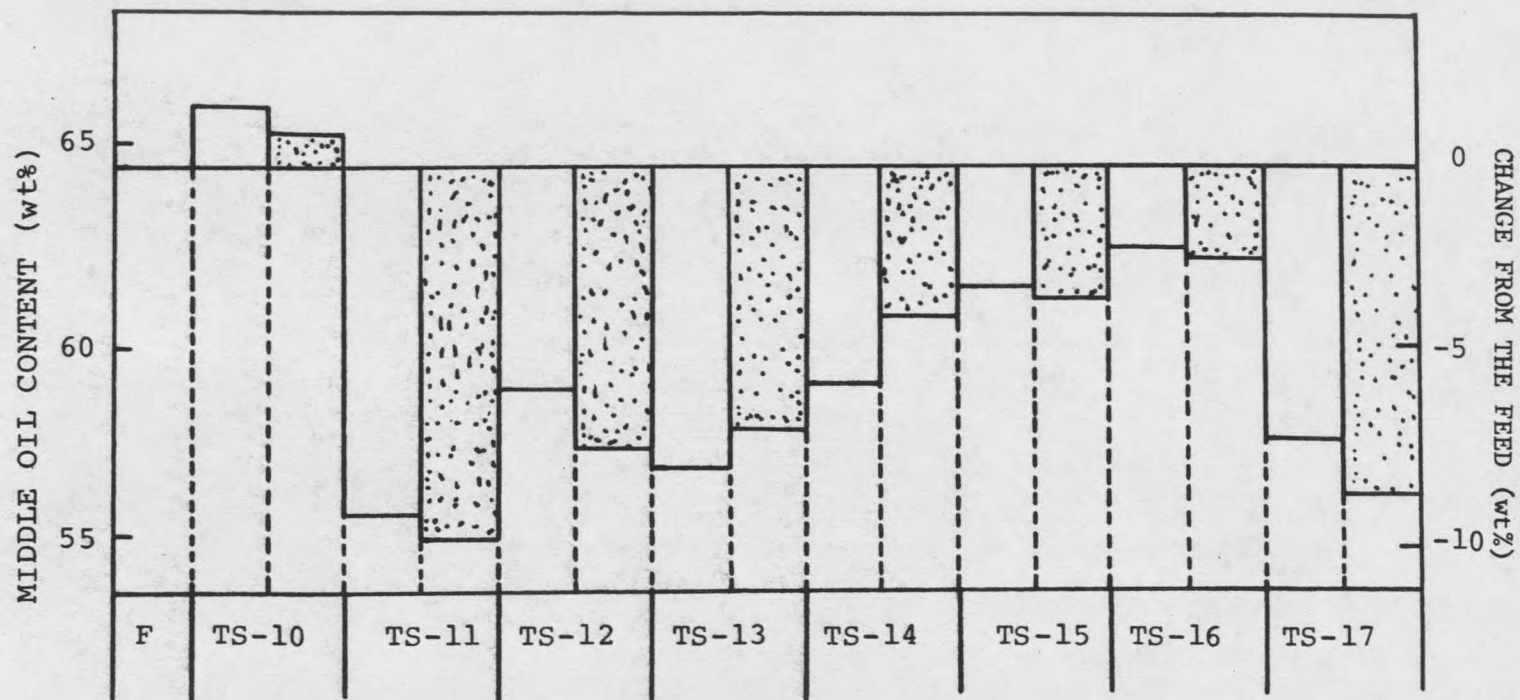


Figure 11. The Effect of Metal Combinations and Water Addition on Middle Distillate

F = Feed, TS-10; blank carrier (alumina, Katalco), TS-11; Co+Mo, TS-12; Co+Mo+W, TS-13; Co+W, TS-14; Co+Mo+Ni+W, TS-15; Ni+W, TS-16; Ni+Mo+W, TS-17; Ni+Mo.

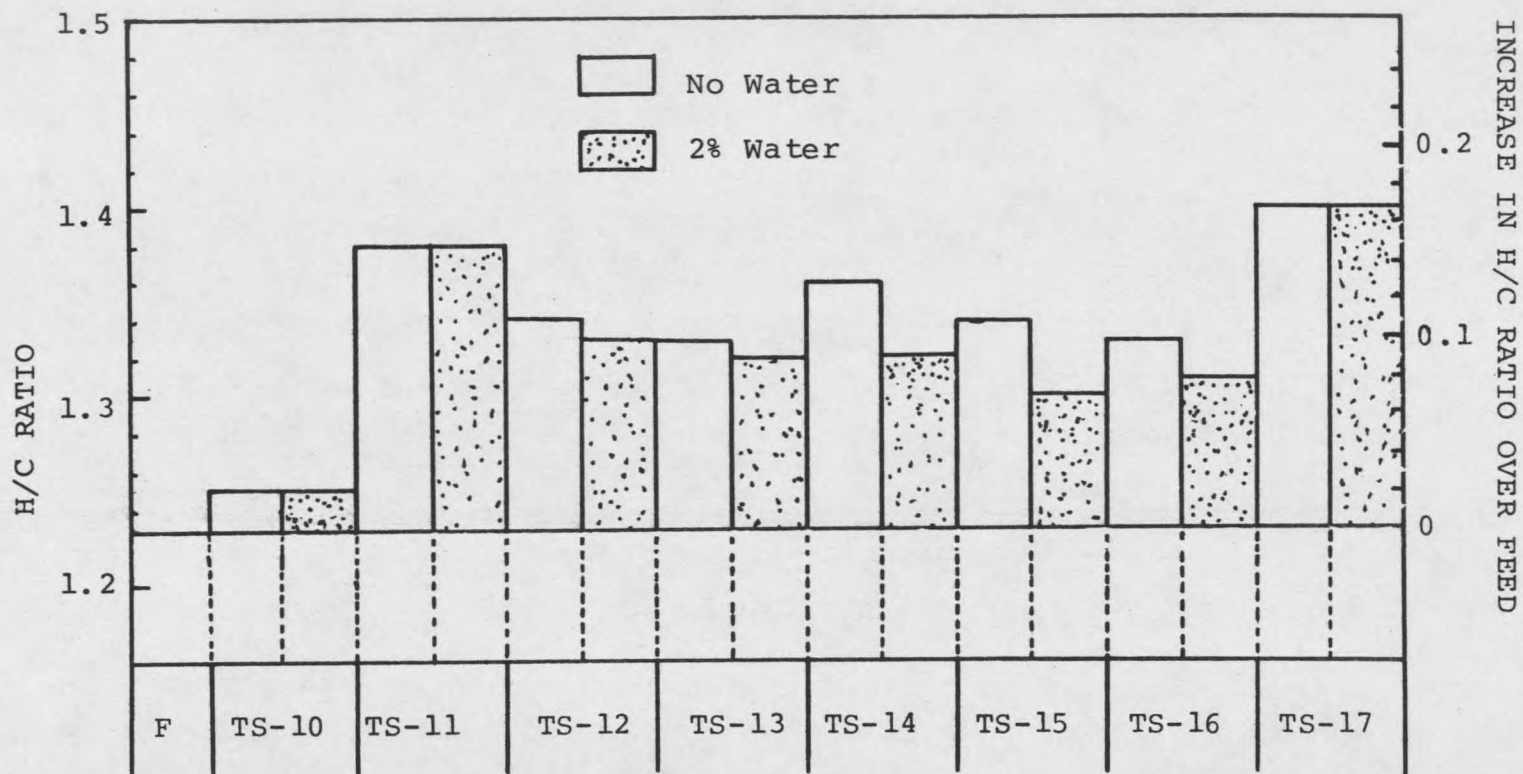


Figure 12. The Effect of Metal Combinations and Water Addition on H/C Ratio (atoms hydrogen per atom carbon)
 F = Feed, TS-10; blank carrier (alumina, Katalco), TS-11; Co+Mo, TS-12;
 Co+Mo+W, TS-13; Co+W, TS-14; Co+Mo+Ni+W, TS-15; Ni+W, TS-16; Ni+Mo+W,
 TS-17; Ni+Mo.

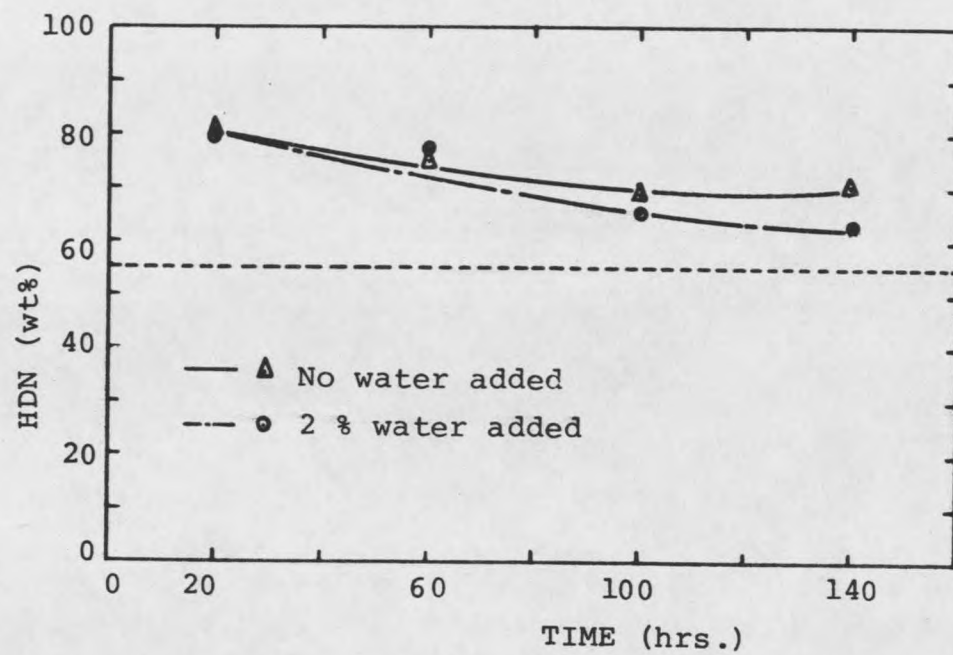


Figure 13. Hydrodenitrogenation vs. Time for the Catalyst TS-11 (4 wt% Co, 16 wt% Mo)

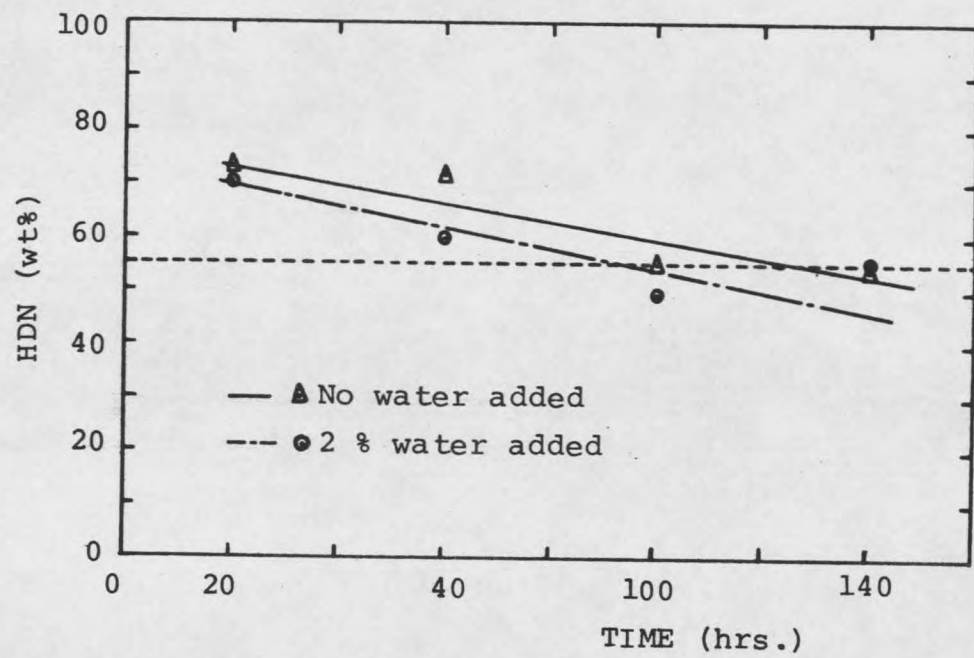


Figure 14. Hydrodenitrogenation vs. Time for the Catalyst TS-12 (4 wt% Co, 8 wt% Mo, 8 wt% W)

enhanced the product quality (see Table 7). H/C ratio remained about the same. Therefore, the improvement in light oil production may be because of enhancing effect of water on H/C activity of this catalyst. This catalyst produced specification grade product (less than 0.3 wt% N in the product oil) initially, but it started producing lower grade product at the end.

Fig. 15 shows the HDN results of the catalyst TS-13 (4% Co, 16% W). The activity of this particular catalyst was very low without water addition; however, water increased HDN from 49 wt% to 63 wt%. Without water addition, the catalyst was not able to produce specification grade product (see Table 5). A similar effect of water was observed for product quality. Light oil production increased from 8.9% to 11.2% (see Table 6 and Fig. 10), and a higher percentage of heavy oil was converted to lighter fractions. In contrast to the positive effect of water on HDN and the product quality, H/C ratio remained about the same (Tables 5 and 7 and Figures 10 and 12). This indicates the enhancing effect of water on H/C.

Fig. 16 shows the HDN results of the Catalyst TS-14 (2% Co, 8% Mo, 2% Ni, 8% W) as a function of time. HDN activity of the catalyst was moderately good without water addition even though deactivation was faster. However, water reduced HDN from 57 wt% to 46 wt%. The catalyst produced specification grade product when time averaged over 140 hours without water addition, but started producing non-specification grade product at the end of the run. The effect of water on the product quality was also inhibitive for this particular catalyst (see Tables 6 and 7 and Figures 10 and 11). Light oil production was

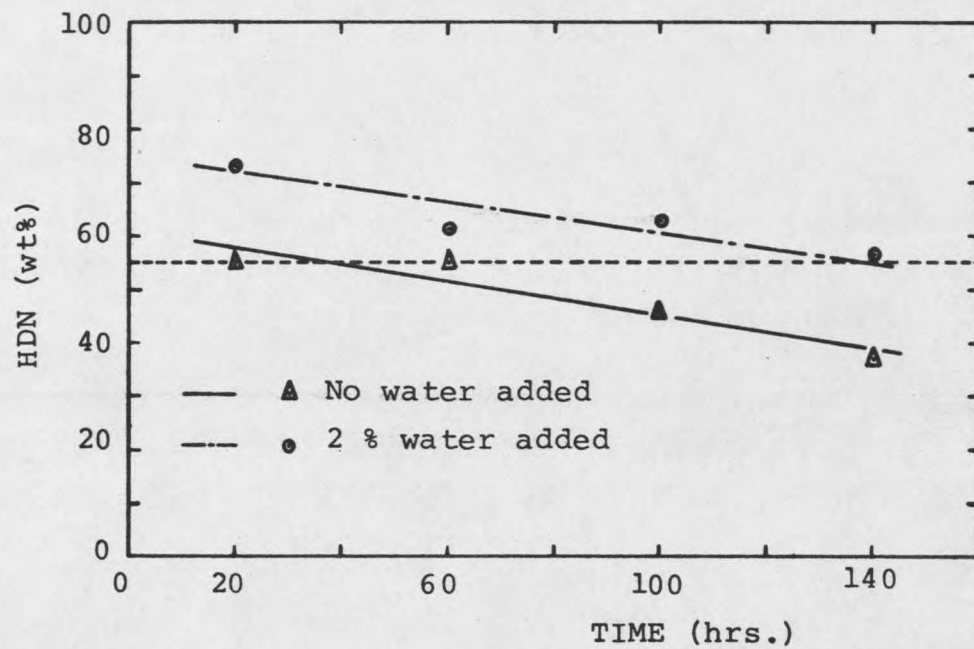


Figure 15. Hydrodenitrogenation vs. Time for the Catalyst TS-13 (4 wt% Co, 16 wt% W)

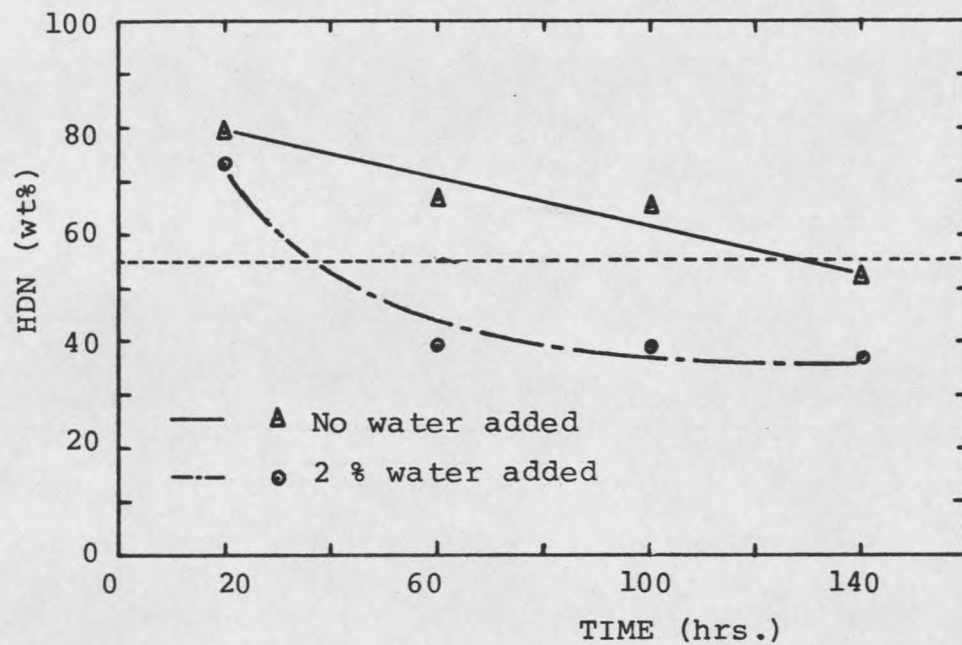


Figure 16. Hydrodenitrogenation vs. Time for the Catalyst TS-14 (12 wt% Co, 8 wt% Mo, 2 wt% Ni, 8 wt% W)

reduced from 7.7% to 5.5%. H/C ratio was reduced from 1.36 to 1.32 indicating that water inhibited HYD activity (Fig. 12).

Fig. 17 shows HDN results of the catalyst TS-15 (4% Ni, 16% W). This catalyst was one of the poorest for both HDN and product quality (Tables 5 and 6 and Figures 9 and 10). Catalyst deactivation was also faster than for the other catalysts. This catalyst did not produce a specification grade product with or without water addition. Water slightly inhibited HDN activity, 39 wt% vs. 35 wt%. The effect of water on product quality was not significant (see Tables 6 and 7 and Figures 10 and 11). H/C ratio for the run with water addition was lower, even though both runs produced about the same amount of light oil (Fig. 12). This indicates the enhancing effect of water on HYC for this catalyst.

Fig. 18 shows the HDN results of the catalyst TS-16 (4% Ni, 8% Mo, 8% W). This was the least active catalyst for both HDN and product quality. It did not produce specification grade product even at the beginning of the run, indicating extremely poor activity. The effect of water on HDN was insignificant, but light oil production slightly increased. Nevertheless, the production of light oil was the lowest of any catalyst tested (see Tables 6 and 7 and Fig. 10). The effect of water on H/C ratio was inhibitive (Fig. 12), therefore, it enhanced HYC activity.

Fig. 19 shows the HDN results of the catalyst TS-17 (4% Ni, 16% Mo). This catalyst had the highest HDN and HYD activity among the catalysts evaluated in this group. Catalyst deactivation was slower than for all the other catalysts except TS-11 (Co+Mo), especially

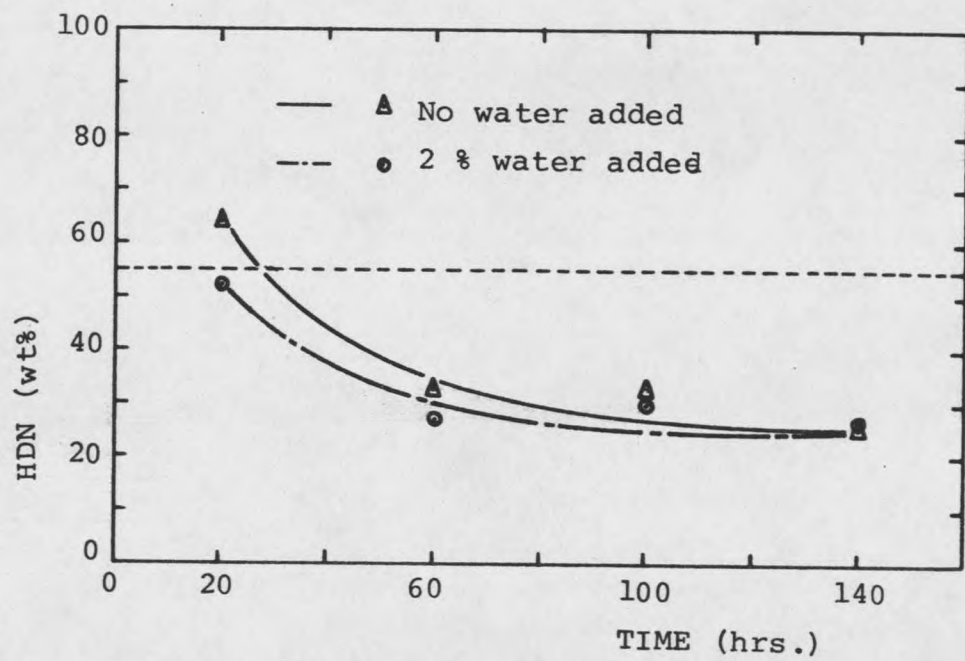


Figure 17. Hydrodenitrogenation vs. Time for the Catalyst TS-15 (4 wt% Ni, 16 wt% W)

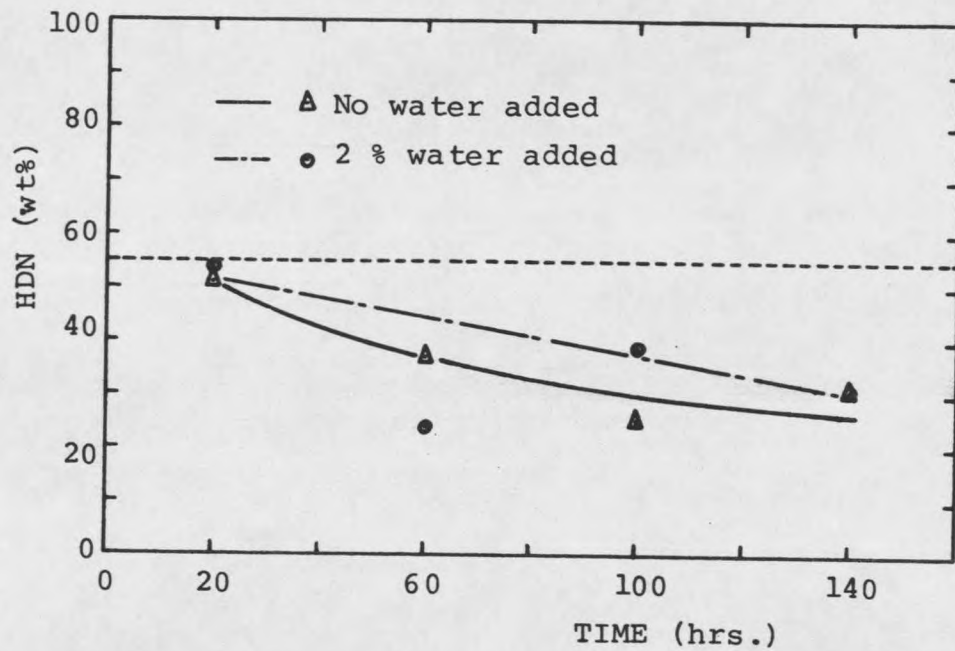


Figure 18. Hydrodenitrogenation vs. Time for the Catalyst
TS-16 (4 wt% Ni, 8 wt% Mo, 8 wt% W)

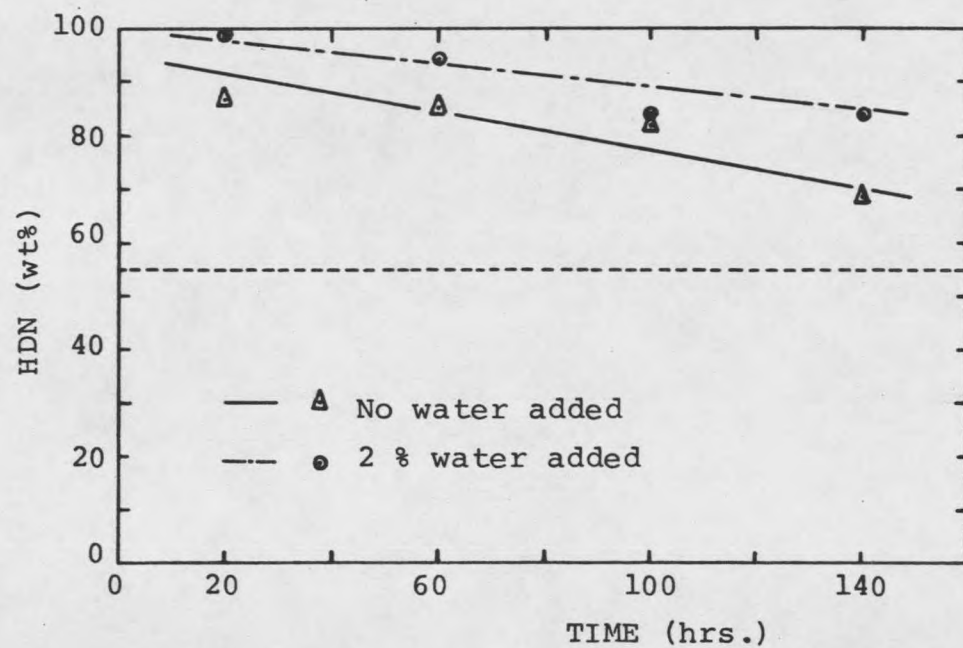


Figure 19. Hydrodenitrogenation vs. Time for the Catalyst TS-17 (4 wt% Ni, 16 wt% Mo)

when water was added to the feed. The effect of water on both HDN and the product quality was positive (Tables 6 and 7 and Figures 10 and 11). H/C ratio remained about the same for both runs. This indicates the positive effect of water on HYC since the light oil production was improved by water addition.

To see the relationship between activities of W and Mo, HDN results are plotted as a function of W/(W+Mo) ratio in Fig. 20. HDN activity decreased with increasing amount of W on the catalysts generally. However, when 2% water was added, HDN activity of Co-W catalyst increased significantly. With this exception in mind, in general Mo is preferable to W for HDN of SRC-II Light Ends Column Feed under the conditions of this study.

When all the catalysts evaluated in this group are compared, the most active metal combinations for HDN, product quality and H/C ratio (or HYD) can be given in the following order:

1. For HDN;

a) No water,

$$\text{Ni+Mo} > \text{Co+Mo} > \text{Co+Mo+W} > \text{Co+Mo+Ni+W} > \text{Co+W} > \text{Ni+W} > \text{Ni+Mo+W}$$

b) With water,

$$\text{Ni+Mo} > \text{Co+Mo} > \text{Co+Mo+W} = \text{Co+W} > \text{Co+Mo+Ni+W} > \text{Ni+Mo+W} \\ = \text{Ni+W}$$

2. For product quality (or light oil production);

a) No water,

$$\text{Co+Mo} > \text{Ni+Mo} > \text{Co+W} > \text{Co+Mo+Ni+W} > \text{Co+Mo+W} > \text{Ni+W} > \text{Mo+W}$$

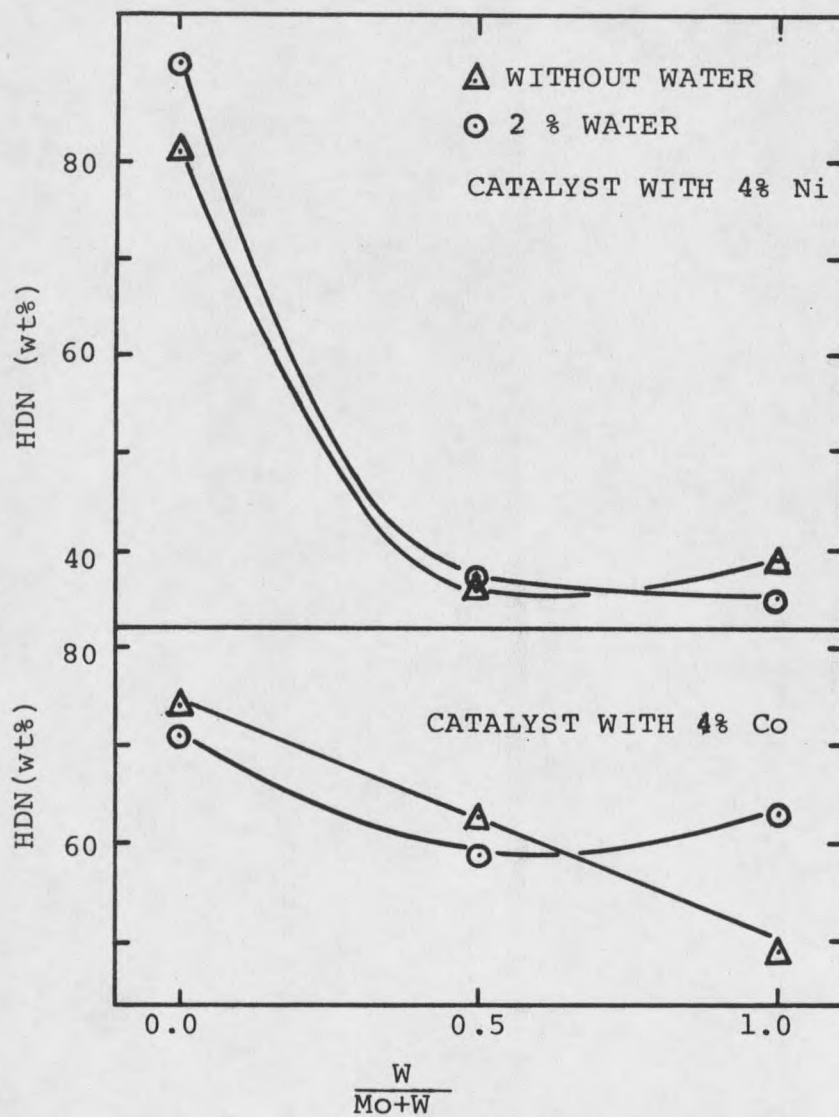


Figure 20. HDN activity of W as a function of metal load.

b) With water,

$$\text{Co+Mo} > \text{Ni+Mo} > \text{Co+W} > \text{Co+Mo+W} > \text{Co+Mo+Ni+W} > \text{Ni+W} > \text{Ni+Mo+W}$$

3. For H/C ratio (or HYD);

a) No water,

$$\text{Ni+Mo} > \text{Co+Mo} > \text{Co+Mo+Ni+W} > \text{Co+Mo+W} = \text{Ni+W} > \text{Ni+Mo+W} = \text{Co+W}$$

b) With water,

$$\text{Ni+Mo} > \text{Co+Mo} > \text{Co+Mo+W} > \text{Co+W} = \text{Co+Mo+Ni+W} > \text{Ni+Mo+W} > \text{Ni+W}$$

Carbonaceous material deposited on the catalyst was determined by air burnoff, and is given in Table 5. In general, water reduced the amount of carbonaceous material deposited. However, it is not easy to single this out from the data listed, because of the fact that the more active catalysts produced more carbonaceous material. When water enhanced the activity of a catalyst significantly, there was also an increased amount of carbonaceous material on the catalyst (see TS-13 and TS-17 in Table 5). This is probably due to the dual character of coke formation. Unreactive coke poisons reaction sites. Reactive coke is subsequently converted to reaction products [210]. Fig. 21 supports this proposition. The amount of coke on the catalyst significantly increased with increasing HDN activity. Indeed, water reduced the amount of carbonaceous material on the inert support, used as a diluent for every catalyst tested without any exception (not shown here).

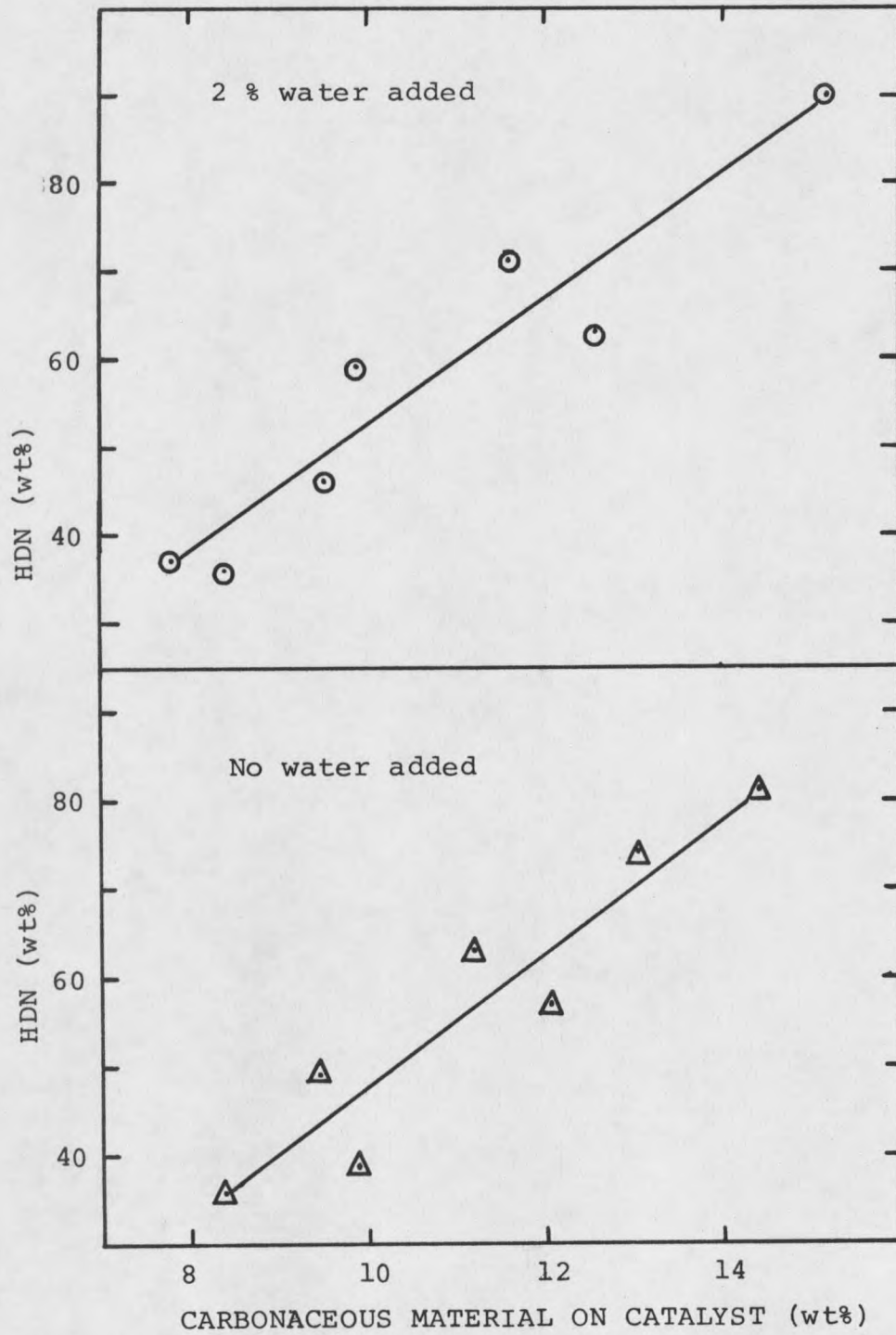


Figure 21. Relationship between HDN activity and carbonaceous material deposited on the Catalyst.

EFFECT OF IMPREGNATION TECHNIQUE

Two of the best catalysts, Co-Mo and Ni-Mo, evaluated in the previous section were subjected to two different impregnation techniques as described in Chapter 3. In both cases, Mo was impregnated in a single step (batchwise). Co or Ni was then impregnated in one case in two steps (TS-21 for Co-Mo and TS-20 for Ni-Mo) and in a single step (batchwise) in the other case (TS-18 for Co-Mo and TS-19 for Ni-Mo). The catalysts TS-18 (Mo+Co) and TS-19 (Mo+Ni) were prepared by Co and Ni impregnation on Mo, respectively. The catalysts TS-20 (Ni:s+Mo:b) and TS-21 (Co:s+Mo:b) had a reverse sequence of metal deposition. Activities of these catalysts are compared in the following paragraphs.

Ni-Mo Catalysts: Since TS-17 (Ni+Mo, step) was discussed in the previous section, it will not be discussed here. Instead, only comparative references will be made to it.

Fig. 22 shows HDN results of the catalyst TS-19 (16% Mo, 4% Ni) as a function of time. This catalyst was as active as TS-17 for HDN. In contrast to catalyst TS-17 (Ni+Mo, step), water did not have any significant effect on HDN for TS-19 (Mo+Ni). When the results given in Tables 8, 9, and 10 and Figures 23, 24 and 25 are compared, H/C ratio for TS-19 (Mo+Ni) is slightly higher than TS-17 (Ni+Mo, step), and the light oil production is significantly higher. Light oil production was 12.7% and 12.3% with and without water addition, respectively. The effect of water on both product quality and H/C ratio was not significant. As a result, HYC activity was not affected by water.

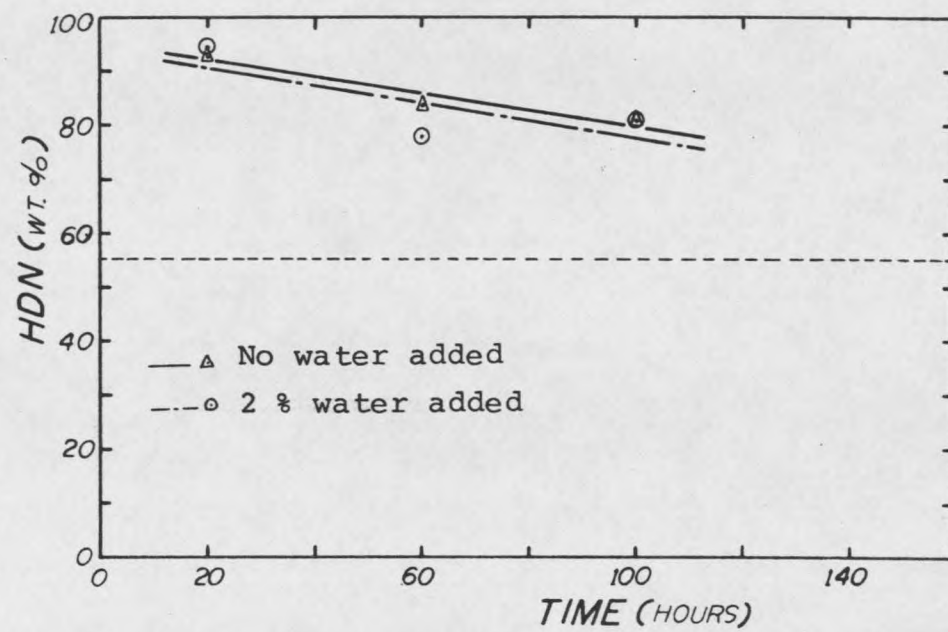


Figure 22. Hydrodenitrogenation vs. Time for the Catalyst TS-19 (16 wt% Mo, 4 wt% Co)

Table 8. The Effect of Impregnation Technique and Water Addition on HDN, Product Quality (Distillation Fractions) and Catalyst Coking

Catalyst & Run	Product Nitrogen (wt%)	HDN (wt%)	H/C ^a (wt%)	LO ^b (wt%)	MO ^c (wt%)	HO ^d (wt%)	C ^e (wt%)	RON ^f for LO
TS-11NW* (Co+Mo, step)	0.17	75	1.38	35.0	55.5	8.9	13.06	89.0
TS-11W*	0.17	74	1.38	36.2	55.0	9.1	11.61	
TS-18NW (Mo+Co)	0.09	87	1.38	39.2	53.0	7.9	14.29	85.4
TS-18W	0.12	82	1.36	38.0	54.2	7.8	15.53	
TS-21NW (Co:s+Mo:b)	0.15	78	1.37	36.9	55.0	8.1	14.53	89.4
TS-21W	0.20	71	1.37	36.8	54.7	8.5	14.24	
TS-17NW (Ni+Mo, step)	0.10	86	1.40	33.9	57.3	8.8	14.40	82.0
TS-17W	0.05	92	1.40	35.8	56.0	8.3	15.25	
TS-19NW (Mo+Ni)	0.10	86	1.41	36.8	54.5	8.7	16.25	82.4
TS-19W	0.11	84	1.40	36.4	54.8	8.8	15.53	
TS-20NW (Ni:s+Mo:b)	0.11	82	1.41	37.0	54.4	8.7	14.89	82.3
TS-20W	0.12	82	1.41	36.5	55.4	8.1	15.80	

* NW = No water addition, W = 2 % water added.

^a Hydrogen to carbon atomic ratio.

^b Light oil fraction in boiling range 40 - 205 °C.

^c Middle oil fraction in boiling range 205 - 298 °C.

^d Heavy oil fraction in the boiling range of 298 °C to the end point.

^e Carbonaceous material deposited on the catalyst.

^f Research octane number.

Table 9. Change in H/C Ratio, Light Oil (LO), Middle Oil (MO), and Heavy Oil (HO) from the Feed

Catalyst & Run	Composition Change From the Feed				Percent Relative Change From the Feed for Each Category			
	H/C	LO	MO	HO	H/C	LO	MO	HO
TS-11NW* (Co+Mo, step)	0.15	10.9	- 9.1	-2.3	12.2	47.7	-14.4	-19.8
TS-11W*	0.15	12.1	- 9.8	-2.1	12.2	48.6	-15.1	-18.0
TS-18NW (Mo+Co)	0.15	15.1	-11.8	-3.2	12.2	62.7	-18.2	-28.8
TS-18W	0.13	13.7	-10.0	-3.3	10.6	57.7	-16.4	-29.7
TS-21NW (Co:s+Mo:b)	0.14	12.8	- 9.7	-3.1	11.4	53.1	-15.1	-27.0
TS-21W	0.14	12.7	-10.0	-2.7	11.4	52.7	-15.6	-23.4
TS-17NW (Ni+Mo, step)	0.17	9.8	- 7.5	-2.4	13.8	38.6	-11.7	-15.3
TS-17W	0.17	11.7	- 8.8	-2.9	13.8	48.6	-36.5	-25.2
TS-19NW (Mo+Ni)	0.18	12.7	-10.3	-2.5	14.6	52.7	-15.9	-21.6
TS-19W	0.17	12.3	-10.0	-2.3	13.8	51.0	-15.4	-20.7
TS-20NW (Ni:s+Mo:b)	0.18	12.9	-10.4	-2.5	14.6	53.5	-16.1	-21.6
TS-20W	0.18	12.4	- 9.3	-3.1	14.6	51.5	-14.5	-25.2

* NW = No water added, W = 2 % water added.

Table 10. The Effect of Water on HDN, H/C Ratio and Light Oil (LO), Middle Oil (MO) and Heavy Oil (HO) Contents for the Co-Mo and Ni-Mo Catalysts

Catalyst & Run	Difference in % Composition Between Runs NW and W (W-NW)*				
	H/C	LO	MO	HO	HDN
TS-11 (Co+Mo, step)	0.00	1.2	-0.7	-0.5	-1.0
TS-18 (Mo+Co)	-0.02	-1.4	1.0	0.4	-5.0
TS-21 (Co:s+Mo:b)	0.00	-0.1	-0.3	0.4	-7.0
TS-17 (Ni+Mo, step)	0.00	1.8	-1.3	-0.5	7.0
TS-19 (Mo+Ni)	-0.01	-0.4	0.3	0.2	-2.0
TS-20 (Ni:s+Mo:b)	0.00	-0.5	1.1	-0.6	0.0

NW = No water added, W = 2% water added

Fig. 26 shows HDN results of the catalyst TS-20 (4% Ni, 16% Mo). HDN activity of this catalyst was slightly lower than both TS-19 (Mo+Ni) and TS-17 (Ni+Mo, step) (see Table 8), and water did not show any significant effect on HDN, product quality and H/C ratio (see Tables 9 and 10 and Fig. 23 and 25). Light oil production was about the same as TS-19 (Mo+Ni).

Co-Mo Catalysts: Since TS-11 (Co+Mo, step) was discussed in the previous section, those results will not be given here. Some references will be made whenever necessary. Tables 8, 9 and 10 and Figures 23, 24 and 25 will provide necessary comparisons for Co-Mo catalysts.

Fig. 27 shows HDN results of the catalyst TS-18 (16% Mo, 4% Co) as a function of time. HDN activity of this catalyst was higher than TS-11 (Co+Mo, step) (see Table 8), and deactivation was reasonably slow. The effect of water on HDN activity was negative (see Table 10). The best product quality was obtained with this catalyst. The light oil production was over 15% (see Table 9 and Fig. 23). The

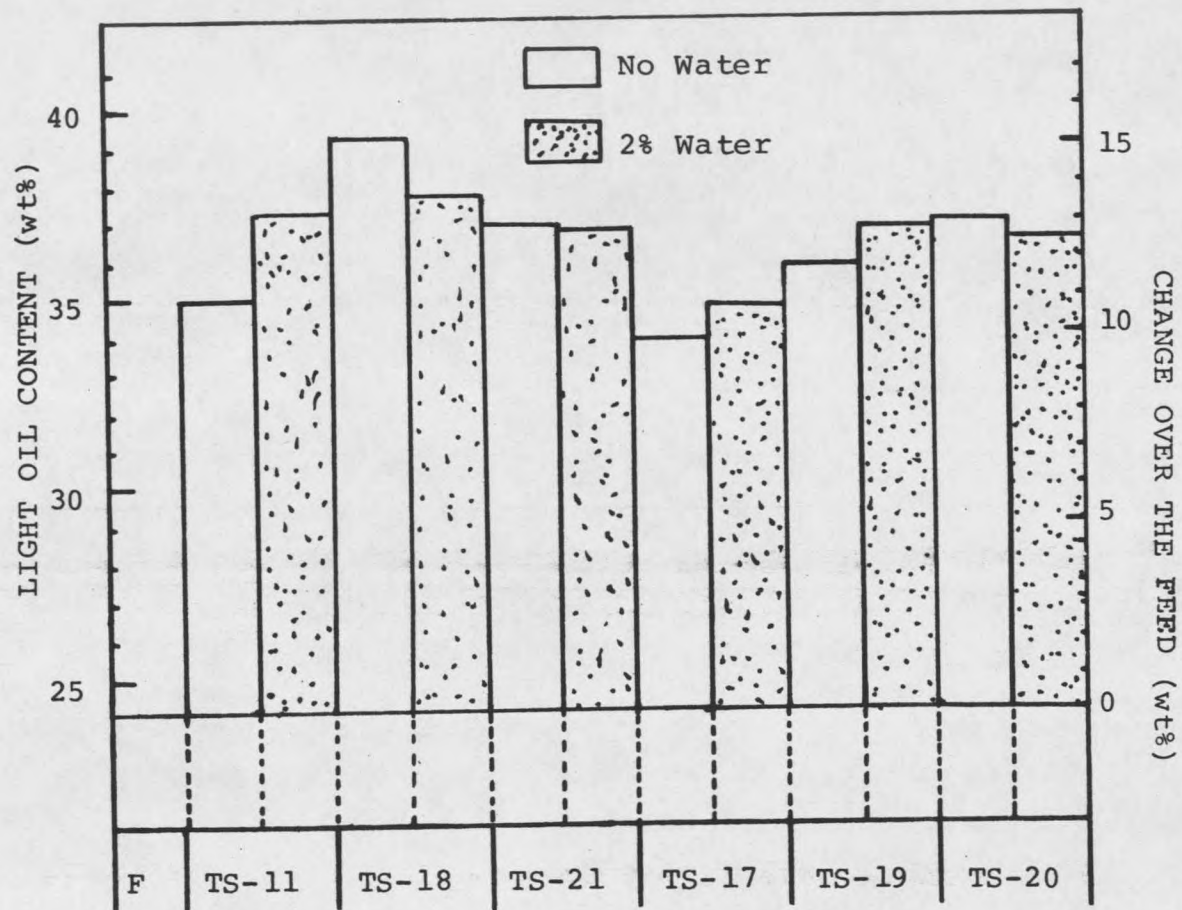


Figure 23. Light Oil (40 - 205°C) Yield for Ni-Mo and Co-Mo Catalysts
 F = Feed, TS-11; Co+Mo, step, TS-18; Mo+Co, TS-21; Co:s+Mo:b,
 TS-17; Ni+Mo, step, TS-19; Mo+Ni, TS-20; Ni:s+Mo:b.

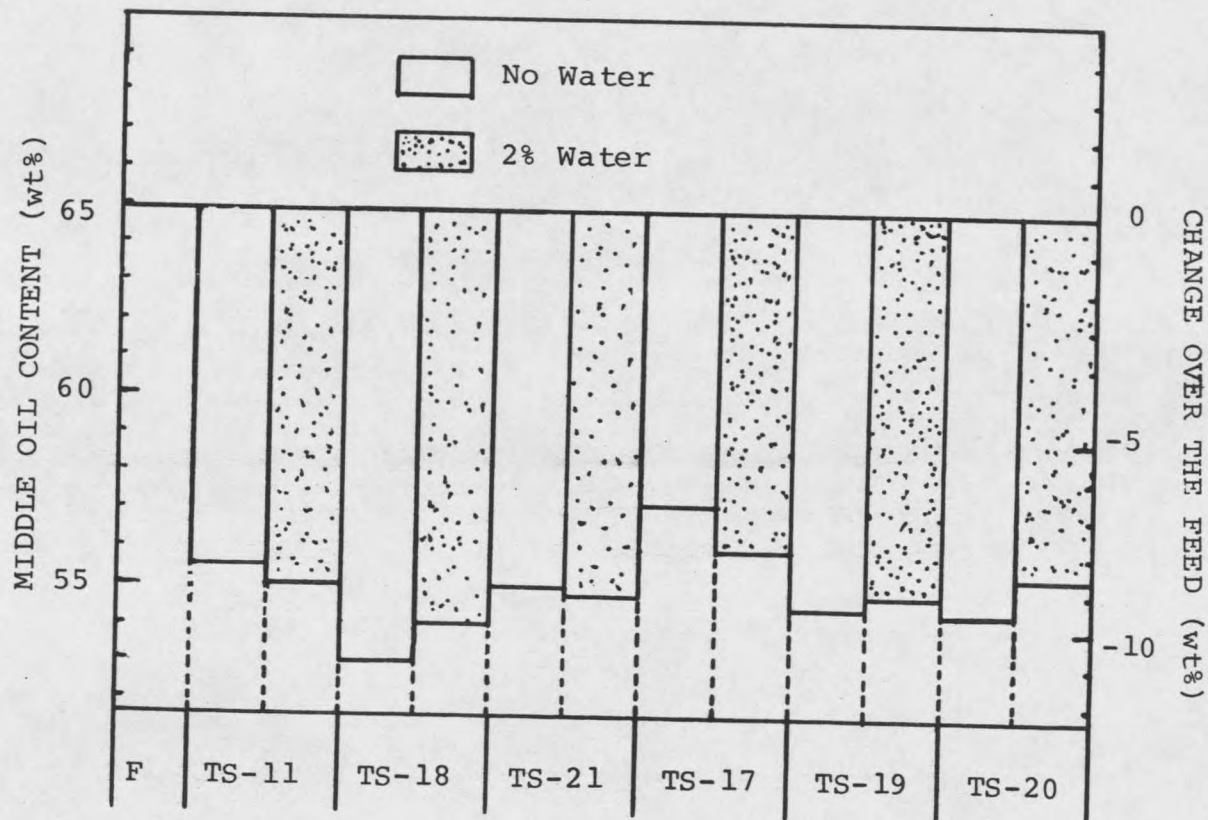


Figure 24. Middle Oil (205 - 298 °C) Yield for Ni-Mo and Co-Mo Catalysts
 F = Feed, TS-11; Co+Mo, step, TS-18; Mo+Co, TS-21; Co:s+Mo:b,
 TS-17; Ni+Mo, step, TS-19; Mo+Ni, TS-20; Ni:s+Mo:b.

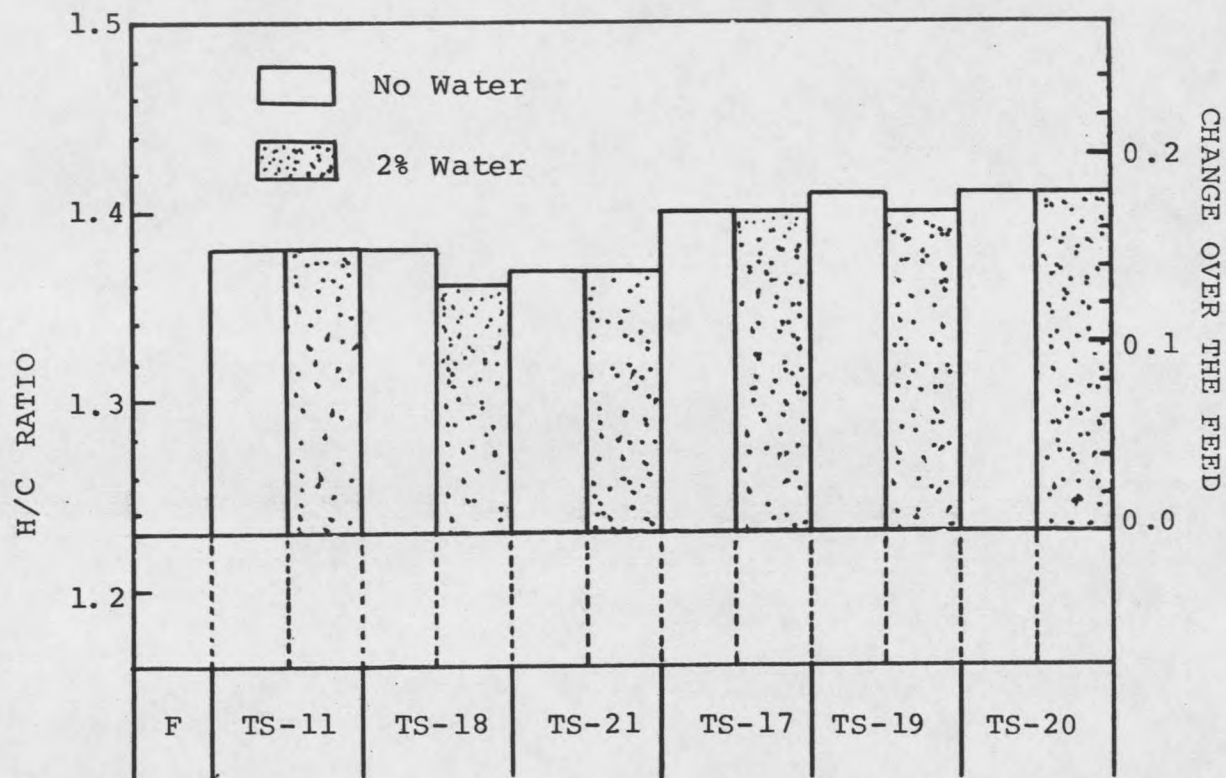


Figure 25. The Effect of Impregnation Technique and Water Addition on H/C Ratio for Ni-Mo and Co-Mo Catalysts

F = Feed, TS-11; Co+Mo, step, TS-18; Mo+Co, TS-21; Co:s+Mo:b, TS-17; Ni+Mo, step, TS-19; Mo+Ni, TS-20; Ni:s+Mo:b.

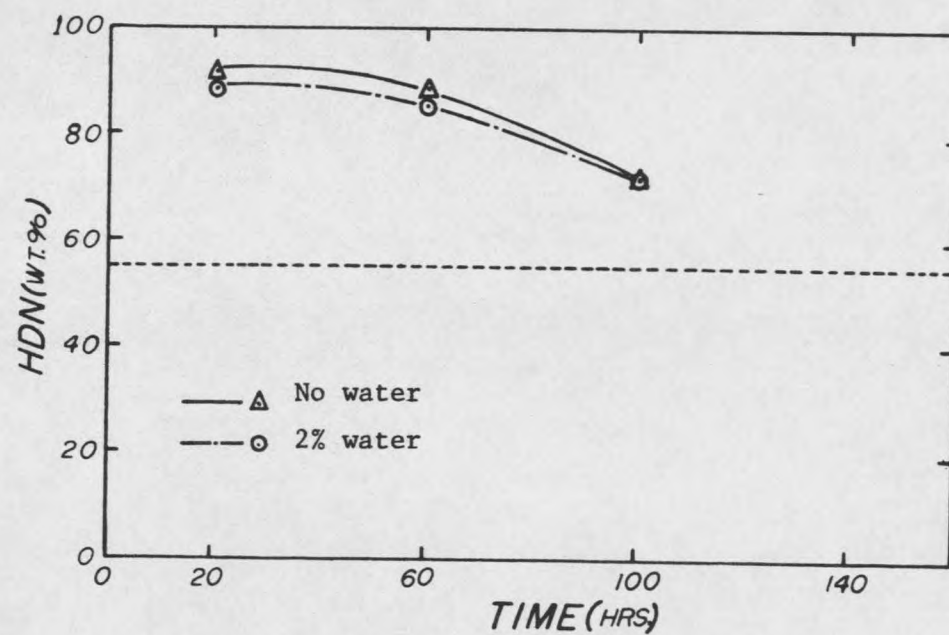


Figure 26. Hydrodenitrogenation vs. Time for the Catalyst TS-20
(4 wt%:s, 16 wt% Mo:b)

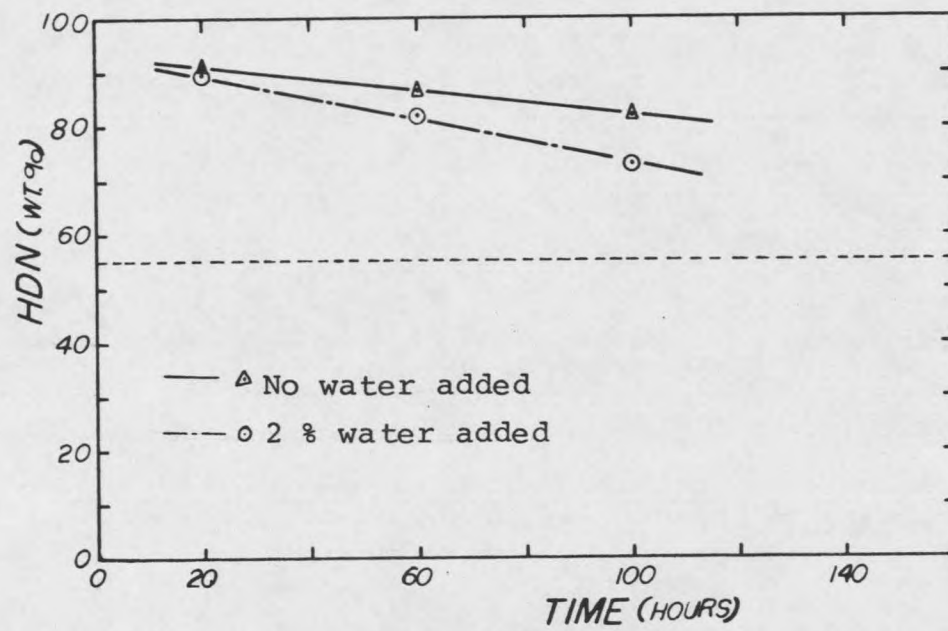


Figure 27. Hydrodenitrogenation vs. Time for the Catalyst TS-18 (16 wt% Mo, 4 wt% Co)

effect of water on the product quality and H/C ratio was negative, indicating an inhibitive effect of water on HYD activity. HYC activity was probably not affected since the heavy oil fraction was reduced about the same amount in both runs (see Table 9).

Fig. 28 shows HDN results of the catalyst TS-21 (4% Co, 16% Mo). HDN activity of this catalyst was slightly better than TS-11 (Co+Mo, step) but less than TS-18 (Mo+Co) (see Table 8). Water inhibited HDN activity. The effect of water on the product quality and H/C ratio was not significant. Light oil production was more than TS-11 (Co+Mo, step) but less than TS-18 (Mo+Co).

Summary, Impregnation Techniques: Activities of the Ni-Mo catalysts are not affected greatly by impregnation technique, but activities of the Co-Mo catalysts are. When Mo is impregnated first and then Co, the activity of the catalyst was improved considerably. HDN and HYC activities were affected most. When catalyst TS-18 (Mo+Co) is compared with Ni-Mo catalysts, its activity for HDN is about the same and better for HYC, but less for HYD. This gives an advantage to this catalyst over Ni-Mo catalysts. It selectively removes nitrogen and cracks high molecular-weight hydrocarbons with less hydrogen consumption. Impregnation technique has an effect only on the product quality for Ni-Mo catalysts. In general, when Mo was impregnated batchwise, light oil production was improved, basically because of improved HYC activity since HYD activity remained nearly the same (see Fig. 23).

Research octane numbers (RON) were determined for the light oil fractions from the runs without water addition (see Table 6). Results

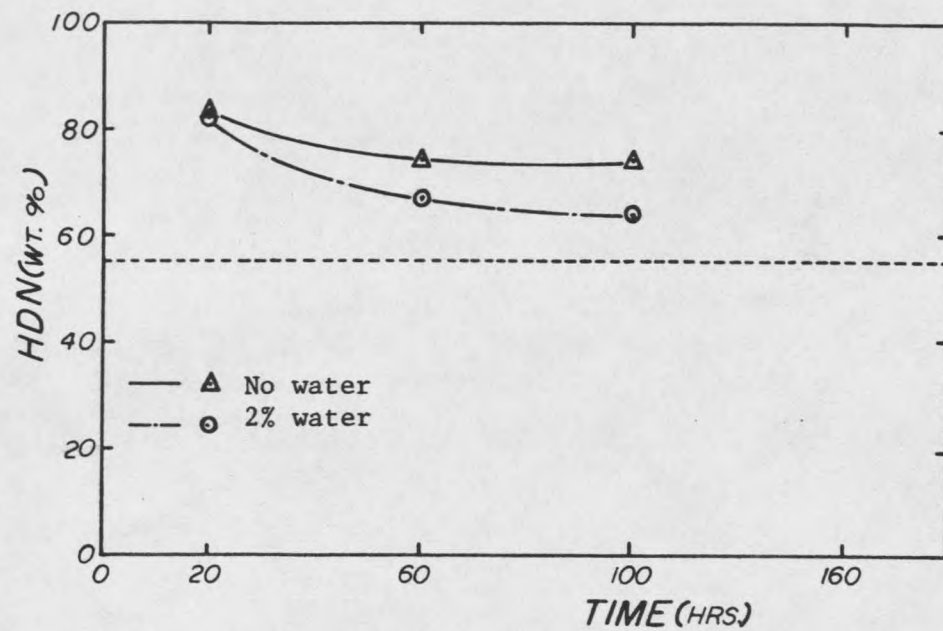


Figure 28. Hydrodenitrogenation vs. Time for the Catalyst TS-21
(4 wt% Co:s, 16 wt% Mo:b)

support the above discussion. The Co-Mo catalysts produce products with higher octane numbers than the Ni-Mo catalysts do. This shows the higher HYC activity of the Co-Mo catalysts.

THE ESCA (XPS) ANALYSIS

ESCA measurements were done for every catalyst evaluated to correlate catalytic activity with the chemical structure and distribution of metals on the support. (The peak binding energies are given in Appendix D.). First, the effect of impregnation technique on the chemical structure will be given, and then that of the metal combinations.

Effect of Impregnation Technique: Mo 3d and Ni 2p spectra of Ni-Mo catalysts are given in Fig. 29 and Fig. 30, respectively. These spectra include some reference compounds and sulfided catalysts as well as the oxide catalysts. Determining the surface structure only from the figures is difficult because of charging problems in ESCA (XPS) analyses. Although the charging was corrected by carbon 1s peak binding energy, its reliability is questionable [36, 191]. In addition to the shifts in binding energies (as shown in the figures), FWHM (Full Width at Half Maximum band) and binding energy differences between specific band peaks (such as Al 2p, O 1s and S 2p) and Ni $2p_{3/2}$ and Mo $3d_{5/2}$ will be utilized in analyzing the data. Binding energy differences (ΔE) eliminate error carried by the C 1s correction since all the spectra in question are subject to the same error source [191]. These are shown in Tables 11, 12 and 13.

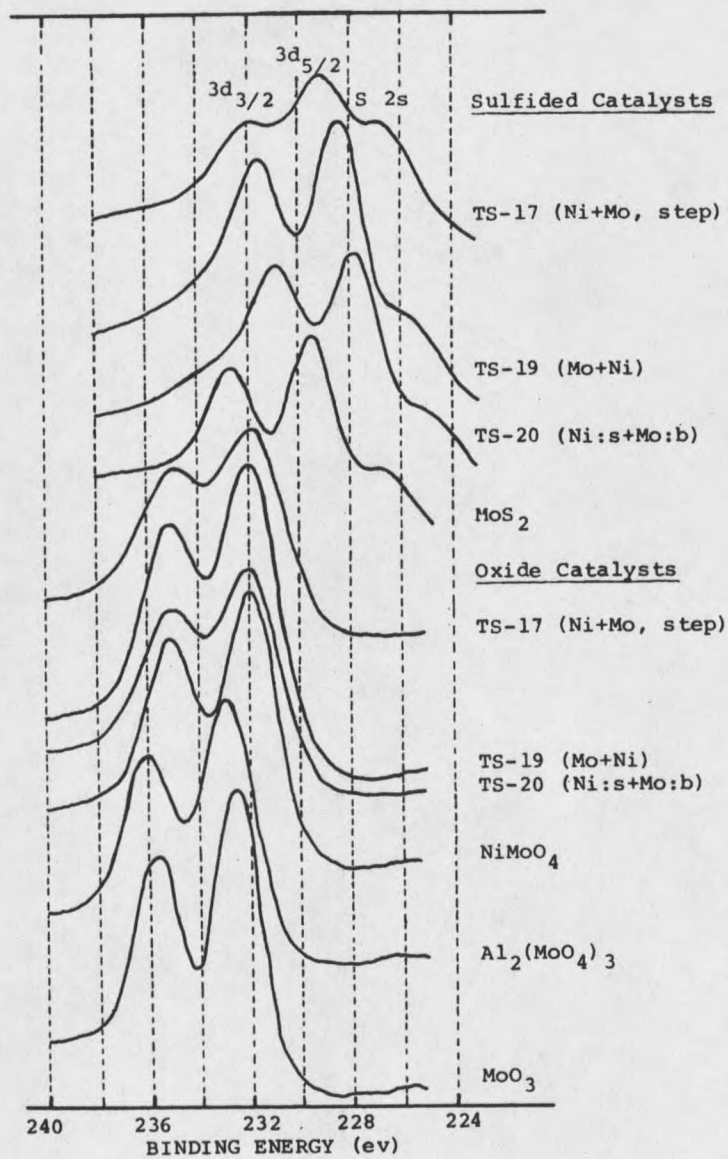


Figure 29. The Effect of Impregnation Technique on the XPS Mo 3d Spectra of the Ni-Mo Catalysts

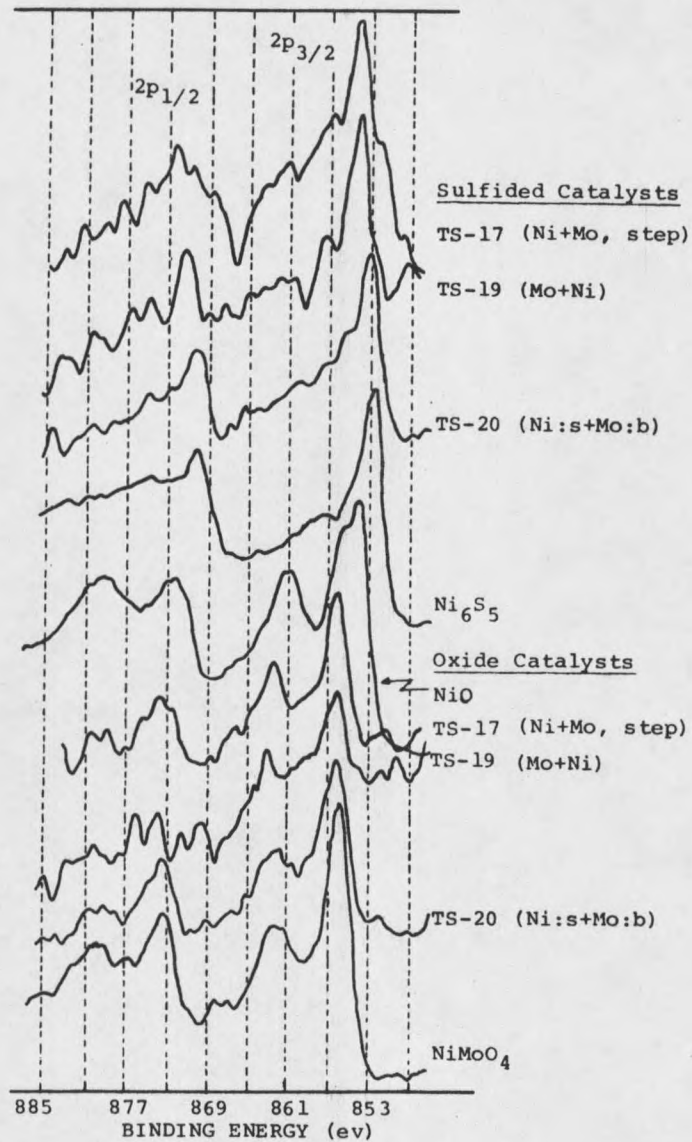


Figure 30. The Effect of Impregnation Technique on the XPS Ni 2p Spectra of the Ni-Mo Catalysts

Table 11. The Effect of Impregnation Technique on the FWHM of the Ni-Mo Catalysts

Catalyst or Compound	Mo 3d (ev)	Al 2p (ev)	Al 2s (ev)	O 1s (ev)	S 2p (ev)
TS-17 (Ni+Mo, step)	5.8	3.0	3.7	3.4	NA
TS-19 (Mo+Ni)	5.4	2.9	3.8	3.4	NA
TS-20 (Ni:s+Mo:b)	5.5	3.0	3.8	3.5	NA
NiAl ₂ O ₄ Support	NA	3.0	3.6	3.1	NA
Al ₂ (MoO ₄) ₃	5.3	2.9	3.2	2.8	NA
MoO ₃	5.3	NA	NA	2.4	NA
NiO ₃	NA	NA	NA	2.7	NA
TS-17S* (Ni+Mo, step)	7.4	4.9	5.9	5.3	4.3
TS-19S* (Mo+Ni)	5.7	3.2	3.8	3.9	3.0
TS-20S* (Ni:s+Mo:b)	6.0	4.6	5.0	5.0	2.9
MoS ₂	5.2	NA	NA	5.0	2.9
Ni ₆ S ₅	NA	NA	NA	2.6	3.4

* Sulfided form

FWHM = Full Width at Half Maximum band

NA = Not available or not applicable

Mo 3d spectra of TS-17 (Ni+Mo, step) is broadened when compared with that of TS-19 (Mo+Ni) and TS-20 (Ni:s+Mo:b). Some investigators [31] attribute this broadening to the charging effect when they compare the spectra of impregnated and unimpregnated catalysts. Since both impregnated and unimpregnated catalyst samples are of the insulating type (in oxide form), they are subject to a similar charging effect. This phenomena can be seen from Table 11 when FWHM of Al₂(MoO₄)₃ and NiMoO₄ are compared with that of TS-19 (Mo+Ni) and TS-20 (Ni:s+Mo:b). They have about the same FWHM (5.3 vs. 5.4 ev).

Table 12. Specific Binding Energy Differences (ΔE) for the Ni-Mo Catalysts.

Catalyst or Compound	Mo	O	Mo	Al	Ni	Al	Ni	Mo	Ni	O
	$3d_{5/2}$ (eV)	1s	$3d_{5/2}$ (eV)	2p	$2p_{3/2}$ (eV)	2p	$2p_{3/2}$ (eV)	$3d_{5/2}$	$2p_{3/2}$ (eV)	1s
TS-17*	299.2		158.2		NA		624.1		NA	
TS-19*	298.2		158.1		799.8		623.9		NA	
					802.1					
TS-20*	298.8		158.1		799.3		624.0		NA	
					800.5		627.0			
					804.0					
NiMoO ₄	298.0		NA		NA		624.0		326.0	
NiO	NA		NA		NA		NA		325.0	
MoO ₃	298.0		NA		NA		NA		NA	
Al ₂ (MoO ₄) ₃	298.6		158.6		NA		NA		NA	
TS-17S**	303.0		154.3		796.2		625.4		322.4	
					797.8		628.0		325.0	
					800.7				320.7	
TS-19S**	304.0		154.1		796.9		625.6		321.6	
					800.2		629.0		325.0	
					802.2				320.7	
TS-20S**	304.0		153.3		796.5		625.9		321.9	
					799.0		628.1		324.1	
					800.2					
					801.2					
Ni ₆ S ₅	NA		NA		NA		NA		320.6	
MoS ₂	302.6		NA		NA		NA		NA	

* TS-17 (Ni+Mo, step), TS-19 (Mo+Ni), TS-20 (Ni:s+Mo:b).

** Sulfided form

NA = Not available or not applicable

Table 13. Specific Binding Energy Differences (ΔE) of the Sulfided Ni-Mo and Co-Mo Catalysts

Catalyst or Compound	Mo $3d_{5/2}$ -S 2p (ev)	Ni $2p_{3/2}$ -S 2p (ev)
TS-17S (Ni+Mo, step)	67.4	692.7
TS-19S (Mo+Ni)	66.7	692.4
TS-20S (Ni:s+Mo:b)	66.7	692.7
Ni ₆ S ₅ MoS ₂	NA	691.5
		Co $2p_{3/2}$ -S 2p
TS-11S (Co+Mo, step)	67.4	615.5
		618.1
		620.7
		621.6
TS-18S (Mo+Co)	67.0	617.3
		618.1
TS-21S (Co:s+Mo:b)	66.9	617.2
		617.7
Co ₉ S ₈	NA	616.6

NA = not applicable

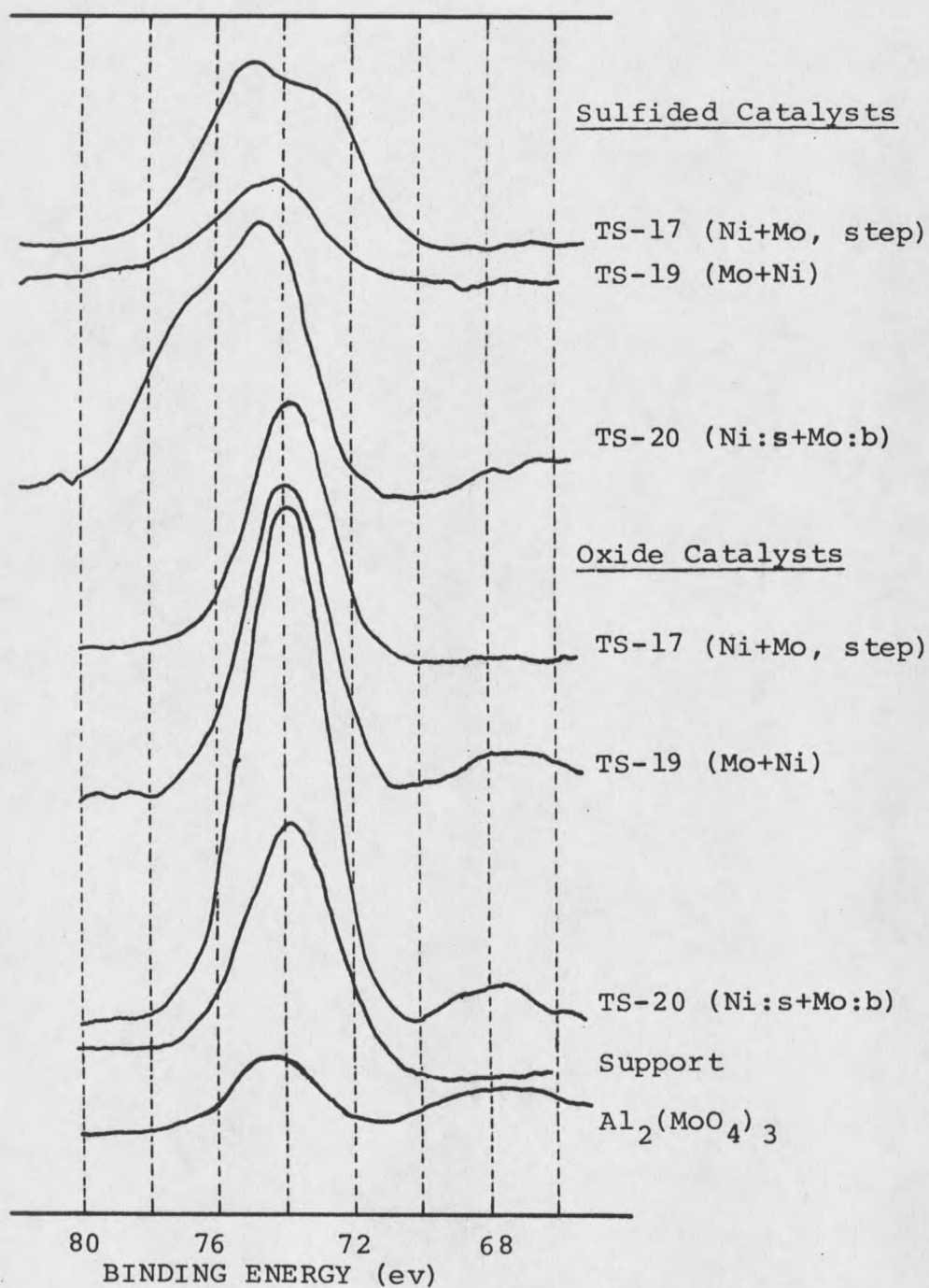


Figure 31. The Effect of Impregnation Technique on the XPS Al 2p Spectra of the Ni-Mo Catalysts

Therefore, in this study, the band broadening will be attributed to the appearance of more than one chemical [182] or geometrical state of the compound on the catalyst surface. More evidence of this will be given and discussed in the following pages. As a result, it is believed that Mo is present in more than one phase in TS-17 (Ni+Mo, step).

When the sulfided form of the TS-17 (Ni+Mo, step) catalyst is considered (upper section of Fig. 29), it has even larger FWHM (7.4 ev) than the oxide form. This is probably due to a partially sulfidable or non-sulfidable form of Mo present on the catalyst surface. Similar broadening of Mo 3d spectra occurs with TS-19 (Mo+Ni) and TS-20 (Ni:s+Mo:b) upon sulfiding. However, it is less with these latter catalysts (5.4 vs. 5.7 with TS-19 and 5.5 vs. 6.0 ev with TS-20). A similar band broadening is observed with Al 2p (see Fig. 31), Al 2s, S 2p and O 1s spectra (see Table 11). Broadening associated with these spectra is larger for TS-17 (Ni+Mo, step).

The difference between TS-17 and TS-19 is that both Ni and Mo are impregnated stepwise in TS-17, but batchwise with the reverse impregnation sequence in TS-19. In TS-20 batchwise impregnation of Mo and two-step impregnation of Ni was used (four step in TS-17). Recalling this background information, it can be postulated that the catalyst TS-17 (Ni+Mo, step) contains the most partially sulfidable phases combined with Al_2O_3 . Since Mo 3d band for TS-17 (Ni+Mo, step) is broader in both the sulfided and oxide forms than these bands in TS-19 (Mo+Ni) and TS-20 (Ni:s+Mo:b), the presence of some $\text{Al}_2(\text{MoO}_4)_3$ type phase can be postulated. It is a structure probably formed by

movement of Mo into the alumina lattice. This structure gives characteristics of $\text{Al}_2(\text{MoO}_4)_3$ although the complete structure may not be in the normal molybdate form. Moreover, involvement of some Ni in this phase can not be excluded as discussed below. This phase is partially sulfidable since both Mo 3d and Al 2p bands were broadened upon sulfiding. The S 2p spectra was also broadened for this catalyst, supporting the argument above. Probably sulfur is present in a different chemical state and/or geometrical position in this structure as compared to the other sulfur structures that will be discussed below.

When Mo 3d spectra of TS-19 (Mo+Ni) and TS-20 (Ni:s+Mo:b) are compared with that of TS-17 (Ni+Mo, step), it can be said that formation of $\text{Al}_2(\text{MoO}_4)_3$ type phase in these catalysts is not likely, or insignificant if it is formed at all. The other possible structures possibilities are NiMoO_4 , MoO_3 and a polymolybdate phase.

The presence of MoO_3 is questionable. Even if it exists, it should not be in an amount large enough to be detected by ESCA. MoO_3 would have been sulfided to MoS_2 if it had existed in significant quantity. The data from the sulfided catalysts do not give evidence of MoS_2 formation. ΔE (Mo $3d_{5/2}$ -S 2p) and ΔE (Mo $3d_{5/2}$ -O 1s) for TS-19 (Mo+Ni) and TS-20 (Ni:s+Mo:b) are less than that for MoS (see Tables 12 and 13). ΔE (Mo $3d_{5/2}$ -S 2p) for MoS_2 comes close to the value for TS-17 (Ni+Mo, step), but it can be an anomaly of the data caused by the other phases being present on this particular catalyst or it may really represent the MoS_2 phase. The formation of MoS_2 on TS-17 (Ni+Mo, step) is possible as will be discussed below.

When ΔE (Mo $3d_{5/2}$ -Ni $2p_{3/2}$) values are compared (see Table 12), formation of NiMoO₄ type structure is possible. However, a distinctive NiMoO₄ phase may not have developed under the concentration ranges of this study. It is probably a phase intermediate between a polymolybdate and NiMoO₄ resembling a structure close to NiMoO₄. This phase is probably less developed in TS-17 (Ni+Mo, step). Upon sulfiding, this phase is probably converted to a Ni-Mo-S phase well dispersed on the Al₂O₃ surface. It may contain some oxygen in its structure. In the case of TS-17 (Ni+Mo, step), this phase may be converted to Ni-Mo-S and some MoS₂ (well dispersed among the other phases) since the majority of the Ni will be in the Al₂O₃ lattice. Since the spectra of TS-19 (Mo+Ni) and TS-20 (Ni:s+Mo:b) do not give evidence for the formation of MoS₂ and Ni₆S₅ in significant quantities, the above assignment is justifiable. Under the sulfiding conditions of this study, MoS₂ and Ni₆S₅ should have formed if they were completely sulfided [201]. The formation of a similar phase (Co-Mo-S) with Co-Mo catalysts is discussed in the literature [191, 211, 212]. The Ni-Mo-S phase can be formulated as Ni_xMo_{1-x}S_{2±δ} by analogy to Co-Mo catalysts.

Analyses of Ni 2p spectra are more difficult than that of Mo 3d since the peak binding energies of different Ni phases differ by only 0.2 to 0.5 ev. This small difference can easily be masked by charging effects and experimental errors. Resolution of the band is a problem also.

The formation of the NiAl₂O₄ type phase under almost any kind of impregnation technique is possible [55]. Therefore, this phase will not be excluded in this study even though spectra for NiAl₂O₄ is not

available. There is always some Ni moved into the Al_2O_3 lattice occupying tetrahedral sites which is not sulfidable. When Ni $2p_{3/2}$ spectra of sulfided catalysts are compared, the secondary peaks appearing at higher binding energy level are assignable to NiAl_2O_4 type structure. This peak is stronger in the Ni $2p_{3/2}$ spectra of the catalyst TS-17 (Ni+Mo, step) indicating the presence of more Ni in NiAl_2O_4 type phase as expected. In fact, stepwise impregnation of Ni should cause movement of more Ni into the Al_2O_3 lattice similarly to the discussion by Chung and Massoth [29, 30] with Co-Mo catalysts. The presence of some Ni in the $\text{Al}_2(\text{MoO}_4)_3$ type phase is possible if the broader Ni $2p_{3/2}$ and Ni $2p_{1/2}$ bands are taken as the evidences of this involvement. However, the nature of this interaction is not clear.

Probably there is no distinct NiO phase in these catalysts since the Ni $2p_{3/2}$ peak of NiO appears at substantially lower binding energy. The rest of the Ni may be present in the NiMoO_4 type phase or other minor phases. The presence of Ni_2O_3 can not be excluded in these catalysts. This phase can not be distinguished from NiMoO_4 by ESCA since their peak binding energies are very close to each other.

Since Al 2p, Al 2s and O 1s bands are broadened for all of the Ni-Mo catalysts, the presence of some partially sulfidable Ni phase in the Al_2O_3 lattice is possible. As discussed above, the broadening of these bands is larger for the catalyst TS-17 (Ni+Mo, step). The broadening increases in the order TS-17 > TS-20 > TS-19. Since Ni was loaded in four steps on the catalyst TS-17, two steps on the catalyst TS-20 and a single step on the catalyst TS-19 (reverse sequence of

metal impregnation for this catalyst) and the stepwise impregnation of Ni causes movement of more Ni into the Al_2O_3 lattice, these band broadenings are probably caused by a partially sulfidable Ni phase associated with the Al_2O_3 structure in addition to $\text{Al}_2(\text{MoO}_4)_3$ type phase in TS-17 (Ni+Mo, step). If the phase was not associated with Al_2O_3 , the Al 2p and Al 2s bands would not be effected. When the Ni-Mo catalysts are sulfided, there is a possibility of the formation of some Ni_6S_5 (a more stable form of Ni). Indeed, the shoulders appearing on the lower binding energy side of the Ni $2p_{3/2}$ spectra (see Fig. 30) coincide with Ni_6S_5 (see also Table 12). However, the amount of this phase should be small compared to the other sulfided Ni phase (Ni-Mo-S) since its peak appears as a weak shoulder. It can be speculated here that the Ni_6S_5 phase comes from the sulfidation of separate Ni phases such as Ni_2O_3 if it is assumed that Ni present in the surface NiMoO_4 type phase is converted only to the Ni-Mo-S phase.

In summary, stepwise impregnation of Ni and Ni+Mo (Ni first) impregnation order caused movement of more Ni into the Al_2O_3 lattice and the amount is related to the number of steps of Ni impregnation. Stepwise impregnation of Mo also caused movement of Mo into the Al_2O_3 lattice forming a phase similar to $\text{Al}_2(\text{MoO}_4)_3$, but some Ni may also present in this structure. Some of the Ni and Mo in the Al_2O_3 lattice appears to be partially sulfidable. The rest of Ni and Mo is probably present in NiMoO_4 type structure and in some surface Ni_2O_3 . However, the assignment of Ni_2O_3 is a speculation at this stage. The NiMoO_4 type phase seems to be sulfidable to an intermediate phase resembling a structure like $\text{Ni}_x\text{M}_{1-x}\text{S}_{2+w}$.

The Mo 3d and Co 2p spectra of the Co-Mo catalysts are shown in Fig. 32 and Fig. 33 respectively. The Mo 3d spectra of the catalyst TS-11 (Co+Mo, step) is very similar to that of the catalyst TS-17 (Ni+Mo, step). The band is broadened to almost the same amount upon sulfiding. The Al 2p, Al 2s, O 1s and S 2p bands of the catalyst TS-11 (Co+Mo, step) are also broadened (see Fig. 34 and Table 14) more than those of the catalysts TS-18 (Mo+Co) and TS-21 (Co:s+Mo:b). However, the broadening is less when compared to the Ni-Mo catalysts. This difference can be due to the difference between Ni and Co.

As a result some Mo was moved into the Al_2O_3 lattice when it was impregnated stepwise. This is again an $\text{Al}_2(\text{MoO}_4)_3$ type structure and some Co may be involved in this structure as will be discussed below. The presence of $\text{Al}_2(\text{MoO}_4)_3$ type phase in the catalysts TS-18 (Mo+Co) and TS-21 (Co:s+Mo:b) is not likely or insignificant if it exists at all. The rest of Mo in the catalyst TS-11 (Co+Mo, step) is probably present as a surface polymolybdate phase. It may interact with some Co but the interaction seems very weak (see Table 15, WE (Co $2p_{3/2}$ -Mo $3d_{5/2}$)). This is expected because most of Co is tied to Al_2O_3 . The majority of Mo in the catalysts TS-18 (Mo+Co) and TS-21 (Co:s+Mo:b) is probably present as a surface phase similar to CoMoO_4 (it is probably less developed in the catalyst TS-21), a phase intermediate between polymolybdate and CoMoO_4 . This assignment can be supported by WE (Mo $3d_{5/2}$ -O 1s) and WE (Mo $3d_{5/2}$ -Al 2p) in Table 15. Similarly to the Ni-Mo catalysts, the presence of MoO_3 is questionable because of the absence of a detectable MoS_2 . However, MoO_3 may present in insignificant quantities in every catalyst.

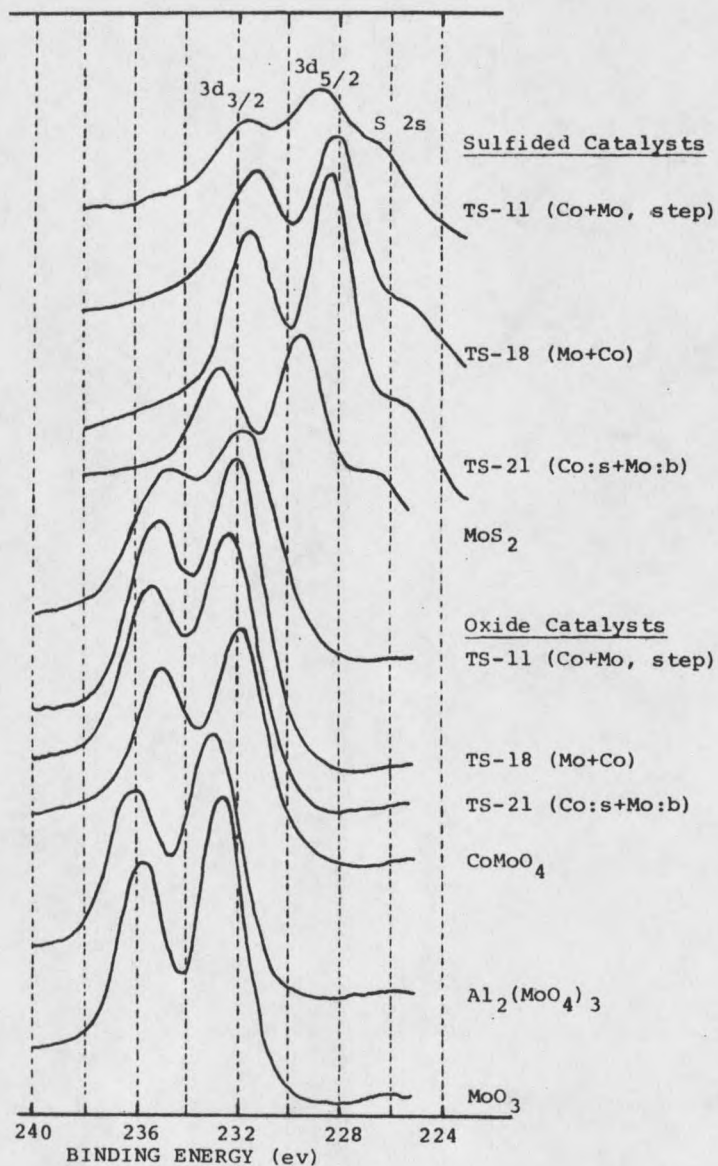


Figure 32. The Effect of Impregnation Technique on the XPS Mo 3d Spectra of the Co-Mo Catalysts

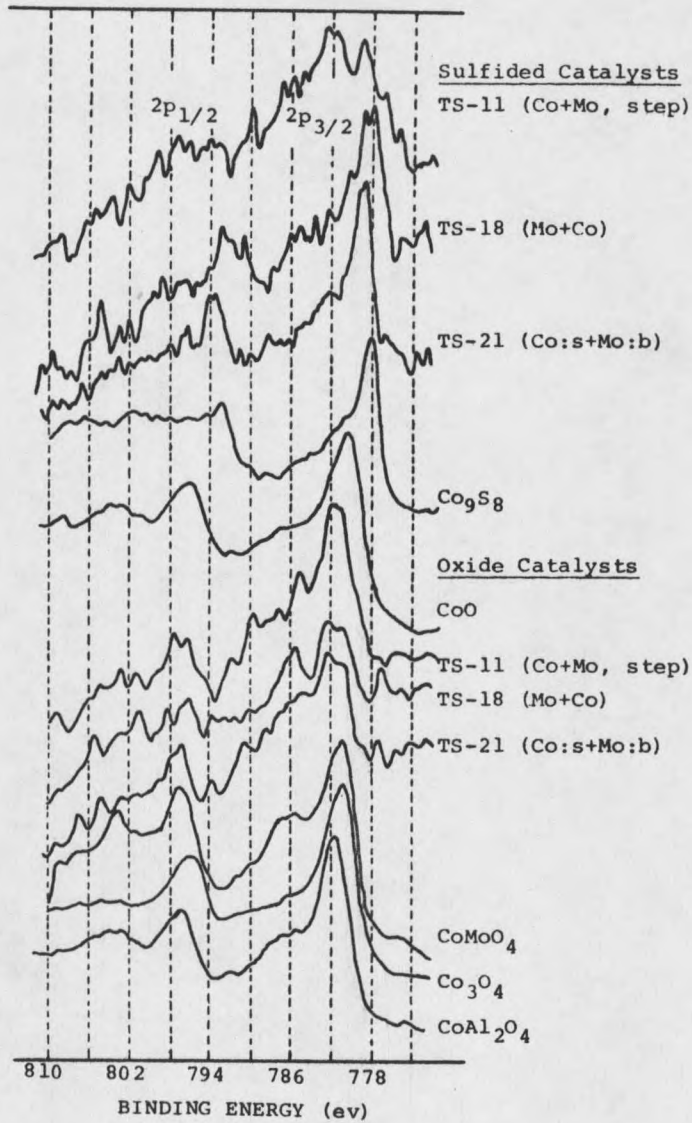


Figure 33. The Effect of Impregnation Technique on the XPS Co 2p Spectra of the Co-Mo Catalysts

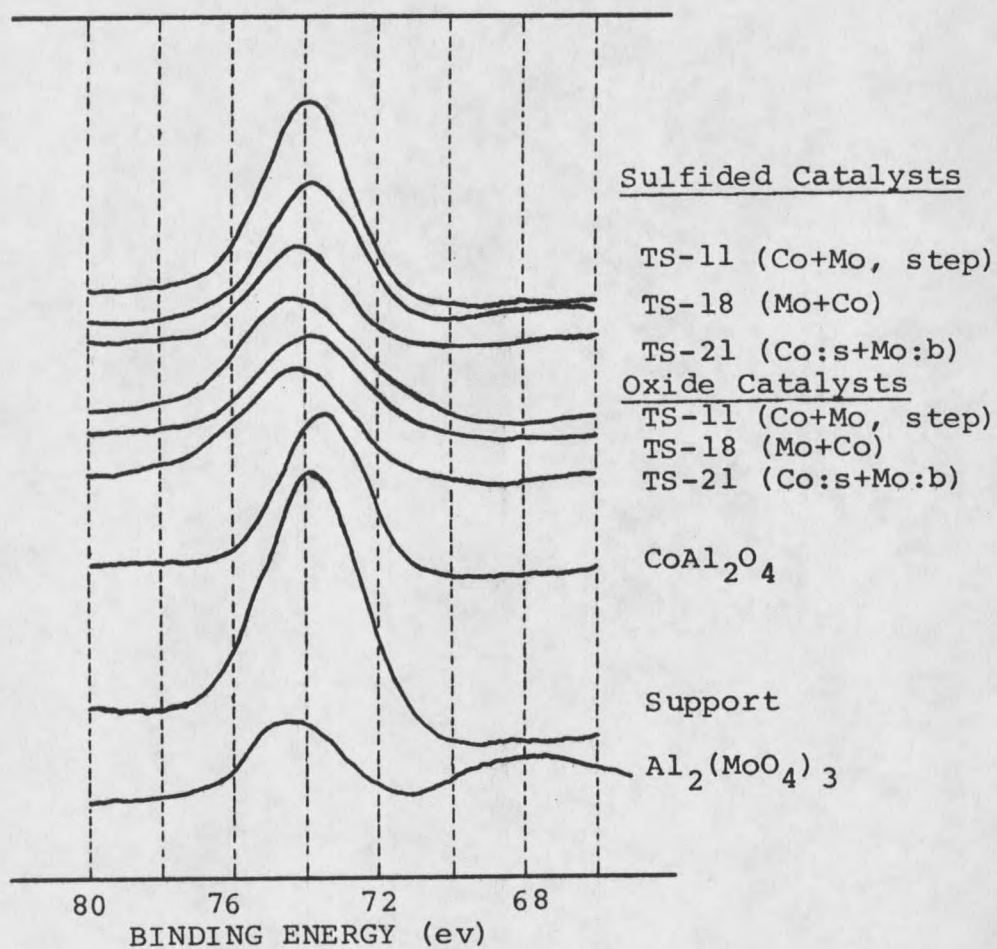


Figure 34. The Effect of Impregnation Technique on the XPS Al 2p Spectra of the Co-Mo Catalysts

