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The Effect of Antimony and Fluoride on Alumina-Based
Co-Mo and Ni-Mo Hydrotreating Catalysts

by

Alison M. Walker

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "The Effect of Antimony and Fluoride on Alumina-Based Co-Mo and Ni-Mo Hydrotreating Catalysts" submitted by Alison M. Walker in partial fulfillment of the requirements for the degree of Master of Science.



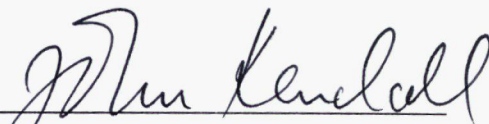
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ABSTRACT

The objective of this project was to develop hydrotreating catalysts which were capable of being used under relatively mild temperatures. It was speculated that by increasing the surface acidity of a conventional Co-Mo (or Ni-Mo) alumina catalyst, that hydrocracking could be achieved at lower temperatures. The aim was to increase the surface acidity of the catalyst by adding small amounts of antimony to an alumina support, followed by addition of fluoride and then Co-Mo (or Ni-Mo). It was anticipated that a "superacidic" surface could be formed in this manner which would emulate the behavior of SbF_5 . By changing the alumina starting material, the impregnation order and the catalyst preparation technique, an optimum preparation procedure was devised. The catalysts were then synthesized with varying concentrations of antimony. The catalyst functions were analyzed using model compound reactions with cumene and thiophene. The catalysts were studied in their reduced and sulfided forms for their hydrocracking activity with cumene, and in their sulfided forms for their hydrodesulfurization ability with thiophene. Infrared spectroscopic studies were performed on the oxidic species in order to determine surface acidity by using the pyridine adsorption technique. In order to determine the oxidation state of antimony on the oxidic catalyst, some XPS spectra were also obtained. The results obtained from the model compound studies indicate that antimony actually deactivates the

catalyst. However, on a conversion per area basis (from surface area measurements) the catalysts containing antimony are more active than those without the additive. The catalysts which contained fluoride were more active (due to enhanced surface acidity) than conventional Co-Mo (or Ni-Mo) hydrotreating catalysts.

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To Mommy and Daddy

To Mikey

To My supervisor

To whom it may concern!

To the men of the world

To my friends

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CHAPTER 1

INTRODUCTION

In the early 1950's, the total amount of recoverable, conventional crude oil in Alberta was close to three billion cubic meters¹. Today, less than fifty percent remains to be produced. Factors such as conservation, alternative forms of energy, and the reduced population growth rate will help to moderate the demand for oil products. However, even by taking these into account, it is estimated that Canadian sources of oil must be doubled by the early 1990's in order to obtain energy self sufficiency². Where will this new supply come from? The bulk of it must be produced from unconventional sources such as the bitumen and heavy oil deposits found in Alberta.

The huge resource in the tar sands can form the basis of a continued source of supply. The bitumen in place from Alberta's four major tar sands deposits (Athabasca, Wabasca, Peace River and Cold Lake), has been estimated to be more than two hundred billion cubic meters³. The recoverable amount is closer to forty billion cubic meters, with eight billion from surface mining and close to thirty-two billion produced in situ. Even after subtracting extraction and upgrading losses, synthetic crude production could reach thirty-four billion cubic meters. The ultimate production potential of the tar sands is more than ten times that of conventional crude.

1.1 UPGRADING

The general properties of Athabasca bitumen are shown in Table 1.1⁴.

Table 1.1
General Properties of Athabasca Bitumen

Specific Gravity, 16/16°C	1.009
Ash (wt %) 700°C	0.59
Iron (ppm)	358
Nickel (ppm)	67
Vanadium (ppm)	213
Conradson Carbon Residue (wt %)	13.3
Pentane Insolubles (wt %)	15.5
Benzene Insolubles (wt %)	0.72
Sulphur (wt %)	4.48
Nitrogen (wt %)	0.43
Oxygen (wt %)	0.95
Carbon (wt %)	83.36
Hydrogen (wt %)	10.52
+525°C Residuum (wt %)	48.03

As can be seen, heavy oils and bitumen exhibit several undesirable properties. The metals present tend to deactivate upgrading catalysts. The Conradson Carbon Residue is a measure of the portion of the residue which will form coke. Coke is a high molecular weight, carbon-rich complex which is left by the destructive distillation of the bitumen. Coke formation also causes

problems by deactivating the catalysts. The presence of nitrogen and oxygen compounds (electron donors) is undesirable since they form strong bonds with the acidic sites on the catalyst support⁴. The strongly adsorbed species will stay on the catalyst long enough for polymerization to occur. Polymerization results in an increase of catalyst carbon content which is not desired. Heavy oils also have high viscosities (greater than one million centistokes) which create headaches for those involved in production and transportation.

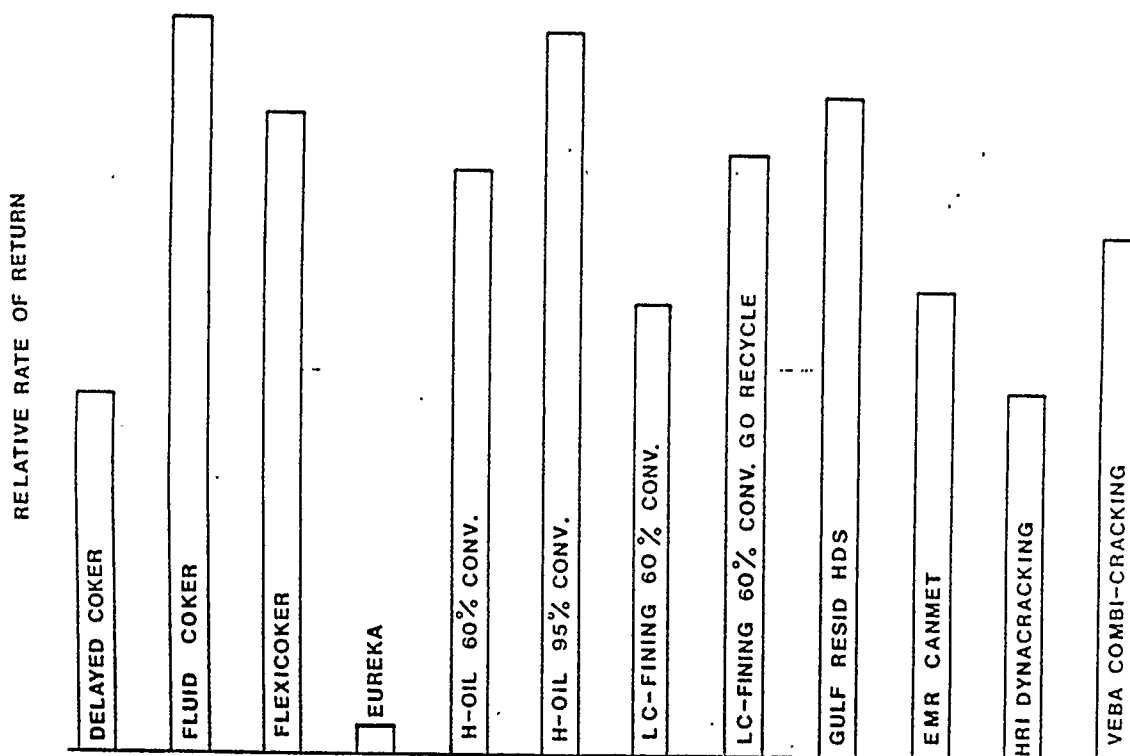
The process which takes bitumen and converts it into an acceptable fuel oil is known as upgrading. The hydrogen to carbon ratio is increased and the viscosity is reduced to less than one hundred centistokes. The vacuum bottoms which are normally about fifty percent by volume are eliminated, and the specific gravity is improved¹. The asphaltenes, metals, nitrogen and sulfur content are all substantially reduced.

The processes used to upgrade bitumen are generally classified as either carbon rejection or hydrogen addition processes. Carbon removal is accomplished by thermal cracking, which involves coke formation. Hydrogen addition can be accomplished by either adding hydrogen and a catalyst (hydrotreating) or by utilizing a donor solvent. The net result of the upgrading process is the production of a light, clean, synthetic crude oil.

There are many upgrading processes used industrially. An economic comparison of the more feasible processes was performed by Husky Oil Ltd., in order to determine which upgrader should be employed in their proposed Lloydminster plant⁵. The results of this

study are shown in Fig. 1.1. These results are not universally applicable since they depend on a number of factors, including feedstock, size, product quality, residue utilization/marketability, price and environmental constraints. However, they do serve as a good medium by which to compare the various upgrading techniques.

Fig. 1.1
Economic Comparison of Various
Upgrading Processes.



The first four processes (delayed coking, fluid coking, flexicoking and Eureka) are all carbon rejection processes which are used industrially. The rest of the processes involve hydrogen addition.

1.1.1 Carbon Rejection Processes

The easiest technique to remove carbon from bitumen is a simple vacuum distillation. Unfortunately, over fifty percent of the feedstock would be rendered into a useless, low value product if this was attempted. Instead, the heavier molecules of bitumen are thermally cracked at temperatures between 450 and 700°C to lighter products. These are then fractionated into coker distillates while the remainder of the bitumen is converted simultaneously to a heavier molecular weight product or coke. The more common industrial processes are outlined below.

Delayed coking is the current commercial technology utilized by Suncor in Fort McMurray, although they have recently started engineering work on an expansion. Delayed coking is a semi-continuous process where heated feedstock is transferred to large coking drums to allow cracking reactions to proceed to completion^{6,7}. The cracked products leave through the top of the reactor, whereas the coke deposits form on the inner walls of the vessel. This process produces a quality liquid product, but the yield is lower than that of other techniques.

Fluid coking is a continuous process which uses the fluidized solids technique to convert bitumen to more valuable products. The

bitumen is coked by being sprayed into a fluidized bed of hot, fine coke particles⁸. The coking reactions can be conducted at higher temperatures and shorter contact times than in delayed coking. These conditions result in decreased yields of coke and greater quantities of liquid products⁹. Until recently, Syncrude had utilized only this upgrading technique at their Alberta plant. However, they now have embarked on an expansion which involves combining fluid coking and hydrocracking technologies, as will be discussed later¹⁰.

In order to decrease the amount of coke formed during processing, a coke gasifier has been added to a fluid coker¹¹. The process is known as flexicoking, and the heat required to run the reactor is supplied by the coke. Since the coke is converted into by-product gas, the energy integration of a flexicoker is greater than that of a fluid coker.

The last carbon rejection process to be discussed is the Eureka process, which is operating successfully on a commercial scale in Japan¹². It has also been used for a pilot plant test¹³. The temperature of the Eureka process is lower than that of the other thermal cracking processes, which results in a lower cracked gas yield and a higher cracked oil yield. The process operates on a cycle similar to that of a delayed coker, except that the cycle time is of the order of four hours. The cycle time for a delayed coker is typically twenty-four hours. As a result of the short cycle time, the bottom material (pitch) avoids excessive thermal treatment and becomes homogeneous, enabling it to be handled in a molten state.

There are two major problems associated with the coking operations which have been discussed previously. First, about fifteen to twenty percent of the starting material forms coke, which contains transition metals and heteroatoms, thereby ruining the possibility of it being used as a fuel. A second point to note is the fact that the upgraded product is still higher in aromatic content than conventional crude, causing problems in downstream processing¹⁴.

Most new upgrading technologies involve hydrogen addition, which can involve either a donor solvent or hydrogen and a catalyst. The bitumen is reacted with hydrogen at fairly high temperatures (although not as high as coking) and pressures. The differences in the processes involve either varied process equipment arrangements or the use of different catalyst systems. The most common donor solvent process is Gulf Oil Ltd.'s DRB process, whereas the hydrogen addition processes include H-Oil, L.C. Fining, Gulf's resid. HDS, Canmet, dynacracking and Veba Combi Cracking.

1.1.2 Donor Solvent

The Gulf Donor Refined Bitumen (DRB) process is basically thermal hydrocracking with hydrogen supplied via a circulating donor stream¹⁵. The donor stream is a middle distillate containing substituted tetralins as the active components. In the hydrocracking step, the tetralins are converted to naphthalenes, providing hydrogen for the feed conversion reactions. The donor is recovered from the reaction mixture by conventional atmospheric distillation. It is

then hydrotreated under moderate conditions and recycled to the thermal hydrocracking section. The presence and availability of hydrogen at the cracking step result in products that are more saturated than those formed by coking. The Gulf DRB process is competitive with current and emerging hydrogen addition processes.

1.1.3 Hydrogen Addition Processes

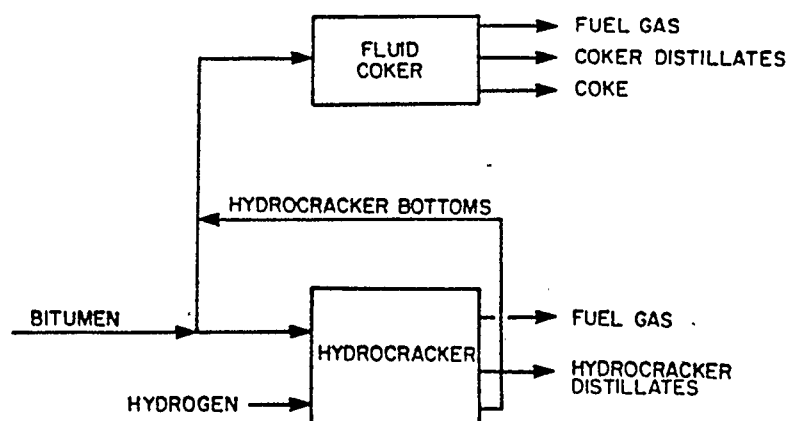
The H-Oil process has been chosen by Husky Oil Ltd. to be used in their upgrader at Lloydminster⁵. H-Oil is a catalytic hydrogenation process of heavy oils in an upflow ebullated-bed reactor. The conversion level can be varied by changing the reaction conditions. Husky has selected a combination of low conversion hydrocracking followed by delayed coking for their upgrader. This combined technology enables Husky to minimize their initial investment, while maximizing synthetic crude yield and financial performance.

As mentioned earlier, Syncrude has just completed a capacity addition program which utilizes the combined technology of fluid coking and hydrocracking. The technology for the hydrocracker is licensed from Lummus Crest Inc., in association with Cities Service and Amoco, and is known as L.C. Fining. L.C. Fining is a low conversion ebullated-bed hydrocracking process which has two variations from conventional hydrocracking technologies¹⁶. Firstly, the powdered catalyst which is employed eliminates the need for a recycle pump. Secondly, an inexpensive demetallization catalyst upstream from the conventional reactor cuts make-up catalyst costs.

The catalyst in the reactor behaves like a fluid, allowing for addition of fresh catalyst without any interruption of operations.

The integration of the hydrocracker with the fluid coker is shown in Fig. 1.2¹⁷.

Fig. 1.2
Integration of the Hydrocracker
with the Fluid Cokers



The combination of expanded bed hydrocracking and coking for the upgrading of bitumen is an improvement in technology over the present use of carbon rejection processes alone. This combination of hydrocracking and coking results in incremental liquid yields in excess of one-hundred liquid volume percent, and reduced sulfur dioxide emissions per barrel of synthetic crude oil. The integration of L.C. Fining and fluid coking also provides the opportunity for future expansions at Syncrude as more hydrocrackers can easily be added.

The Canmet hydrocracking process is a high conversion, high demetallization, residuum hydrocracking process. It uses an additive to suppress coke formation and achieve high conversions of high boiling-point hydrocarbons into lighter products. The process was initially inspired by the German "Combi" process. The catalyst used is iron sulfate impregnated on coal, which is an inexpensive catalyst that deactivates rather rapidly. In the process, feedstock is mixed with additives, heated, contacted with hydrogen and then sent to an upflow reactor¹⁸. The product is withdrawn overhead and separated into a hydrogen-rich recycle gas stream, process gas, distillates and a residual pitch fraction. The sulfur and nitrogen removal from heavy gas oil is ninety and seventy percent respectively. In general, the Canmet process has demonstrated the ability to achieve high conversion of what appears to be an unlimited range of heavy feedstocks.

Much interest has recently been shown by AOSTRA in Veba OEL's combi-cracking process (VCC). It is now ready for commercial application in Alberta as extensive testing of Alberta feedstocks has been completed in a large scale pilot plant in Gelsenkirchen, West Germany¹⁹. The VCC process is a high conversion, hydrogen upgrading process which combines thermal hydrocracking in a liquid phase reactor with catalytic hydrotreating in a gas phase reactor. It provides a high yield of excellent quality, synthetic crude oil from bitumen²⁰.

From the foregoing discussion, it is apparent that hydrogen addition schemes are gaining industrial acceptance due to their

superior liquid yield. The carbon removal processes, liquid coking and flexicoking, are still widely used since the residue stream is utilized for internal fuel, thereby minimizing operating expenses.

1.2 THE CATALYSTS

The focus of this research project is the preparation of hydrotreating catalysts. Since hydrotreating includes hydrocracking, hydrodesulfurization, hydrodenitrogenation, and the saturating of some of the unsaturated species in the feedstock, it is very demanding on the catalyst employed. The catalyst has to perform two functions. First, it has to crack species of high molecular weight into smaller fractions, then it must catalyze the hydrogenation of the unsaturated smaller fractions in order to avoid polymerization²¹. It is in this second step where the removal of heteroatoms (iron, vanadium, nickel, sulfur, nitrogen and oxygen) should also be accomplished. Widespread research is being directed at understanding the role of various catalysts that are used industrially, and in developing improved catalysts which can withstand the severe processing conditions required to remove heteroatoms.

The catalysts involved in hydrotreating all belong to the same family. They are the sulfides of metals of group VI A (i.e. Mo,W) promoted by the sulfides of metals of group VIII (i.e. Co,Ni)²². The various pairs of sulfides have different activities for various chemical conversions. The metal sulfides are usually dispersed on a large surface area support such as alumina, silica or carbon. The combination of desired catalyst acidity, total pore volume, surface

area and pore size distribution restricts the selection of the catalyst support²³.

When designing a catalyst, one attempts to build in the important attributes of activity, stability, selectivity and catalyst lifetime. The most crucial aspect is the catalyst lifetime, since deactivation is a major problem. There are three types of deposits which deactivate a catalyst surface, with the major one being coke formation²⁴. Deactivation also occurs from the organometallic species present in bitumen, and inorganic particles of clay or sand which have not been removed from the bitumen²⁵. The deactivation is the result of the pores of the support becoming plugged. This drastically reduces the effective surface area of the catalyst²⁶.

High conversions can be obtained in hydrotreating by increasing the temperature. Unfortunately, an accompanying exponential increase in catalyst deactivation by coke formation renders this unacceptable²⁷. In order to obtain optimum performance, researchers must try to balance conversion levels with catalyst lifetimes.

It has been suggested that there is a steady state amount of coke deposited on a catalyst (for a particular feedstock and a particular set of operating conditions) regardless of the presence of special additives which are designed to inhibit coke formation. This indicates that changes in catalyst composition cannot alter the amount of coke deposited on a catalyst at steady state²⁸. However, changing the catalyst composition can improve the conversions obtained. Fluorine compounds are known to increase the surface acidity of catalysts^{29,30}. Since catalytic cracking conversion is

related to surface acidity, the addition of fluoride ion results in higher conversions at lower operating temperatures²¹. The tendency for coke to form on the catalyst surface is reduced by proceeding at lower temperatures, thereby increasing the catalyst lifetime.

1.3 PROJECT OVERVIEW

In this study, an attempt to further increase the acidity of the catalyst surface was made by adding antimony as well as fluoride. It is known that highly acidic surfaces can be prepared by treating alumina with SbF_5 ³¹. Unfortunately, the SbF_5 rapidly disappears when subjected to the severe conditions required for hydrotreating³². In an attempt to increase the surface acidity of conventional Co-Mo/ Al_2O_3 and Ni-Mo/ Al_2O_3 catalysts, small amounts of antimony were incorporated into the oxide lattice of alumina. This was followed by the addition of fluoride, molybdenum and cobalt or nickel. It was anticipated that a superacidic surface could be formed in this manner, which would emulate the behavior of SbF_5 .

The catalyst preparation method utilized in this project was important since the desired fluoro-antimony species must be anchored to the surface of the alumina. A systematic investigation was started with the following objectives:

- 1) To choose whether boehmite ($\alpha\text{-Al}(\text{OH})_3$), which is converted to $\gamma\text{-Al}_2\text{O}_3$ upon calcination at 450°C , or $\gamma\text{-Al}_2\text{O}_3$ should be used as the starting material for the preparation of the catalyst support.

- 2) To determine whether coprecipitation of antimony and aluminum oxides, or impregnation of antimony onto the alumina surface is the most desirable preparation method for the catalyst support.
- 3) To determine in which order, and by which technique, the promoters should be deposited on the catalyst.

In order to delineate an optimal preparation procedure for the oxidic catalysts, the catalysts were dried, calcined and then activated by reduction and/or sulfidation. These were then tested for their catalytic activity with the model compounds of cumene (cracking, hydrocracking) and thiophene. Activities were compared, and a preparative procedure was chosen.

On the basis of these results, a series of catalysts were prepared and a correlation between their activities and surface acidities was attempted. Surface acidity studies were performed by adsorbing pyridine on thin wafers of the catalysts and then recording the infrared spectrum. Studies were performed on the oxidic precursors of the active sulfidic catalysts. Changes in the surface acidity (both Brönsted and Lewis) with various catalytic additives could be determined in this manner.

Detailed studies of the catalyst activities were performed using model compound reactions. The catalysts were studied in their oxidic forms for their cracking activity and in their reduced and sulfided forms for their hydrocracking ability. Cumene was chosen as a model compound since three different types of reactions could be studied at the same time. The hydrodesulfurization activities were monitored by

the reaction of hydrogen with thiophene over the catalysts. Further information, and results, are found throughout the thesis in the appropriate sections.

CHAPTER 2

EXPERIMENTAL METHODS

The laboratory work which has been required for this project can be divided into three major areas: preparation of catalysts, characterization methods, and model compound reactions. The preparation entailed making the catalyst support, and then devising the most effective route by which to incorporate active ingredients onto it. Catalyst characterization was accomplished by obtaining x-ray powder diffraction patterns, x-ray photoelectron spectra, and Fourier transform infrared spectra. Surface areas of the catalysts were also measured. Catalytic activities were determined through the use of the model compounds, cumene and thiophene. Cumene was used to determine cracking and hydrocracking activity, whereas thiophene was used for hydrodesulfurization reactions.

2.1 PREPARATION OF CATALYSTS

There are many different parameters which must be recognized when synthesizing hydrotreating catalysts. An attempt has been made to control the important parameters, and delineate an appropriate preparation sequence, based on results from characterization studies and model compound reactions. This is discussed in detail in Chapter 5, "Preparation of Catalysts".

2.1.1 Preparation of the Support

Three different techniques were used to anchor the antimony into the alumina lattice. The different approaches involved either impregnating varying amounts of antimony onto alumina (boehmite, α -AlOOH or gamma alumina, γ -Al₂O₃) or co-precipitating the two components. In all cases, the catalysts were dried at 110°C for at least 12 hours, and then calcined (in a stream of air) by heating in a tube furnace (Lindberg, Sola Basic) at 475°C for 4 hours. The temperature was raised from room temperature to 475°C by the use of a programmed temperature controller with the heating rate set at 4°C/minute.

An example of the preparation of a support, containing an antimony to aluminum atomic ratio of 1:50, by impregnation onto boehmite is outlined below. Boehmite (8.980 g AlOOH, ALFA Products) and antimony oxide (0.437 g Sb₂O₃, Fisher Scientific) were mixed dry. Distilled water (2.6 ml) containing ammonium hydroxide (1.6 ml) was added, and the mixture was mulled for at least five minutes. Additional water (0.8 ml) containing nitric acid (3 micropipette drops) was then poured onto the mixture, and it was mulled again. The support was then left at room temperature to allow for evaporation of any excess water prior to drying at 110°C and calcining at 475°C.

The impregnation of antimony oxide onto gamma alumina followed the same procedure, the only difference being the fact that the boehmite was dried and calcined prior to use.

The co-precipitation method was used for the preparation of several supports. The antimony oxide was dissolved in hydrochloric

acid and heated. The boehmite was dissolved in a potassium hydroxide solution. The concentrations of both solutions were the same. The solutions were mixed simultaneously, with the pH of addition being monitored. The fine white precipitate which formed was allowed to settle, and the supernatant was decanted. Since potassium chloride was also precipitated, the solid was washed several times with excess distilled water. The support was then dried and calcined as before.

2.1.2 Addition of Promoters

Promoters were incorporated into the support by either co-impregnation or sequential impregnation routes. In the samples which were prepared by sequential impregnation, the promoters were added in varying orders to the calcined antimony/alumina support. The catalysts were then dried and/or calcined between additions. The results obtained from the preparation studies are given in Chapter 5.

The incorporation of promoters into the catalyst began by dissolving ammonium paramolybdate, ammonium fluoride, and nickel nitrate (or cobalt nitrate) separately. The total volume of all the liquid which was added was approximately equal to the pore volume of the support. The quantities of the metal salts were calculated to give 15 wt % MoO_3 and 3 wt % NiO (CoO) on the catalyst surface upon calcination. The fluoride concentration was varied from 0 wt % to 6.9 wt %. A sample preparation procedure (for catalyst AMW-16) is outlined on the following page.

Preparation of AMW-16

1. The mixed oxide support was formed by adding 8.980 g AlOOH (7.5×10^{-2} moles Al_2O_3) to 0.437 g Sb_2O_3 (1.5×10^{-3} moles Sb_2O_3) and using the preparation technique outlined in Section 2.1.1 "Preparation of Support", to give 1 Sb:50 Al atoms.
2. Addition of fluoride: 1.131 g NH_4F (3.0×10^{-2} moles F) was dissolved in 2 ml of H_2O and added to the calcined support. An additional 2 ml of H_2O was added after mixing, the catalyst was mulled for 5 minutes, then dried (110°C) and calcined as before (475°C) to give a ratio of 4F:20 support atoms (6.9 wt % F).
3. Addition of NiO/MoO_3 : 1.933 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ (1.1×10^{-2} moles Mo) was dissolved in 2 ml of H_2O containing 1.8 ml of NH_4OH (7.0M), 1.223 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.2×10^{-3} moles Ni) was dissolved in 1 ml of H_2O containing 3 drops of HNO_3 . These solutions were added to the catalyst, mulled thoroughly, and then the catalyst was dried and calcined.

2.2 CHARACTERIZATION OF CATALYSTS

Several techniques were used to identify and characterize the prepared catalysts and supports. X-ray powder diffraction patterns and surface areas of catalysts were obtained. Antimony x-ray photoelectron spectra were recorded for several of the samples in order to determine the antimony oxidation state in the oxidic catalysts. Pyridine adsorption was used to determine the surface acidity of each catalyst by employing Fourier transform infrared spectroscopy.

2.2.1 X-ray Diffraction

X-ray powder diffraction patterns of several samples were obtained through the cooperation of the Department of Geology at this university. The instrument which was used was a Norelco X-ray diffractometer with Ni-filtered Fe-K α radiation. The powder patterns obtained were compared to those published in the literature in order to identify the species present in the support and on the catalysts.

X-ray powder diffraction patterns are determined by the type of crystal lattice, and by the spacings in the lattice. They are useful as fingerprinting devices for the identification of compounds³³. As such, they are particularly suited for distinguishing between the various transition aluminas, as shown in Chapter 3 (Alumina).

2.2.2 Surface Area

The surface area of each catalyst was determined by using a Micromeritics model 2200 high speed surface area analyzer which is based on the Brunauer-Emmett-Teller (BET) method. The surface areas of powdered or porous solid materials are measured by determining the quantity of gas necessary to form a single layer of gas molecules (monolayer) on a sample³⁴.

The testing is accomplished by using nitrogen gas at liquid nitrogen temperatures. Under these conditions, the gas molecules are strongly adsorbed to the solid surface. At liquid nitrogen temperatures, the space occupied by each adsorbed molecule is known within relatively narrow limits. The sample is warmed to ice water temperatures, and the volume of gas which is adsorbed by the catalyst

between the two temperature limits is measured. This volume is then corrected for liquid nitrogen temperature variation (with changes in atmospheric pressure) and the true surface area of the catalyst is obtained.

2.2.3 X-ray Photoelectron Spectroscopy

In order to determine the oxidation state of antimony in several oxidic samples, x-ray photoelectron spectroscopy was used. The binding energy of an electron increases with increasing oxidation state. The observed shift in binding energy caused by changes in atomic charge results in the measurement of the oxidation state of a particular element.

The spectra were obtained by Dr. S. Sunder, using the x-ray photoelectron spectroscopy facilities located at the Whiteshell Nuclear Research Establishment (Atomic Energy of Canada, Pinawa, Manitoba). Copper coupons were used as substrates for powder samples, and the C 1s peak position (B.E. = 284.8 eV) was used for charge correction.

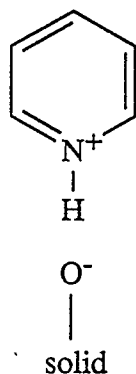
2.2.4 Pyridine Adsorption

Surface acidity studies were performed by adsorbing pyridine onto the catalyst surface and then studying the interaction by Fourier transform infrared spectroscopy. Pyridine was used to study the Brönsted and Lewis acidity of the surfaces since the Lewis and Brönsted acid sites can easily be distinguished by their pyridine adsorption spectra.

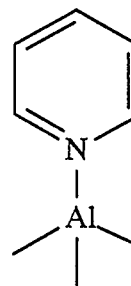
Figure 2.1

Brönsted and Lewis Held Pyridine

Brönsted



Lewis



The vibrational modes used to make the distinction between the two are shown in Table 2.1³⁵.

Table 2.1

Assignment of Vibrational Modes of Pyridine
Adsorbed on Brönsted and Lewis Acid Sites

Vibrational Mode	PyH ⁺ (cm ⁻¹)	Py:L (cm ⁻¹)
A ₁	1655 strong	1595 very strong
B ₁	1627 strong	1575 medium
B ₁	1550 medium	1455-1442 strong
A ₁	1490 very strong	1490 strong

The Lewis sites present on the surface are characterized by the band at $\sim 1455\text{ cm}^{-1}$, whereas the Brönsted sites are characterized by the band at $\sim 1545\text{ cm}^{-1}$.

2.2.4.1 Experimental

Thin wafers of catalysts ($\sim 25\text{ mg}$) were prepared and put in sample holders. These were then placed in a specially designed cell which could hold four of the pellets for comparative studies, and would ensure that the pre-treatment conditions of each sample were identical. The oxidic sample was then placed onto a high vacuum line and degassed for at least 16 hours. The temperature program was as follows: room temperature to 100°C at a rate of $2.5^\circ/\text{min}$, held at 100°C for 1 hour, then heated to 500°C at a rate of $5^\circ/\text{min}$ and held. The sample was then calcined by admitting oxygen into the system and holding the temperature at 500°C for 16 hours. The purpose of this was to burn off any carbonaceous material from the surface. The oxygen was pumped off and background spectra of the clean surfaces were obtained.

Pyridine was adsorbed at 100°C for at least 30 minutes. It was then desorbed for 1 hour (at 100°C) while still on the vacuum line. The spectra of the catalysts with pyridine were then recorded (using a Nicolet 8000 interferometer, at a resolution of 2 cm^{-1}). The spectra for pyridine adsorbed on each sample were then obtained by the subtraction of these two sets of spectra.

2.3 MODEL COMPOUND TESTING

Catalytic activities were measured by using the model compounds cumene and thiophene. Model compounds are useful since they allow for the rapid verification of the suitability of a solid acid as a catalyst. Cumene undergoes several reactions on catalysts and can therefore be used to determine the cracking and hydrocracking ability of oxidic, reduced and sulfided catalysts. Thiophene is used as a guide to determine the hydrodesulfurization ability of catalysts.

2.3.1 Cumene as a Model Compound

On hydrotreating catalysts, cumene undergoes dealkylation, dehydrogenation and side chain cracking reactions. The relative significance of these reactions depends on the catalyst and the operating conditions. Under the conditions used in this experiment, cumene was either dealkylated to benzene, dehydrogenated to α -methyl styrene, or the alkyl chain was cracked to ethyl benzene. A reaction scheme for cumene conversion is shown in Fig. 2.2.

Cumene dealkylation to benzene is the most important reaction for characterizing the Brönsted acid sites on the catalysts. This simple reaction can be considered as an electrophilic substitution of an isopropyl ion by a proton, as can be seen in Fig. 2.3³⁶.

The rate of cracking of cumene to benzene is proportional to the number of cumene molecules chemisorbed on the active sites of the catalyst³⁷. The reaction exhibits zero order kinetics at high cumene pressure, so it is possible to calculate the number of active sites by using absolute rate theory.

Fig. 2.2
Products Obtained When Cracking Cumene

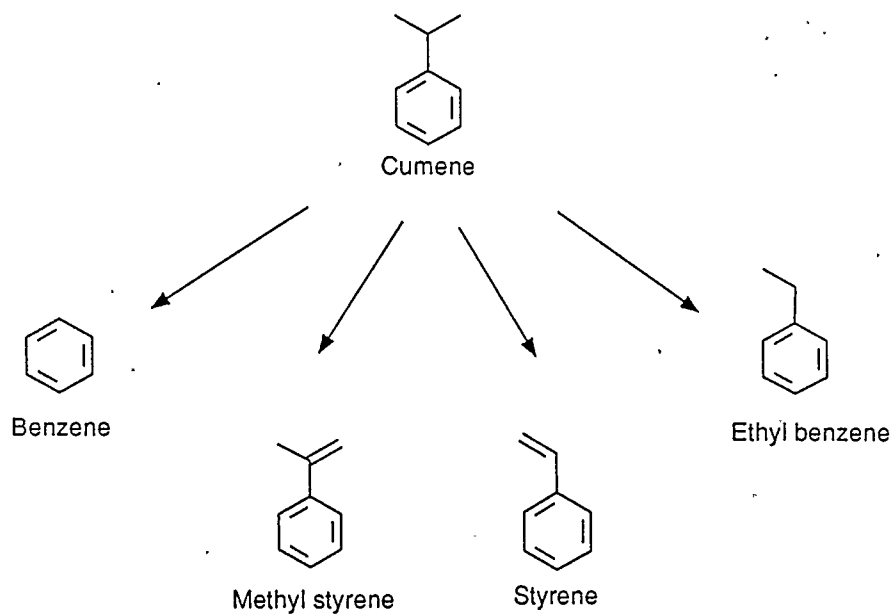
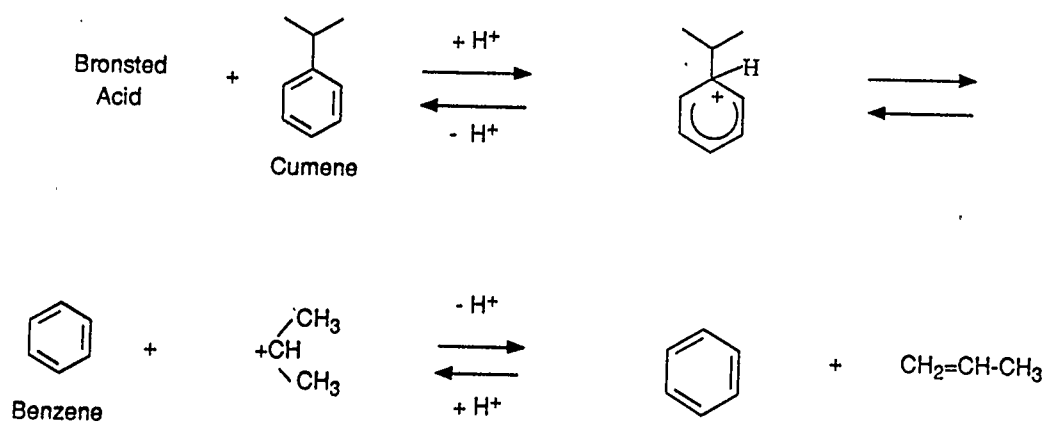


Fig. 2.3
Mechanism for Cumene Dealkylation to Benzene

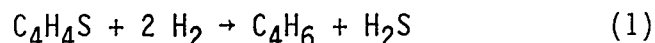


The cumene reactant must be extremely pure before use since it has been shown that impurities of 0.05% hydroperoxide can cause the reaction rate to decrease by a factor of two.

The secondary reactions which accompany the transformation of cumene to benzene include the production of α -methyl styrene and styrene. On alumina, between 350 and 550°C, it has been shown that cumene cracks roughly 50% by an ionic mechanism and 50% by a radical mechanism³⁸. The formation of styrene and α -methyl styrene is thought to occur through the radical mechanism. On all catalysts, coke is a significant product which tends to cause deactivation. This is apparent since the reaction mixture contains aromatics and olefins which are well known coke precursors³⁹.

2.3.2 Thiophene as a Model Compound

The hydrodesulfurization activities of each catalyst were determined through their reaction with thiophene. The catalytic reaction of thiophene in hydrodesulfurization experiments is generally represented by the following overall steps:



The major products which are detected include H_2S , $n\text{-C}_4\text{H}_{10}$, n -butene-1, and cis and trans-butene-2. Previous studies indicate that since butadiene is not easily detected, reaction (1) is thought to be

irreversible and reaction (2) is much more rapid than either (1) or (3)⁴⁰.

In our experiments, thiophene was reacted with hydrogen over the catalyst while samples of the output stream were collected every ten minutes. The reaction products (a mixture of butenes) were analyzed by gas chromatography but were not resolved.

2.3.3 The Testing Apparatus

The catalyst testing was carried out in a stainless steel, continuous flow, fixed bed bench top reactor. The reactor (15 mm i.d.) was packed with 0.150 g of catalyst (80-100 mesh) supported between layers of quartz wool.

The cumene (or thiophene) was contained in a pre-saturator which was held at a constant temperature by use of a cooling water bath set at -18°C . Prior to reaction with the catalyst, several background samples were obtained in order to determine the purity of cumene or thiophene and also, in the case of cumene, to determine the amounts of ethyl benzene and α -methyl styrene present.

The effects of contact time, activation temperature and reaction temperature had previously been studied by Dr. Z. Sarbak in this laboratory. The optimum conditions for the conversion of cumene were determined to be 500°C for activation, and 400°C for reaction with a contact time of 450 g hours per mole of cumene.

The catalyst was activated by heating for $1\frac{1}{2}$ hours at 500°C with a gas flow rate of $30\text{ cm}^3/\text{min}$. The gas used depended on the catalyst state required. Helium was used for the oxide forms

(cracking experiments), hydrogen for pre-reduction (hydrocracking runs) and 10% $\text{H}_2\text{S}/\text{H}_2$ for pre-sulfidation (hydrocracking and hydrodesulfurization experiments). After activation, and obtaining the background gas chromatograms (GC's) the model compound was reacted with the catalyst at 400°C . For cracking experiments, the sweep gas was helium while for hydrocracking and hydrodesulfurization runs, it was hydrogen. In the cumene studies, samples of the output stream were collected every 20 minutes in a sample loop collector (Valco Instruments). This was directly connected to a gas chromatograph [HP 5890, thermal conductivity detector; column description: 10 m length x 0.53 mm i.d. x $2.0\ \mu\text{m}$ film thickness, 50% phenyl, 50% methyl polysiloxane (HP-17)]. This was then connected to an integrator (HP 3392a). For the thiophene hydrodesulfurization experiments, the products were analyzed every 10 minutes by an on-line gas chromatograph [Varian 3700 flame ionization detector, column description: 10 m length x 0.53 mm i.d. x $1.33\ \mu\text{m}$ film thickness, carbowax 20 m (HP-20M)]. A schematic diagram of the catalytic testing system is shown in Fig. 2.4.

2.3.4 Calculations

The gas chromatograph signals were used to calculate the total number of moles of each product in the output stream after being corrected for their background concentrations and detector sensitivity. For the cumene studies, the response factors were determined (relative to cumene) by injecting known amounts of each substance into the gas chromatograph. The areas obtained for each

allowed the calculation of the response factors which were then corrected relative to that for cumene. These are shown in Table 2.2.

Fig. 2.4
Catalyst Testing Network

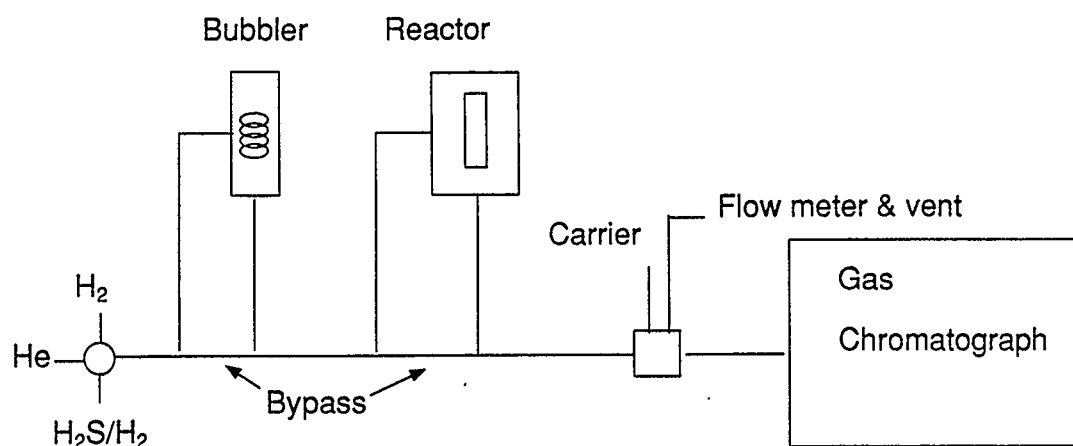


Table 2.2
Relative Response Factors

cumene	1.000
benzene	1.371
ethylbenzene	1.058
α -methyl styrene	1.106

In the hydrodesulfurization studies with thiophene, the mixture of butenes obtained (which were not resolved) were assumed to have the same detector response as thiophene.

2.3.4.1 Cumene Conversion and Yields

For these calculations, the area of cumene was taken from the chromatographs obtained. The other areas were determined by subtracting the background values obtained and multiplying by the relative response factor. The total conversion is defined as the sum of all the aromatic products (except cumene) divided by the sum of all the aromatics including cumene. The yield of a particular aromatic is defined as its area divided by the sum of all the aromatics except cumene.

The method of calculation is based on the assumption that the aromatic ring is not cracked under the conditions of these experiments. The aliphatic products are not included in the calculation. A computer program was written to calculate the cumene conversion results and yields.

2.3.4.2 Thiophene Conversion

The thiophene conversion was calculated by subtracting the percentage of the thiophene in the product stream from the percentage of thiophene in the reactant stream (which was determined by collecting background GC's). This total was then divided by the value obtained from the background GC's (i.e. thiophene in reactant stream) in order to obtain a percentage conversion. The preceding calculation assumes that the detector response is the same for all the butenes produced, and for the thiophene.

CHAPTER 3

THE SUPPORT: ALUMINA

In early publications, researchers referred to the support as a carrier. The catalytic material was distributed over a carrier in order to decrease the cost of the catalyst. Another purpose of the carrier was to provide mechanical strength to a weak catalyst. As the years passed, a greater understanding of the carrier led to it becoming known as the support. In many cases, the support actually contributes to the catalytic activity and assumes an essential role in the catalyst system.

There are at least seven physical characteristics in a support that must be controlled for proper performance of the catalyst or support. These characteristics are hardness, density, total pore volume, pore distribution, pore size, particle size and particle shape⁴¹. All of these support characteristics are interrelated. An example of this relationship can be shown by focussing on pore volume. As the pore volume increases, the hardness and the pore size will decrease. Due to these relationships existing between the support characteristics, the ultimate catalyst must represent a blend of these factors, with some of them compromised, in order to achieve optimum performance for a given operation.

Most industrial hydrotreating operations use aluminas as the catalyst supports. However, several research groups have recently been studying the effect of the support on catalytic activity. Compounds which have been used to disperse the active reagent include

silica, activated carbon, titania, magnesia, and various zeolites⁴²⁻⁴⁸. One recent report investigates the activities of sulfided molybdenum catalysts (under high hydrogen pressure) towards the hydrogenation, hydrocracking and hydrodesulfurization of various compounds. The reactivity order of the supports towards hydrogenation was found to be $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{MgO} > \text{SiO}_2$, while for hydrocracking and hydrodesulfurization it was $\text{TiO}_2 > \text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO}$ ⁴⁸. The catalytic activities of the supports depended on the structure and the properties of the metal oxide precursor to the active sulfide species. High hydrogenation activity was obtained for Al_2O_3 and TiO_2 where highly dispersed paramolybdate structures formed. In contrast, high hydrocracking activity was observed when an electronegative molybdenum species was present, which resulted in the formation of Brönsted acid sites. Hydrodesulfurization activity was catalyzed through both kinds of active sites.

One surprising feature which has been discovered through activity studies with various supports is the fact that iron, nickel and cobalt, which are used as catalysts for a large number of industrial reactions, are never supported on carbon. The reason for this is the ease with which these elements form inactive carbides during the manufacturing process⁴⁷. Through activity studies on various supports, it is apparent that the support plays an active role in the catalytic process.

The industrial preference for aluminas as the support is due to a number of factors. Aluminas are readily available in large quantities and in high purity at relatively low costs. They are

thermally very stable, and have surface areas in the 100-250 m²/g range. The pore volumes can be controlled during formation, and bimodal pore size distributions can be attained⁴⁹. Aluminas are amphoteric, therefore they possess both acidic and basic properties. These are controlled by the surface groups or ions which terminate the crystallites. The surface chemical properties of aluminas are important since they are involved in the formation and stabilization of the catalytically active components which are supported on their surfaces.

3.1 STRUCTURES OF ALUMINAS⁵⁰⁻⁵⁶

The name, alumina, has been commonly used for a broad range of products derived from aluminum hydroxides. Their nature, and consequently their uses, is closely related to the structure of the hydroxides and their behavior during thermal decomposition. There are three classes of compounds which are called aluminas.

1. Aluminum trihydroxides, with the formula $\text{Al}(\text{OH})_3$
2. Aluminum oxyhydroxides, with the formula AlOOH
3. Aluminum oxides, in which it is necessary to distinguish further between transition aluminas and corundum ($\alpha\text{-Al}_2\text{O}_3$).

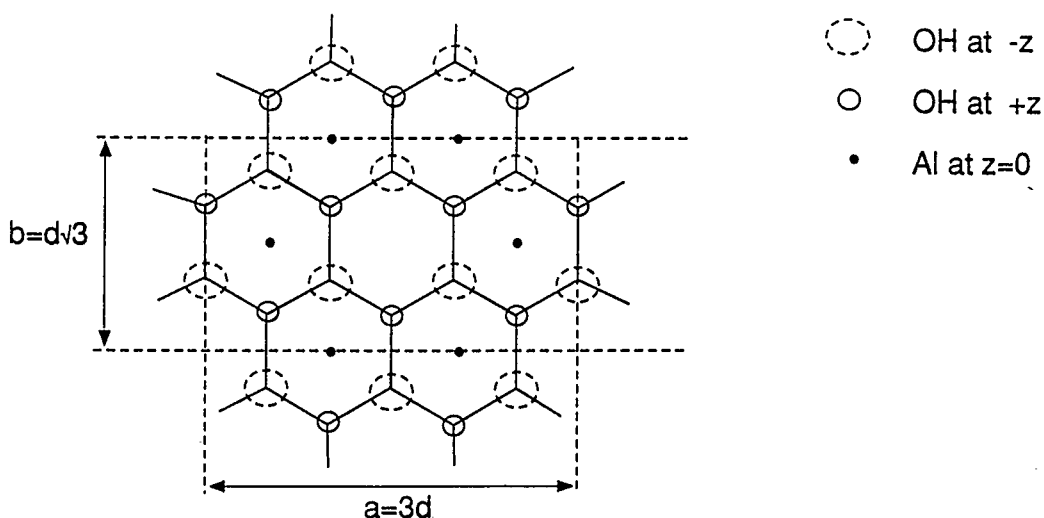
3.1.1 Aluminum trihydroxides - $\text{Al}(\text{OH})_3$

Three forms of trihydroxides are known. These are gibbsite ($\alpha\text{-Al}(\text{OH})_3$), bayerite ($\beta\text{-Al}(\text{OH})_3$) and nordstrandite. Gibbsite and nordstrandite both occur naturally. Gibbsite is the principle constituent of the bauxites found in North and South America, and nordstrandite is found in Serawa and Guam. All three trihydroxides

can be obtained synthetically from amorphous hydroxides under well defined conditions of temperature and pH.

The crystal structure of the trihydroxides is based on a double layer (AB) of closely packed hydroxyl ions. Two-thirds of the octahedral holes are filled with aluminum ions. The lattice is somewhat deformed due to the alternations of occupied and vacant octahedra, with the empty octahedra being larger than those that are filled. The stacking of the double layers in gibbsite can be represented as ABBAABBA, with the double layers being kept together by hydrogen bonds between the hydroxyl ions. The stacking of the double layers in bayerite can be represented as ABABABAB. Nordstrandite is a combination of the stacking of both gibbsite and bayerite, and can be represented as ABABBAAB. A schematic representation of a trihydroxide double layer is shown in Fig 3.1⁵⁰.

Fig. 3.1
Schematic Representation of the Structure of a
Trihydroxide Double Layer. Projection on (001) Plane.



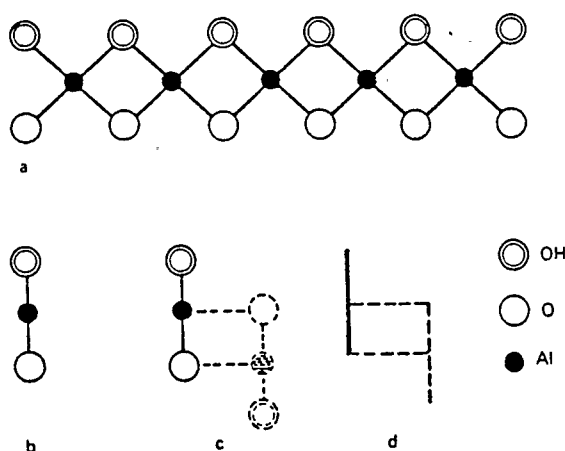
3.1.2 Aluminum Oxyhydroxides - $\text{AlO}(\text{OH})$

There are two known structures, boehmite and diaspore, that correspond to the molecular formula: $\text{AlO}(\text{OH}) \cdot \text{XH}_2\text{O}$. A third form called pseudoboehmite or gelatinous boehmite should also be mentioned since it is structurally derived from boehmite but has specific properties. The products of calcination of pseudoboehmite exhibit high surface areas and are stable at higher temperatures than aluminas obtained via other routes. As a result, pseudoboehmite is frequently chosen as a precursor to catalyst supports²³.

The structure of the oxyhydroxides can be described in the following manner. In the direction of the a-axis there are HO-Al-O chains (shown schematically in Fig. 3.2)⁵⁵.

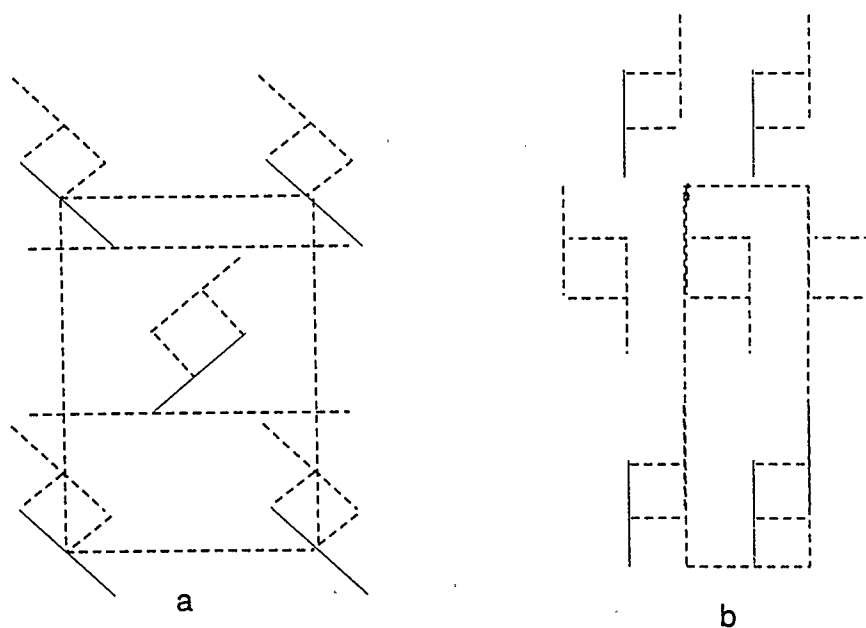
Fig. 3.2

Schematic Representation of Boehmite: (a) Al-O-OH chain; (b) Profile of One Chain; (c) Profile of Two Anti-parallel Chains (d) Schematic Representation of (c).



Two of these chains can be placed in positions anti-parallel to each other in such a way that the oxygen atoms of the second chain are at the same level as the aluminum atoms of the first chain. The difference between boehmite and diasporite is in the arrangement of the extended double molecules, as shown in Fig. 3.3⁵⁵.

Fig. 3.3
Schematic Representation of Structures:
(a) Diasporite; (b) Boehmite.



The structural characterization of pseudoboehmite has been a matter of controversy. The principal features are an excess of water, and a shift and broadening of the (020) XRD peak, which are irreversibly reduced by drying or hydrotreating. This had been interpreted as either extra water bound with strong hydrogen bridges between the layers of the boehmite⁵³, or as extra water bound to

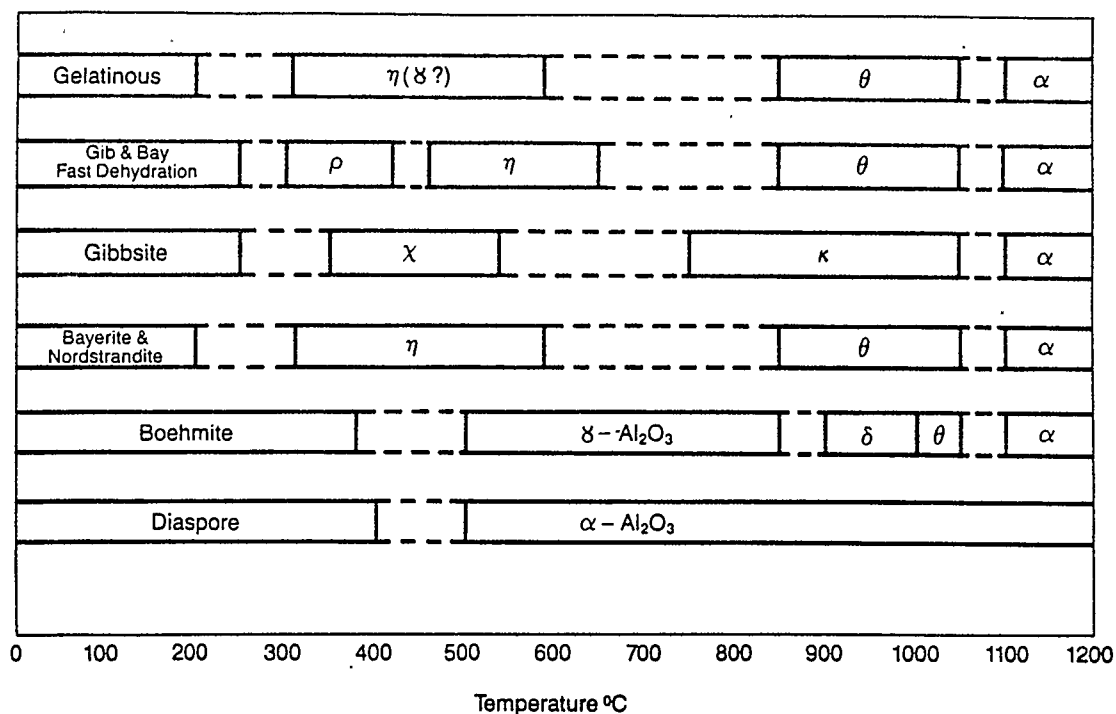
aluminum atoms on the border of the sheets⁵⁷. A model which fits the experimental results better has been proposed that involves stacking defects. A defect amplitude of one angstrom makes the distance between blocks of normally spaced sheets large enough to allow the intercalation of water⁵³. An excellent agreement between measured and calculated values is thus obtained.

3.1.3 Transition Aluminas

The partial dehydration of aluminum trihydroxides and oxyhydroxides leads to compounds which are generally poorly crystallized, and have the formula $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$, with $0 < X < 1$. The nature of the product obtained by calcination depends on the starting hydroxide and the temperature used. In all cases, the ultimate product of dehydration is corundum, $\alpha\text{-Al}_2\text{O}_3$. The six principle phases are identified by the Greek letters chi (χ), kappa (κ), eta (η), theta (θ), delta (δ) and gamma (γ). A dehydration scheme for the aluminum oxides is shown in Fig. 3.4⁵⁹.

The catalytically most important transition aluminas are η -alumina (derived from bayerite), and γ -alumina (derived from boehmite or pseudoboehmite). The dehydration mechanisms to form η and γ -alumina are different⁶⁰. The dehydration of the trihydroxides (bayerite) occurs through loss of water from two hydroxyl groups in the same close-packed layer of hydroxyl groups forming one side of the cleavage plane. In order to obtain a cubic close packed lattice, the resulting layers have to shift, which may be prevented from happening by isolated hydroxyl groups on the surface.

Fig 3.4
Decomposition Sequence of Aluminum Hydroxides.



In boehmite, the water molecules expelled arise from two hydroxyl groups across the cleavage plane. The layers can slip in the direction of the hydrogen bonds, giving a cubic close-packed oxygen lattice. This difference in dehydration mechanisms may explain the differences in the microporous texture of the spinel type aluminas and, at the same time, the differences in their crystallographic texture.

Both γ and η -alumina possess defect spinel lattices which are slightly tetragonally distorted, with the γ -phase distortion being more pronounced⁶¹. The difference is in the distribution of aluminum cations over the octahedral and tetrahedral sites. Octahedral sites are preferentially occupied by aluminum in both configurations, with

the fraction of cations in tetrahedral positions slightly higher in $\gamma\text{-Al}_2\text{O}_3$ than in $\eta\text{-Al}_2\text{O}_3$.

The unit cell consists of thirty-two oxygen atoms and twenty-one and one-half aluminum atoms. There are thus two and two-third vacant cation positions per cell (causing the defect spinel structure)⁶⁰. $\eta\text{-Al}_2\text{O}_3$ has a strong, one-dimensional disorder of the cubic close-packed stacking, resulting in a lower packing density than $\gamma\text{-Al}_2\text{O}_3$. The oxygen sublattice of $\gamma\text{-Al}_2\text{O}_3$ is fairly well ordered (cubic close-packed) whereas the tetrahedral aluminum lattice is strongly disordered⁶¹. The main structural differences between the two modifications are found in the lower packing density of the oxygen lattice in $\eta\text{-Al}_2\text{O}_3$ and the slightly higher occupation of tetrahedral sites in $\gamma\text{-Al}_2\text{O}_3$.

3.2 CHARACTERIZATION OF ALUMINAS

The most practical tool for identifying the various aluminas has proven to be x-ray diffraction (XRD) of powder samples. Interpretation of powder data is not always straightforward as most aluminas are poorly crystallized. Since the transition forms represent different stages of re-ordering of the lattice, line broadening and the possible presence of several transition forms together represent complications in interpretation. Characteristic line spacings and the relative intensities of x-ray powder diffraction patterns for the aluminum hydroxides and corundum are shown in Table 3.1. The patterns for the transition aluminas are shown in Table 3.2⁵⁴.

Table 3.1

X-ray Powder Diffraction Patterns for Aluminum Hydroxides and Oxide

Gibbsite		Bayerite		Nordstrandite		Boehmite		Diaspore		Corundum		Experimental ALFA Products α -alumina(H_2O)		CATAPAL boehmite	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
4.82	100	4.72	100	4.79	10	6.11	100	4.71	13	3.48	74	6.13	100	6.31	100
4.34	40	4.36	70	4.37	2	3.16	65	3.99	100	2.55	92	3.17	87	3.16	94
4.30	20	3.19	25	4.31	4	2.35	53	3.21	10	2.38	42	2.35	76	2.35	77
3.35	10	3.08	1	4.21	4	1.98	6	2.56	30	2.17	1	1.97	7	1.98	7
3.31	6	2.69	3	4.15	4	1.86	32	2.43	3	2.09	100				
3.17	8	2.45	3	3.88	3	1.85	27	2.39	5	1.74	43				
3.08	4	3.24	6	3.60	3	1.77	6	2.36	8	1.60	81				
2.44	15	2.28	3	3.46	2	1.66	13	2.32	56	1.55	3				
2.42	4	2.21	67	3.02	2	1.53	6	2.13	52	1.51	7				
2.37	20	2.14	3	2.82	2	1.45	16	2.08	39	1.40	32				
2.28	4	2.06	2	2.71	1	1.43	9	1.90	3	1.37	48				
2.23	6	1.97	3	2.49	1	1.41	1	1.82	8	1.28	2				
2.15	8	1.91	1	2.48	3	1.40	2	1.73	3	1.29	16				
2.03	12	1.83	1	2.45	2	1.38	6	1.71	15	1.19	6				
1.98	10	1.76	1	2.39	7	1.37	2	1.68	3	1.16	1				
1.95	2	1.71	26	2.26	7	1.31	15	1.63	43	1.15	4				
1.90	7	1.68	2	2.22	1	1.30	3	1.61	12	1.14	1				
1.79	10	1.64	1	2.03	1	1.22	1	1.57	4	1.13	5				
1.74	9	1.59	4	2.01	5	1.21	2	1.52	6	1.10	6				
1.67	9	1.56	2	1.90	5	1.18	3	1.48	20	1.08	3				
1.65	3	1.55	4	1.78	4	1.17	1	1.43	7	1.08	7				
1.63	1	1.52	1	1.72	1	1.16	3	1.42	12	1.04	13				
1.58	3	1.48	1	1.70	1	1.13	5	1.4	6	1.02	1				
1.57	1	1.47	1	1.68	1	1.09	1	1.38	16	1.00	11				
1.55	2	1.45	7	1.67	1	1.05	2	1.34	5	0.98	2				

Table 3.2
X-ray Powder Diffraction Patterns for Transition Aluminas

d^a	I/I_0^b	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	EXPERIMENTAL	
												Calced	ALFA
												d	I
2.40	50	2.76	20	4.60	30	6.10	10	5.04	40	5.47	5	1.40	100
2.30	10	2.43	30	2.76	20	4.48	5	4.57	60	5.06	5	1.98	100
2.13	30	2.29	30	2.40	50	3.05	30	4.07	70	4.57	10	2.54	20
								2.87	20	4.02	5	4.54	15
1.98	20	2.12	6	2.30	30	2.81	50	2.74	50	2.86	60	2.67	15
1.54	10	1.99	90	1.99	100	2.73	5	2.59	10	2.73	100	2.45	15
1.40	100	1.97	40	1.51	20	2.59	100	2.46	40	2.46	80	2.80	10
		1.52	20	1.40	100	2.42	20	2.29	20	2.31	40		
		1.40	100	1.21	10	2.33	35	1.99	30	2.26	30		
								1.95	10	2.03	80		
		1.14	10	1.14	10	2.17	5	1.91	10	1.19	40		
						2.13	90	1.81	10	1.80	5		
						2.07	5	1.54	45	1.54	20		
						1.99	15	1.51	40	1.48	20		
						1.95	5	1.50	40	1.46	20		
						1.88	30	1.46	80	1.43	10		
						1.83	5	1.43	60	1.41	30		
						1.64	20	1.39	100	1.39	100		
						1.49	5	1.30	40				
						1.45	5	1.26	20				
						1.44	50	1.14	40				
						1.40	95						
						1.34	5						

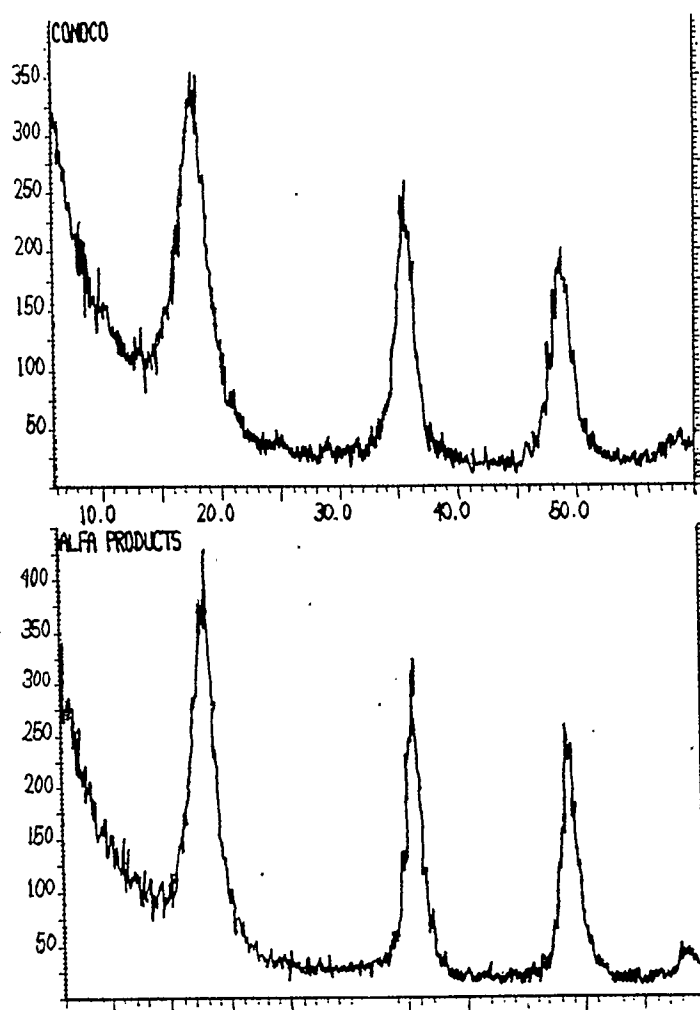
NOTE: Filtered $\text{CuK}\alpha$ radiation was used.

^a d denotes line spacings.

^b I/I_0 denotes relative intensities.

The alumina used in this project was alpha aluminum oxide (90% Al_2O_3 , 9% H_2O , 40 micron) supplied by Alfa Products. This was a different source than that previously used by our research group (80% Catapal SB and 20% Catapal N, obtained from Continental Oil Co., Peterboro, New Jersey). X-ray powder diffraction patterns of both aluminas (before calcining) were obtained to ensure that both samples were boehmite. The XRD spectra for both samples are shown in Fig. 3.5.

Fig. 3.5
XRD Patterns for Boehmite Samples



As can be seen for the patterns obtained, and the d-spacings shown in Table 3.1, both samples are boehmite.

The boehmite samples were converted to gamma alumina using the procedure outlined in Chapter 2 (drying and calcining). Confirmation that the boehmite was transformed to γ -alumina was achieved by comparison of the x-ray diffraction patterns of the calcined samples with literature data (see Table 3.2).

As can be seen, the differences between γ and η forms are quite small and are easily concealed in the XRD results especially in the case of mixtures. The first difference is that the 1.98 Å peak is doubled for γ , whereas it is unsymmetrical for η -Al₂O₃. The next point is the fact that the 4.6 Å line of γ is very broad, while for η -Al₂O₃ it is sharp. A third criterion which can be used for differentiating η and γ is the ratio of the heights of the 2.4 Å and 2.28 Å peaks, although this is not always successful⁵³.

3.3 SURFACE MODELS OF ALUMINA^{40,49}

The surface of alumina is made up of a combination of aluminum and oxygen ions, which may each have a coordination number lower than that existing in the bulk. These superficial ions constitute vacant sites that are always occupied at ambient temperature by either coordinated water molecules, or hydroxyl groups resulting from the dissociative adsorption of water. This returns them to their normal coordination, octahedral or tetrahedral for aluminum and octahedral for oxygen. Dehydration and dehydroxylation leads to the appearance

of coordinately unsaturated aluminum (Lewis acid site) and oxygen (Lewis base site).

The first surface model of alumina was proposed by Peri in 1965⁶², and was based on the hypothesis that spinel type aluminas preferentially expose planes with Miller indices of (100). This somewhat idealized model proved to be quite helpful in understanding and visualizing the surface of alumina. The limitation was the fact that at high temperatures, the (111) plane is energetically most favorable. More recently, Knozinger and Ratnasamy⁶³ have proposed a model which is based on the assumption that a mixture of low index planes (111, 110 and 100) are exposed on the surface of the crystallites. The relative abundance of the faces is assumed to vary for the different transition aluminas.

Five different types of hydroxyl groups are proposed to occur on the idealized surface of aluminas. These correspond to the coordination of a hydroxyl group to a tetrahedral aluminum, to an octahedral aluminum, and to a combination of each of them or to them both. The five OH group configurations are shown in Fig. 3.6 on the following page.

The most important result from this model is the fact that each surface hydroxyl group has a different net charge due to its environment. Table 3.3 shows the hydroxyl group configurations and OH stretching frequencies of transitional aluminas⁶³. Since the net charges are different, it is expected that the various sites have different properties. Type III, which has a net positive charge of +0.5 is expected to be the most acidic (lowest wavenumber).

Fig. 3.6
OH Group Configurations for Alumina

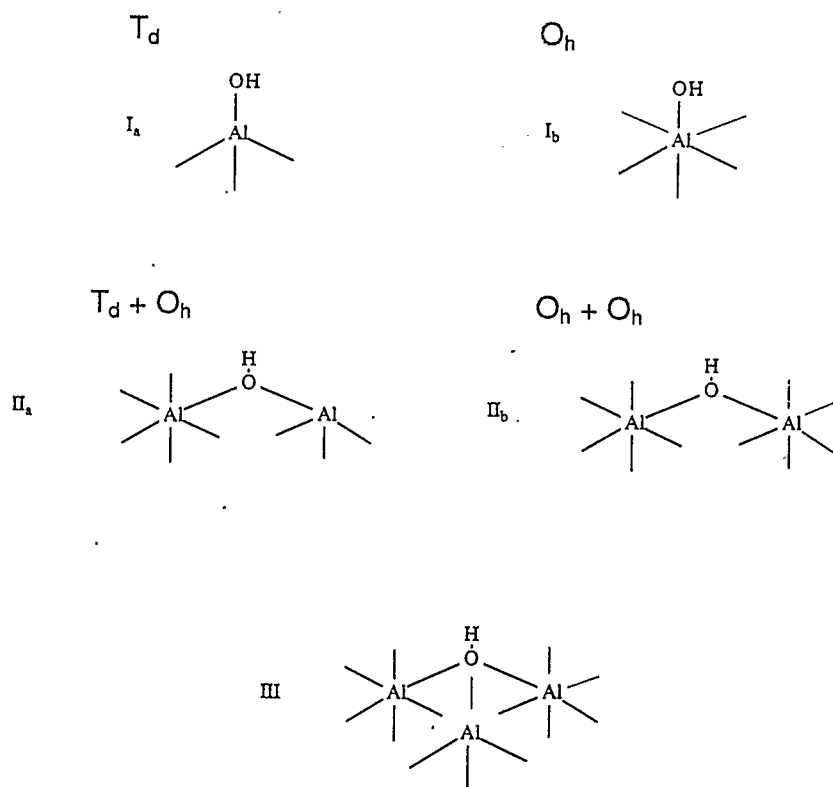


Table 3.3
Hydroxyl Group Configurations and OH Stretching
Frequencies of Transitional Aluminas.

OH-type	Coordination number			Net charge at surface anion		$\bar{\nu}_{OH}/cm^{-1}$
	Al ³⁺ _{total}	Al ³⁺ _{oct}	Al ³⁺ _{tet}	O	OH	
Ia	1	-	1	-1.25	-0.25	3760-3780
Ib	1	1	-	-1.5	-0.5	3785-3800
IIa	2	1	1	-0.75	+0.25	3730-3735
IIb	2	2	-	-1.0	0	3740-3745
III	3	3	-	-0.5	+0.5	3700-3710

The assignment of the IR (infrared) stretching frequencies has been made on the basis of the formal net charge located on the hydroxyl group depending on its coordination to aluminum on the surface. As a consequence of the various possible coordination numbers of the hydroxyl groups and of aluminum, all five configurations can be expected on (111) faces of η and γ - Al_2O_3 . Only Ia, Ib and I Ib are possible for (110) faces, and the (100) face would bear exclusively Ib type groups. From these considerations, it has been concluded that the particles of transition aluminas must be terminated by these three low indexed planes. The relative contributions of each plane is probably dependent on various preparation parameters and on the particular crystallographic modification.

It is apparent that the process of dehydroxylation which leads to the formation of Lewis acid and base sites depends on a large number of factors. The structure of the alumina, the relative proportion of the exposed crystallite sides; and the temperature involved, all play important roles. In spite of the information offered by this model of the alumina surface, much still needs to be learned about the surface of industrial alumina supports.

CHAPTER 4

THE PROMOTERS

Seventy years ago it was stated that "it has recently been discovered that there are other substances which, when added in minute quantity to a catalyst, increase its activity"⁶⁴. These substances became known as promoters. Numerous studies have since been conducted which focus on the use of additives to modify interactions between the active phase and the carrier in supported metal catalysts. Changes in active phase-support interactions can affect the chemical state and the dispersion of the active phase. The overall result is that the catalytic activity is altered.

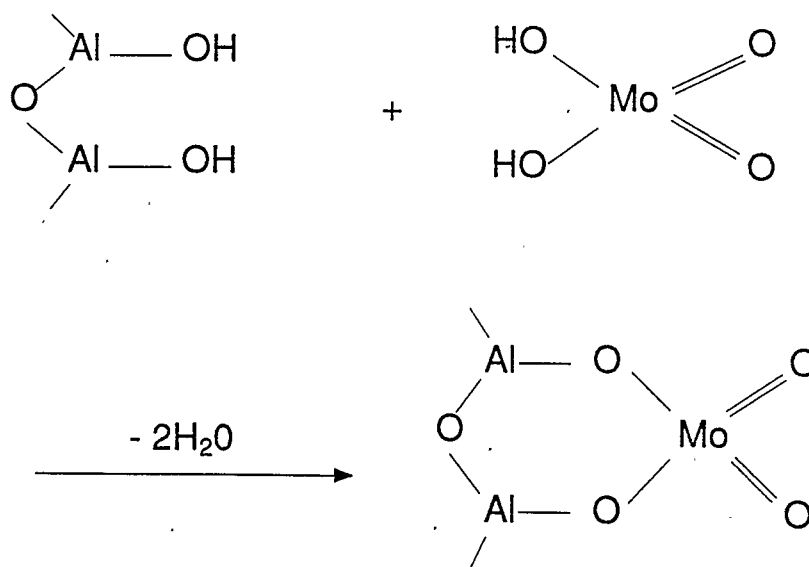
4.1 STRUCTURE OF THE CATALYSTS

The surface properties of Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ have been studied extensively⁶⁵⁻⁶⁷. The effects of foreign ions on the dispersion of catalytically active phases, and on the solid-solid interaction between these phases and alumina, have also been investigated^{68,69}. Before we can embark on a discussion of the promoters and their effects on the catalyst, we must know something about the structure of the catalyst surface. Models of the surface have been suggested through careful analysis, and the interpretation of various spectroscopic results (IR, XRD, XPS, EXAFS).

4.1.1 Structure of the Oxidic Catalyst

The structure of $\text{Mo}/\text{Al}_2\text{O}_3$ has been studied thoroughly. It has been shown that the oxidic catalyst consists of a monolayer of molybdena (MoO_3) on the catalyst surface⁷⁰. A simple model for the monolayer formation is shown in Fig. 4.1.

Fig. 4.1
Monolayer Formation



The species present upon drying and calcining include MoO_3 and $\text{Al}_2(\text{MoO}_4)_3$ ⁷¹. The molybdate layer has been characterized by the presence of Brönsted acid sites and one type of strong Lewis acid site⁷². Promoter ions such as Co and Ni are thought to be deposited on the molybdena layer.

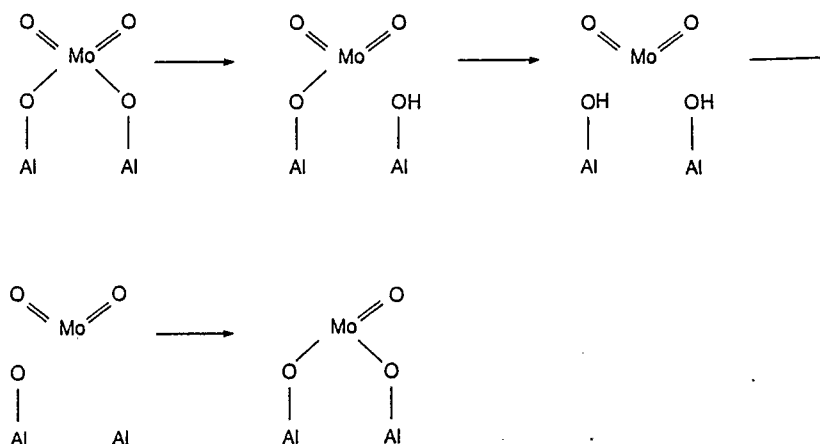
When the calcination is done at 500°C , the promoter ions are still on the catalyst surface⁷³. This has been concluded since no

cobalt or nickel aluminate species were observed, and the Brönsted acid sites on the surface were neutralized. The interaction between cobalt or nickel and the molybdate layer is manifested by the appearance of a new Lewis acid site⁷³. At higher calcination temperatures, the cobalt ions remain near the molybdate surface and form CoAl_2O_4 . On the other hand, in the nickel catalyst the promoter ions diffuse into the interior of the catalyst and get lost in the alumina lattice, forming bulk NiAl_2O_4 .

4.1.2 The Reduced Catalyst^{74,75}

A model of the catalyst during reduction has been proposed by observing changes in the hydroxyl groups present on the surface, and in the concentration of oxygen chemisorption sites. It is easiest to consider this on the unpromoted catalyst surface. Fig. 4.2 shows the scheme of activation of a molybdenum catalyst by reduction with hydrogen⁷³.

Fig. 4.2
Scheme of Activation of Molybdenum
Catalyst by Reduction with Hydrogen



Activation by reduction with hydrogen takes place from Mo^{6+} to Mo^{4+} with the breaking of Mo-O bonds in the Mo-O-Al bridge of model tetrahedral molybdenum. The formation of oxygen chemisorption sites is connected with the reduction of Mo^{6+} to at least Mo^{4+} . The hydroxyls on the aluminas are probably the intermediates in the formation of oxygen chemisorption sites⁷⁴.

Several researchers have proposed different Mo^{6+} species in $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts⁷⁵⁻⁷⁷. These are: (1) a non-reducible phase of tetrahedral molybdenum which is similar to $\text{Al}_2(\text{MoO}_4)_3$; (2) an easily reducible phase of bulk MoO_3 , and (3) an intermediate reducible phase (probably octahedral molybdenum) whose reducibility is increased by cobalt addition. Species like $\text{Al}_2(\text{MoO}_4)_3$ could be formed by a decrease of the coordination state of the molybdenum monolayer species from octahedral to tetrahedral by oxygen removal during reduction, or by solid state reaction between molybdenum species with the support.

Recent studies on the reduction of $\text{Ni}/\text{Al}_2\text{O}_3$ determined the influence of alumina on the behavior of the dispersed nickel^{78,79}. During catalyst preparation, substitution of nickel into the alumina lattice, and dissolution of alumina, facilitates the formation of NiAl_2O_4 -like species. The surface NiAl_2O_4 is formed in highly dispersed clusters. The initiation sites for the NiAl_2O_4 formation are thought to be defects in the alumina lattice, such as oxygen vacancies. During activation, a portion forms nickel crystallites and the remainder is incorporated into the support as Ni^{2+} . This can be visualized as a reaction with NiO , and results in the location of

the Ni^{2+} cation in a tetrahedral or octahedral position somewhere within the solid. The accompanying O^{2-} ion cannot find any position in the support lattice and remains at the surface. The surface enriched in oxygen ions can then offset the excess positive charge which exists at the near surface. Similar mechanistic steps have also been proposed for $\text{Co}/\text{Al}_2\text{O}_3$, $\text{Mo}/\text{Al}_2\text{O}_3$ and also $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts⁷².

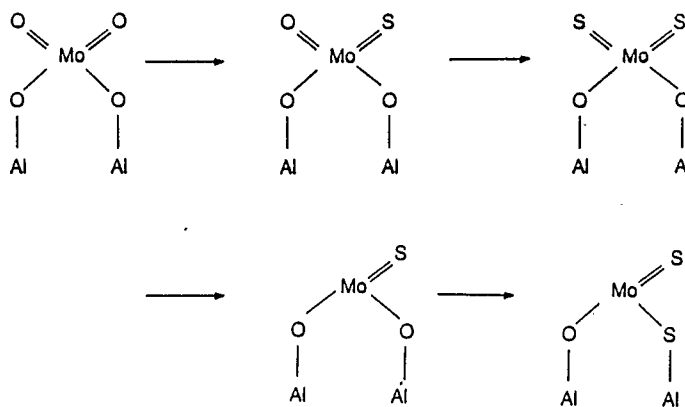
4.1.3 Sulfided Catalysts

The relative abundance of species present on the surface of a catalyst changes when a fresh oxidic catalyst is converted to its sulfidic form⁸⁰. This structural change affects both the activity and the selectivity of the catalyst⁸¹.

An activation mechanism based on an $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst reduced by hydrogen sulfide in a hydrogen atmosphere is shown in Fig. 4.3⁷⁴.

Fig. 4.3

Scheme of Activation of the Molybdenum Catalyst by Reductive Sulfidation with a Mixture of Hydrogen and Hydrogen Sulfide



This model was originally proposed by Arnol'dy, whereby surface molybdenum oxide is transformed by reactions with hydrogen sulfide to oxysulfides⁸². These decompose at higher temperatures to give Mo^{4+} and sulfur. The sulfidation can continue to produce bulk MoS_2 which is no longer bound to the support. The intermediates in the reaction are surface molybdenum complexes with hydroxyl and sulfhydryl groups, which have been characterized. Hydrogen sulfide has been found to preserve the dispersion of molybdenum species on the surface because it attacks terminal $\text{Mo}=\text{O}$ of surface molybdenum oxide rather than the $\text{Mo}-\text{O}-\text{Al}$ bridges, which are attacked when hydrogen is used to activate the catalyst⁷³.

4.1.4 Structure of the Promoted Catalysts (Ni-Mo or Co-Mo)

The original model for the structure of the promoted sulfided species was based on a monolayer of molybdate on the alumina surface, stabilized by cobalt (or nickel) ions. The promoter ions occupied tetrahedral positions in the alumina lattice and replaced an equivalent amount of aluminum ions. The aluminum ions were then incorporated into the molybdate monolayer and helped to stabilize the active molybdate surface⁷². Later, DeBeer and co-workers proposed a modified monolayer model where the function of the alumina support was to disperse the molybdate⁸³. During sulfidation, MoS_2 crystallites form which are promoted by intercalation of cobalt ions. The cobalt ions must come out of the alumina in order for this intercalation to occur. DeBeer attempted to show that the transport of cobalt ions

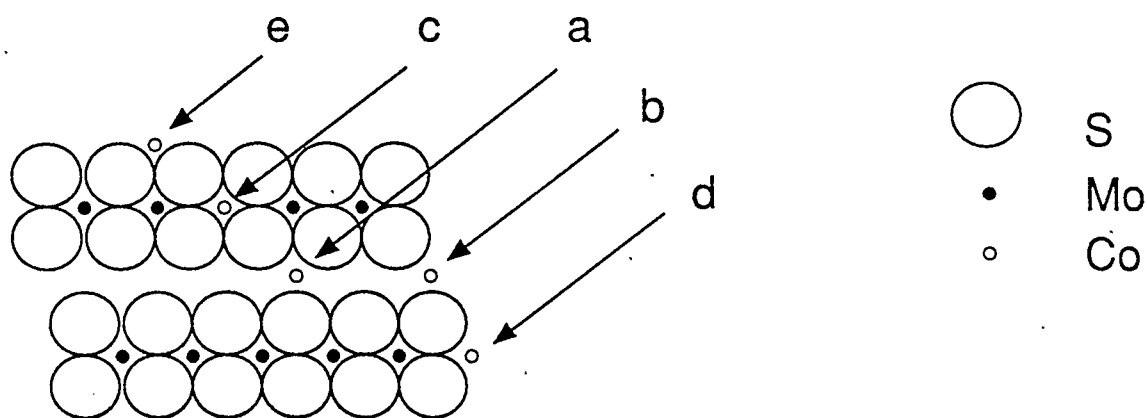
from the alumina lattice into the sulfided molybdate layer took place.

Much evidence has recently been presented which suggests that the promotion of the hydrodesulfurization activity of Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts are related to the presence of the promoter ions in a so-called Co-Mo-S or Ni-Mo-S phase⁸⁴⁻⁸⁸. The new phase can be considered to be cobalt or nickel atoms located at edge positions of a MoS₂ structure^{89,90}.

The MoS₂ structure with some of the possible locations of cobalt is shown in Fig. 4.4⁸⁹.

Fig. 4.4

Schematic Picture Showing Some of the Possible Locations of Co in the MoS₂ Structure



Position (a) represents the position where cobalt would sit in the original intercalation model. Position (b) represents the edge or "pseudo-intercalated" cobalt atom whereas, (c) shows cobalt substituting for molybdenum in the lattice. In position (d), cobalt is located at the edges of the slabs; and in (e), cobalt is found at basal planes.

The only positions for cobalt which are consistent with spectroscopic measurements of Co-Mo-S are the basal plane (e) and edge positions (d)⁸⁹. It had been difficult choosing between the two positions (although the edge positions were favored) until recently. The bonding between S-Mo-S slabs is comprised of weak van der Waals forces. Consequently, MoS₂ will readily cleave along a van der Waals gap. The exposed basal plane surfaces will be relatively inert since none of the covalent bonds are broken by such a cleavage. In contrast, the edge surfaces have coordinatively unsaturated molybdenum atoms. As a result, the Co-Mo-S (Ni-Mo-S) phase can be considered to be cobalt (nickel) atoms located at the edge positions of a MoS₂ structure⁸⁸.

Two types of sites are present on the surface of Co-Mo/Al₂O₃ catalysts. These have different activities towards hydrodesulfurization and hydrogenation. A strong influence of the catalyst composition has been observed, and specified in the following manner⁸⁷.

Unpromoted catalysts. Hydrodesulfurization and hydrogenation are associated with sites on the edges of the MoS₂ structures. The

unpromoted sites have relatively low hydrodesulfurization activity, but they have high selectivities towards hydrogenation.

Promoted catalysts. (with Co or Ni:Mo < 0.5). These catalysts have increasing coverage of the MoS₂ edges with increasing promoter content. This interaction results in the formation of Co-Mo-S or Ni-Mo-S phases, and is accompanied by a corresponding decrease in the number of unpromoted sites. The hydrodesulfurization activity is mainly determined by the concentration of promoted sites, and is much higher on promoted sites than on unpromoted ones.

Catalysts with high promoter content. These catalysts show activity towards hydrodesulfurization and hydrogenation, but it is quite low. This results from the formation of separate Co or Ni sulfides (Co₉S₈, Ni₉S₈)⁸⁷. The hydrodesulfurization activity is directly proportional to the amount of cobalt (nickel) atoms which are present in the MoS₂-like phase. With this in mind, the effects of other promoters can be discussed.

4.2 ADDITIONAL PROMOTERS

Careful spectroscopic analysis has shown that ions such as beryllium, magnesium and lithium inhibit the formation of both cobalt and nickel aluminates on the catalyst surface. They also decrease the concentration of promoter ions which diffuse into the outer layers of the support surface⁹⁰. On the other hand; sodium, potassium, rubidium, cesium, zinc, calcium, strontium, barium, gallium and germanium ions strongly stimulate the formation of surface epitaxial aluminates by enhancing the diffusion of cobalt ions into tetrahedral

sites of the alumina support^{76,91}. This results in a higher cobalt/nickel to aluminum ratio on the catalyst surface.

Cobalt or nickel aluminates are generally undesirable compounds on a catalyst surface due to their low reactivities towards oxidation-reduction and sulfurization reactions. In some cases, the increased formation of the aluminates has been found to be connected with a large increase in the cobalt dispersion on the support surface⁷⁶. Proper control of the active phase-support interactions, to give a balance between the best state of dispersion and the minimum quantity of CoAl_2O_4 or NiAl_2O_4 present, is important for maximizing catalytic activity.

A recent study on the influence of boron on the chemical state and dispersion of $\text{Co/Al}_2\text{O}_3$ reveals that the dispersion of cobalt decreases with increasing boron content⁹². The two additional promoters which have received the most attention are phosphorus and fluorine.

4.2.1 Phosphorus Promoted Catalysts⁹²⁻⁹⁷

Phosphate anion has been considered to be one of the most effective additives to molybdenum based hydrotreating catalysts. In fact, it appears as a component in a number of commercial catalysts. Phosphate anion strongly interacts with alumina through a mechanism involving surface basic sites⁹². It competes with molybdate in the adsorption process onto alumina. If it is the first species to be added, it limits the amount of Mo(VI) which can be adsorbed. As phosphorus content increases, the isomerization activity of alumina decreases in parallel with the adsorption of Mo(VI) . The mechanism

for this transition is based on the fact that strained Al-O-Al groups (which have the character of Lewis conjugated acid-base sites) are responsible for the adsorption properties and the catalytic activity⁹³. The role of phosphate is unique in stabilizing and/or deactivating these strained sites.

The effect of phosphorus addition on the initial activity of coal liquids upgrading catalysts (Ni-Mo/Al₂O₃) was recently investigated⁹⁴. The addition of phosphorus had a significant effect on the ability of the catalyst to convert heavy coal liquids into lighter products. However, the phosphorus addition did not improve the hydrogenation activity and caused only a slight increase in the hydrodesulfurization and hydrodenitrogenation activities. These results contradict those which are reported in the literature for the use of phosphorus containing catalysts for hydrotreating light petroleum feedstocks^{95,96}. They also indicate that if phosphorus has any use in upgrading catalysts it will be in the area of catalyst deactivation.

4.2.2 Fluorine Promoted Catalysts⁹⁸⁻¹⁰¹

Fluorination of alumina increases its catalytic activity for many reactions including cracking, isomerization, alkylation-dealkylation, polymerization and disproportionation. It is now well established that these reactions proceed via carbocation intermediates which are formed and stabilized on surface protonic sites¹⁰⁰. The activity of the catalyst is increased due to the enhancement of its acidic properties when fluoride is incorporated into the surface.

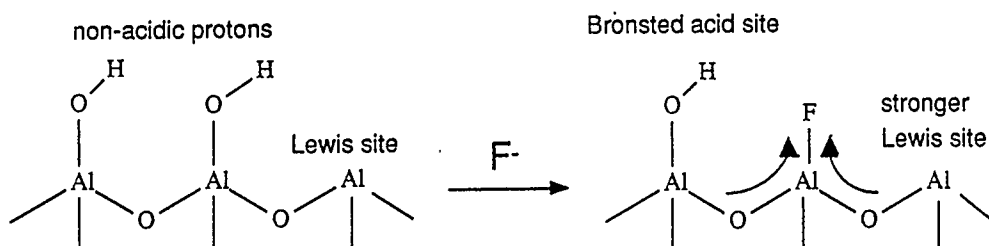
The acidity of both protonic (Brönsted) and non-protonic (Lewis) sites is increased when fluorine replaces surface oxygen or hydroxyl groups. This is due to fluorine's large electronegativity, which polarizes the lattice more than the groups which it is replacing¹⁰¹. As a result of the increased activity, fluorinated alumina has been shown to be a very active, selective, and stable catalyst for many reactions.

4.2.2.1 Structure of Fluorinated Alumina

As a result of fluorination, the less acidic hydroxyl groups are removed, while hydroxyls of strong acidity are created⁹⁹. The following reaction mechanism has been proposed to explain the modification of the alumina surface by fluorine¹⁰². However, controversy still exists as to the nature and number of acid sites created on the surface.

Fig. 4.5

Reaction Mechanism for Fluorination of Alumina



According to the mechanism, a decrease in the number of Lewis acid sites, as well as the creation of Brönsted sites occurs during fluorination. Considering the surface as a dynamic system, the replacement of some hydroxyl groups by fluoride will influence the overall acidity of the remaining centers. A change in both the number of Brönsted and Lewis acid sites, and in their strength occurs when fluoride is added. The total number of Lewis acid sites decreases with increasing fluoride content. On the other hand, the total number of Brönsted sites increase with increasing fluoride. The number of both Brönsted and Lewis acid sites with strong acidity reaches a maximum at two to four percent fluorine content¹⁰³.

4.2.2.2 Structure of F/Ni-Mo/Al₂O₃ Catalysts

The oxidic and sulfidic states of a series of fluorided Ni-Mo/Al₂O₃ catalysts containing constant nickel and molybdenum loadings, and various amounts of fluorine, have just been characterized^{104,105}. In the oxidic precursor state, the following species were detected:

- 1) A supported molybdate phase in which a fraction of the supported nickel is incorporated in octahedral sites.
- 2) α -NiMoO₄
- 3) NiAl₂O₄

The relative concentration of these three phases was independent of fluorine content. Fluorination does not appear to change the structure of the supported phase in the oxidic catalyst¹⁰⁴.

Fluorination inhibited the extent of sulfidation and/or reduction of Mo(VI), and the sulfidation of nickel(II). With increasing fluoride content both of these effects, as well as the intrinsic hydrodesulfurization activity of the catalysts, increased. The variation in the activity with the surface coverage of the active phase led to the conclusion that the promoting effect of fluoride is mainly due to the fact that these ions increase the surface coverage of the supported molybdenum and nickel. The number of active sites per unit surface area of the catalyst also increases. The increase in surface coverage has been attributed to both the increase in dispersion of the catalytic species and the decrease in the specific surface area¹⁰⁵.

It is important to note that the fluorination of alumina decreases its specific surface area. The decrease depends on the fluorine content and the procedure of fluorination. The surface area shows a rapid initial decrease followed by a slower decrease once the fluorine content increases above 5 to 10%^{99,101,106}. A part of the alumina is consumed to form AlF_3 during the preparation. Since AlF_3 has a low surface area, this species is considered to cause the large decrease in surface area.

4.3 SUPERACID CATALYSTS

In order to enhance the surface acidity of fluorinated alumina, antimony has been used as an additional promoter. No previous studies have been performed where all three promoters are present (Ni or Co, Sb, F). Some studies have been completed using antimony

pentafluoride on graphite, silica and alumina; and also on the promoting effect of antimony on alumina based platinum catalysts¹⁰⁷.

Liquid superacids (SbF_5 , HF-SbF_5 , $\text{SbF}_5\text{-FSO}_3\text{H}$) have been extensively investigated and many interesting phenomena which occur only in superacid solutions have been observed¹⁰⁸⁻¹¹⁰. One of the distinct features is the formation of carbonium ions which result from the addition of a proton to alkanes. From these, carbonium ions can be formed which undergo skeletal rearrangements and yield isomerized alkanes. A liquid superacid is therefore capable of acting as a catalyst for the skeletal isomerization of alkanes at low temperatures³¹. This result, coupled with the fact that there are difficulties separating the original liquid superacids from the products obtained, has stimulated the research effort on solid superacids.

4.3.1 SbF_5 Intercalated Graphite¹¹¹⁻¹¹⁴

SbF_5 intercalated graphite is an active catalyst for hydroisomerization at low temperatures. Up to 75% of the SbF_5 can be incorporated into the graphite lattice. Unfortunately, this catalyst poisons quickly when heavy feedstocks are used. Better stability of the catalyst has been found if the graphite is fluorinated prior to SbF_5 treatment. The SbF_5 then bonds more strongly to the substrate. It is thought that this enhances the stability as a result of SbF_5 being released from the intercalate and creating new active sites on the surface of the fluorinated graphite¹⁰¹. The intercalation of SbF_5 in graphite leads to several advantages over SbF_5 alone. These include:

- 1) Reactions are less violent and easier to control since the graphite behaves like a solvent and dilutes the superacid.
- 2) Product/catalyst separation is very easy as it can be done by filtration.
- 3) Certain steric requirements must be met for access to active sites, thereby affecting sensitivity and selectivity.

The activity of the SbF_5 intercalated graphite catalyst decreases with time. This is a result of leaching out of the SbF_5 and also the reduction of SbF_5 to SbF_3 . The activity is also thought to decrease because of the poisoning of the acidic sites by carbonaceous products¹¹⁴. Thus, this catalyst is not a good candidate for industrial development as the deactivation process cannot be slowed down sufficiently. However, due to the mild conditions employed and its efficiency in reacting with hydrocarbons, it has been used successfully to study the initial steps in isomerization and cracking reactions.

4.3.2 SbF_5 on Silica-Alumina^{31,32,101}

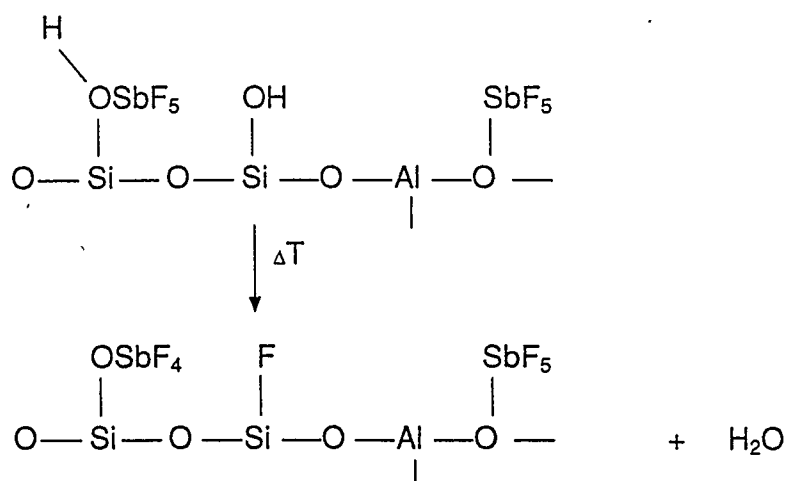
Solid superacid catalysts were prepared by treating a number of metal oxides with various superacids including SbF_5 ³¹. It was shown that SbF_5 alone did not have considerable activity, however, it became active when adsorbed on different metal oxides. The activity depended on the metal oxide employed, with the highest activity being observed when silica-alumina was used as a support. SbF_5 is not

merely mounted on the supported surface, it actually reacts with it.

The reaction of SbF_5 with $\text{SiO}_2\text{-Al}_2\text{O}_3$ is shown in Fig. 4.6.

Fig. 4.6

The Reaction of SbF_5 with $\text{SiO}_2\text{-Al}_2\text{O}_3$



At low temperatures, SbF_5 coordinates to the hydroxyl group on the silicon atom, and to the oxygen atom adjacent to the aluminum atom of the Lewis acid site. Coordination to the hydroxyl group increases the acid strength of the hydroxyl group. Coordination to the oxygen atom increases the acid strength of the Lewis acid site. At higher temperatures, SbF_5 reacts with the hydroxyl group to give OSbF_4 and HF . The HF produced may react with another hydroxyl group to form water as the fluorine gets bound to either silicon or aluminum.

Infrared results show that both Brönsted and Lewis acid sites are present on the surface when the metal oxide is treated with SbF_5 at temperatures below 100°C ³². Only Lewis acid sites are present

when the temperature is raised to 300°C. The amount of SbF_5 incorporated onto the catalyst was highest at 0°C when approximately 50% of the surface, or a monolayer, was covered. At higher temperatures the coverage dropped to less than 10%³¹. The surface area of the catalyst also decreased as the amount of SbF_5 incorporated increased. It is apparent from these results that SbF_5 incorporated on alumina cannot be used as a hydrotreating catalyst.

4.3.3 Additional Antimony-Promoted Catalysts

Most of the other solid superacid catalysts which have been reported in the literature are patents, and therefore cannot be discussed in great detail. One such catalyst, which contains alumina, molybdena and antimony oxide¹¹⁵, has been used to produce maleic anhydride from the vapor phase oxidation of butenes.

In 1977, a hydrocarbon cracking catalyst was patented by Phillips Petroleum Company, which contained 0.005 to 5% Sb on a silica-alumina mixed oxide support¹¹⁶. With a 0.5% loading of antimony, the catalyst gives gasoline yields of 61% and 12% coke. This compares favorably with the figures obtained for the unpromoted catalyst of 56% gasoline and 13% coke.

Gulf Oil Ltd. applied for a patent in 1984 for a commercial cracking catalyst prepared through their research and development department¹¹⁷. It was designed for cracking high metal content feedstocks and contained 40% alumina which was impregnated with tin or antimony and then calcined. Nickel and vanadium were also present on the catalyst. The gas oil conversion obtained with the straight

Ni-V/ Al_2O_3 catalyst was 60%, whereas it increased to 66% when the antimony was added as a promoter. It has been suggested that the antimony was added as an "anti-poison" in order to minimize the detrimental effect of heteroatoms in the feedstock, as these cause coke formation and high gas yields¹¹⁸.

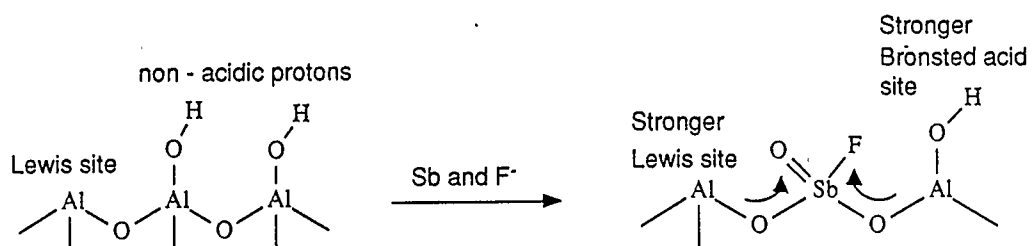
4.4 ANTIMONY PROMOTION OF F/Ni-Mo(Co-Mo)/ Al_2O_3 CATALYSTS

The goal of this project was to produce catalysts with high surface acidity by adding small amounts of antimony to the alumina support. Since alumina treated with SbF_5 tends to lose the SbF_5 under the conditions required for hydrotreating, Sb_2O_3 was used. The basic idea was to produce γ -alumina with antimony incorporated in the lattice, and then fluorinate the entire surface. The optimum situation would be to convert Sb(III) to Sb(V) in this process, as the higher oxidation state of antimony would enhance the electronegativity of the entire group. This is predicted to make the surface hydroxyl groups more acidic, as shown in Fig. 4.7.

The antimony and fluoride would emulate the behavior of SbF_5 when added to alumina and the disadvantages associated with the liquid superacid would be avoided. Using an appropriate preparation method, we hoped to be able to anchor the fluorantimony species to the surface of the alumina.

Fig. 4.7

Reaction Mechanism for Sb + F Addition to Alumina



CHAPTER FIVE

PREPARATION OF CATALYSTS

The heterogeneous catalysts used in hydrotreating consist of small crystallites of catalytically active compounds on a porous support of high surface area. For these catalysts to develop high activity, the active phase must be present in high dispersion. The dispersion, and the nature of the supported active oxide phase, are critically determined by the support and the preparation method¹¹⁹. The preparation of supported catalysts involves three steps; contacting the active ingredients with the support, drying the support to remove excess liquid, and activating the catalyst by calcining, reducing or other appropriate treatments.

5.1 DEPOSITION OF PRECURSORS ON A SUPPORT

The deposition of the active ions on the surface is the most crucial step in the preparation sequence. There are two common methods used to load promoters onto a support. The first of these is impregnation of the support, in one or more steps, with solutions of the promoter ions. The second method, co-precipitation, involves mixing two or more solutions, causing precipitation to occur. When preparing supported catalysts in this manner, the carrier is usually present in a suspension and the activators are added as salt solutions.

5.1.1 Impregnation¹²⁰⁻¹²²

In impregnation, the active material is sorbed (usually in solution) onto a solid, powdered or granulated support. The solvent used is usually water. This technique can be classified as either wet or dry impregnation, depending on the prior state of the support. In wet impregnation, the pore volume of the support is saturated with water beforehand, and the solute is transferred into the support by means of diffusion. In dry impregnation, the solution is sucked into the porous support by capillary action and any diffusional transport of the solute is superimposed on the convective flow. As the solute moves into the pore space of the support, it can be adsorbed onto the surface of the pore wall. The distribution of the immobilized solute governs the catalyst uniformity.

Other solutes can be added to the impregnating solution in addition to the catalyst precursor in order to control the distribution of catalytically active species. This is achieved through competition for adsorption sites on the support surface. When several solutes are used in the impregnating solution, the process is known as simultaneous impregnation or co-impregnation. Often, multi-component impregnation is carried out in stages. When this is the case, it is called sequential impregnation or successive impregnation.

5.1.2 Precipitation^{123,124}

In the usual precipitation procedure, an aqueous metal salt solution is contacted with an aqueous alkali (ammonium hydroxide or

carbonate) solution to cause the precipitation of an insoluble metal hydroxide or carbonate. This then converts to the metal oxide upon calcination. The metal nitrate salt is often used since it is water soluble, readily available and inexpensive. Ammonium hydroxide is used frequently since it is removed easily either by washing or by subsequent thermal treatment. The precipitation method can generate a catalyst with high, uniform activity. One drawback of this method is the fact that it uses much more metal than impregnation techniques.

The crystal properties of the precipitate which forms are dependent on several variables. These include concentration and pH of the solutions, temperature, and the rate and order of the precipitation. Since these parameters directly influence the catalytic activity, they must be optimized.

5.2 DRYING THE CATALYST^{120,124,125}

Before drying, the catalyst is saturated with liquid so that a thin film covers the surface. Drying first evaporates the surface liquid and then the liquid in the pores. The vapor generated in the pores forces the evaporating liquid out. If the drying rate is too fast, the vapor will be generated within the catalyst faster than the moisture can be forced out of the pores. This results in the pores exploding. As the drying process continues, the free liquid will vaporize, and adsorbed and bound water will remain in the pores. This water will ultimately be removed during calcination. Another phenomenon also occurs inside pellets which have varying pore sizes.

The moisture which remains will be preferentially pulled into the smaller pores by capillary force. Thus, the drying of pores will proceed in stages, with the smallest pores being the last to dry.

5.3 DRYING AND IMPREGNATION PARAMETERS¹²⁶⁻¹³⁵

The mass transfer processes involved in both drying and impregnation do not necessarily reach equilibrium. This results in non-uniform impregnation profiles. The radial distribution of the active species, as well as the nature of the surface species and their dispersion, are strongly influenced by the preparation conditions¹²⁵. Consequently, the influence of different preparative conditions on the catalyst is very important. Researchers who have analyzed the influence of impregnation and drying steps on the distribution of active components have reported that metal loadings, impregnation time, pH, drying temperature, and rate are all parameters which must be taken into account¹²⁶⁻¹³⁵.

5.3.1 Metals Loading

The metal loading is a very important preparation parameter. It has been found that hydrodesulfurization and hydrodemetallation activities reach a maximum at about 15% molybdena for a commercial Ni-Mo/Al₂O₃ catalyst¹²⁶. Higher concentrations lead to a loss of hydrodesulfurization activity. The decrease in activity has been explained by the formation of clusters over the initial active centers. In addition, micropore plugging during drying stages (for

heavy molecules) has been suggested as a cause for this deactivation¹²⁷. The ideal cobalt and nickel ratios have been found to be 0.3 NiO (CoO):MoO₃ or about 3% by weight^{126,128}.

5.3.2 Impregnation Time

Short contact times for the impregnation of dry and wet alumina pellets with nickel solutions renders degenerate shell catalysts¹²⁹, where the catalytic species is restricted mainly to the catalyst surface. Longer impregnation times increase the surface concentration of the adsorbed nickel and produce a more uniform catalyst distribution.

5.3.3 Effect of pH

Various ions adsorb differently into alumina depending on the pH of the solution. The pH of the impregnating solution also affects both the distribution and dispersion of the tetrahedral and octahedral species present in both Ni-Mo/Al₂O₃ and Co-Mo/Al₂O₃ catalysts^{130,131}. As a result, the catalytic activity is affected.

5.3.4 Drying Temperature and Rate

The influence of drying conditions on the molybdenum distribution and catalytic activity of a Co-Mo/Al₂O₃ catalyst has been reported¹²⁶. The temperature of drying, and the gas flow were varied over the catalyst. The mildest drying conditions gave the best macroscale distribution and catalytic activity. If drying conditions are not moderate, the catalyst pore structure can be damaged.

However, if conditions are too mild, drying times will be excessive. It has been found that a catalyst is more active if dried at higher humidity and lower temperatures, around 100°C. In order to determine optimum drying conditions, the catalyst must be dried at various temperatures and humidities. The performance of the catalysts can then be tested, and by correlating the data obtained, the drying behavior of the catalyst can be optimized.

5.3.5 Other Parameters

Recent studies on Co-Mo/Al₂O₃ catalysts focused on obtaining cobalt and molybdenum concentration profiles by careful control of impregnation parameters^{132,133}. It was shown that apart from the aforementioned variables, other factors played important roles in the shape and extent of ion incorporation. These included the preparation procedure, solute concentration, ratio of solution volume to the weight of the support, state of the support (wet or dry) and the amount of stirring of the solution. The amount of molybdenum entering the alumina pores, and the proportion of octahedrally coordinated molybdenum species, is favored by using large solution volumes and stirred solutions¹³³. The thiophene hydrodesulfurization activity was observed to increase in catalysts prepared by using low solution volumes, ammonia as a competitor, and dry supports or stirred impregnation solutions¹³⁴. This seemingly endless list of parameters which must be controlled during preparation also includes the ionic strength of the impregnating solution, the concentration of metal

salts in the solution¹³⁵, and the sequence of incorporation of the metal salts into the support¹²⁷.

5.4 ACTIVATING THE CATALYST

In the final stage of preparation, the catalyst is converted into its oxidic form, normally by calcining at temperatures around 500°C. If reduction is required for the activation, it can be accomplished by performing the calcination in a reducing atmosphere (such as hydrogen), or as a separate activation step. For hydro-treating catalysts, where the active form is the sulfided species, a further activation step must be performed. The catalytic activity of the final catalyst is dependent on several parameters which can be varied during activation. These include temperature, heating rate (during each activation step), degree of reduction or sulfidation, and the nature of the sulfur compound which is used during sulfidation.

5.4.1 Calcination

The purpose of calcination is to convert the metallic species to their oxide state. At the same time, the unstable anions and cations which are present in the impregnating solutions are also eliminated (ammonia, nitrates, etc.). The temperature required for this transformation is usually between 400 and 700°C.

5.4.1.1 Effect of Temperature

Optimum activity is obtained when Co-Mo/ γ -Al₂O₃ catalysts are calcined at a lower temperature, 500°C¹³⁶. Topsoe and co-workers have shown that upon increasing the calcination temperature, a decrease in catalytic activity is observed¹³⁸. This decrease is accompanied by an increase in the concentration of cobalt in tetrahedral coordination and a decrease in the amount of octahedrally coordinated cobalt. These results have led to the conclusion that the octahedrally coordinated cobalt present at the surface is a precursor to the active Co-Mo-S phase which is present after sulfiding. The tetrahedrally coordinated cobalt plays only a minor role in the promotion, and is located in subsurface positions of the alumina. The decrease in activity observed with increasing calcination temperature has thus been attributed to cobalt (or nickel) diffusing from octahedral surface positions to tetrahedral positions in the catalyst interior. It is interesting to note that the configuration of the molybdenum atoms does not significantly change during increases in calcination temperature.

It is generally accepted that Co-Mo/ γ -Al₂O₃ catalysts are more active for hydrodesulfurization reactions than Ni-Mo/ γ -Al₂O₃ catalysts¹³⁹⁻¹⁴¹. Recent interest in Ni-Mo/ γ -Al₂O₃ catalysts has been attributed to the increasing price of cobalt on the world market. One study comparing Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts shows that the nickel catalysts are actually the most active for hydrodesulfurization when they are calcined at 475°C⁷¹. The difference between the activities of the two catalysts has been attributed to

the fact that the inactive spinel, NiAl_2O_4 , forms more readily in nickel catalysts¹⁴²⁻¹⁴⁴. This is because nickel will diffuse from the surface to the bulk more readily than cobalt. Nickel appears to be a better promoter than cobalt (for hydrodesulfurization) if a suitable calcination temperature is used.

The rate of the increase in the temperature of calcination also affects the activity of the catalyst¹²⁶. Higher activity is observed with a lower rate of increase (50°C/hr.). Thermogravimetric studies show two well defined peaks for water loss ($100/120^\circ\text{C}$) and ammonia loss ($200/250^\circ\text{C}$) with the low rate. With higher rates (100°C/hr.), the peaks are less defined. Also, x-ray diffraction results indicate that there is slightly lower crystallinity in the catalysts which were prepared at higher rates of temperature increase.

One of the problems which occurs if the temperature of calcination is too high is sintering. Excessive sintering results in a reduction of activity since both the pore size and the surface area of the catalyst are reduced.

The activity of a catalyst can be improved during the calcination step by passing a stream of hot air over the catalyst. This results in more controlled heat transfer, oxidation of ammonia, and the sweeping of gaseous products from the catalyst.

5.4.2 Reduction

Catalyst activation often involves changing the oxidic form produced from calcination to a reduced form. This is done either by non-isothermal (temperature programmed) or isothermal addition of

hydrogen. The major variables which have to be considered are the heating rate during reduction, the temperature of reduction, the time of reduction and the hydrogen space velocity^{74,135}.

The ideal temperature range for reduction is between 400 and 500°C⁷⁴. The state of the catalyst after treatment with hydrogen at different temperatures was characterized by measuring the concentration of surface hydroxyl groups and sites for oxygen chemisorption. The unreduced oxidic catalyst has no capacity for chemisorption, but does have some surface hydroxyl groups. These have been ascribed to the support surface (alumina) which is not covered by promoters¹⁴⁵. The formation of hydroxyl groups and oxygen chemisorption sites proceeds only above 400°C. A decrease in hydroxyl concentration is found above 500°C, so the ideal temperature range is between 400 and 500°C.

Relatively little work has been done concerning the effects of reduction of Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ oxide catalysts on their catalytic activity. Several reports have stated that pre-reduction hinders the subsequent sulfidation for both catalysts, thereby lowering the hydrodesulfurization activity^{139,146-148}. The initial hydrodesulfurization activity for pre-reduced catalysts is high, but it drops off to a steady state level which is lower than that for non-pre-reduced catalysts¹⁴⁹⁻¹⁵².

5.4.3 Sulfidation

Hydroprocessing catalysts must be sulfided prior to use to ensure that at least part of the oxide ions in the catalyst are

replaced by the more active sulfur ions. The reaction is highly exothermic and therefore needs to be carefully controlled. It is well known that the performance of the catalyst is strongly dependent on how the sulfiding is carried out¹⁴⁷.

The sulfidation of hydroprocessing catalysts is generally carried out at moderate temperatures (300 to 450°C), under pressures between 200 and 5000 kPa of sulfiding and reducing agents. The effectiveness of the catalysts depends on the nature of the activating molecules, the activation procedure, and the sulfidation temperature. It has been shown that these parameters modify both the activity and the selectivity of the catalysts¹⁴⁹.

5.4.3.1 The Activating Molecules

The various commercial sulfiding technologies fall into four general categories¹⁵³:

1. Those that use H_2S/H_2 gas mixtures in contact with the catalyst.
2. Those that use the native organic sulfur compounds in the feedstock.
3. Those that spike the feedstock with a sulfur-donating species (mercaptans, thioethers, carbon disulfide).
4. Those that impregnate the catalyst with a sulfur containing compound (ammonium sulfide).

The most common laboratory sulfiding agent is an $\text{H}_2\text{S}/\text{H}_2$ gas mixture¹⁵⁴. Other sulfiding molecules such as thiophene, carbon disulfide and butanethiol have been studied, but are not as effective¹⁵⁵.

5.4.3.2 Activation Procedure

A recent study by Delmon et al. shows the influence of two different activation procedures on the catalytic properties and structural changes of a hydrodesulfurization catalyst as a function of temperature⁷⁷. The activation procedure was by either consecutive reduction-sulfidation or by simultaneous reduction and sulfidation using $\text{H}_2/\text{H}_2\text{S}$. It was concluded that the activation by consecutive reduction-sulfidation reactions at temperatures above 400°C produced a strong catalytic activity loss. The activation by simultaneous reductions and sulfidation produced catalysts with optimal activity in an extended temperature range (400 to 650°C). Other authors have reached the same conclusions^{82,156,157}.

The relative abundance of species present on the surface of a catalyst has been shown to change when a fresh oxidic catalyst is converted to its sulfided form. This structural change affected both the activity and selectivity of the catalyst⁸¹. The activity sequence among various pre-treated catalysts in descending order was found to be sulfided > pre-reduced/sulfided > fresh > reduced. The promoting effect of sulfidation was suppressed significantly once the catalyst was reduced. Reduction prior to sulfidation decreased the active cobalt (nickel) site population. Since catalytic activity is

ascribed to either cobalt or nickel, the deterioration of the catalytic activity upon reduction was concluded to be due to the decrease in the active species site population.

The effect of sulfidation time was also studied⁸⁷. After two hours of sulfidation, no further improvement in catalytic activity was observed.

5.4.3.3 Sulfidation Temperature

The sulfidation temperature is also an important parameter. The following structural changes have been observed when the temperature of sulfidation is above 400°C⁷⁷. The support (alumina) and the supported phases tend to sinter together, causing a loss in dispersion and surface area. The concentration of the sulfides of the promoter ions increase. Since these are inactive, the activity of the catalyst also decreases. Also, the concentration of the active Co-Mo-S (Ni-Mo-S) phase decreases due to the fact that the promoter ions are shifted from octahedral coordination sites to tetrahedral ones. The decrease in the concentration of this active phase causes a drastic decrease in the hydrodesulfurization activity of the catalyst^{87,138}.

In catalyst activity/structure studies, it is essential to know the exact conditions which the catalyst has been subjected to during preparation. Some of the conflicting reports which appear in the literature may well arise from differences which were undetected in the preparation procedure.

5.5 DELINEATION OF THE PREPARATION METHOD USED IN THIS STUDY

In order to prepare the antimony and fluoride promoted catalysts used in this project, a systematic study was performed on a first series of catalysts. The three objectives were:

1. To choose whether boehmite (α -AlOOH), or gamma alumina (γ -Al₂O₃) should be used as the starting material for the preparation of the support.
2. To determine whether co-precipitation of antimony and alumina, or impregnation of antimony onto the alumina surface was the most desirable method for preparing the support.
3. To find the optimum concentrations of antimony and fluoride needed for maximum catalytic activity.

The catalyst functions were analyzed by cumene cracking and hydrocracking reactions. X-ray powder diffraction patterns were also obtained for several samples. In this early stage, the catalysts were not studied in their sulfided state. It was known that direct relationships exist between the oxidic catalysts and their corresponding sulfided forms²⁷. Also, the sulfided forms are x-ray amorphous¹¹⁶.

5.5.1 Preparation Techniques

The different preparation techniques which were investigated were discussed previously in Chapter 2. The approaches involved impregnating antimony onto either boehmite or gamma alumina, or co-precipitating the two components.

5.5.2 Results

The cumene cracking results, hydrocracking results and the x-ray powder diffraction patterns obtained for some of the catalysts in the first series are shown in the following tables. The antimony loading was varied as was the fluoride content. No other promoters were involved in the first series of catalysts. Unless otherwise stated, all catalysts were prepared by impregnation of the antimony and/or fluoride onto boehmite.

Table 5.1
Cumene Cracking Results (Series 1)

Catalyst	additives		(%) Cumene Conversion				yield (4 hr.)		
	Sb(a)	F(b)	(c) ₁	2	3	4	benz.	et.benz.	α -Me
γ -Al ₂ O ₃	0	0	6.9	5.4	4.8	4.3	0	0	4.3
Sb ₂ O ₃	-	0	6.2	5.3	5.2	4.8	0	0	4.8
AMW-2	1	0	5.0	4.5	4.8	3.9	0	0	3.9
AMW-6	2	0	6.4	6.1	5.9	6.1	0	0	6.1
AMW-3	3	0	5.1	4.9	4.8	4.7	0	0	4.7
AMW-7(d)	3	0	14.7	14.2	14.1	14.1	0	0	14.1
AMW-8	0	2	76.5	75.3	75.5	75.5	72.3	0	2.3
AMW-9(e)	0	2	64.6	53.4	47.2	43.9	39.1	0.1	4.8
AMW-4	3	1	5.4	5.7	6.1	6.3	0.1	0	6.2
AMW-5(d)	3	1	6.9	6.4	6.4	6.4	0.1	0	6.4
AMW-10(e)	3	1	17.4	14.4	13.4	12.6	0.1	0	12.5
AMW-11(f)	3	1	3.9	3.7	3.9	3.8	0	0	3.8

(a) number of Sb atoms per 20 Al atoms.

(b) number of F atoms per 20 (Al + Sb) atoms.

(c) number of hours of reaction

(d) co-precipitation of Al + Sb support.

(e) impregnation of promoter onto γ -Al₂O₃.

(f) impregnation of promoter onto co-precipitated support.

* benz. = benzene, et. benz. = ethyl benzene and α -Me = α -methyl styrene.

Table 5.2
Cumene Hydrocracking Results (Series I)

Catalyst	additives		(%) Cumene Conversion				yield (4 hr.)		
	Sb(a)	F(b)	(c) ₁	2	3	4	benz.	et.benz.	α -Me
γ -Al ₂ O ₃	0	0	0.7	0.7	0.7	0.7	0	0	0.7
Sb ₂ O ₃	-	0	0.7	0.4	0.5	0.6	0	0	0.6
AMW-2	1	0	0.5	0.6	0.6	0.6	0	0	0.6
AMW-8	0	2	59.5	59.1	59.1	59.0	58.9	0.1.	0
AMW-9(e)	0	2	77.0	77.7	78.1	79.3	79.3	0	0
AMW-10(e)	3	1	0.5	0.5	0.7	0.4	0	0	0.4

* Note: Please see Table 5.1 for description of legend.

Table 5.3
X-ray Diffraction Results

Al ₂ O ₃ (calcined)			Sb ₂ O ₃ (calcined)			AMW-3 (impregnation)			AMW-7 (co-precipitation)		
d	I	identity	d	I	identity	d	I	identity	d	I	identity
1.40	100	γ-Al	3.07	100		2.61	100		3.14	100	KCl
1.98	100	γ-Al	3.21	68	Sb ₂ O ₃	2.04	95		2.22	43	KCl
2.54	20		3.44	35		1.98	87	γ-Al	1.41	17	KCl
4.54	15	γ-Al	1.97	29	Sb ₂ O ₃	2.34	79	γ-Al	1.82	10	KCl
2.67	15		2.94	27		8.28	77		1.57	9	KCl
2.45	15	γ-Al	2.78	23	Sb ₂ O ₃	1.41	71		1.41	6	γ-Al
2.80	10	γ-Al	1.72	21		1.40	65	γ-Al	1.40	6	γ-Al
			1.68	21	Sb ₂ O ₃	1.40	53				
			2.65	19		3.09	51				

5.5.3 Discussion of results

The cumene cracking results for the co-precipitated catalysts were ambiguous. Although the catalyst containing just antimony (AMW-7) showed relatively high activity, upon addition of fluoride (AMW-5) this activity was greatly reduced. This could be a consequence of the presence of potassium chloride, a by-product of the co-precipitation procedure which was employed. Potassium chloride was readily identified in the x-ray diffraction results (Table 5.4), and is known to decrease the activity of a catalyst.

In comparison, the catalysts prepared by the addition of fluoride onto the impregnated support resulted in an increase of activity (see AMW-3, AMW-4). On the basis of these results, it was decided that impregnation was a better preparation technique than co-precipitation for these catalysts.

The cracking and hydrocracking results that were obtained for fluorinated alumina indicated that the impregnated boehmite was more active in cumene cracking experiments. However, the catalyst which was prepared by impregnating the already calcined alumina was much more active in hydrocracking. It is important to note that when fluoride is added, the product distribution changes drastically. The antimony-alumina supports were incapable of catalyzing the dealkylation of cumene to benzene. They were only involved in the dehydrogenation of cumene to α -methyl styrene.

By looking at these preliminary results, and comparing them with unpublished results¹⁵⁸ obtained when antimony was initially used as an additive by our research group, several things were apparent.

First, the mixed antimony alumina support was no more active in reactions with cumene than gamma alumina alone. It therefore appeared as if there was no further enhancement of the catalyst acidity if Sb_2O_3 was added to alumina (without fluoride). Also, it was decided that the next stage was to prepare catalysts with lower amounts of antimony and larger concentrations of fluoride.

Subsequently, one catalyst was prepared (AMW-12) with an antimony to aluminum ratio of 1:50. This was prepared by impregnating fluoride onto a calcined antimony-alumina support. The fluoride ion content was raised to 4 atoms per 20 support atoms. The cracked cumene conversion obtained after 4 hrs of reaction was 39.1%, with 36.5% being benzene. In the analogous hydrocracking reaction, a conversion of 30.9% was attained. Since these were promising results, a second series of catalysts was prepared containing the same amount of antimony and fluoride, and the additional promoters, nickel and molybdenum. The order of addition of the active species (fluoride, nickel and molybdenum) was varied in an attempt to delineate an appropriate preparation sequence. All other preparation parameters were kept constant.

5.6 PREPARATION OF Ni-Mo PROMOTED CATALYSTS

The second series of catalysts which was prepared contained nickel, molybdenum and fluoride on the previously prepared antimony-alumina mixed oxide support. The active ingredients were added to the support as salt solutions (as described in Chapter 2) by either sequential or co-impregnation routes.

5.6.1 Results

The results obtained from cumene cracking and hydrocracking reactions on AMW-12 to AMW-16 are shown in Tables 5.4 and 5.5. All catalysts contain 1 antimony per 50 aluminum atoms and 4 fluorine atoms per 20 (Al + Sb) atoms.

Table 5.4
Cumene Cracking Results (Series II)

Catalyst	additives		(%) Cumene Conversion					yield (4 hr.)		
	Ni	Mo	1	2	3	4	benz.	et.benz.	α -Me	Other
AMW-12	0	0	47.4	42.6	42.7	39.1	36.5	0	2.6	0
AMW-13 ^a	3	15	30.5	31.3	32.8	30.7	4.7	0	25.2	0.8
AMW-14 ^b	3	15	32.6	33.1	32.8	31.7	2.2	0	26.8	2.7
AMW-15 ^c	3	15	32.1	28.9	29.5	28.7	5.0	0	21.1	2.6
AMW-16 ^d	3	15	35.8	34.8	32.2	32.3	2.1	0	27.3	2.9

- a) Ni-Mo addition, dry, F addition, dry, calcine.
- b) Ni-Mo addition, dry, calcine, F addition, dry, calcine.
- c) co-impregnation
- d) F addition, dry, calcine, Ni-Mo addition, dry, calcine.

Table 5.5
Cumene Hydrocracking Results (Series II)^a

Catalyst	additives		(%) Cumene Conversion					yield (4 hr.)		
	Ni	Mo	1	2	3	4	benz.	et.benz.	α -Me	Other
AMW-12	0	0	35.5	33.0	32.6	30.9	30.9	0	0	0
AMW-13	3	15	49.6	52.3	52.0	51.7	45.9	0.9	4.9	0
AMW-14	3	15	71.9	71.8	70.7	69.8	65.2	0.5	4.1	0
AMW-15	3	15	40.1	39.4	40.4	40.1	36.4	0.7	3.0	0
AMW-16	3	15	72.2	72.1	71.5	70.4	67.2	1.1	2.1	0

a) For preparation sequence, see Table 5.4.

5.6.2 Discussion of Results

From both the cracking and hydrocracking results, it appears that the catalyst prepared by impregnation of fluoride prior to addition of nickel and molybdenum is most active. It should be noted, however, that there is approximately a five percent error in the results obtained, leading to some uncertainty in this conclusion. This error was determined by repeating a run three times with the same catalyst. It can be seen (by comparing the results for AMW-15 with those of the other three Ni-Mo catalysts) that for this catalyst system the stepwise impregnation sequence is much more effective than the co-impregnation technique.

These results indicate that the lower levels of antimony and higher loading of fluoride in the catalysts are nearer to optimum than those used in Series One. The evidence for this is seen in the higher overall conversions of cumene.

It has been found in this study that the preparation method which yields the highest conversions of cumene was a stepwise impregnation sequence. The support was prepared initially by impregnation of antimony onto boehmite, followed by calcination. The promoters were then added with fluoride first, followed by nickel and molybdenum. The remainder of catalysts which were prepared in this study were synthesized in a similar manner.

CHAPTER 6

RESULTS AND DISCUSSION

A final series (Series III) of catalysts was prepared using the technique outlined in Chapter 5. The concentration of antimony in the support was varied from 8.3 to 31 weight percent (corresponding to antimony/aluminum ratios of 1:50 and 1:10 respectively). The percentage of antimony in the final catalysts, which contained the promoters fluoride, molybdenum and nickel (cobalt), was between 6.2 and 23 weight percent. The catalysts were characterized by using the techniques which were outlined in Chapter 2. These included surface area measurements, x-ray powder diffraction patterns, x-ray photoelectron spectra, and infrared spectroscopy with pyridine as a probe molecule. The catalysts were tested for their activities through reactions with the model compounds, cumene and thiophene.

6.1 SURFACE AREA MEASUREMENTS

The results which were obtained from surface area measurements (using the BET method) are shown for each catalyst in Table 6.1. The composition of each catalyst is also shown. It is apparent from these results that the surface area of the catalysts decrease with increasing promoter content. The sharp decrease in surface area with the addition of fluoride has been noted previously for catalysts which were prepared in a similar manner^{104,105}. The decrease in surface area has been attributed to AlF_3 , a low surface area phase

which is formed during the preparation, as a result of the reaction of alumina with fluoride¹⁰¹.

Table 6.1
Composition and Surface Area of Series III Catalysts

Catalyst	Additives				Surface Area (m ² /g)
	Sb ^a	F ^b	CoO/NiO ^c	MoO ₃ ^c	
γ -Al ₂ O ₃	0	0	0	0	200.2
AMW-9	0	2	0	0	181.2
AMW-12	1:50	4	0	0	141.9
AMW-19	0	4	3 Ni	15	115.9
AMW-20	0	4	3 Co	15	112.5
AMW-16	1:50	4	3 Ni	15	97.6
AMW-18	1:50	4	3 Co	15	98.7
AMW-23 ^d	1:50	4	3 Ni	15	105.5
AMW-21	1:30	4	3 Ni	15	102.1
AMW-22	1:30	4	3 Co	15	100.2
AMW-24	1:10	4	3 Ni	15	91.4
AMW-25	1:10	4	3 Co	15	93.7

a) number of Sb atoms per x Al atoms.

b) Number of F atoms per 20 (Al + Sb) atoms

c) weight percent

d) HOOH used in preparation to try to oxidize Sb to +5.

The further decline in surface area which is observed with addition of antimony may be a result of sintering, which reduces the dispersion of the catalyst and also its surface area. It has been noted by ceramicists that low melting oxides, such as antimony, can sharply reduce the melting point of catalyst supports. If this reduction is severe enough, objectionable levels of sintering can occur at relatively low temperatures¹⁵⁹.

Another factor which must be considered when comparing surface area measurements is the number of calcination steps involved during the preparation. The surface area decreases significantly from γ -alumina and fluorided alumina (AMW-9) to the catalysts which contain three promoters (e.g. AMW-16, AMW-18). The former have surface areas which approach $200 \text{ m}^2\text{g}^{-1}$ and involve only one calcination step, whereas the latter catalysts require three calcination steps with the resulting surface areas being reduced to $\sim 100 \text{ m}^2\text{g}^{-1}$.

6.2 X-RAY DIFFRACTION (XRD) RESULTS

Typical x-ray powder diffraction data obtained for a Series III catalyst are shown in Table 6.2. Also indicated are the literature values for molybdena and nickel oxide, as well as the possible identity of some of the lines.

The XRD results for AMW-16 show the presence of γ -alumina, and also traces of nickel oxide and molybdena. No evidence of either antimony or fluoride was found. This result is similar to recent findings by Lycourghiotis et. al.^{104,105} with respect to fluorinated nickel molybdenum catalysts.

Table 6.2
X-ray Diffraction Results for AMW-16

$\gamma\text{-Al}_2\text{O}_3$		Sb_2O_3 senarmonite		MoO_3 molybdate		NiO bunsenite		Catalysts AMW-16(a)		
d	I	d	I	d	I	d	I	d	I/Imax	identity?
1.98	100	3.22	100	3.26	100	2.09	100	1.40	100	$\gamma\text{-Al}_2\text{O}_3$
1.40	100	1.97	42	3.81	82	2.41	91	3.31	72	MoO_3
2.39	80	2.79	40	3.46	61	1.48	57	1.98	62	$\gamma\text{-Al}_2\text{O}_3$
2.28	50	1.68	35	2.66	35	0.98	21	1.90	40	MoO_3
4.56	40	1.28	12	6.93	34	0.85	17	2.03	33	NiO
1.52	30	6.44	12	2.31	31	1.26	16	3.52	32	MoO_3
2.80	20	2.56	11	1.85	21	1.21	13	3.10	30	MoO_3
1.14	20			2.70	19			2.46	29	NiO
0.81	10			2.27	18			6.17	27	MoO_3
1.03				1.96	17			2.83	26	$\gamma\text{-Al}_2\text{O}_3$
				1.73	17			5.36	25	
				1.57	16			4.09	24	MoO_3
								2.65	24	MoO_3
								1.50	21	NiO

a) The composition of AMW-16 is 1 Sb per 50 Al atoms, 4 F per 20 (Al + Sb) atoms, 3% NiO and 15% MoO_3

They found evidence of γ -alumina, but could detect no crystallized solid phases. The phases which are thought to be present include AlF_3 , NiAl_2O_4 , $\text{Al}_2(\text{MoO}_4)_3$ and NiMoO_4 (each of which has been characterized by other spectroscopic techniques and are known to exist on catalyst surfaces).

The XRD powder patterns which were obtained for the other catalyst samples were all very similar to the AMW-16 pattern. No discernible differences were observed, although some spectra were slightly weaker than others. Moreover, no visible differences were seen in the alumina diffraction lines. It could be expected that some shifting of the lines would be observed as a result of the polarization of the alumina lattice, which occurs upon addition of fluoride. However, no such effect was apparent. It is clear, therefore, that XRD is not a powerful technique by which to characterize the catalyst surface, and differentiate between samples. This is mainly a result of the poor crystallinity of the samples. However, XRD is a useful technique to distinguish between the various transition aluminas, and to detect problems which can occur during the calcination of the support, causing incomplete formation of γ -alumina from boehmite.

6.3 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) RESULTS

The XPS spectra of several catalyst samples were obtained in order to determine the oxidation state of antimony within the catalyst supports. The results are shown in Table 6.3 along with the

literature values which are expected for several antimony compounds^{160,161}.

Table 6.3
Antimony XPS Results and Literature Values

Sample	Measured Binding Energy, eV				
	Observed			Corrected	
	C 1 _s	3 d _{3/2}	4d	3 d _{3/2}	4d
<u>Catalysts</u>					
AMW-12	285.4	545.0	39.9	540.7	35.6
AMW-16	285.3	544.4	39.4	541.0	36.0
AMW-21	285.2	543.8	38.9	541.2	36.6
AMW-24	285.6	544.3	39.4	540.5	35.6
<u>Literature</u>					
Sb ₂ O ₃	287.2	541.6	37.3	539.4	35.1
Sb ₂ O ₅	286.9	542.2	37.8	540.2	35.9
SbF ₃	286.0	542.2	37.4	541.2	36.4
SbF ₅ ⁵		550.9(gas phase)			

Please note that compositions are given in Table 6.1.

The XPS results indicate that antimony is either in a +5 oxidation state, and/or that it is coordinated to fluoride. This is apparent when looking at the binding energy values (3d_{3/2}: 540.5-541.2) which are higher than the literature values for Sb₂O₃ (3d_{3/2}: 539.4 eV) and Sb₂O₅ (3d_{3/2}: 540.2 eV). The fact that the binding

energies are higher than those observed for the antimony oxides indicates that the antimony present in the catalyst supports is in a more polarizing environment. This is in keeping with the incorporation of antimony into the γ -alumina lattice, and also to the presence of electronegative fluoride ions. It is clear that the antimony, which was impregnated as Sb_2O_3 , has changed its chemical environment as a consequence of the preparation procedure.

It can also be seen from the comparison of the results from AMW-12 (containing Sb and F) and the other three catalysts (containing Sb, F, NiO and MoO_3), that the nickel oxide and molybdena present on the catalyst do not affect the binding energies to any significant extent. Most of the shift in binding energy of the antimony lines is a result of the presence of both fluoride ions and alumina.

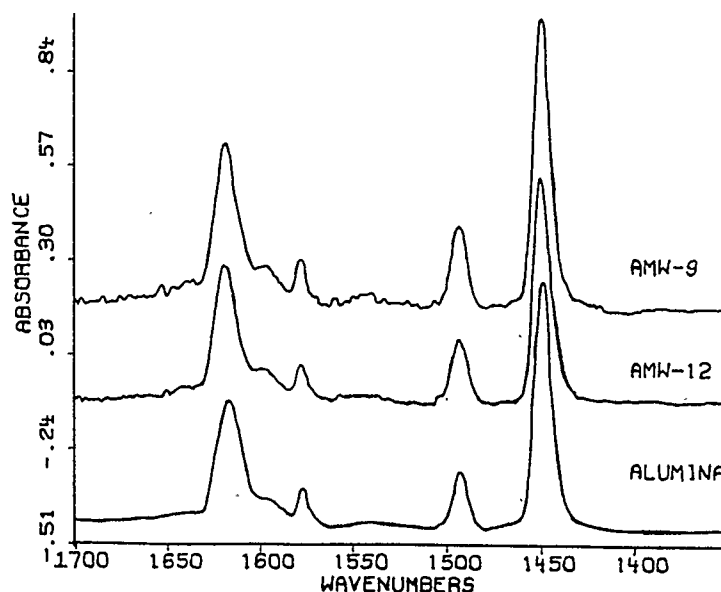
6.4 PYRIDINE ADSORPTION STUDIES

The infrared spectra for pyridine adsorbed on γ -alumina, fluorided alumina (AMW-9) and fluorided antimony-alumina (AMW-12) are shown between 1700 and 1350 wavenumbers in Fig. 6.1. It appears that the Brönsted band at ~ 1540 wavenumbers (cm^{-1}) is larger for fluorided alumina (AMW-9) than for either of the other two samples. However, it is difficult to discern due to the increased background noise levels for AMW-9 (which could be a result of the pellet being of poorer quality and transmitting less light). In order to compare the Brönsted acidity of the three samples, the ratio of the peak heights of the 1490 cm^{-1} and 1450 cm^{-1} peaks was calculated. The peak at 1490 cm^{-1} is due to both Brönsted and Lewis acid sites, whereas the

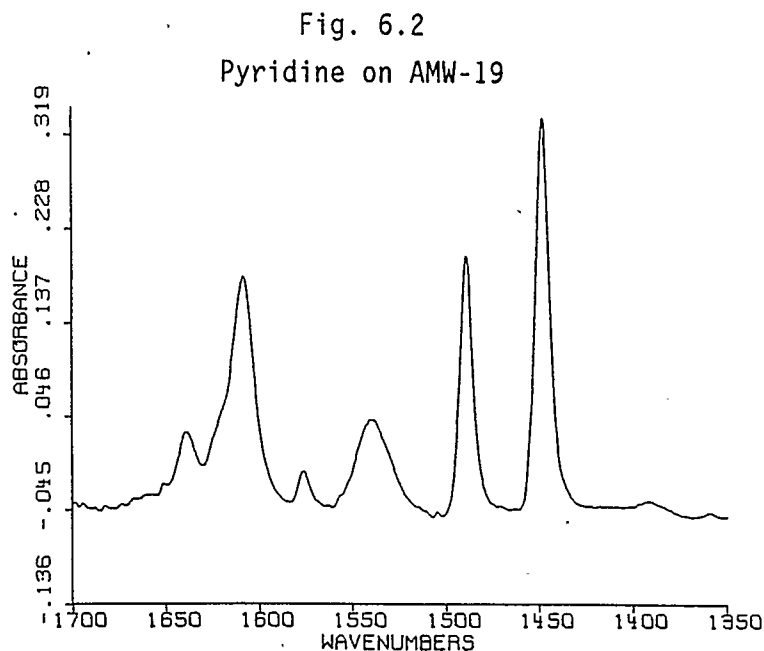
peak at 1450 cm^{-1} is a result of Lewis acidity. The consequence of this is the fact that the ratio of the two peaks will give an indication of the relative Brönsted acidity of the samples. It should be noted that the ratioing will only be valid if the spectra are measured on the same absorbance scale, which in this case is true.

The ratio (of the two peaks) which is obtained for γ -alumina is 0.23, while the ratio for the other two samples is 0.28. It can be concluded that the addition of fluoride increases the Brönsted acidity of the alumina as expected. On the other hand, the addition of antimony appears to reduce both the Brönsted and Lewis acidity of the fluorided alumina. The ratio of the two peak heights is the same, but the intensity of both peaks are lower than those obtained for fluorided alumina (AMW-9).

Fig. 6.1
Infrared Spectra of Pyridine Adsorbed on $\gamma\text{-Al}_2\text{O}_3$,
 $\text{F}/\gamma\text{-Al}_2\text{O}_3$ (AMW-9) and $\text{F}/\text{Sb}_2\text{O}_3/\text{Al}_2\text{O}_3$ (AMW-12).



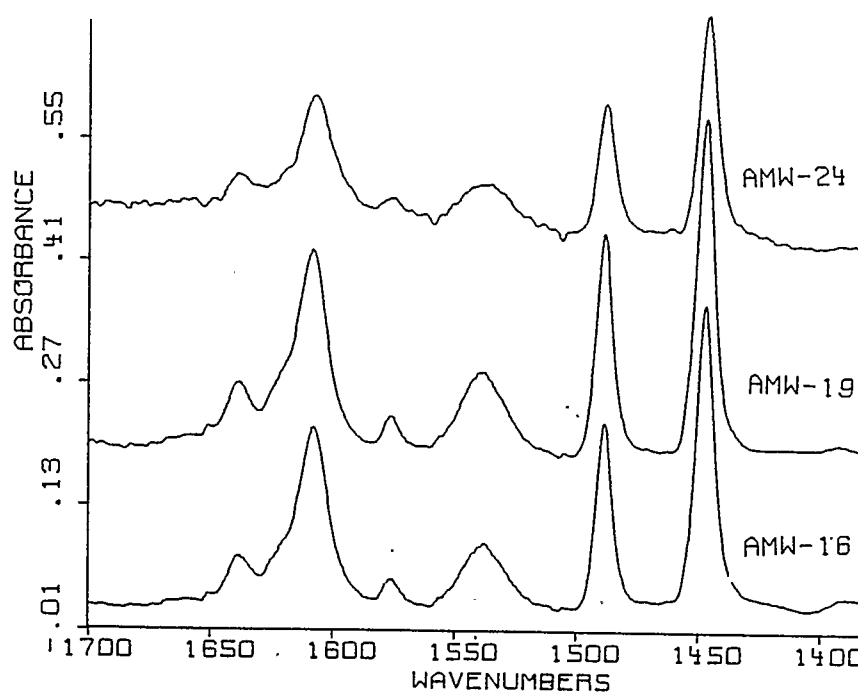
The infrared spectrum of pyridine adsorbed on AMW-19 (Ni-Mo, F/ γ -Al₂O₃) is shown in Fig. 6.2.



The infrared spectrum obtained for pyridine adsorbed on AMW-19 (Ni-Mo/F/ γ -Al₂O₃) gives results which are similar to those which have been previously reported for the analogous Co-Mo/F/ γ -Al₂O₃ catalysts¹⁶². On the basis of the infrared absorption band that is observed at ~ 1540 cm⁻¹, it can be deduced that the Brönsted acidity of AMW-19 (Ni-Mo/F/ γ -Al₂O₃) is larger than that of AMW-9 (F/ γ -Al₂O₃). This is a result of the addition of molybdena (MoO₃), which produces Brönsted acid sites. It is speculated that this enhanced acidity is associated with hydroxyl groups present on either molybdenum species or on the alumina surface adjacent to the molybdenum¹⁶². It has been shown that these sites disappear upon reduction with hydrogen, whereas the sites created by fluoride remain¹⁶⁴.

The spectra of AMW-16 (1 Sb:50 Al), AMW-19 (no Sb) and AMW-24 (1 Sb:10 Al) are shown between 1400 and 1700 wavenumbers in Fig. 6.3. A comparison of the three spectra shows that both the Lewis and Brönsted acidity decreases with increasing antimony loading. However, when doing a direct comparison of AMW-16 and AMW-19 (taking the ~20% loss in surface area from AMW-19 to AMW-16 into account), the acidity appears to be similar and may even be enhanced.

Fig. 6.3
Infrared Spectra of Pyridine Adsorbed on AMW-16 (1 Sb:50 Al),
AMW-19 (no Sb) and AMW-24 (1:10 Sb:Al)



* All catalysts contain 4F:20 (Al +Sb) atoms, 15 wt % MoO₃ and 3 wt % NiO.

6.5 HYDRODESULFURIZATION ACTIVITY

The hydrodesulfurization activity was determined by reacting hydrogen with thiophene over each catalyst. The results obtained are shown in Table 6.4.

Table 6.4
Thiophene HDS Results

catalyst	Sb ^a content	% Thiophene Conversion				corrected for surface area	
		1	2	3	4	S ₂ A. (m ² /g)	conversion per m ²
γ -Al ₂ O ₃	0	1.4	1.5	1.5	1.4	200	0
AMW-9	0	1.5	1.5	1.5	1.4	181	0
AMW-12	1:50	1.1	1.1	1.0	1.0	142	0
AMW-19	0	23.8	22.3	21.4	20.4	116	1.2
AMW-20	0	19.8	18.8	18.0	17.6	113	1.0
AMW-16	1:50	17.2	16.6	15.9	15.4	98	1.0
AMW-18	1:50	14.6	14.0	13.8	13.3	99	0.9
AMW-23	1:50	13.8	13.2	12.6	12.5	106	0.8
AMW-21	1:30	11	10.6	10.4	10.1	102	0.7
AMW-22	1:30	12.8	11.5	11.3	11.4	100	0.8
AMW-24	1:10	8.8	8.5	8.2	8.2	91	0.6
AMW-25	1:10	10.4	10.1	9.7	9.7	94	0.7

^a number of Sb atoms per x Al atoms

Please note that the compositions are given in Table 6.1

The most active catalysts for thiophene hydrogenolysis are those which contain no antimony. It appears that an increasing amount of antimony deactivates the catalyst towards hydrodesulfurization. The effect is not just a result of the surface area decrease, which occurs upon addition of antimony. The thiophene conversions which are obtained when taking the surface areas into account are lower for those catalysts containing antimony than for those without.

The deactivation may be a result of the increased acidity of the catalysts. It has been suggested that the increasing acidity, resulting from the polarization of the alumina lattice by fluoride, will increase the Lewis acidity of the molybdenum sites, and therefore increase the carbon-sulfur hydrogenolysis capability of catalysts⁹⁸. However, our results (as well as those reported by others^{103,105,165}) do not support this idea. In fact, studies of F/Co-Mo/ γ -Al₂O₃ and F/Ni-Mo/ γ -Al₂O₃ catalysts show decreases in hydrodesulfurization activity for fluoride loadings higher than 3 wt %. These results suggest that the increased acidity may disrupt the delicate oxidation/reduction balance which is postulated in some hydrodesulfurization mechanisms⁷⁶.

It is apparent that cobalt (or nickel) and molybdenum are necessary in order for thiophene conversion to proceed. The γ -alumina, fluorided alumina (AMW-9) and fluorided antimony-alumina (AMW-12) have virtually no catalytic activity towards hydrodesulfurization of thiophene. This is in agreement with the currently accepted model for hydrodesulfurization which involves the formation of Co-Mo-S (Ni-Mo-S) phases with cobalt (nickel) on the edge

positions of the MoS_2 structure^{89,90}. The presence of antimony may cause the blockage of some of the active sites, or possibly, promote the formation of inactive sulfide phases such as Co_9S_8 or Ni_9S_8 .

The nickel promoted catalysts (AMW-16, 19, 21 and 24) appear to be more active than the cobalt promoted ones (AMW-18, 20, 22 and 25) towards thiophene hydrogenolysis. This is in agreement with literature reports which have stated that $\text{Ni-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts are more active than the analogous $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts if a suitable calcination temperature is used during catalyst preparation⁷¹.

The catalyst which was prepared with oxidation of the antimony in mind (AMW-23) shows lower activity than either of the other two catalysts with similar antimony loadings (AMW-16, 18). This could indicate that the lattice is slightly more polarized in AMW-23, causing the catalyst to have increased acidity. If this is the case, a small decrease in activity is expected since the increased acidity seems to inhibit thiophene conversion.

6.6 ACTIVITY STUDIES USING CUMENE

The catalysts were studied in their reduced and sulfided forms for their hydrocracking activity with cumene. The results for the reduced catalysts are shown in Table 6.5, and the results obtained for the sulfided catalysts are given in Table 6.6.

From the cumene hydrocracking results for the reduced catalysts (Table 6.5), several points can be made. It is apparent that the catalysts with no promoters, or low fluoride ion content, are inactive towards cracking reactions.

Table 6.5
Cumene Hydrocracking Results (Reduced Catalysts) Series III

catalyst	Sb ^a	% Cumene conversion				yield (4 hrs)			
	content	1	2	3	4	benz.	et.benz.	α-me	other
γ-Al ₂ O ₃	0	0.7	0.7	0.7	0.7	0	0	0.7	0
Sb ₂ O ₃	0	0.7	0.4	0.5	0.6	0	0	0.6	0
AMW-9	0	77.0	77.7	78.1	79.3	79.0	0	0	0
AMW-12	1:50	47.4	42.6	42.7	39.1	36.5	0	2.6	0
AMW-19	0	82.6	81.6	81.5	79.9	75.8	0.8	0	3.3
AMW-20	0	77.6	76.8	75.6	76.4	71.0	0.5	0	4.9
AMW-16	1:50	72.2	72.1	71.5	70.4	67.2	1.1	2.1	0
AMW-18	1:50	71.0	69.9	70.9	70.0	64.6	0.3	0	5.0
AMW-23	1:50	78.6	75.9	74.4	74.1	68.8	0.9	0	4.3
AMW-21	1:30	63.6	59.8	62.7	60.6	55.6	0.5	0	4.6
AMW-22	1:30	69.8	68.3	66.0	61.3	56.3	0.2	0	4.9
AMW-24	1:10	47.6	46.3	47.2	48.1	40.7	0.5	2.7	4.2
AMW-25	1:10	42.8	43.7	44.8	44.2	40.1	0.5	0.8	2.8

^a number of Sb atoms per x Al atoms

Please note that the compositions are given in Table 6.1

Table 6.6
Cumene Hydrocracking Results (Sulfided Catalysts) Series III

catalyst	% Cumene conversion				yield (4 hrs)			
	1	2	3	4	benz.	et.benz.	α -me	other
γ -Al ₂ O ₃	0	0	0	0	0	0	0	0
AMW-9	80.6	79.8	78.7	79.6	79.5	0.1	0	0
AMW-12	34.5	37.8	38.0	38.3	38.3	0	0	0
AMW-19	84.7	84.6	83.5	83.2	79.5	0	0	3.8
AMW-20	77.8	80.8	85.9	85.0	81.9	0	0	3.1
AMW-16	86.5	85.3	84.7	84.8	83.4	0.1	0	1.3
AMW-18	69.3	69.1	70.8	73.9	73.3	0	0	0.6
AMW-23	84.7	84.3	83.7	83.8	81.7	0	0	2.1
AMW-21	76.5	78.6	78.5	78.3	75.9	0	0	2.4
AMW-22	77.7	77.1	76.9	77.2	76.3	0.1	0	0.8
AMW-24	44.5	52.6	51.1	50.9	48.4	0.2	0.8	1.5
AMW-25	49.8	48.1	48.4	47.2	45.1	0.2	0.6	1.3

Please note that the compositions are given in Table 6.1

The product distribution in each of these cases is 100% α -methyl styrene which is the product obtained by the dehydrogenation of cumene. The fact that only α -methyl styrene is seen suggests that there are no Brönsted acid sites present on these catalysts. The catalyst containing only antimony and fluoride (AMW-12) is quite

active towards cracking reactions, with over 90% of the product obtained being benzene. This is a direct result of the fluoride ions increasing the acidity of the alumina surface. Higher conversions are obtained by fluorided alumina alone (AMW-9) where almost 100% of the product obtained is benzene. The fluoride ions are polarizing the lattice more strongly than the hydroxide ions that they replace. The addition of antimony reduces the cracking activity of fluorided alumina. Some of this decrease can be related to the differences in surface area between AMW-9 and AMW-12 (181 and 142 m²g⁻¹ respectively). However, even with this in mind, a drop in activity is still apparent. The addition of antimony may actually decrease the acidity of the fluorided alumina, as was shown in the FT-IR results section.

The hydrocracking results for both the reduced and sulfided catalysts in Series III indicate several things. First, it is apparent that catalysts with high antimony loadings are less active than those with lower loadings. Secondly, with a few exceptions, the catalysts with nickel present as a promoter appear to be more active than those containing cobalt (as in the HDS case). Finally, the catalyst which was intentionally oxidized (AMW-23) demonstrated higher activity than either AMW-16 or AMW-18. This could be an indication that more antimony is present in the +5 oxidation state, causing a greater polarization of the alumina lattice, and resulting in a more acidic catalyst. However, another possibility is the fact that the addition of hydrogen peroxide stabilizes the molybdates in the catalyst. It has recently been reported that hydrogen peroxide

can change the distribution of both cobalt and molybdenum present on the catalyst¹⁶⁵.

The catalysts which contain no antimony (AMW-19 and AMW-20) are the most active in both their reduced and sulfided forms. This is thought to be a consequence of the reduced surface areas which occur upon addition of antimony. The conversions obtained for each catalyst (after 4 hours on stream) have been expressed in Table 6.7 in terms of their surface areas.

Table 6.7
Cumene Hydrocracking Results for Reduced and Sulfided
Catalysts Expressed in Terms of their Surface Area

catalyst	Sb ^a content	surface area m ² /g	% conversion after 4 hours.			
			reduced activity per m ²	reduced activity per m ²	sulfided activity per m ²	sulfided activity per m ²
AMW-19	0	116	79.9	4.6	83.2	4.8
AMW-20	0	113	76.4	4.5	85.0	5.0
AMW-16	1:50	98	70.4	4.8	84.8	5.6
AMW-18	1:50	99	70.0	4.7	73.9	5.0
AMW-23	1:50	106	74.1	4.7	83.8	5.3
AMW-21	1:30	102	60.6	4.0	78.3	5.1
AMW-22	1:30	100	61.3	4.1	77.2	5.1
AMW-24	1:10	91	48.1	3.5	50.9	3.7
AMW-25	1:10	94	44.2	3.1	47.2	3.3

^a number of Sb atoms per x Al atoms

Please note that the compositions are given in Table 6.1

Looking at the results which are expressed in terms of surface area (Table 6.7), it is apparent that the catalysts with the lowest antimony loadings (AMW-16, AMW-18) are as active (or more active) than those which contain no antimony. It can therefore be concluded that the loss of activity which is observed upon addition of antimony is entirely due to the associated surface area decrease. The antimony seems to act as a catalyst poison at higher loadings, possibly by blocking the active sites on the alumina surface, or reducing the dispersion of the catalytically active components.

6.7 CONCLUSION

It has been shown that the most effective manner to incorporate antimony oxide into an alumina lattice is by dry impregnation of the antimony oxide into boehmite. This is then calcined, and additional promoters, fluoride, molybdenum and nickel (or cobalt) are added in a step-wise fashion. This method of preparation yields catalysts with high activities towards cumene hydrocracking. The catalytic cracking activity observed for these catalysts is higher than that obtained for conventional Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts. However, it is lower than that observed for the catalysts which contain no antimony. This has been attributed to the loss of surface area which occurs when antimony is present. The surface area reduction is proposed to be caused by the antimony oxide sintering on the catalyst surface, decreasing the dispersion and collapsing some of the pore structure of the catalyst.

The x-ray photoelectron spectroscopy results indicate that the antimony is in a different chemical environment than before impregnation. However, it is apparent from the hydrocracking results and infrared spectroscopic studies that the catalysts containing antimony are no more acidic than those which contain fluoride alone. When the antimony is present in the lowest concentration, the catalyst is more active for hydrocracking per unit surface area. Upon increasing the antimony loading, the catalyst is deactivated.

The results which were obtained from the thiophene hydrogenolysis reactions indicate that the presence of antimony and fluoride is detrimental to the hydrodesulfurization reaction. It appears that the polarization of the lattice induced by fluoride addition (which improves the catalysts' hydrocracking ability by enhancing the proton donating character) reduces the hydrogenolysis ability. Although this decrease in hydrodesulfurization is important, it must be noted that in the hydrotreating of real feedstocks there must be a balance between the hydrocracking and hydrodesulfurization activities of a catalyst. The cracking of large molecules which are present in industrial feedstocks will expose more heteroatoms to the catalyst surface. The enhancement of hydrocracking ability of these catalysts over conventional $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts may offset the detrimental effects observed in the hydrodesulfurization reactions.

6.8 FUTURE WORK

It is apparent, from the results which have been obtained in this study, that the behavior of SbF_5 has not been emulated (by using Sb_2O_3 , fluoride addition and oxidation during preparation). Investigations should be launched into preparation methods utilizing SbF_5 , and stronger fluoriding agents such as HF , in an attempt to keep the superacidic functionalities on the catalysts¹⁶⁷.

Further experiments should be conducted into the continued reduction of antimony loadings on the catalysts. Recent reports involving elements in the same group as antimony (phosphorus and arsenic) on alumina-based catalysts suggest that low loadings (less than 2 wt. %) are desirable^{97,168}. Loadings of 0.5 wt. % P_2O_5 can lead to better dispersion of active components, and enhancement of hydrodesulfurization activities. At higher loadings, AlPO_4 forms and the surface areas of the catalysts reduce dramatically. Similar results reported for As_2O_5 show decreases in activity with increasing arsenic content (from 0.01 to 3.6 wt. %)¹⁶⁹. Arsenic alters the electronic structure of the Co-Mo-S phase due to interactions with Co. Loadings of ~1 wt. % Sb_2O_5 may be small enough to enhance both hydrodesulfurization and hydrocracking activities without having detrimental effects on the surface area.

The testing of these catalysts with real feedstocks is also important. It must be determined whether the advantages gained in hydrocracking outweigh the disadvantages observed to date in the hydrodesulfurization reaction. At the same time, studies can be

performed on catalyst lifetimes to see if any advantage is gained by using the additional promoters.

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