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Secondary Promoters in Alumina-Supported Nickel-Molybdenum Hydroprocessing Catalysts

by

Jenny Marie Lewis

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THE UNIVERSITY OF CALGARY FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Secondary Promoters in Alumina-Supported Nickel-Molybdenum Hydroprocessing Catalysts" submitted by Jenny Marie Lewis in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Abstract

Two secondary promoters, phosphorus and fluoride, have been investigated for their influences on the physicochemical properties of alumina-supported nickelmolybdenum hydroprocessing catalysts. Model compound reactions and infrared spectroscopy were used to probe the functionalities of the different catalysts, and the catalysts were also tested in the hydroprocessing of a low-nitrogen and a high-nitrogen (quinoline-spiked) gas oil feed to assess the utility of the model compound reaction studies.

Fluoride-promoted catalysts with high cumene hydrocracking activity, i.e. high surface Brønsted acidity, and with comparable thiophene hydrodesulphurisation (HDS) activity to Ni-Mo/Al₂O₃ can be prepared by coimpregnation of the F, Ni and Mo additives. This preparation method allows nearly quantitative retention of fluoride after calcination. Accelerated aging studies indicate that the metal additives promote coking of cyclohexene, while the F-associated Brønsted acid sites only promote coke formation of species which polymerize more easily, such as α -methylstyrene. Catalyst characterization methods indicate that the additives accumulate to some extent in the smaller pores of alumina and access to these sites by the model compounds is blocked through coke formation. Fluoride was found to promote both the hydrogenation (HYD) and HDS activity of Ni-Mo/Al₂O₃ in the hydroprocessing of a low-nitrogen feed. This is thought to be because sterically-hindered aromatic and thiophenic structures can be cracked on F-associated Brønsted acid sites, and are then better able to adsorb flat on hydrogenation sites. Fluoride promotes the quinoline hydrodenitrogenation (HDN) activity of Ni-Mo/Al₂O₃ catalysts, probably through the promotion of C-N bond cleavage reactions which are thought to occur on acid sites, but this reaction also leads to poisoning of these sites.

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Infrared studies of the phosphorus promoted Ni-Mo/Al₂O₃ catalysts indicate that H₃PO₄ modifies the surface hydroxyl distribution on alumina and also provides new hydroxyl groups. The interaction of Mo species with the H₃PO₄-modified surface was found to be very different to that with unmodified alumina and results in Mo species which are more easily converted to the active sulphide phase in HDS reactions. Impregnation of phosphorus prior to the metal additives results in catalysts which are more active in HDS because the Mo species are more easily sulphided, and probably because phosphate blocks sites on which catalytically-inactive NiAl₂O₄ may form, thereby allowing more Ni to be incorporated into the active "Ni-Mo-S" phase. Phosphorus also increases indirectly the Brønsted acidity of the catalyst by increasing the activity of the MoS₂-associated acid sites, which are of sufficient strength to crack diisopropylbenzene to cumene. Phosphorus promotes both the HDS and HYD activities of Ni-Mo/Al₂O₃ in the hydroprocessing of the low-N feed and the P-promoted catalysts cope well with the high-N feed. A promotional effect of phosphorus is also seen in quinoline HDN, probably as a result of increased HYD activity.

P- and F-promoted Ni-Mo/Al₂O₃ catalysts are very active in quinoline HDN and maintain good activity in HDS and HYD of the high-N feed. Preliminary studies suggest that these catalysts have increased acidity due to fluoride, but the addition of phosphorus tempers this acidity and also improves the HYD activity so that the acid sites are less susceptible to coking and poisoning.

Thiophene HDS was found to be a good reaction for probing the activity of catalysts in the HDS of sterically-unhindered molecules, but an inaccurate probe for the HDS of hindered compounds. Where direct comparisons were possible, the model hydrocracking reactions also provided a good indication of the hydrocracking activity of the catalysts for the real feeds.

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To Dave and Mum & Dad

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Symbols and Abbreviations

AEM Analytical electron microscopy AOSTRA Alberta Oil Sands Technology and Research Authority αMS α -methylstyrene Benz. Benzene BET Adsorption isotherm model proposed by S. Brunauer, P. H. Emmett and E. Teller CANMET Canada Centre for Mineral and Energy Technology c.u.s Coordinatively unsaturated DHQ Decahydroquinoline DIPB 1,3-diisopropylbenzene EtB Ethylbenzene EXAFS Extended X-ray fine structure FID Flame ionization detector F^{*}NiMoA1 F, Ni, Mo containing alumina-supported catalysts, Ni-Mo followed by F stepwise impregnation; asterisk indicates after which step the final calcination was performed FNiMo*A1 F, Ni, Mo containing alumina-supported catalysts, F followed by Ni-Mo stepwise impregnation FNiMoA1 Coimpregnated F, Ni, Mo containing alumina-supported catalysts FTIR Fourier-Transform infrared spectroscopy FT-nmr Fourier-Transform nuclear magnetic resonance GC Gas chromatography GC-MS Gas chromatography - Mass spectrometry H:C Hydrogen-to-carbon ration

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HDN	Hydrodenitrogenation
HDS	Hydrodesulphurization
H-Oil	Hydrocarbon Research Incorporated H-Oil (heavy oil) process,
	currently owned by Husky Oil
HP	Hewlett Packard
HREM	High resolution electron microscopy
IR	Infrared
LC-Finer	Lummus Crest Inc. licenced hydrocracking process
MoAl	15 wt% MoO ₃ /Al ₂ O ₃ catalyst
NiAl	3.0 wt% NiO/Al ₂ O ₃ catalyst
nmr	Nuclear magnetic resonance
nPB	<i>n</i> -Propylbenzene
OPA	o-Propylaniline
PB	Propylbenzene
РСН	Propylcyclohexane
PFM	Phosphorus, fluoride and Ni-Mo containing catalyst (order of
	stepwise impregnation indicated)
PMF	Phosphorus, Ni-Mo and fluoride containing catalyst (order of
·	stepwise impregnation indicated)
psi	Pounds per square inch
Q	Quinoline
RRF	Relative response factor
SCĊ	side-chain-cracked products of cumene (excluding benzene)
STP	Standard temperature and pressure (0 °C and 1 atmosphere)
Syncrude	Synthetic crude oil
TCD	Thermal conductivity detector

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THN	Tetrahydronaphthalene
TISAB IV	Total ionic strength adjustor buffer - developed by ORION Research
1THQ	1,2,3,4-Tetrahydroquinoline
5THQ	5,6,7,8-Tetrahydroquinoline
UV-VIS	Ultraviolet-visible spectrophotometry
vol%	Volume percent
wt%	Weight percent
xFNiMoAl	Coimpregnated F, Ni, Mo containing alumina-supported catalysts; x
	gives the wt% F present
xNiMoP _y	Ni, Mo, P containing catalyst; x gives the preparation method used as
	described in the Experimenal Section and y gives the wt% P present
xPAl	H ₃ PO ₄ /Al ₂ O ₃ catalysts; x gives the wt% P present
XPS	X-ray photoelectron spectroscopy
Ia	Type Ia hydroxyl of alumina - OH bonded to one tetrahedral Al
	centre
Ib	Type Ib hydroxyl of alumina - OH bonded to one octahedral Al
ι,	centre
Π	Type II hydroxyl of alumina - OH bridging one tetrahedral Al centre
	and one octahedral Al centre or two octahedral Al centres
Ш	Type III hydroxyl of alumina - OH triply-bridging three octahedral Al
	centres

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Chapter 1: Introduction

1.1. Upgrading Methods

Canada has vast deposits of bitumen in the Alberta Oil Sands. It has been estimated that they contain approximately 151 billion cubic metres of bitumen, a resource 17.5 times larger than the conventional crude oil deposits in Canada(1). Approximately 10 % of this deposit can be surface mined (up to a depth of 45 m) and is done so by Suncor Inc. and Syncrude Canada Ltd. Because of its viscous nature, bitumen lying deeper than 45 m must be recovered by *in situ* techniques, and a great deal of research has been and is still being conducted to develop these techniques.

The recovered bitumen must undergo primary upgrading to reduce its viscosity before it can be pumped through a pipeline to distant refineries. There are two basic methods for upgrading bitumen and heavy oils, coking and hydrocracking. A third method, fluid catalytic cracking is a widely used refining method, but it is generally used for cleaner feeds. All these methods improve the liquid product quality by increasing the H:C ratio, removing metals and some sulphur and nitrogen compounds and decreasing the viscosity. The first method, coking, is a so-called carbon rejection process, while the second method, hydrocracking, is a hydrogen addition method.

Coking is a thermal process in which the feed is heated at high temperature in order to crack large molecules into smaller ones by mechanisms which involve free radicals. Some of the radicals produced by thermal cracking abstract hydrogen from other molecules to form lighter products which are distilled off. Other radicals combine to form even heavier molecules, i.e. coke. In delayed coking, the feed is heated in a large drum at around 465 °C for long residence times to allow the cracking reactions to

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go to completion(2). To enable continuous operation two coking drums are used; while one is on stream the other is cleaned of the coke which builds up on its inner surface. This coking method is used by Suncor Inc. at their plant near Fort McMurray.

In delayed coking about 23 wt% bitumen is lost as coke. This is an unusable by-product because of its high metals content and it can be environmentally unfriendly. Consequently, from an economic viewpoint it is desirable to have high liquid yields and low coke yields. Fluid coking can achieve this to some extent. In this process the bitumen is sprayed into a bed of coke particles which are fluidized by means of steam blown upwards from the bottom of the reaction vessel. This is operated at much higher temperatures (530 °C) and the contact time is much shorter than that used in delayed coking. As a result the cracked, smaller molecules are removed from the reactor before they can recombine to form coke. The fluidized coke particles eventually grow in size from the deposited coke and settle to the bottom of the reactor where they can be removed without shutting down operation. Consequently fluid coking is a continuous process. Fluid coking of partially-topped bitumen together with hydrocracking is used by Syncrude Canada Ltd. at Mildred Lake in their "LC-Finer" process.

The liquid yields can be increased substantially if hydrogen gas is added to the bitumen at elevated pressures and at a temperature of 430-470 °C. This method, hydrocracking, is particularly useful for converting the undistillable bitumen material (vacuum bottoms or residues) to lighter products. Usually hydrocracking is done in the presence of a catalyst such as in Husky Oil's "H-Oil" process, Syncrude's "LC-Finer" process, and in the CANMET hydrocracker. Both the H-Oil and LC-Finer processes use ebullated bed hydrocrackers in which the catalyst bed is dispersed in the liquid residue and expanded by bubbling hydrogen and liquid feed through the system.(3) The catalyst can be added and withdrawn from the reactor without interrupting operations. The

hydrocracking processes require catalysts with cracking and hydrogenation components. These acid catalysts are optimized for the type of feedstock and are usually based on silica-alumina or zeolite-supported Pt, Pd, Ni, Co, Mo, and W catalysts(4) although the CANMET process utilizes a cheap iron/carbon catalyst.

Because it is produced from thermal methods the chemical nature of the primary upgraded product is quite different from that of conventional crude oil. In particular, all fractions (i.e. Naptha (82-177 °C), Mid-Distillates (177-343 °C) and Gas Oil (343-525 °C)) are higher in S and N contents than those specified for subsequent refining steps(5). Therefore, the primary upgrading product must be further upgraded to decrease the sulphur and nitrogen content. At the same time product quality can also be improved in other ways, for example, by decreasing the aromaticity of the middle-distillate fraction which is important for the production of jet fuels. This second upgrading method is called hydroprocessing and involves the selective hydrogenation of C-N and C-S bonds (hydrotreating), together with further C-C bond breaking (hydrocracking) to convert higher boiling feedstocks into lower boiling ones. The product obtained from this second upgrading method is synthetic crude oil or syncrude. Hydroprocessing is carried out at temperatures of 300-450°C and hydrogen pressures of 700 to 2800 psi(6). Conventional catalysts used for hydroprocessing are alumina-based Mo or W catalysts promoted by Ni or Co. The requirements of hydroprocessing catalysts are discussed in the next section.

1.2. Hydroprocessing Catalysts

There are a number of requirements which must be met by hydroprocessing catalysts. The chemical requirements include the need for cracking, hydrogenation,

hydrodesulphurisation (HDS, sulphur removal) and hydrodenitrogenation (HDN, nitrogen removal) components. The physical requirements include the need for a cheap, high surface area, porous support material which allows a high dispersion of the chemical functionalities, and which allows easy diffusion of feed molecules to these sites. Also, the catalyst must have good thermal stability since it has to survive long times on stream and rigorous regeneration methods. In addition the catalyst should have good mechanical properties. For example, the catalyst powder or paste is often pelletized by extrusion and therefore requires suitable rheological properties; also these pellets must have high resistance to attrition (abrasion). The chemical components of the catalyst are of more interest in this research work and are therefore discussed in more detail.

A schematic representation of a hydroprocessing catalyst is given in Figure 1.2.1. It consists of a high surface area support material upon which the active metals are dispersed. Cracking reactions are generally accepted to occur on Brønsted acid sites which are provided by the support itself. The conventional support material, γ -alumina, possesses surface hydroxyl groups and these may be transformed into acidic Brønsted acid sites by the addition of certain additives. For example, H₂SO₄, F⁻, Cl⁻ and H₃BO₃ all increase the hydrocracking activity of the support (7,8). There are two factors which influence the hydrocracking activity of the support - the quantity and the strength of the acid sites. In general, the greater the number of acid sites the more active the catalyst will be in hydrocracking, while the acid strength will determine the types of products obtained(9).

The hydrogenation component of the catalyst is commonly provided by a group VIB metal, namely Mo or W. The HDS and HDN activities can be increased substantially if small amounts of Group VIIIB metals (Co or Ni) are introduced.



Figure 1.2.1: Depiction of a hydroprocessing catalyst

Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts are the most widely used, with Co-Mo having higher HDS activity and Ni-Mo having higher HDN activity(10).

The metal components are usually introduced to the support as aqueous salt solutions by a method known as incipient wetness impregnation. In this method the total volume of water used for the solutions is equal to the pore volume of the support and so just fills the pores with the impregnating solutions. The metal salts are then converted to their respective oxides by calcination, i.e. by heating in a flow of air at 450-500 °C(11). The active forms of the metal additives for HDS and HDN are the sulphides, MoS₂ and WS₂, the activities of which are increased by the Co or Ni promoter metal sulphides. The metal oxides are usually converted to the metal sulphides *in situ*, a process which can, itself, determine the activity of the catalyst(12-14). More detail of this is given in the next section which discusses the nature of the active sites in HDS and HDN.

Other additives besides the metal sulphides may also be present in hydroprocessing catalysts. Additives which improve the cracking activity of the catalyst have already been mentioned. In addition, species which increase the hydrogenation, HDS or HDN activities, for example by increasing the metals dispersions, can also be present. These additives are called secondary promoters, Co and Ni being the primary promoters. More will be said about these additives in the following sections.

1.3. Models for Active Sites

Heterogeneous catalysts for hydroprocessing are extremely complex systems and there are few techniques which can be used to study their surface structure *in situ* together with their chemical reactivity. Therefore, determining the active sites for reactions such as HDS and HDN has been no trivial matter. The understanding of these catalysts has been gained through measurements of catalyst activity (for example, refs. 15-20), the study of model metallic complexes and bimetallic cluster compounds (for example, refs. 21-25) and through chemisorption studies(25-29) and the use of spectroscopic techniques. The spectroscopic techniques include: Infrared and Raman spectroscopies(29-33); a host of ultra-high vacuum techniques(34,35) such as X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS)(36,37); high resolution and analytical electron microscopies (HREM and AEM)(38); and Mössbauer emission spectroscopy(32,39,40). The latter technique has proved to be extremely useful in studying sulphided Co-Mo/Al₂O₃ catalysts *in situ* and has lead to many recent advances. There is such an intensive research effort in this area that there are frequent reviews in the literature (for example, refs. 41-46).

MoS₂ forms hexagonal platelets on the surface of alumina, either bonding through the basal planes or through edges, as seen by HREM(47,48) and as depicted in Figure 1.2.1. The edge sites of these MoS₂ crystallites are those responsible for the catalytic activity of MoS_2 in HDS(46). Doping catalysts with radioactive ⁵⁷Co allows the study of the promoter environment in the catalyst by Mössbauer emission spectroscopy. This technique can be used in situ since the high-energy γ -rays can easily penetrate the catalyst under reaction conditions. This technique has allowed the identification of the different sulphided Co-species on the Co-Mo/Al₂O₃ catalyst(40). In addition to cobalt aluminate and cobalt sulphide (Co_9S_8) another phase, which has been termed Co-Mo-S was also found. This Co-Mo-S phase is proposed to consist of cobalt located in the edge sites of MoS₂ crystallites, as is depicted in Figure 1.2.1. EXAFS has confirmed that the Mo in Co-Mo-S resembles Mo in $MoS_2(45)$. Also, AEM has confirmed that Co is located in the edge sites of the MoS₂ platelets(49,50). These Co-Mo-S sites are very active in HDS(45) and are thought to be responsible for the

promotional effect of Co in MoS_2/Al_2O_3 catalysts in HDS. There is evidence that the analogous nickel promoted MoS_2/Al_2O_3 system has a similar catalytically important Ni-Mo-S phase(51,52).

There is some dispute, however, as to whether the Mo atoms in Co-Mo-S (or Ni-Mo-S) play a direct role in catalysis, and it has been suggested that MoS_2 may just be a 'support' for generating active Co sites.(17,53). This is because highly active Co/C catalysts can be prepared(54). Cobalt in the Co-Mo-S phase and in sulphided Co/C catalysts has been linked to cobalt in an octahedral environment, and therefore the fraction of octahedral cobalt in these catalysts correlated well with the HDS activity(55).

In the sulphided Co-Mo and Ni-Mo/Al₂O₃ systems some of the Mo atoms in MoS_2 crystallites remain bonded to the support by Mo-O-Al bonds, probably via bonding of the edges of the MoS_2 platelets(45), and these bonds may be broken by sulphiding at high temperature (875-1275 K) to form even more active HDS catalysts. The low temperature sulphided phase has been termed Type I Co-Mo-S, while the high temperature sulphided, high activity phase is termed Type II Co-Mo-S. This Type II phase is thought to form more easily on inert support materials such as carbon(45).

From the foregoing discussion the use of secondary promoters may be recognized; they can (i) change the interaction between MoO_3 and Al_2O_3 so that the dispersion (and therefore size) of MoS_2 crystallites is modified and the total number of edge sites controlled, (ii) prevent the formation of inactive cobalt (or nickel) aluminates so that more promoter atoms occupy MoS_2 edge sites, (iii) provide new catalytic sites.

<u>1.4. Project Overview</u>

The objectives in this project were to examine the effect of two secondary promoters, F and P, on the activity of Ni-Mo/Al₂O₃ in hydroprocessing reactions. Ni-Mo, as opposed to Co-Mo/Al₂O₃, was studied since the former is more active in HDN. In the hydroprocessing of real feeds particular problems are posed by nitrogen compounds which are not effectively removed by Co-Mo/Al₂O₃ and which poison acidic reforming catalysts used further downstream.

As mentioned earlier, fluoride increases the Brønsted (and Lewis) acidity of alumina, and thus provides new catalytic sites for hydrocracking. It was of interest to examine the effect of this increased acidity in other hydroprocessing reactions such as HDS and HDN, and also the deactivation properties of these catalysts compared to less acidic ones (Chapter 3).

Phosphorus on the other hand promotes HDS and HDN reactions but it is still unclear as to whether it increases the number or the strength of active sites (and how this is achieved), or if it also provides some new (i.e. different) catalytic sites, such as hydrocracking or hydrogenolysis (C-S, C-N bond cleavage) sites. This then was another objective of this work - to examine the influence of P on Mo and Ni impregnation, sulphidibility and reactivity in HDS (and HDN), and its effect on the surface acidity of alumina (Chapter 4).

Since phosphorus promotes heteroatom removal and fluoride promotes hydrocracking, it was also of interest to see if both these properties could be merged in catalysts containing both P and F (Chapter 5).

The catalysts were studied using infrared spectroscopy to examine the surface interaction between phosphorus and metal additives, model compound hydrocracking and HDS reactions to test the reactivity of specific sites, and real feed hydroprocessing. The feeds used in the latter case were a gas oil and the same gas oil spiked with quinoline; a nitrogenous base, to probe the catalytic activity in HDN (Chapter 6).

More detailed discussions of previous research carried out in each of these areas are given at the start of each chapter or section.

Chapter 2: Experimental Methods

<u>2.1. Catalyst Preparations</u>

All catalysts were prepared using the incipient wetness method. Salts of the additives were dissolved in a volume of water no greater than the pore volume of the γ -alumina support (0.5-0.6 mL g⁻¹), and then impregnated onto the dry support material. The total volume of water used was approximately the same in all cases (0.55 ± 0.05 mL g⁻¹). The source of Mo, Ni, F and P were (NH₄)₆Mo₇O₂₄.4H₂O (Fisher Scientific), Ni(NO₃)₂.6H₂O (Baker Chemicals), NH₄F (Fisher Scientific) and 85% H₃PO₄ (Fisher Scientific) respectively. Unless stated otherwise, the amounts of these salts used were equivalent to 15 wt% MoO₃, 3 wt% NiO, and varying F and P content; these were relative to the mass of the γ -alumina support only, i.e. there was no correction of weight percent as a consequence of the other additives present. Conversion of the salts to the respective metal oxides or desired surface species was acheived by heating the sample under a flow of air at 4 °C min⁻¹ to 475 °C and then holding this temperature for 4 h, unless otherwise specified. Catalysts were usually prepared in 10 g batches. The different catalysts studied are outlined in the following section and any difference to the procedure described here is explained.

2.1.1. γ -alumina Support

The support material in all the catalysts studied was γ -alumina which was prepared from boehmite as follows: 50 g boehmite (α -AlOOH) (Alfa Products, 40 μ m, 90 % Al₂O₃, 9 % H₂O) was mulled for 3-5 min with 16 mL distilled water. A further 10 mL distilled water was added in 5 mL portions with mulling for 3-5 min after each addition. The powder was left to dry in air at room temperature overnight before being

dried at 120 °C overnight. Finally the powder was calcined by drawing air through it while heating at 4 °C min⁻¹ to 500 °C and then holding this temperature for 4 h. The formation of γ -alumina was confirmed by X-ray powder diffraction and the surface area was 190-200 m²g⁻¹.

2.1.2. Fluoride Promoted Catalysts

F/Al₂O₃:

Two catalysts with nominal loadings of fluoride of 3.6 and 6.9 wt% were prepared. Calcination was achieved at 475 °C for 2 h.

Ni-F,

 $Mo-F/Al_2O_3$:

These two catalysts were prepared by addition first of the metal salt solution to the alumina, followed by the fluoride salt solution, with mulling between each addition. They were dried and calcined as described in Section 2.1.

Ni-Mo-F/Al₂O₃: Catalysts containing 0, 1.8, 3.6 and 6.9 nominal wt% F were prepared by simultaneous impregnation of the additive salts; Mo followed by Ni, followed by F, with mulling for 1 - 2 min after each addition. Drying and calcining was performed as described earlier. In addition, two catalysts containing 3.6 wt%F were also prepared by stepwise impregnation of the additives for comparison. In the first case, a Ni-Mo/Al₂O₃ catalyst was made, as described above, and F⁻ impregnated onto this and dried and calcined at 475 °C for 2 h for this second calcination step. In the second case, the metal salts were impregnated onto F/Al₂O₃ (calcined 2 h) and dried and calcined as usual.

2.1.3. Phosphorus Promoted Catalysts

 P/Al_2O_3 :

Catalysts with phosphorus loadings of 0 - 7 wt% P were prepared

by impregnating γ -alumina with H₃PO₄ solutions which had been adjusted to pH 2 by the addition of NH₄OH solution. Calcination was at 475 °C for 4 h.

 $Mo-P/Al_2O_3$:Catalysts containing 0 - 4.9 wt% MoO_3 supported on γ -Al_2O_3 oron 1 wt%P/Al_2O_3 were prepared by the impregnation of the metalsalt onto the relevant support material followed by calcining for 2h at 475 °C.

Ni-P,

 N_i/Al_2O_3 : These catalysts containing 3.0 wt % NiO were prepared in an analogous manner to the Mo-P/Al₂O₃ catalysts.

Ni-Mo-P/Al₂O₃: Three series of Ni-Mo-P catalysts were prepared with varying phosphorus contents of 0 - 7 wt%. In Method 1 all three additives were dissolved in the <u>same</u> impregnating solution; in some cases a few drops of nitric acid was added to stabilize the impregnating solution. In Method 2 three separate impregnating solutions were used and the catalysts were calcined prior to (4 h) and after (2 h) the addition of H_3PO_4 . In Method 3 separate impregnating solutions were used but the phosphoric acid was added first (calcined 4 h), then the metal salts added and calcined for 2 h.

2.1.4. Phosphorus and Fluoride Promoted Catalysts

Ni-Mo-F-P/

 Al_2O_3 :

Two series of catalysts containing 3.6 nominal wt % F and varying P contents (0 - 3 wt%) were prepared by a summer student, Phyllis H. Van Rhyn. In the first series the order of addition was P then Ni-Mo then F with a drying and calcination step after each

addition (2 h, 4 h, 2 h calcination times respectively). In the second series the order of addition was P then F then Ni-Mo with drying and calcination steps after each addition (2 h, 2 h, then 4 h calcination times).

2.2. Model Reaction Studies

2.2.1. Cumene Cracking and Hydrocracking

Cumene cracking and hydrocracking have been used extensively as model reactions for probing catalyst surface acidities (56-63). Cumene undergoes different reactions on different sites on the catalyst surface as shown in Figure 2.2.1. The



Dehydrogenation

Cracking (Acid Sites)

(Metal Sites)

Figure 2.2.1: Major products in cumene cracking and hydrocracking reactions

formation of benzene is a particularly useful probe of the surface acidity of the catalyst, since cracking of cumene to benzene occurs on Brønsted acid sites(64).
A suitable temperature program for separating the different products was determined and is shown in Figure 2.2.2. The detector response factors to each of the



Figure 2.2.2: Separation of cumene reaction products

major products and to cumene were determined by injection into the gas chromatograph of toluene and cyclohexane solutions containing known amounts of the different products. Then, plots of moles of substance versus area (from the GC traces) could be constructed, the slopes of which gave the detector response factors (mol/unit area). By dividing all response factors by that for cumene, relative response factors (RRF's, relative to cumene) were obtained. These are summarized in Table 2.2.1 together with the retention times of the different compounds. Thus, the relative number of moles of a particular substance produced in the cumene cracking or hydrocracking reaction is obtained by multiplying the area under the GC trace for the substance by the RRF for that substance. The yield of a particular product is given by:

Product Area x RRF

 Σ (Area of Aromatics x RRF) (except cumene)

- 15 -

and

Substance	RRFª	Retention Time (min)
Benzene	1.371	2.6
Ethylbenzene	1.058	6.6
Cumene	1.000	8.2
α-methylstyrene	1.106	10.7

 Table 2..2.1:
 Cumene reaction product RRF's

^aRRF=Relative Detector Response Factor

Cumene Conversion = $\frac{\Sigma(\text{Area of Aromatic x RRF})(\text{except cumene})}{\Sigma(\text{Area of Aromatic x RRF}) (\text{including cumene})}$ assuming that the benzene ring is not cracked.

The cumene was used as supplied from Eastman Kodak. The major impurity was ethylbenzene (< 1% from the GC). Prior to performing a catalytic reaction, gas chromatograms of the starting cumene reactant were obtained and the amounts of impurities determined. These areas were subtracted from the areas of the corresponding product peaks in the reaction in order to correct for the impurities.

The catalyst testing was carried out in a stainless-steel continuous-flow, fixed-bed microreactor operating at 400 °C and approximately atmospheric pressure. The reactor (15 mm i.d.) contained 0.150 g catalyst (80-100 mesh) between layers of quartz wool. Activation of the catalysts was achieved by heating at 500°C for 90 min under the appropriate gas (He for the oxide forms, H₂ for pre-reduction and 10% H₂S/H₂ for pre-sulphidation) at a flow rate of 30 mL min⁻¹. Cumene was admitted to the reactor from a presaturator held at 20 ± 2 °C in a stream of the required gas. Under cracking conditions the sweep gas was He, while under hydrocracking conditions the sweep gas was H₂. The products were analysed every 20 min by an on-line gas chromatograph (HP 5890, TC Detector; column description: 10m length x 0.53mm i.d. x $2.0\mu m$ film thickness, 50% phenyl 50% methyl polysiloxane (HP-17)).

Under hydrocracking conditions one other minor product, in addition to those shown in Figure 2.2.1 was observed over certain catalysts. This was identified as npropylbenzene on the basis of GC-MS of the product mixture (HP5890 GC equipped with HP5970 mass selective detector). Two other minor products were sometimes seen under cracking conditions; these have been identified in our laboratory as omethylstyrene and o-ethyltoluene(65).

2.2.2. Thiophene Hydrodesulphurisation (HDS)

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The types of sulphur compounds present in petroleum feedstocks include thiols, disulphides, sulphides, thiophenes, dibenzothiophenes, benzonaphthothiophenes *etc.*(66). Generally, the heavier the sulphur compound the less reactive it is towards HDS. Thus, thiols are very reactive whereas thiophenes are much less reactive. Both benzothiophene(67-71) and thiophene(54,67,68,72-77) have been widely used as model compounds for studying the HDS characteristics of hydroprocessing catalysts. Some of these studies have compared the reactivities of thiophene and dibenzothiophene(67,68) but few have compared the model compound reactivities with those of real feeds over the same catalysts(78).

Thiophene HDS is the most commonly used model compound reaction since atmospheric H_2 pressures are sufficient for easily measurable conversions. The usual products in thiophene HDS are butenes and butane, while some authors observe trace amounts of butadiene, and tetrahydrothiophene has only been observed at higher H_2 pressures(79). Numerous mechanisms for thiophene HDS have been proposed on the basis of model reaction studies(72,80-83) and these have been reviewed recently by Prins <u>et al</u>.(46).

In our model thiophene HDS studies the C_4 products were not separated by the GC conditions used. However, detector response factors to 1-butene, cis- and trans-2butene and n-butane were found to be very similar. These were determined by injecting known volumes of the gaseous products into the GC and integrating the peak areas. They are listed in Table 2.2.2 together with detector response factors to thiophene and tetrahydrothiophene. Since the detector response to thiophene was an order of

Compound	mol/Area (x10 ⁻¹⁴)	Retention Time (min)			
Thiophene	5.75	0.88			
Tetrahydrothiophene	0.40	1.38			
Butane	0.12	0.37			
1-Butene	0.13	0.39			
cis-2-Butene	0.13	0.39			
trans-2-Butene	0.13	0.39			

 Table 2.2.2: Detector response factors to possible thiophene HDS products

magnitude better than that to the C_4 products, and since no tetrahydronaphthalene was observed in our catalytic studies, and since the thiophene used (Aldrich Chemicals) had high purity as seen by GC, the % thiophene HDS was calculated as:

100 - % Thiophene out (exit stream) = % C_4 out

Early thiophene HDS studies (Fluoride work, Chapter 3) were carried out in a reactor similar to that used for the cumene reactions but equipped with a 500 μ L sampling loop in a gas sampling valve. Injections were made every 15 min into an on-

line gas chromatograph (Varian 3700, FI detector; column description: 10 m length x 0.53 mm i.d. x 1.33 μ m film thickness, carbowax 20M (HP-20M)) at 50 °C under isothermal conditions. The thiophene was contained in a presaturator at 15 ± 1 °C and was passed over the catalyst at 400 °C in a stream of H₂ at a total gas flow of 30 mL min⁻¹. The sulphiding procedure was the same as that used in cumene hydrocracking.

Because of integrator problems, in later studies (Phosphorus and P-F work, Chapters 4 and 5) the cumene reactor system was also used to carry out the thiophene HDS reactions so that a different detector and column were used (see Section 2.2.1). The presaturator and reaction temperatures were the same and an isothermal GC temperature of 50 °C was employed as described above. The % conversion in these later studies was consistently higher by about 4-6 % which appeared to be a result of more thermal HDS occurring on the "cumene" reactor system.

2.2.3. m-Diisopropylbenzene Cracking and Hydrocracking

1,3-Diisopropylbenzene (DIPB) is much more reactive in dealkylation than cumene(7) and so provides a more sensitive probe of surface acidity; i.e. DIPB dealkylation can occur on weaker Brønsted acid sites than cumene dealkylation. The products of DIPB cracking and hydrocracking are given in Figure 2.2.3.

Cumene and α -methylstyrene were easily identified by addition of samples of these compounds to the trapped product mixture and analysis by GC. The remainder of the products in Figure 2.2.3 were identified by GC-MS of the product mixture. The identity of 1-n-propyl-3-isopropylbenzene was confirmed by nmr decoupling experiments of the product mixture: The ¹H nmr of the product mixture (Bruker AC 200 Spectrometer) showed triplets at 2.48 and 0.93 ppm and a multiplet at 1.61 ppm due to the n-propyl group; upon irradiating at 1.6 ppm, the two triplets collapsed to form two singlets, thus confirming n-propyl connectivity.



Figure 2.2.3: 1,3-Diisopropylbenzene reaction products

The two dehydrogenated products of DIPB are the major products under cracking conditions, while cracked and rearranged products predominate under hydrocracking conditions. If sufficient cumene is formed then small amounts of α -methylstyrene are observed. Detector response factors were not calculated for the products due to the unavailability of some of the compounds; this does not affect the trends in yields of products over different catalysts however.

The catalyst testing procedure was similar to that used in the cumene model reactions. The DIPB was held in a presaturator at 20 ± 1 °C and the products analysed every 30 min by on-line GC. The DIPB conversion is defined as the sum of all aromatics except DIPB divided by the sum of all aromatics including DIPB, as determined from the gas chromatograms (areas). Similarly, the yield of a particular aromatic product is defined as the area of that product peak divided by the sum of all

areas due to aromatics, including DIPB. This assumes that cracking of the benzene ring does not occur under the conditions of the experiments.

2.3. Catalyst Characterization

2.3.1. Surface Area Measurements

The surface areas were measured by the BET method using a Micromeritics high speed surface area analyser after degassing the samples for 30 min at 200 °C. The BET equation(84) is given by :

$$\frac{P}{V_s(P_o - P)} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_o}$$

where P = equilibrium pressure, V_s = volume adsorbed at S.T.P. of gas, P_o = vapour pressure of adsorbate at temperature of adsorbant, V_m = volume at S.T.P. of gas required to form a monolayer and C = Constant. A plot of P/V(P-P_o) vs P/P_o is linear in the range P/P_o = 0.05 to 0.35, and the sum of the slope and intercept is equal to $1/V_m$. Since the area occupied by an N₂ molecule is known accurately (0.162 x 10^{-18} m²) the surface area of the sample may be calculated from the monolayer volume if the mass of the sample is measured.

The surface area analyser used measures one point on the adsorption isotherm only, at $P/P_o = 0.30$, and assumes the plot $P/V(P-P_o)$ vs P/P_o passes through the origin, and thus calculates the slope based on this one measurement. The error in V_m as a result of ignoring the intercept increases as the surface area of the sample increases, up to 1.5 cm³ for a surface area of 300 m²g⁻¹. However, a correction is made for this so that the actual error is reduced to about 0.1 cm³. Even so, the reproducibility of the measured surface areas was determined to be of the order of $\pm 5 \text{ m}^2\text{g}^{-1}$.

2.3.2. Pore Size Distribution Measurements

Some of the catalysts were characterized by mercury porosimetry using a Quantachrome Autoscan 60. The measurements were made by Sunil Chaudrhy at Nova Husky Research Corporation. Mercury is forced into the pores of the catalysts at increasing pressure increments, and the radii of the pores (r) is related to the pressure (P) by:

$$r > \frac{2 \gamma |\cos \phi|}{P}$$

where γ =surface tension of mercury; ϕ =contact angle between mercury and solid. From the volume taken up at each pressure interval, pore size distribution plots (dV/dr vs r) may be obtained.

2.3.3. X-Ray Powder Diffraction

X-Ray diffraction powder patterns of the γ -alumina and the P/Al₂O₃ catalysts were determined using a Norelco X-ray diffractometer with graphite monochromated Fe-K_{α} radiation.

2.3.4. Fluoride Analysis

The fluoride analysis was performed by measuring the voltage sensed by a fluoride-sensitive electrode in a solution containing the digested catalyst sample and a TISAB IV buffer, and comparing this to standard solutions prepared in the same way by the digestion of γ -alumina. Plastic vessels were used throughout the analysis since fluoride reacts with glass, and prior to the digestion, the catalyst samples were dried at 100 °C overnight and cooled and stored in a desiccator. The procedure followed for the digestion of the alumina catalyst samples was similar to that described by Swift and Schaefer(85). The finely powdered sample of weight equivalent to approximately 50 mg

 γ -alumina (i.e. account is taken of the metal loadings to try an maintain a constant concentration of Al³⁺ in the analyte solutions) was weighed into a clean, dry porcelain crucible. Then 0.25 g Na₂CO₃ was added and the two solids mixed with a glass rod. A further 0.25 g Na₂CO₃ was weighed into a nickel crucible and spread evenly over the base of the crucible. The sample-Na₂CO₃ mixture was transferred to the centre of the nickel crucible. NaNO₃ (0.25 g) was weighed into the porcelin crucible and mixed with any remaining sample particles before also being transferred to the centre of the nickel crucible. Finally, 0.5 g NaOH pellets was added and the crucible tapped so that the pellets settled into the mixture.

The crucible was placed on a triangle and heated (lid on) slowly under a bunsen flame until all the solids had melted. The crucible was then allowed to cool (lid on) and the solidified melt dissolved in 5 mL water and transferred using a plastic pipette to a plastic bottle. 95 mL TISAB IV was added as a buffer and Al³⁺ complexing agent. (This was also used to rinse out the nickel crucible.)

The standard solutions were prepared in a similar fashion using γ -alumina and dissolving the solidified melt in 5 mL of a sodium fluoride standard solution. A calibration curve of mV versus F⁻ concentration could be constructed from the readings obtained using the fluoride-sensitive electrode in the standard solutions. Thus the concentration of F⁻ in the analyte solutions could be determined from the response of the electrode in these solutions.

2.3.5. Phosphorus Analysis

Catalysts were analysed for phosphorus by the phosphovanadomolybdate method(86). Firstly, the catalysts were digested in a hot mixture of concentrated HF and $H_2SO_4(87)$. The powdered sample (0.5 g) was weighed accurately into a Teflon beaker. At the same time a similar amount was weighed into a crucible and placed in an oven at

110 °C overnight to assess the moisture content. To the sample in the teflon beaker, 20 mL conc. H_2SO_4 and 10 drops of conc. HF was added slowly. A further 5 mL conc. HF was added and the mixture heated (and stirred) in an oil bath at around 80 °C for about 2 h. After this time there was, in most cases, still sample remaining and so the solution was cooled on ice and a further 10 mL conc. HF added dropwise, before being heated again at 80 °C overnight. This was always sufficient to dissolve all of the catalyst sample. After this time 20 mL H₂O was added slowly and the solution heated at 80 °C for at least 2 h to drive off HF. The solution was then transferred, while hot, to a 100 mL volumetric flask and allowed to cool before being made up to the mark with water and then transferring to a plastic bottle for storage.

The ammonium vanadate solution was prepared by dissolving 0.625 g NH_4VO_3 in 125 mL hot water and adding 5 mL conc. HNO₃. Upon cooling the solution was diluted to 250 mL in a volumetric flask. The ammonium molybdate solution was prepared by dissolving 12.5 g (NH_4)₆Mo₇O₂₄.4H₂O in warm water and diluting to 250 mL in a volumetric flask upon cooling.

The standard phosphorus solutions were prepared by dissolving accurately weighed amounts of KH_2PO_4 (equivalent to 5, 10, 15 and 20 mg P) in water in 100 mL volumetric flasks, adding 20 mL conc. H_2SO_4 and diluting to the mark. The H_2SO_4 was added since this was also present in the samples.

5 mL of standard <u>or</u> sample solutions + 25 mL H_2O + 5 mL $NH_4VO_3(aq.)$ + 5 mL $(NH_4)_6Mo_7O_{24}(aq.)$ were pipetted into a 50 mL volumetric flask and diluted to the mark. The absorbance at 465 nm was determined on a Cary 16 UV-VIS spectrophotometer against a blank prepared in the same manner.

2.3.6. OH Groups by Fluoride Exchange

The method used to measure the exchangeable OH groups on the surface of γ -

alumina and P/Al₂O₃ catalysts was similar to that used by Yamagata <u>et al.</u>(88). A 0.4 g catalyst sample was put in 10 mL of an aqueous solution of NH₄F (0.0572 M) and left for 3-4 days with occaisonal shaking. To 5.0 mL of the filtrate 5.0 mL of TISAB IV was added and the fluoride remaining in the filtrate measured using a fluoride-sensitive electrode; this is where the procedure differed to that used by Yamagata <u>et al.</u>(88). The difference between the initial and final fluoride ion concentrations is equal to the number of exchanged surface OH groups.

2.4. Spectroscopic Studies

2.4.1. OH Region Investigations

The infrared spectra were recorded on a Nicolet 8000 FT-IR spectrometer, at 2 cm⁻¹ resolution, using a liquid-nitrogen cooled InSb detector. Approximately 15 mg of powdered catalyst was pressed into a self-supporting wafer (10,000 psi for 2 min) and mounted in a cell for pretreatment. The cell design was such that four wafers could be treated simultaneously, and also, infrared spectra could be recorded without contacting the catalyst wafers to the atmosphere. For the P/Al_2O_3 samples the pretreatment conditions were as follows: First the wafers were cleaned overnight under $\frac{1}{2}$ atm. O₂ at 600 °C. They were then evacuated for 24 h at 700 °C whereupon a vacuum of < 10⁻⁵ Torr was achieved upon cooling.

For the Mo/Al₂O₃, Mo-P/Al₂O₃, Ni/Al₂O₃ and Ni-P/Al₂O₃ catalysts cleaning was achieved under $\frac{1}{2}$ atm O₂ at 500 °C overnight and the subsequent evacuation was at 600 °C overnight. Reduction or sulphiding of the catalysts was performed after the cleaning procedure by admitting $\frac{1}{2}$ atm of H₂ or 10% H₂S/H₂ respectively to the cell and heating to 500 °C overnight. The cell was then evacuated at 600 °C overnight before

being cooled to room temperature and the spectra recorded.

2.5. Gas Oil Studies

2.5.1. Batch Reactor System

The hydrotreating system was assembled by T. Oswald under AOSTRA agreement #358(89) but required some attention to be operational once more. It consists of a 300 mL Hastalloy C stirred autoclave with a system for introducing and venting gases to and from the reactor. The control system is an Apple II plus computer which controls the reactor temperature and also monitors the temperature, pressure and stirring rate, and is programmed to shut down the reaction (by means of water cooling coils within the reactor) in the event of a system failure. Computer control of heating, cooling, stirring and rapid cooling at the end of the reaction allows for good reproduction of experimental conditions which is very important for comparing the effects of different catalysts.

The feed used was a Syncrude combined gas oil-fuel oil obtained from the Alberta Research Council. There were three steps in every hydrotreating run. The first step involved sulphiding the catalyst. The catalyst (1.00 g, 40 - 60 mesh) and 2 mL CS₂ were sealed in the autoclave and pressurized to 1000 \pm 50 psig H₂ after purging the system first with Ar then H₂. The autoclave was heated (not stirred) to 440 °C and allowed to cool to room temperature after 3 h. The second step consisted of a redistribution process to remove excess sulphur. The autoclave was vented slowly, purged with Ar then H₂ and, finally, repressurized to 1000 \pm 50 psig with H₂. The redistribution conditions were the same as those for sulphiding. The third and final step was the hydrotreating reaction itself. The autoclave was vented and purged with Ar.

Then 22.1 \pm 0.3 g of feed was poured into the reactor under a positive Ar pressure to minimise contact of the catalyst to the atmosphere. The autoclave was resealed, flushed with Ar then H₂ and then pressurized to 1000 \pm 50 psig. The reaction was carried out for 3 h at 407 \pm 4 °C (stirred) before cooling rapidly to room temperature. The gases were vented from the system and were not analysed. The autoclave was purged with Ar and then opened and the liquid product and spent catalyst separated. The liquid product was analysed for density, C, H, N and S wt%, and % aromatic carbon as described in the following sections.

2.5.2. Quinoline-Spiked Feed

The quinoline-spiked feed (5.0 vol%) was prepared as follows: 50.00 mL quinoline was pipetted into a 1 L volumetric flask, diluted with the Syncrude combined gas oil and stirred overnight. The flask was then made up to 1 L and stirred thoroughly.

The hydrotreating experiments using the quinoline-spiked feed involved an identical procedure to that described in Section 2.5.1. The quinoline HDN products were analysed by GC so that the extent of HDN could be assessed (Section 2.5.7).

2.5.3. Density Measurements

The densities of the liquid products were measured at 16.5 ± 0.5 °C using an Anton Paar DMA40 Digital Density Meter. This instrument determines the period of oscillation of a U-shaped capillary containing the different substances. The frequency of oscillation is related to the mass, elastic constant and internal volume of the hollow tube, and also to the density of the substance in the tube. Thus, since the volume of sample is fixed, the constants in the experiment may be determined by using substances of known density (air and water) so that the densities of the gas oil samples can be calculated from the frequency (actually the period) of oscillation of the tube. The precision is $\pm 1 \times 10^4$ g/cm⁻³.

2.5.4. Sulphur Analysis

The hydroprocessed gas oil samples were analysed for sulphur using a Princeton Gamma-Tech Model 100 Chemical Analyser. This is an X-ray fluorescence analyser; the sample is excited by X-rays from a radioisotopic source and then upon relaxation the emitted X-rays are detected. The intensity of the emitted X-rays is proportional to the wt% S as determined from a calibration curve constructed from reference samples prior to the measurements. The absolute error in the measurements is ± 0.02 wt% S.

2.5.5. C, H, N Analysis

The liquid products were analysed for their C, H, N content by Dorothy Fox in the Analytical Services Laboratory in the Department of Chemistry using a C.E.C. 440 Elemental Analyser. The absolute precision of this instrument is better than ± 0.3 %.

2.5.6. % Aromatic Carbon Determination

The quantitative ¹³C nmr sprectrum of a 40:60 mixture of sample:CDCl₃ was recorded using a Bruker AC 200 MHz FT-nmr spectrometer. An inverse gated decoupling experiment was used to remove nuclear Overhauser effects, together with a long delay between scans (20 s). The solvent signal was used as a reference. This method required overnight acquisition and therefore the procedure was modified by using a 0.05 M CDCl₃ solution of chromium (III) acetylacetonate, instead of pure CDCl₃, as a relaxation agent. This method allowed 1 second delays so that acquisition (2000 scans) was completed in an hour. There was good agreement between the % aromatic carbon obtained in these two ways(65). The % aromatic carbon content is given by the integrated area of the aromatic region (160-110 ppm) divided by the sum of the integrated areas of the aromatic and aliphatic (60-5 ppm) regions multiplied by 100. The major error in both procedures arises from phase correcting peaks which are superimposed on a broad background and, consequently, the absolute uncertainty in the

% aromatic carbon is of the order of $\pm 2-3$ %.

2.5.7. Quinoline Hydrodenitrogenation (HDN) Analysis

The quinoline HDN reaction network is quite complex and has been widely investigated(90-97). The reaction network proposed by Satterfield and Yang(93) is given in Figure 2.5.1. Most of the major products in this reaction could be obtained, Q from Fischer Scientific, 1THQ, 5THQ, DHQ, OPA, PB from Aldrich Chemical Co., and PCH from Alfa Products. These liquids were distilled prior to use and suitable GC conditions determined to separate such a product mixture. The separation obtained is shown in Figure 2.5.2 together with the column description.



Figure 2.5.2: Separation of major quinoline HDN products

The detector response factors to each of these liquids was determined and these are listed in Table 2.5.1 together with the retention times.

The analysis of the hydroprocessed spiked feed was performed by using tetrahydronaphthalene (THN, Aldrich Chemical Co.) as an internal standard. Approximately 1.0 g of sample and 0.1 g THN were accurately weighed into a vial and diluted in 10 mL acetone (Fischer Scientific). Approximately 0.2 μ L of this solution was injected into the GC (GC conditions described in Figure 2.5.2) and the number of moles



Figure 2.5.1: Quinoline HDN reaction network (adapted from 93). Q = quinoline, 1THQ = 1,2,3,4-tetrahydroquinoline, 5THQ = 5,6,7,8-tetrahydroquinoline, DHQ = decahydroquinoline, OPA = *o*-propylaniline, PCHA = propylcyclohexylamine, PCHE = propylcyclohexenes, PCH = propylcyclohexane, MPCP = methylpropylcyclopentane.

Sample	RRFª	Retention Time (min)
PCH	0.87	2.34
PB	0.90	2.57
cis- and trans-DHQ	0.97	5.30, 5.70
5THQ	0.89	6.48
Q	1.00	6.65
OPA .	1.03	6.88
1THQ	0.90	7.95

 Table 2.5.1: Detector response factors to quinoline HDN products

^aRelative response factor (relative to quinoline)

of each product determined from the areas of the corresponding peaks. The response factor of THN was determined to be 0.83 relative to quinoline(65) and so, since the weight of THN is known accurately, the moles of product per gram sample could be calculated from:

$$mol_p/g = \frac{Wt_{THN}}{A_{THN} \times RRF_{THN}} = \frac{A_p \times RRF_p}{MW_p \times Wt_s}$$

where

 mol_p = number of moles of product, p Wt_{THN} = weight of THN in solution A_{THN} = area of THN peak from GC RRF_{THN} = detector response to THN relative to Q = 0.83 A_p = area of product peak from GC RRF_p = detector response to product relative to Q (from Table 2.5.1) MW_p = molecular weight of product Wt_s = weight of sample

The injections were repeated at least four times and average values taken. The % HDN is given by {[(mol/g Q in feed) - (Σ mol/g N-containing compounds in sample)]/(mol/g Q in feed)} x 100; and the absolute error was better than ± 1 % in most cases and ± 3 % in the worst cases.

2.5.8. Characterization of Spent Catalysts

The spent catalysts were washed with 10 mL CH_2Cl_2 , filtered and dried at 100 °C before being analysed for their surface areas and C, N and, where applicable, fluoride contents as described in Sections 2.3.1, 2.5.5 and 2.3.4 respectively.

<u>2.6. Carbon Coating/Deactivation Studies</u>

The F-Ni-Mo/Al₂O₃ catalysts were subjected to carbon coating of their surfaces by cyclohexene polymerization(98). A 2 g sample of catalyst was placed in a calcination tube and heated under dry N₂ (20 mL min⁻¹) to 600 °C at a rate of 10 °C min⁻¹ and then held at this temperature for 30 min. After this time the N₂ flow was passed first through a presaturator containing cyclohexene at room temperature and then over the catalyst at 600 °C for 6 h. Finally, the catalyst was allowed to cool to room temperature under a flow of dry N₂.

These catalysts were characterized by surface area measurements and C analysis and were tested for their activities in cumene cracking and hydrocracking and in thiophene HDS using the methods described earlier in this chapter.

Chapter 3: Fluoride Promotion

3.1. Introduction

Additives such as fluoride and chloride are commonly used in Pt/alumina reforming catalysts. The acidity of alumina is enhanced greatly by the addition of such additives and a proposed mechanism for the generation of acidity is given in Figure 3.1.1(60); fluoride replaces surface hydroxyls and generates Brønsted acid sites and strengthens Lewis acid sites because of its electronegativity.



Figure 3.1.1: Generation of acid sites on alumina by fluoride; adapted from 60.

Evidence for this mechanism is provided in the work of Okamoto and Imanaka(99) who investigated the effect of fluoride loading on the γ -alumina OH stretching region by infrared spectroscopy. They observed decreasing v(O-H) intensities , with increasing fluoride loading, particularly for the most basic OH groups which are expected to be more easily displaced by F⁻.

A consequence of this increased acidity is a dramatic increase in activity in reactions involving carbonium ion intermediates, such as cracking, hydrocracking, alkylation-dealkylation, olefin polymerization and isomerization(64). Isomerization is particularly important in reforming where branched alkanes and alkenes (high octane

numbers) are desired.

Hydrocracking is used extensively in petroleum refining for the production of gasoline, jet fuels and lubricants. The purpose of hydrocracking is to convert high boiling feeds to lower boiling fractions by the cracking and hydrogenation of hydrocarbon molecules. When hydrocracking is accompanied by selective hydrogenation to remove sulphur (and nitrogen) compounds the refining method is known as hydroprocessing. Thus, an acidic functionality is critical in refining processes, and the degree of acidity required depends on the desired properties of the product. As a consequence, fluoride promotion has also been investigated in catalysts which are commonly used in hydroprocessing; i.e. alumina supported Co-Mo and Ni-Mo catalysts. One of the rationales for this is that with more acidic catalysts, hydrocracking may be carried out at lower temperatures and thus coking reactions may be avoided.

The acidity has been studied both by model cracking reactions(7,62,63,100) and by the adsorption of nitrogenous bases monitored by IR spectroscopy(62,101-103). Furthermore, the influence of fluoride on sulphur removal has been examined using thiophene HDS as a model reaction(8,63,104-107). Boorman <u>et al.</u>(108) demonstrated the utility of fluoride as a secondary promoter in Co-Mo/alumina catalysts in the hydroprocessing of bitumen where it was seen to have a positive effect in sulphur removal. This was explained in terms of fluoride promoting acid-catalysed cracking reactions of high molecular weight molecules in the feed and thus exposing sulphur atoms within such molecules to the catalyst surface.

It has also been proposed that fluoride not only has the direct effect on activity described above, but also may have an indirect effect on catalyst activity by influencing the impregnation and dispersion of MoO_3 on alumina(106,109).

The work discussed in this chapter is divided into two sections. In the first

section the importance of catalyst preparation method is investigated by using model cracking, hydrocracking and HDS reactions. In the second section the deactivation properties of these catalysts are considered to examine their susceptibility to coking and fluoride leaching. This is extended somewhat in Chapter Six which deals with the hydroprocessing properties of F-Ni-Mo/Al₂O₃ catalysts for a gas oil feed and a feed with a high basic nitrogen content.

3.2. Preparation Method and Model Compound Studies

While it is well established that fluoride increases the acidity of alumina it appears that the nature of the surface produced depends upon the sequence of steps involved in the impregnation(7,60,62,100). The effect of fluoride on the thiophene HDS reaction has been investigated by several authors. Jirátová and Kraus(8) saw an increase in HDS rate at a concentration of 3 wt% fluoride. Muralidhar and coworkers(7) also found an increase in HDS activity for low loadings of fluoride (0.2 wt%) but at higher loadings (1.7 wt% F) they observed a decrease in activity for Co-Mo catalysts impregnated in a stepwise manner. In another more recent study(104,105), the HDS activities of fluorided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts prepared by successive impregnation of the additive ions were examined. It was found that although substantial changes in surface area resulted from this impregnation method, a small amount of fluoride (up to 0.8 wt%) increased the thiophene HDS reactivity per square metre of surface for both the Ni- and Co-promoted cases. However, at slightly higher loadings (2 wt%) the activity per square metre of the Co-promoted catalyst dropped substantially while that of the Ni-promoted catalyst continued to increase. Although these results from different laboratories are not consistent in detail (the weight percent at which the

fluoride changes its effect from a positive one to a negative one is not the same), it does appear that, for catalysts prepared by stepwise impregnation, small concentrations of fluoride promote HDS activity while larger amounts inhibit it, at least for the Co-Mo/Al₂O₃ catalysts. The inconsistencies are probably related to the different impregnation techniques used and the different nature of the surfaces which result; in particular there may be differences in the actual amount of fluoride retained by the support as a consequence of the different preparation methods, as shown later in this Section.

A practical hydroprocessing catalyst must be capable not only of sulphur removal but also of cracking the high molecular weight components of the feed. Indeed, cracking may well be necessary to expose the S atoms in order to ensure that the HDS process is effective. In previous studies in this laboratory, the effect of fluoride impregnation on the cracking, hydrocracking, and HDS activities of Co-Mo/Al₂O₃ catalysts was studied(60,62,63). These catalysts were prepared by simultaneous impregnation of all the additives, rather than by stepwise impregnation. The results showed a dramatic increase in hydrocracking activity upon fluoridation but a decrease in thiophene HDS activity.

The present work seeks to extend previous investigations of the effect of fluoride from Co-promoted catalysts to Ni-Mo/Al₂O₃ catalysts. The better hydrogenation capability of nickel-promoted catalysts(10) and the effect of fluoride on the acidity of the alumina support suggest that F⁻-Ni-Mo/Al₂O₃ would be an attractive hydroprocessing catalyst. Consequently, a series of co-impregnated fluorided nickel-promoted catalysts, analogous to the previous cobalt-promoted series, was prepared and studied. A more complete investigation of the thiophene HDS reaction over these fluorided catalysts was also undertaken. Furthermore, because the sequence of steps in the impregnation process appears to have an important influence on the nature of the surface and its activity, different preparation methods were also examined in this study.

3.2.1. Preparation Method and Fluoride Retention

In order to investigate the importance of catalyst preparation method for fluoride retention by the γ -alumina support, three catalysts with the same nominal weight percents of the additives (3.0 wt% NiO, 15.0 wt% MoO₃) were prepared in three different ways. The composition of these catalysts are given in Table 3.2.1. It is clear

Tabl	e 3.2.1:	Effect of	preparation	n method o	n fluoride	retention
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Catalyst ^a	Preparation method	Wt%F ^b _{nom.}	Wt%F ^c _{meas.}	Surface Area (m ² g ⁻¹)			
F*NiMoAl	NiMo followed by F	3.6	0.9	. 128			
FNiMo*Al	F followed by NiMo	3.6	1.0	120			
FNiMoAl	Coimpregnated NiMoF	3.6	3.5	165			

^a * denotes after which additive the final calcination was performed. ^b nominal weight percent fluoride.

^c measured weight percent fluoride.

that for coimpregnation of all the additives the fluoride is retained quantitatively, while stepwise addition of the additives results in substantial loss of fluoride regardless of whether the fluoride is impregnated before or after the metal additives. It is well known that molybdate interacts strongly with the alumina support by reacting with surface hydroxyl groups(110). Furthermore, a loading of 15.0 wt% MoO₃ is more than that required for monolayer coverage of the alumina surface, assuming the constituent MoO₆ octahedra in MoO₃ occupy 0.25 nm² each (calculated from reference 99). Therefore at this loading of molybdate there is expected to be few surface hydroxyls remaining to react with fluoride. This may explain the low retention of fluoride for F*NiMoAl.

Similarly, for FNiMo*Al the fluoride bonded to the alumina surface in the first calcination step may be displaced by molybdate in the second impregnation step, again leading to loss of fluoride upon calcination. A recent study has provided evidence for this(109). Alternatively, the second calcination step in both these preparation methods may result in loss of fluoride. However, this seems unlikely on the basis of fluoride retention after model compound reaction conditions (see Section 3.3.7).

In the case of the coimpregnated catalysts it appears that all of the fluoride is able to react with the alumina surface. This necessarily implies that the molybdate is less dispersed in this system. In this regard, both a decrease in dispersion of Mo(109) and a larger MoS_2 slab size upon sulphidation(106) have been observed in $Mo-F/Al_2O_3$ catalysts.

The second thing to note from Table 3.2.1 is that both stepwise preparation procedures result in a greater loss in surface area than does coimpregnation. (Surface area of the γ -alumina support is 198 m²g⁻¹.) Since sintering of the γ -alumina support, and accompanying reduction in surface area, is time as well as temperature dependent(111), the extra calcination step involved in F*NiMoA1 and FNiMo*A1 procedures is presumably partly responsible for the greater decrease in surface area.

3.2.2. Compositions, Surface Areas and Thiophene HDS

The surface areas of all the catalysts studied are listed in Table 3.2.2 together with their compositions and thiophene HDS activities. For catalysts prepared by coimpregnation of additives, i.e. all but 0.9F*NiMoAl and 1.0FNiMo*Al, good retention of fluoride during the preparation was observed.

The addition of molybdate to alumina results in a large decrease in surface area relative to the γ -alumina support. This is consistent with MoO₃ blocking the pores of γ -alumina thereby reducing the surface area. The other additives are present at lower

Catalyst ^a	C	Composition		Surface Area	HDS	
	MoO ₃	NiO	F _{meas.}	(m ² g ⁻¹)	(% Conv. ^b)	
NiMoAl	15	3	0	154	30	
0.8FNiMoA1	15	3	0.8	161	30	
3.5FNiMoA1	15	3	3.5	165	29	
6.4FNiMoAl	15	3	6.4	129	22	
0.9F*NiMoAl	15	3	0.9	128	25	
1.0FNiMo*Al	15	3	1.0	120	20	
MoAl	15	0	0	139	10	
2.4FMoAl	15	0	2.4	133	17	
NiAl	0	3	Ô	189	2	
3.2FNiAl	0	. 3	3.2	157	6	
6.5FA1	0	0	6.5	177	0	
3.6FA1	0	· 0	3.6	186	0	
γ-alumina	0	0	0	198	0	

 Table 3.2.2:
 Surface areas and thiophene HDS conversions

^a For catalyst designation see footnotes of Table 3.2.1 ^b After 4 h on stream at 400°C

loadings and cause much smaller changes in surface area. While all additives decrease the surface area compared to y-alumina, the large changes in surface area associated with fluoridation noted by Lycourghiotis et al.(105), were not evident for the samples prepared for this study. In particular, for the simultaneously impregnated samples, the molybdenum additive has a larger effect than does the fluoride. For the two catalysts

which were prepared by a stepwise procedure (0.9F*NiMoAl and 1.0FNiMo*Al) a larger decrease in surface area was found, both when F⁻ was added last and when the Ni-Mo additives were added last. However, the changes found for these two catalysts were not as large, proportionally, as those obtained by Lycourghiotis <u>et al.</u>(105), who found a drastic decrease (up to 50%) in surface area upon fluoridation for catalysts prepared by a stepwise impregnation of the various additives.

The results of the thiophene HDS studies after 4 h on stream are also given in Table 3.2.2; the changes in reactivity with time were very minor for this reaction. It is clear that the presence of the Ni-Mo phase is essential in this reaction. This is not surprising since it is well known that a Ni-Mo-S phase provides very active sites for thiophene HDS(45).

Interestingly, fluoride promotes HDS in both the F-Mo and F-Ni systems. The reason for this is unclear; Miciukiewicz <u>et al.</u>(106) observed a small decrease in thiophene HDS activity of Mo/Al₂O₃ catalysts with increasing fluorine content. One may speculate that if fluoride promotes larger MoS₂ slab formation as proposed by them, then optimum fluoride loadings may result in a higher edge site:corner site ratio. i.e. If the MoS₂ slabs are too small there are more corner sites than edge sites per slab, and if the slabs are too large then the total number of edge sites will decrease. Since the edge sites are thought to be active in HDS, a concomitant increase in thiophene HDS activity may be observed at optimum slab size (and fluoride content). Topsøe <u>et al.</u>(112) have demonstrated that true edge atoms in MoS₂/Al₂O₃ are more active in HDS than corner atoms and that smaller MoS₂ particles have the lowest activity per Mo edge atom. In the case of the F-Ni system, the fluoride may react with anion vacancies in the support and thus prevent the formation of catalytically inactive nickel aluminate. While this has not been demonstrated for fluoride, it has been demonstrated for other anions such as

phosphate(113).

The effect of fluoride on the HDS activity of Ni-Mo/Al₂O₃ is less clear. Loadings of up to 3.5 wt% F leave the activity virtually unchanged while very high loadings (6.4 wt%) decrease the activity. Similar results were found for the coimpregnated F-Co-Mo/Al₂O₃ catalysts(63). This is in agreement with the work of Muralidhar <u>et al.</u>(7) who studied very low (0.2 wt%) and higher (1.7 wt%) loadings of fluoride. At 0.2 wt% F an increase in the HDS rate was reported, while 1.7 wt% F caused a decreased activity. Apparently extremely small amounts of F are required in order to see a promotional effect in thiophene HDS. The detrimental effect of larger amounts of F may be associated with a decrease in the amounts of easily reduced/sulphided molybdenum and nickel as reported by Papadopoulou <u>et al.</u>(105).

Jirátová and Kraus(8) suggested that the electron-withdrawing effect of F^- would increase the Lewis acidity of the Mo sites and thereby increase the C-S hydrogenolysis capability. The results presented here give no evidence in support of this. However, fluoride does affect the alumina surface as can be seen in the cumene conversion studies which are discussed in Section 3.2.3.

3.2.3. Cumene Reaction Studies

The results of the cumene cracking and hydrocracking reactions over the different catalysts are given in Table 3.2.3. The values given are those determined after 4 h on stream. Cumene cracking involves the reaction of cumene over a catalyst in the absence of H₂. The formation of α -methylstyrene (α MS) provides an indication of the dehydrogenation (and therefore hydrogenation, by the principle of microreversibility) ability of the catalyst, while benzene production is indicative of many/strong Brønsted acid sites on the surface. Benzene may be produced in two ways: First, via protonation of the aromatic ring on acidic sites, followed by cleavage of the ring-side-chain

Catalyst	Cracking (oxides)			Hydrocracking (reduced)			Hydrocracking (sulphided)				
	% Conv.	% Yields ^a		% Conv.	% Yields			% Conv.	% Yields		
		Benz.	αMS	ΣSCC		Benz.	αMS	nPB		Benz.	nPB
γ-alumina	4.1	0.3	3.8	0.0	0.5	0.0	0.5	0.0	0.0	0.0	0.0
NiAl	6.8	0.2	6.6	0.0	0.8	0.0	0.8	0.0	0.0	0.0	0.0
3.2FNiAl	38.3	29.7	7.7	0.9	48.7	47.0	0.5	1.1	61.5	60.5	0.9
MoAl	27.7	0.4	24.0	3.2	2.6	0.9	0.6	0.6	2.9	2.3	0.5
2.4FMoAl	34.3	2.7	26.7	5.0	50.7	45.8	0.5	4.3	60.0	57.2	2.0
NiMoAl	31.0	0.7	28.0	2.4	2.1	0.9	0.6	0.6	4.1	2.8	1.3
0.8FNiMoAl	36.5	1.4	29.4	5.7	10.9	8.8	0.3	1.9	24.6	22.4	2.2
1.8FNiMoAl	33.0	3.0	25.5	4.5	43.1	36.1	0.6	6.4	75.2	71.7	3.5
3.5FNiMoAl	38.5	7.0	25.4	6.0	52.2	46.7	0.0	5.5	84.5	80.9	3.6
6.4FNiMoAl	38.2	6.9	27.0	4.3	45.0	41.0	0.6	3.7	61.8	60.3	1.5
0.9F*NiMoAl	36.7	1.8	29.2	5.7	29.0	25.5	0.0	3.4	34.7	29.0	5.6 ·
1.0FNiMo*Al	36.2	2.2	29.5	4.4	16.3	14.0	0.0	2.3	24.0	19.2	4.8

Table 3.2.3: Cumene conversions and yields after 4 h on stream at 400 °C

^a Benz. = Benzene; $\alpha MS = \alpha$ -methylstyrene; $\Sigma SCC =$ sum of the side-chain-cracked products (excluding benzene); nPB = n-propylbenzene

bond(114); second, via a mechanism involving dehydrogenation over the metal phase to form α MS followed by protonation of the side-chain over the Brønsted acid sites and subsequent rearrangements and/or cleavage reactions(62). This second mechanism also gives rise to other side-chain-cracked (SCC) and rearranged products.

From Table 3.2.3 it is clear that alumina itself is weakly acidic and provides some dehydrogenation sites. The latter are most likely anion vacancies in the surface structure. The presence of either metal oxide, particularly MoO₃, enhances the dehydrogenation-hydrogenation properties, as evidenced by the increased yield of α MS, while the acidity is unchanged. This demonstrates that the molybdenum-associated Brønsted acid sites on MoO₃/Al₂O₃ are either too weak to crack cumene or are poisoned rapidly. It has been suggested that these acid sites are rapidly destroyed under the reducing hydrocarbon atmosphere and therefore play no role in this reaction(60).

The addition of fluoride to NiAl or MoAl results in an increase in benzene yield while the α MS yield is virtually unchanged. For 3.2FNiAl the amount of benzene produced is far greater than that produced over 2.4FMoAl. The reason for this, which is discussed in more detail in Section 3.3, is that α MS may polymerize over the F-associated Brønsted acid sites and thus poison them. This coking mechanism is more apparent over 2.4FMoAl since this catalyst has a higher dehydrogenation activity.

For the coimpregnated FNiMoAl catalysts there is a steady increase in benzene production which seems to level out at higher F loadings. This is more apparent in the cumene hydrocracking reaction as discussed below. The two stepwise-impregnated catalysts have comparable activities in cumene cracking to 0.8FNiMoAl. This is not surprising considering that they have similar loadings of fluoride.

Cumene hydrocracking involves the reaction of cumene over a catalyst in the presence of H_2 . This reaction is a common probe for investigating the Brønsted acidity

of catalysts since the presence of Brønsted acid sites results in cracking of the side-chain. This work has also demonstrated that cumene hydrocracking is a better probe for surface acidity than cumene cracking, since dehydrogenation to α MS is suppressed by H₂ and so little coking of the acid sites occurs.

It is clear from Table 3.2.3 that the addition of fluoride dramatically increases the Brønsted acidity of alumina. There appear to be two differences between the Ni-Mo and Co-Mo catalysts: Firstly, a maximum in the cumene conversion between 3.5 and 6.4 wt% F⁻ was observed for the Ni-promoted catalysts (cf. 3.5FNiMoAl and 6.4FNiMoAl), whereas for the analogous Co-containing catalysts a maximum in conversion had not yet been reached even after the more severe fluoride treatment(62,63). Secondly, the sulphided Ni-Mo catalysts are more active in cumene hydrocracking than the reduced counterparts, which was not observed for the Co-Mo/Al₂O₃ catalysts(63). It has been suggested by Ledoux and coworkers(115) that the lower oxidation state of molybdenum in MoS_2 is more able to dissociate H_2 , and thus sulphided molybdenum catalysts have a higher hydrogenation capability. Similarly it has been reported that Ni-Mo/Al₂O₃ catalysts have a higher hydrogenation ability than Co-Mo/Al₂O₃ catalysts(10). This higher hydrogenation activity may reduce the amount of coking on the acid sites thereby allowing higher activity. Alternatively, it has been demonstrated that MoS_2 itself is capable of generating Brønsted acid sites by dissociation of $H_2S(116)$. This may provide an additional source of acid sites for the cracking of cumene. However, cumene hydrocracking over sulphided MoAl suggests that these sites are too weak to crack cumene.

3.2.4. Impregnation Sequence

From the results for 0.8FNiMoAl, 0.9F*NiMoAl and 1.0FNiMo*Al, all of which have similar fluoride content after calcination, it appears that the order of impregnation

has virtually no effect on the cracking ability of these catalysts, but does have a small effect on their HDS activity. The HDS results are in agreement with the results of Muralidhar and co-workers(7) who also observed a decrease in HDS activity when fluoride was impregnated prior to or after the metal additives. However, the impregnation sequence does influence the hydrocracking activity of both the reduced and sulphided catalysts. Comparison of 0.8FNiMoAl, 0.9F*NiMoAl and 1.0FNiMo*Al indicates that impregnation of the F⁻ after the metal additives results in a more acidic surface, since more benzene and side-chain-cracked products are observed for 0.9F*NiMoAl. This suggests that both coimpregnation (0.8FNiMoAl) and impregnation of the metal additives after fluoride (1.0FNiMo*Al) result in catalysts in which acid sites generated by fluoride are blocked by the metal oxides. This is easily visualized for the stepwise method where pores containing fluoride-associated Brønsted acid sites may be blocked by the metal oxides during the second impregnation/calcination step.

3.2.5. Summary of Preparation Methods and Model Compound Studies

This study of fluorided, Ni-promoted Mo/Al₂O₃ catalysts produced results very similar to those found for Co-promoted catalysts in a previous study in this laboratory: Fluoride and molybdenum introduce two distinct types of Brønsted acid sites when impregnated on γ -alumina; reduction of the catalysts with H₂ results in the destruction of the Mo-associated Brønsted acid sites, while the F⁻-associated sites persisted; and cobalt or nickel have no effect on the γ -alumina surface acidity. It was also clear from this work that the fluoride-associated Brønsted acid sites were responsible for virtually all of the cracking activity of the catalysts. Only minor differences in trends between the Ni-and Co-promoted catalysts were noted: The Ni containing catalysts showed a maximum in cumene conversion at less than the maximum wt % F⁻ studied, and increased cumene conversion upon sulphiding. Neither of these trends was observed for the Co containing

catalysts.

The results of the current study underscore the importance of the impregnation procedure in determining the quality of the catalysts formed. Surface areas and fluoride content are both adversely affected by step-wise impregnation. Furthermore, while impregnation of fluoride after the metal additives results in a more acidic surface than the coimpregnated catalyst with a similar fluoride loading, coimpregnation of fluoride (up to 3.5 wt%) allows the maintenance of a high thiophene HDS activity. In contrast, for stepwise impregnated F-Ni-Mo catalysts, even low loadings of fluoride (1 wt%) decrease the thiophene HDS activity. In this regard, the coimpregnated catalysts are superior to those prepared in a stepwise manner since high hydrocracking activity can be achieved in the former case, without any adverse affect in HDS.

3.3. Deactivation Studies

While a F-Co-Mo/Al₂O₃ catalyst has been shown to have superior HDS activity to unpromoted Co-Mo/Al₂O₃ in bitumen hydrocracking(108), there has been some criticism of the utility of acidic catalysts in hydroprocessing reactions(117). There are two reasons for this. Firstly, the basic nitrogen compounds in the feeds may adsorb strongly on the Brønsted acid sites, poisoning them and leading to coke formation(118,119). Secondly, olefin polymerization, which is well known to be acid catalysed, is thought to be one of the primary routes to coke formation(120).

Coke formation leads to catalyst deactivation due to active-centre blocking, blocking of narrow pores or partial pore mouth blocking by deposited carbon(121,122). This results in loss of surface area and pore volume and a loss of activity(119,123,124). From an economic point of view it is therefore important to minimise catalyst deactivation so that catalyst lifetime is increased and regeneration or recharging of the catalyst (with possible shutdowns in production) is needed less frequently.

Olefin polymerization over catalysts in an inert atmosphere has been used to accelerate Co-Mo/Al₂O₃ catalyst aging(125). The aim of the present study was to use this method to assess the deactivation properties of the F-Ni-Mo/Al₂O₃ catalysts. The activities of the coked catalysts in hydrocracking and HDS were then compared to those of the fresh catalysts in order to gain some insight into the sites for coking.

It should be noted that olefin polymerization can also result in carbon deposition with interesting characteristics. Vissers <u>et al.</u>(98) produced a carbon-covered alumina with increased surface area and pore volume, implying that the deposited coke had a porous structure. Similar findings were observed for Pt-Sn/Al₂O₃ catalysts in the dehydrogenation of hexane(126). While this is not the usual phenomena observed on hydroprocessing catalysts, the present study also investigates whether this type of coking is possible on the F-Ni-Mo/Al₂O₃ systems.

Another valid criticism of the use of fluoride-promoted catalysts is that, under hydroprocessing conditions, the fluoride can be leached from the catalyst, possibly as HF, and this can result in corrosion problems. Furthermore, regeneration of the catalyst may also be a source of corrosion of the reactor system(127). Thus another feature of this study was to examine loss of fluoride both under aging conditions and with time on stream in model compound reaction studies. This is extended in Chapter Six to loss of fluoride during the hydroprocessing of real feeds.

3.3.1. Coking of Alumina

The coking of alumina to form carbon-covered alumina followed the procedure used by Vissers <u>et al.(98)</u> which involved the pyrolysis of cyclohexene over alumina at 600 °C for 6 h. These researchers had reported that high surface area coke could be

deposited on alumina in this manner. While comparable carbon coverage of the alumina was obtained, a decrease, rather than the previously observed increase(98), in the surface area of the resulting support was observed (from 190 m²g⁻¹ for γ -alumina to 144 m²g⁻¹ for C/Al₂O₃). In an attempt to understand this difference, other carbon-covered alumina samples were prepared by varying the pyrolysis time (6 h to 48 h) and by using boehmite or γ -alumina as the precursor support. While increasing weight percent carbon was observed with increasing pyrolysis time, it was not possible to increase the surface area of the precursor support. In fact, a linear decrease in surface area, consistent with a gradual blocking of the smaller pores in alumina, was found (Figure 3.3.1). This decrease in surface area is independent of the precursor support, although boehmite appears to present the more active cyclohexene pyrolyzing surface, as reflected in a higher weight percent carbon deposited on boehmite compared to γ -alumina for the same pyrolysis time, as is demonstrated in Figure 3.3.2.

For both γ -alumina and boehmite precursors the curves in Figure 3.3.2 follow adsorption isotherm type behaviour with apparent monolayer carbon coverage at around 24 and 29 wt% C respectively. These monolayer carbon coverages imply surface areas of approximately 190 m²g⁻¹ for the γ -alumina and 230 m²g⁻¹ for the transformed boehmite (to γ -alumina) if it is assumed that the deposited carbon possesses a graphitelike structure(128). These surface areas agree well with the values expected for γ -alumina prepared from boehmite and indicate that no appreciable loss in surface area occurs as a result of the high temperature employed in the pyrolysis procedure, i.e. the reduction in surface area is due only to coking of the alumina surface.

Vissers <u>et al.(98)</u> recognized the possibility of decreasing surface area with carbon coating if the carbon is deposited as a monolayer. Clearly, the conditions required for the deposition of high surface area hemispherical carbon particles as



Figure 3.3.1: Effect of C on the surface area of γ -alumina(o) and boehmite(Δ).




discussed by them are very exacting, and despite careful adherence to the procedure described by them only low surface area carbon deposition was observed here.

In order to investigate whether monolayer carbon coverage of the alumina had indeed been reached, fluoride was impregnated onto one of the carbon-coated alumina samples with 28 wt.% C. Fluoride has no effect on the acidity of carbon surfaces and furthermore is not retained by this type of surface, particularly under reaction conditions (65). However, the presence of fluoride has a dramatic effect on the acidity of alumina resulting in high cumene cracking activity (60) and, furthermore, the loss of fluoride after such a reaction is quite small (see Section 3.3.7 and reference 129) confirming that fluoride is bonded to the surface. Therefore both cracking reaction and fluoride analysis before and after this reaction will indicate whether any of the alumina surface remains exposed to fluoride at this loading of carbon.

Sufficient fluoride was contacted with the 28% C-Al₂O₃ to produce a catalyst of 3.6 wt.% F. The preparation procedure followed that used for F/Al_2O_3 (see Section 2.1.2) except the catalyst was not subjected to calcination since oxidative degradation of the coke would occur. However analysis indicated that the actual weight percent fluoride present was 1.1%. This is less than that retained by an alumina support (see next section) but does suggest that some of the alumina surface is still accessible to fluoride. Further evidence that the fluoride was bonded to the alumina surface was provided by the analysis of the spent catalyst after cumene cracking which showed that almost all of the fluoride (1.0%) was still retained. However, the activity of the catalyst in this reaction indicated that the surface possessed no surface acidity; the only product at any time during the reaction was α -methylstyrene which presumably forms over the deposited carbon, and a yield of 8.3% is comparable to that seen for 9 wt% C-Al₂O₃ (8.9% as shown in the next section). The conclusions drawn from this are, therefore, that

some of the alumina surface is still accessible to fluoride, possibly small pores or partially-blocked pores of the C-covered alumina, but the Brønsted acid sites which develop are inaccessible to cumene and also to cyclohexene; i.e., a monolayer coverage of carbon has been reached with respect to that part of the surface which is accessible to cyclohexene (and cumene).

It is expected that this coking process will significantly change the pore structure of the alumina. In order to investigate this, mercury porosimetry data was obtained. A comparison of the mercury intrusion/extrusion data for the fresh and coked γ -alumina (9 wt% C) is given in Figure 3.3.3, from which a number of observations can be made. Firstly, at lower pressures (larger pores) a greater volume is intruded into the C/Al₂O₃ sample compared to the fresh γ -alumina. This is a true difference since the reproducibility between samples of the same material is very good (Figure 3.3.4). This surprising result implies that the deposited coke possesses some large pores, although these pores contribute very little to the overall surface area.

The second observation from Figure 3.3.3 is that a lesser volume is intruded into the smaller pores in the coked sample $(0.23 \text{ cm}^3\text{g}^{-1} \text{ compared to } 0.32 \text{ cm}^3\text{g}^{-1})$ indicating that the deposited carbon blocks some of the smaller pores. These pores are responsible for providing the majority of the catalyst surface area, hence the observed decrease in BET surface area upon coking. A third observation is that for both samples an open hysteresis loop is seen. This implies that some of the "smaller pores" are actually "inkbottle" pores(130) (see Figure 3.3.5), whereby mercury cannot enter until the pressure is at a value equivalent to the radius of the entrance capillary at which point the whole pore fills. Upon extrusion, the capillary "neck" of the pore empties at the appropriate pressure but the mercury in the "ink-bottle" part (larger radius) is trapped. Since the coked sample has a greater trapped volume in the hysteresis loop, it must also have a greater



Figure 3.3.3: Mercury porosimetry intrusion/extrusion data for alumina(+) and C/alumina(0); solid line - intrusion, dashed line - extrusion.



Figure 3.3.4: Mercury porosimetry intrusion/extrusion data for two different alumina samples; assessment of errors. Solid line - intrusion data, dashed line - extrusion data.

fraction of "ink-bottle" pores, i.e. some pores of alumina have been converted to ink-bottle pores by coke deposition; a suggested route to this is shown in Figure 3.3.5.



Figure 3.3.5: Possible route to the generation of "ink-bottle" pores.

One may envisage, for the 28 wt% C sample discussed earlier, that if these ink-bottle pores dominate then the narrow capillary neck may admit small species such as fluoride but not larger species such as cumene or cyclohexene. In view of the fact that some fluoride was retained by this sample, (b) in Figure 3.3.5 is the more likely scenario.

It is less easy to comment on the change in average pore size upon coking. The problem in interpreting this data is that there is some uncertainty in the liquid-solid contact angle(131). A contact angle of 127° is usually taken for that of mercury on γ -alumina(132), while 140° is more appropriate for a carbon surface(133). We may assume therefore that a suitable mercury contact angle for 9 wt% C/Al₂O₃ is between these two extremes. Figure 3.3.6 gives the pore volume distributions for the fresh and coked alumina samples for a contact angle of 127° for the fresh catalyst, and both alumina-like and carbon-like extremes (127° and 140° respectively) for the coked



Figure 3.3.6: Pore volume distributions by mercury intrusion for alumina(+) and C/alumina(Δ). A contact angle of 127° was used for both samples in (a), while in (b) contact angles of 127° and 140° respectively were used.

catalyst. If an intermediate contact angle is assumed for the coked catalyst then a slight shift to larger pore radius, consistent with carbon filling the smaller pores of alumina, is seen.

3.3.2. Compositions and Surface Areas of Coked Catalysts

The compositions of the fresh and coked catalysts (after 6 h under cyclohexene/N₂ at 600 °C) are given in Table 3.3.1. together with their surface areas, measured weight percent fluoride and, where applicable, weight percent carbon. The compositions and surface areas of the F-Ni-Mo/Al₂O₃ catalysts may differ slightly to those in Table 3.2.2 since some of those in Table 3.3.1 were prepared in a second batch. The measured wt.% F was in good agreement with the nominal wt.% for the coimpregnated fresh catalysts, as expected from Section 3.2, and fair agreement for the coked catalysts. The apparent lower F content of these catalysts may be due in part to the uncertainty in the precise weight percent carbon they contain (see later).

For all catalysts fluoride produces a small decrease in surface area. Metal additives produce somewhat larger decreases. This has been observed previously for alumina supported fluorided Ni-Mo catalysts (Section 3.2).

Some interesting observations arise from the results of cyclohexene pyrolysis over the alumina catalysts. For those catalysts containing fluoride only, the weight percent of carbon deposited is comparable to that on alumina only (9-10 wt.%) and a similar large decrease in surface area is seen after carbon deposition. This implies that fluoride does not promote cyclohexene polymerization. However, model compound reactions indicate that enough carbon is present to poison the fluoride-associated Brønsted acid sites generated by up to 3.6 wt.% F⁻ (see next two sections). This suggests that while the fluoride does not promote the polymerization, carbon is nevertheless deposited on these sites. In contrast, for catalysts containing metal additives,

Catalyst	Wt% Additives				Wt% C	Surface Area
	NiO	MoO ₃	F ^a nom.	F ^a _{meas.}		(m ² g ⁻¹)
γ-alumina	0	0	0	••	A	190
NiMoAl	3	15	0	-		137
1.8FNiMoAl	3	15	1.8	1.8		125
3.5FNiMoAl	3	15	3.6	3.5	N/A	122
6.4FNiMoAl	3	15	6.9	6.4		113
3.6FA1	0	0	3.6	3.7		186
6.5FA1	0	0	6.9	6.5	*	177
C/alumina	0	0	0	-	9	144
C/NiMoAl	3	15	0	-	· 20	130
C/1.8FNiMoAl	3	15	1.8	1.7	20	105
C/3.5FNiMoAl	3	15	3.6	3.7	19	106
C/6.4FNiMoAl	3	15	6.9	5.4	30	108
C/3.6FA1	0	0	3.6	3.1	10	128
C/6.5FA1	0	0	6.9	4.4	10	116

 Table 3.3.1: Compositions and surface areas of fresh and coked catalysts

^a Quoted wt% F are calculated based on the weight of the alumina support.

substantially more carbon is deposited (19-30 wt.%) and only small decreases in surface area result. This implies that either some of the carbon deposited has a high surface area, or carbon deposition does not occur uniformly over the catalyst, but rather, in 'islands', apparently on the metal sites. Model compound studies, the results of which are discussed in more detail in later sections, indicate the latter. Furthermore, carbon analysis of the metal-containing coked catalysts revealed that these samples only were inhomogeneous (hence quoted C weight percents are approximate, in the range \pm 3 wt.% C for 0-3.5FNiMoAl, and \pm 5 wt.% C for 6.5FNiMoAl). This provides further support for the argument that the carbon is deposited in islands on these catalysts.

One possible explanation of these observations is that both the metal species and fluoride accumulate to some extent in the smaller pores of the catalysts and that the metal species effectively block these pores (hence a large decrease in surface area occurs) while the smaller fluoride ions do not. Such an accumulation of the active species may be expected to occur during the drying stage of the catalyst preparation where the larger pores empty of solution first and the receding liquid film carries solute into the smaller pores (134). Extending this argument to the coked catalysts, we may conclude that the large decrease in surface area resulting from the carbon coating of γ -alumina or F'/Al₂O₃ arises from carbon deposition in smaller pores, while for the metal-containing catalysts only a small decrease in surface area is observed because these pores are already blocked by the metal species and the carbon deposition occurs in islands on the metals themselves.

Evidence for this is provided in the mercury porosimetry data for the catalysts. Figure 3.3.7 shows the porosimetry data before and after Ni-Mo(a) and F(b) impregnation onto alumina, and before and after coking of 3.6FAl(c); a contact angle of 127° was taken in all cases. For each catalyst more than 95% of the surface area is present in pores with radius < 70 Å, and, therefore only changes in the pore volume in this region are expected to influence the catalysts' surface areas. For NiMoAl (Fig. 3.3.7(a)) it is clear that Ni-Mo blocks pores on γ -alumina with radius < 70 Å resulting in a pore volume decrease from 0.32 to 0.22 cm³g⁻¹ in this region. Thus it is not surprising



Figure 3.3.7: Mercury porosimetry intrusion/extrusion data: (a) γ -alumina(+) compared to Ni-Mo/Al₂O₃(Δ); (b) γ -alumina(+) compared to 3.6 wt% F/Al₂O₃(Δ); (c) fresh(+) and coked(Δ) 3.6 wt% F/Al₂O₃. Solid lines show intrusion data while dashed lines show extrusion data.

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that Ni-Mo impregnation decreases the surface area of γ -alumina. Similarly, coking of the catalysts also blocks the small pores as seen in Figure 3.3.7(c) (decrease in pore volume from 0.30 cm³g⁻¹ for 3.6FAl to 0.22 cm³g⁻¹ for C/3.6FAl). The addition of fluoride (Fig. 3.3.7(b)), however, does not decrease the pore volume of the smaller pores (0.32 cm³g⁻¹ for γ -alumina compared to 0.30 cm³g⁻¹ for 3.6FAl), i.e. fluoride does not block these pores and hence does not decrease the surface area. Fluoride does decrease the pore volume of the larger pores (10,000 to 3,000 Å), however. These pores contribute very little to the overall surface area and therefore this change in pore volume does not affect the catalyst surface area very much. It does suggest, however, that impregnation with NH₄F(aq.) tends to collapse these larger pores.

Some insights into the mechanism of coking on these types of catalysts may be obtained assuming that the mechanisms of coking and pyrolysis are similar. There is some validity to this assumption since although neither mechanism is well understood they must both involve polymerization of olefins to some extent (120,128). Interestingly, the active sites for pyrolysis of cyclohexene appear to be associated with the metal additives, rather than fluoride, since the wt% C on C/3.6FAl and C/6.5FAl is similar to that on alumina alone (C/alumina) whereas the wt.% C on the metal-containing catalysts is somewhat higher. Clearly, for a molecule such as cyclohexene which does not polymerize easily over acidic sites, fluoride promotion has little effect on the coking propensity. Fluoride promotion does increase the coking propensity for species which polymerize more easily, however, such as α -methylstyrene. This is discussed in the next section.

A notable feature of these results is that considerable carbon deposition occurs on the metal sites. It has been established that MoO_3 increases both the Brønsted and Lewis acidity on alumina (60,135). The possibility that it is the Mo-associated Brønsted acid sites which are responsible for cyclohexene polymerization seems unlikely on the basis of the carbon deposition over the $F-/Al_2O_3$ catalysts. The polymerization may be associated with the increased Lewis acidity, however. Scaroni <u>et al.</u>(136) observed a reduction in coking of a Co-Mo/Al₂O₃ catalyst after it had been exposed to pyridine, a Lewis base. This led them to the conclusion that coking occurs to some extent on the Lewis acid sites on these types of catalysts. At higher loadings of fluoride (6.4FNiMo) a higher weight percent carbon is deposited suggesting that only at such fluoride concentrations is the acidity sufficient to polymerize cyclohexene on the fluorideassociated Brønsted acid sites.

3.3.3. Cumene Cracking

The results of cumene cracking over the fresh and coked catalysts are given in Table 3.3.2. Comparison of the activity of the fresh and coked support reveals the effect of carbon in this reaction. Alumina, which has few hydrogenation-dehydrogenation sites shows low activity in the production of α -methylstyrene. Interestingly, the coked alumina support is more active in α -methylstyrene production than alumina which implies that the deposited carbon is active in this reaction. This improved hydrogenation-dehydrogenation activity may be important from an industrial viewpoint where the promotion of hydrogen uptake is an essential property of a hydrotreating catalyst. Hence C/Al₂O₃ shows some potential as an alternative support material to alumina. Some investigations of this have been made in this laboratory (137,138).

The effect of fluoride impregnation on the alumina support has been discussed previously (Section 3.1): Fluoride, by polarizing the alumina lattice, generates Brønsted acid sites which are very active in cracking of cumene to benzene. Conversely, the presence of the metals improves the hydrogenation-dehydrogenation ability of all the catalysts as reflected in the increased α -methylstyrene production. This was discussed in

Catalyst		Cracking (oxides)			Hydrocracking (reduced)			Hydrocracking (sulphided)				Thiophene	
	% Conv.	% Yields ^a		% Conv.	% Yields		% Conv.	% Yields			HDS		
		Benz.	αMS	ΣOth.		Benz.	αMS	ΣOth.		Benz.	αMS	ΣOth.	%Conv.
γ-alumina	2.9	0.5	2.4	´ O	0.5	0	0.5	0	0	0	0	0	0
NiMoAl	34.5	0	31.0	3.5	5.1	1.8	1.6	1.7	5.0	5.0	2.0	1.4	24
1.8FNiMoAl	33.0	3.0	25.5	4.5	43.1	36.1	0.6	6.4	75.2	71.7	0	3.5	21
3.5FNiMoAl	39.9	2.9	29.4	7.5	76.4	70.0	0	6.6	78.7	76.1	0	2.4	19
6.4FNiMoAl	37.0	8.2	23.7	5.1	67.8	63.8	0.2	3.8	71.7	70.0	0.5	1.2	16
3.6FA1	71.4	68.8	2.6	0	82.3	82.3	0	0	80.6	80.2	0	0.4	0
6.5FA1	69.6	67.7	1.6	0.3	73.4	73.4	໌	0	81.4	81.4	0	0	• 0
C/alumina	8.9	0	8.9	0	0.9	0	0.9	0	1.1	0	1.1	0	0
C/NiMoAl	20.4	0	20.4	0.	1.6	0	1.6	0	2.2	0	1.7	0.4	6
C/1.8FNiMoAl	20.2	0	20.2	0	2.3	0.8	1.5	0	5.9	2.8	1.5	1.6	4
C/3.5FNiMoAl	12.4	0	12.3	0	4.3	3.2	1.1	0	7.9	4.9	1.7	1.3	4
C/6.4FNiMoAl	36.7	10.9	22.8	3.0	22.7	21.4	1.2	0	27.4	25.3	1.1	1.0	3
C/3.6FA1	16.8	10.0	6.8	0	2.7	1.7	1.0	0	4.3	3.1	1.2	0	0
C/6.5FA1	38.5	32.1	6.4	0	10.2	9.4	0.7	0.1	11.2	10.2	0.8	0.2	0

 Table 3.3.2: Model compound testing results after 4 h on stream at 400 °C

^a Benz. = Benzene; $\alpha MS = \alpha$ -methylstyrene; $\Sigma Oth. =$ sum of other products (side-chain-cracked and rearranged).

more detail in Section 3.2.

With the exception of C/6.4FNiMoAl and C/6.5FAl, carbon deposition onto the alumina catalysts appears to poison both the metal sites and the fluoride-associated Brønsted acid sites. As discussed earlier, pyrolysis of cyclohexene appears to occur preferentially on the metal sites of the catalysts, and so poisoning of both acid and dehydrogenation sites by carbon necessarily implies that these sites are in close proximity. It is interesting that only those catalysts with the highest fluoride loadings (C/6.4FNiMoAl and C/6.5FAl) remain active in cumene cracking to benzene (see also the hydrocracking results). Extending the argument in the previous section we might conclude that at high F⁻ loadings a portion of the impregnated fluoride ions remains. Another notable feature is that, in spite of the large amount of carbon deposited on the metal sites, substantial α -methylstyrene is still formed. Thiophene HDS studies indicate that these metal sites are indeed blocked, leading to the conclusion that it is the deposited carbon itself which is active in the α -methylstyrene production.

3.3.4. Cumene Hydrocracking

The results for cumene hydrocracking over the fresh and coked catalysts, in their reduced and sulphided forms, are also given in Table 3.3.2. The results on the fresh catalysts were similar to those observed previously (Section 3.2 and reference 129), namely, that benzene is the major product for cumene hydrocracking over these catalysts and that the amount of benzene formed increases with increasing fluoride content. Also, the sulphided catalysts are more acidic than their reduced counterparts.

The results of the coked catalysts again indicate poisoning of the active sites by the deposited carbon. For the catalysts containing the highest fluoride loading some Brønsted acid sites persist as evidenced by higher benzene yields for C/6.4FNiMoAl and C/6.5FA1. The acidity of these two catalysts is lower than anticipated on the basis of their cumene cracking results (notice that for the fresh catalysts much more benzene is produced under hydrocracking than under cracking conditions). This tends to suggest that much of the benzene produced over these catalysts under cracking conditions is via mechanism 2 (dehydrogenation followed by protonation then cleavage, see Section 3.2.3) and under hydrocracking conditions this mechanism is suppressed by H_2 . This provides additional evidence that, at least for C/6.5FA1 which contains no metals, dehydrogenation occurs over the deposited carbon.

3.3.5. Thiophene HDS

The results in Table 3.3.2 indicate that those catalysts containing fluoride only had little or no activity in thiophene HDS, indicating (not unexpectedly) that the metal sulphides form the active sites in this reaction. Also, as seen in Section 3.2, very high fluoride loadings decrease the thiophene HDS activity of the fresh catalysts. Thiophene HDS over the coked catalysts confirm that the coke is deposited on the metal sites.

3.3.6. Deactivation Studies

Of the model reactions studied only the cumene cracking deactivation curves were found to be very informative. Figure 3.3.8 shows the percent conversions in cumene cracking for the two series of catalysts as a function of time. The fresh catalysts containing fluoride only have nearly constant activity with time (over the interval studied) and the product distribution is nearly 100 % benzene. The coked catalysts have lower % conversions, especially C/3.6FAl, but behave similarly to the alumina series although some deactivation of C/6.5FAl is apparent over the 4 h reaction time. This deactivation is associated with a slight decrease in benzene production. In the presence of metals, however, marked deactivation does occur; a drop in activity of between 20-40 % is observed for the fresh catalysts over 4 h. The product distribution contains both



Figure 3.3.8: Cumene cracking deactivation curves for F-Ni-Mo/Al₂O₃ before(a) and after(b) accelerated aging. Weight percents of F-NiO-MoO₃ are: ∇ 0-0-0; o 0-3-15; + 1.8-3-15; • 3.5-3-15; \triangle 6.4-3-15; \triangle 3.6-0-0; + 6.5-0-0.

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 α -methylstyrene and benzene and other side-chain cracked products. An example of how the product distribution varies with time is given in Figure 3.3.9 and it is clear from this that the drop in activity is associated with a rapid decrease in benzene formation, i.e. a rapid poisoning of acidic hydroxyls.

The following conclusions may be drawn from these results: Since catalysts containing only fluoride do not deactivate rapidly, cracking to benzene over fluoride-associated Brønsted acid sites via protonation then side-chain cracking does not coke the catalyst; i.e., propene produced by this mechanism behaves similarly to cyclohexene in that it does not polymerize on the acid sites. The second mechanism for benzene formation which involves dehydrogenation over the metal sites followed by protonation over the fluoride-associated Brønsted acid sites and then cleavage and/or rearrangement, does poison acid sites through coking, however. This is evidenced for catalysts containing both F and Ni-Mo in the rapid decrease in the formation of cracked products as a function of time but only a slow decrease in the α -methylstyrene production (Figure 3.3.9), suggesting that it is the acid sites rather than the metal sites where coking occurs; i.e., α -methylstyrene, which can polymerize easily, does so on the acid sites thus coking them. The small deactivation of C/6.5FAI suggests that some of the benzene produced over these catalysts is produced by the second mechanism, where dehydrogenation occurs over the deposited carbon rather than metal sites.

3.3.7. Fluoride Retention

Comparison of the wt% F present on the fresh and coked catalysts (Table 3.3.1) indicates that for loadings of up to 3.6 wt% F there is good fluoride retention under coking conditions (N₂/cyclohexene, 600 °C, 6 h). For the highest fluoride loading studied, however, there is quite substantial loss of fluoride under coking conditions (16% loss for C/6.4FNiMoAl and 32% loss for C/6.5FAl). It is tempting to speculate that



Figure 3.3.9: Product distribution with time for catalyst 6.4FNiMoAl during cumene cracking. Δ % conversion, + % yield benzene, o % yield α -methylstyrene and + % yield others.

fluoride which is blocked by carbon deposition in the smaller pores becomes trapped and is not lost. From the model compound results it was deduced that (C/)6.4FNiMoAl and (C/)6.5FAl had some fluoride deposited outside of the smaller pores and perhaps it is some of this fluoride which is lost under coking conditions. However, analysis of some of the spent 'fresh' catalysts indicates that under model compound reaction conditions fluorine is again retained less by those catalysts with > 3.6 wt% F. These results are shown in Table 3.3.3. The mechanism for this loss of fluoride is unclear and it is not

Catalyst	Reaction	Fluoride Wt%			
	· ·	Before	After		
3.6FA1	Cumene HC ^a , reduced	3.6	3.5		
3.2FNiAl	Cumene HC, sulphided	3.2	2.9		
2.4FMoAl	Cumene HC, sulphided	2.4	2.1		
0.8FNiMoAl	Thiophene HDS	0.8	0.8		
3.5FNiMoAl	Cumene Cracking	3.5	3.0		
6.4FNiMoAl	Cumene HC, reduced	6.4	4.8		

Table 3.3.3: Fluoride retention after model compound reactions

 a HC = Hydrocracking

apparent from this data whether fluoride loss is just a consequence of the high temperature or whether the reacting (or coking) molecules are involved. It is possible that at this fluoride loading surface AlF_3 has started to form and that some volatilization of AlF_3 occurs at elevated temperatures. Weight loss from a 6.8 wt% F/alumina sample at 1200 °C has been explained by this route(106). However, the melting point of AlF_3 is high (1290°C) and so an alternative, or perhaps additional, explanation may be that at

these high F loadings other surface species, based on lower boiling compounds, such as molybdenum oxofluorides may start to form. Indeed, on the basis of XPS measurements, Okamoto <u>et al.</u>(109) have suggested that such species are formed when molybdenum is impregnated onto F/alumina. These would have much lower melting points (186 - 270 °C (139)) and so could be easily lost at reaction and coking temperatures.

3.3.8. Summary of Deactivation Studies

Pyrolysis of cyclohexene on either γ -alumina or boehmite results in a linear decrease in surface area with increasing weight percent carbon. This is possibly a result of some low surface area carbon deposition in the smaller pores of the substrate. The carbon deposition follows adsorption isotherm-type behaviour, with an apparent monolayer coverage of between 24-29 wt% C depending on the alumina precursor, and boehmite presents a slightly more active pyrolysing surface. At this carbon coverage some of the alumina surface is still accessible to small species such as fluoride ions. This alumina surface may be present in "ink-bottle" pores which possess narrow openings through which fluoride may pass but not the larger cyclohexene or cumene molecules. The deposited carbon displays some dehydrogenation-hydrogenation activity, making C/Al₂O₃ a potential new support material.

When cyclohexene is pyrolysed on F-Ni-Mo/Al₂O₃ catalysts it is clear that the metal centres promote the polymerization, possibly through increasing the Lewis acidity of the support, but that the Brønsted acid sites generated by fluoride are not strong enough to effect this reaction. These Brønsted acid sites do promote polymerization (coke formation) of molecules which polymerize more easily, however, such as α -methylstyrene which forms a more stable tertiary carbocation. Model compound reaction studies before and after carbon deposition show that both metal sites and

fluoride-associated Brønsted acid sites are blocked by carbon. Catalyst characterization leads to the suggestion that catalytic species accumulate in smaller pores in the support during the preparation procedure and that carbon deposition also occurs preferentially at these locations. Thus, fluoride-associated Brønsted acid sites and metal sites are in close proximity and both are poisoned through coking on the metal sites. Only at the highest fluoride loading studied did cracking sites remain on the surface after coking. Thus at this loading, a portion of the fluoride remains outside of the (coked) small pores.

Good retention of fluoride is observed for loadings up to 3.6 wt% F during both model compound reactions and cyclohexene pyrolysis. Above this loading some loss of fluoride is observed, however. This may be due to the formation at high fluoride loadings of surface phases such as AlF_3 or molybdenum oxyfluorides which are gradually leached from the catalyst.

3.4. Conclusions

Catalysts which possess high surface Brønsted acidity and which maintain good thiophene HDS activity can be prepared by coimpregnation of F, Ni and Mo onto γ -alumina. Good retention of fluoride is possible by this preparation method. Under accelerated aging studies and model reaction studies catalysts containing up to 3.6 wt% F show good fluoride retention, while some loss of fluoride is apparent from catalysts with higher fluoride loadings. The metal additives promote coking reactions, possibly by generating Lewis acid sites, while the fluoride-associated Brønsted acid sites only promote coke formation of species which polymerize easily, such as α -methylstyrene. All the additives accumulate to some extent in the smaller pores of γ -alumina, and access to these sites is blocked through coke formation.

Chapter 4 Phosphorus Promotion

4.1. Introduction

Phosphorus has been investigated and recommended as a secondary promoter in Ni-Mo catalysts over a period of thirty years or more, and is used in a number of commercial catalysts. This is because phosphorus (usually added as phosphoric acid) improves many of the properties of a hydroprocessing catalyst. Low loadings of phosphorus (0.3-3.8 wt%) have been reported to give improved HDS and HDN activities(140-143), as well as improved hydrogenation ability(144). In addition, the presence of phosphoric acid in the impregnating solution stabilizes high metal ion concentrations and leads to a more uniform impregnation of the support(145) thus producing more active catalysts. Furthermore, phosphorus-containing catalysts have improved resistance to coking(146) and increased strength and stability(147), both of which are important for commercial catalysts which must have as long a lifetime as possible. Although the original patent literature dates back almost forty years, it is only recently that investigations into the mechanism of phosphorus promotion have been initiated(148-159).

It appears that the promotional effect of phosphorus is multifaceted. The role of phosphorus in increasing HDS and HDN activities involves the generation of a greater number of active sites(160) and/or the generation of sites with greater activity(161). Phosphorus increases the metal dispersion(148) and, by reacting with anion vacancies in the support prevents the formation of catalytically inactive nickel or cobalt aluminate(154). As a consequence the promoter metal ions are forced to occupy other sites on the support. An increase in octahedrally-coordinated Ni²⁺ and Co²⁺ has been

observed in the presence of phosphorus(113,154), and these species appear to be precursors to the active phase in HDS and HDN. In addition, phosphorus increases the amount of easily reduced molybdenum species on the alumina surface leading to a promotion in hydrogenation(155) and thiophene HDS(156) activities. The extent of promotion was found to be strongly dependent on the preparation procedure. An additional beneficial effect of phosphorus in quinoline HDN has been proposed(162) whereby AlPO₄ provides additional sites for C-N bond cleavage reactions.

The improved thermal stability of phosphorus-containing catalysts has been attributed to blocking, by phosphorus, of nucleation sites for the transition between γ -alumina and low surface area α -alumina(150).

The resistance to coking which is imparted by phosphorus has been explained in of terms а promotion of the hydrogenation-dehydrogenation activity of $MoO_3/Al_2O_3(150)$ and by a decrease in the surface acidity of the alumina surface(146). The influence of phosphorus on the surface acidity of alumina is still unclear, however. Chadwick et al.(151) observed only a slight increase in surface acidity with increasing P content, using pyridine as a probe. Stanislaus et al.(149), who studied the temperature programmed desorption of ammonia from phosphated alumina, observed an initial decrease in the total surface acidity followed by a progressive increase as the phosphorus content increased. Morales and co-workers(152), who also used ammonia adsorption as a probe of the surface acidity, saw only a progressive increase in the surface acidity of alumina with increasing phosphorus content. Busca <u>et al.</u> studied H_3PO_4/Al_2O_3 by infrared spectroscopy using CO(158), and a number of N-compounds(159) as probe molecules. They found that phosphate poisons the basic sites on the supports but has little affect on the Lewis acidity. Also, in Ni-Mo-P systems it has been proposed that phosphorus, by preventing NiAl₂O₄ formation, decreases the number of strong acid sites

in the support (163).

While the understanding of phosphorus promotion has certainly grown as a result of these studies some of the fundamental questions remain. Among these is the mechanism of phosphoric acid adsorption onto γ -alumina. This is addressed in Section 4.2, while Section 4.3 extends this work to examine the interaction between molybdate and H₃PO₄-Al₂O₃. Finally, in Section 4.4 the importance of preparation procedure on HDS activity is studied. Also, in this section the effect of phosphorus on catalyst surface acidity is probed using model hydrocracking reactions.

4.2. Adsorption Mechanism of Phosphoric Acid on γ-alumina

Two different H_3PO_4 adsorption mechanisms have been proposed on the basis of ammonia desorption studies. Stanislaus <u>et al.(149)</u> extended an earlier model proposed by Gishti <u>et al.(150)</u> whereby H_3PO_4 reacts with conjugated Lewis acid-base sites on alumina forming multiple bonds at low concentrations but single bonds at higher concentrations as shown below:



In contrast, Morales et al.(152) proposed the reaction of H_3PO_4 with isolated basic

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alumina hydroxyls at low concentrations, followed by successive titration of the more acidic alumina hydroxyls. Finally, at higher concentrations condensation between adjacent P-OH groups is proposed to occur. The different types of hydroxyls on γ -alumina can be distinguished easily by infrared spectroscopy(164-166) and it occurred to us that investigation of the OH stretching region of P/Al₂O₃ catalysts would be a useful way of probing this adsorption process. There have been few studies of this type in the literature. Mennour <u>et al.</u>(167) characterized phosphated alumina for samples containing low phosphorus loadings (0-2 wt% P) by infrared spectroscopy. Also, Busca <u>et al.</u>(158) investigated the hydroxyl region for H₃PO₄/Al₂O₃ but for only one phosphorus loading of 2.4 wt% P. Very recently van Veen <u>et al.</u>(168) investigated the adsorption of (NH₄)H₂PO₄ on γ -alumina and deduced that H₂PO₄⁻ reacts predominantly with neutral and acidic hydroxyl groups at higher phosphorus loadings. In the present work the adsorption of H₃PO₄ on γ -alumina is investigated for phosphorus loadings of 0-7 wt%.

4.2.1. Compositions and Surface Areas

The compositions and surface areas of the catalysts used in this study are given in Table 4.2.1. The catalyst notation is given by xPAl where x refers to the weight percent phosphorus on the catalyst and Al refers to the alumina support. Only one of these catalysts was analysed for phosphorus content (5.0PAl) and the result was in excellent agreement with the nominal wt% P. This is a general finding from analysis of other phosphorus-containing catalysts (see Section 4.4) i.e. that H_3PO_4 interacts strongly with alumina and is retained quantitatively. The effect of phosphorus on alumina surface area can be seen from Table 4.2.1. There is an initial rapid decrease in surface area up to a surface concentration of > 10.2 x $10^{13} H_3PO_4$ cm⁻² followed by a much smaller decrease for higher phosphorus loadings. This "levelling off" in the surface area decrease could

Catalyst	Wt% P _{nom.}	Surface Area	Surface concentration		
	· ·	(m^2g^{-1})	(x 10 ¹³ H ₃ PO ₄ cm ⁻²)		
γ-alumina	0	190	0		
0.3PA1	0.3	157	3.1		
1.0PA1	1.0	139	10.2		
3.0PA1	3.0	79	30.1		
5.0PA1	5.0	55	51.2		
7.0PA1	7.0	78	71.6		

Table 4.2.1: Compositions and surface areas of P/Al₂O₃ catalysts

be a result of polyphosphate or $AlPO_4$ formation at the surface, as proposed in Section 4.2.2.

4.2.1. Infrared Spectra of P/Al₂O₃ Catalysts

The IR spectra for catalysts containing 0-5 wt. % P are shown in Figure 4.2.1. The OH stretching region for γ -alumina (Fig. 4.2.1(a)) can be resolved into four bands centred at 3795, 3780, 3736 and 3697 cm⁻¹. These values are in good agreement with those observed by Peri and coworkers(164,165) when γ -alumina is evacuated at 600-700 °C. The five different types of hydroxyls which are expected to be present on the surface of alumina have been assigned by Knözinger and Ratnasamy(166). Figures 4.2.2(a-d) show the idealized low Miller index planes for γ -alumina where the charge balance at the surface is maintained by hydroxide. The different types of OH groups are clearly demonstrated; OH may be bonded to either tetrahedral or octahedral Al leading to Types Ia (3780 cm⁻¹) and Ib (3795 cm⁻¹) hydroxyls respectively. Alternatively hydroxyl groups



Figure 4.2.1: FT-IR spectra of: (a) γ -alumina; (b) 0.3 wt% P/Al₂O₃; (c) 1.0 wt% P/Al₂O₃; (d) 3.0 wt% P/Al₂O₃; (e) 5.0 wt% P/Al₂O₃. Spectra were acquired after heating at 700 °C in vacuo and have been offset along the absorbance axis for clarity.



Figure 4.2.2: Idealized low Miller index surface planes of γ -alumina, where the charge balance at the surface is maintained by hydroxide; (a) A layer, parallel to the (111) plane, (b) B layer, parallel to the (111) plane, (c) C layer, parallel to the (110) plane, (d) D layer, parallel to the (110) plane.

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can bridge two Al centres resulting in Types IIa and IIb hydroxyls which are observed unresolved at 3736 cm⁻¹ in Figure 4.2.1(a). Finally, OH can be triply bridging with an observed v(OH) at 3697 cm⁻¹. Absent from Figure 4.2.2. is the (100) plane which in the ideal case would be a plane of Ib sites only. Since four, and possibly all five, of these OH types are observed in Figure 4.2.1(a) it seems probable that all five of these planes are present in this γ -alumina sample. The wavenumber of the OH stretch is dependent upon its acidity; thus the lower the wavenumber, the more acidic is the hydroxyl group. Therefore, using the notation in Figure 4.2.2, Type Ib hydroxyls are most basic while Type III hydroxyls are the most acidic.

Inspection of the IR spectra of the P/Al_2O_3 samples (Figs. 4.2.1(b-e)) shows a decrease in the Al-OH band intensities with increasing P content with the exception of the 3795 cm⁻¹ band. This indicates that H_3PO_4 reacts with all but the most basic Type Ib OH groups. In fact, the band due to Type Ib hydroxyls appears to increase in intensity up to 1 wt. % P. Also apparent is a new band at 3676 cm⁻¹ which has been assigned to P-OH groups(167); this band increases in intensity with increasing H_3PO_4 content. Finally, for high loadings of H_3PO_4 , a broad absorption at around 3250 cm⁻¹ is observed, which becomes even broader for the 7.0PAl sample (not shown), and suggests interaction between OH groups).

In order to gain more quantitative information on the reactivities of the different hydroxyls, the v(OH) regions of the spectra were curve fitted for the five hydroxyl bands. The results are shown in Figure 4.2.3. The band areas, normalized with respect to sample weight, were plotted against the surface H₃PO₄ concentrations and are given in Figures 4.2.4(a-e).

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From the initial areas (i.e. in γ -alumina) it appears that after the pretreatment



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Figure 4.2.3: OH stretching region in the IR spectra of 0-7 wt% P/Al_2O_3 curve-fitted for five different hydroxyl bands.

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Figure 4.2.4: Effect of the surface concentration of phosphoric acid on the OH stretching region of P/Al₂O₃ samples. (a) 3795 cm⁻¹ band (Ib sites); (b) 3780 cm⁻¹ band (Ia sites); (c) 3736 cm⁻¹ band (IIa and IIb sites); (d) 3697 cm⁻¹ band (III sites); (e) 3676 cm⁻¹ band (P-OH groups). Band areas are normalized with respect to sample weight.

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procedure described above there is a far greater number of Type III hydroxyls and Type II hydroxyls than either Type Ia or Ib. While the extinction coefficient is expected to increase with increasing acidity of OH(169) (i.e. for the lower wavenumber hydroxyl bands) it seems unlikely that this would contribute a ten-fold difference in the band areas. Therefore, it seems that the numbers of Types II and III OH groups on the surface are of the same order of magnitude, but there are fewer Ia sites by a factor of approximately 10, and still fewer Ib sites. The most basic hydroxyls (Ib most basic, then Ia) are expected to be lost most easily by dehydroxylation and so it is perhaps not surprising that these are the least abundant OH groups after heating γ -alumina at 700 °C under vacuum. Also, as discussed by Knözinger and Ratnasamy(166), dehydroxylation of the (111) plane (A and B layers, Figures 4.2.2(a) and (b) respectively) may result in a situation where the more frequently occurring IIa and IIb sites predominate. However, the large area of the Type III hydroxyl ν (OH) band leads one to the suggestion that the (111) plane is preferentially exposed on the γ -alumina surface.

There are a number of features in Figures 4.2.4(a-e) which need to be explained by any adsorption mechanism. Firstly, in the initial portion of the curves, the area of the band due to Ia OH groups (Figure 4.2.4(b)) decreases more rapidly than the Type II sites (4.2.4(c)) which in turn decrease more rapidly than the Type III sites (4.2.4(d)). Secondly, at a surface concentration of about 10 x 10^{13} H₃PO₄ cm⁻² there follows a more gradual decrease in the areas of the latter two bands, while the band due to Type Ia OH groups has been removed completely. Similarly, for the P-OH band at 3676 cm⁻¹ (Figure 4.2.4(e)) there is an initial sharp increase in the area of this band with increasing P content, and a change in slope of this curve occurs at a surface concentration of about 10 x 10^{13} H₃PO₄ cm⁻². Also, a sudden decrease in the integrated intensity of the P-OH band at the highest phosphorus concentration is observed. Finally, the number of Type Ib hydroxyls (3795 cm⁻¹) increases to a maximum value at around 10 x 10^{13} H₃PO₄ cm⁻² (1 wt. % P) and then decreases again to around the original number at higher P loadings (Figure 4.2.4(a)).

To explain the first of these observations, i.e. Type Ia reacting faster than Type II which react faster than Type III hydroxyls, it is necessary to consider the acid-base chemistry of the preparation procedure. γ -alumina develops strong acidity only upon heat treatment above 470 °C in a vacuum, and furthermore there is strong evidence that this acidity is due to the development of Lewis acid centres (not Brønsted acid sites) through dehydroxylation(170). Therefore, it is reasonable to assume that during the preparation procedure, the aqueous phosphoric acid will protonate all types of alumina hydroxyls by an acid-base reaction:

$$A1 - OH + H_3PO_4 (aq.) \longrightarrow A1 - O + H (aq.) (aq.)$$

Presumably water is lost either before or during the calcination process, resulting in the elimination of the bands associated with the O-H stretching vibration of these groups. Clearly the most basic hydroxyls of alumina would be expected to react preferentially with phosphoric acid and hence one would expect Types Ia and Ib to react more quickly than Types II and III. This explains the slopes of the curves in the initial portion of Figures 4.2.4(b-d). While this order of reactivity is not surprising, it is worth noting that it is not the same as that found for $(NH_4)H_2PO_4$; van Veen <u>et al.</u>(168) found that the $H_2PO_4^-$ ion did not adsorb on the basic hydroxyl groups.

At phosphoric acid surface concentrations above $10 \times 10^{13} \text{ H}_3\text{PO}_4 \text{ cm}^{-2}$ the alumina hydroxyl groups start to react less readily as reflected in the change in slope of

Figures 4.2.4(c) and (d) (and (b)). This shape of curve was also observed for the addition of MoO₃ or SO₄²⁻ to alumina(99) and was explained in terms of the formation of polymolybdate species in the former case. It is proposed therefore that at concentrations above 10 x 10^{13} H₃PO₄ cm⁻² phosphoric acid reacts with P-OH groups on the alumina surface in addition to Al-OH groups. Thus polyphosphate species are expected to be formed on the alumina surface. There is some evidence in support of this in the literature. Cordero <u>et al.(157)</u> observed excellent phosphorus dispersion for samples containing up to 0.9 wt. % P (9.2 x 10^{13} phosphate species cm⁻²) which then decreased at higher loadings, due to the formation of phosphate multilayers.

Consistent with this model is the shape of the P-OH band area-concentration curve (Figure 4.2.4(e)). Up to 10 x 10^{13} H₃PO₄ cm⁻² the area of the P-OH band increases rapidly, which is expected since for every Al-OH which reacts with phosphoric acid two P-OH groups are formed. However, above this surface concentration phosphoric acid reacts with some P-OH groups, in addition to Al-OH, and the rate of increase in the P-OH band area becomes less. At still higher phosphorus loadings (> 51 x 10^{13} H₃PO₄ cm⁻² (>5 wt. % P, corresponding to approximately monolayer coverage of H₃PO₄) a sudden drop in the P-OH band intensity occurs, possibly signifying a surface phase change to AlPO₄. Indeed, XRD patterns of the catalysts resembled that of γ -alumina for samples containing low loadings of phosphoric acid, but at high loadings of phosphorus (5 and 7 wt. % P samples) there is an additional, very broad peak near $2\theta = 27^{\circ}$ (possibly the 111 diffraction peak of AlPO₄), which is consistent with the presence of AlPO₄. Furthermore, van Veen <u>et al.</u>(168) observed the formation of an AlPO₄-type phase at above 4.5 wt. % P as evidenced by solid-state NMR spectra of calcined P/Al₂O₃ samples.

The effect of phosphoric acid on the band at 3795 cm⁻¹ (Ib OH groups) is quite

different to that on the other alumina surface OH groups. According to the mechanism proposed here, this hydroxyl should have greater reactivity than the more acidic OH groups, for example Types II and III. However, the number of Ib sites first increases and then decreases and, furthermore, over and above this effect the Ib sites do not appear to react with H_3PO_4 at all. The apparent increase in the number of these sites may be explained by inspection of Figure 4.2.2(b). Reaction of a Type IIb or Type III site with phosphoric acid may result in the formation of Ib sites at low loadings of phosphorus by:



Similarly, reaction of Type IIa hydroxyls with phosphoric acid (Figure 4.1.2(a)) will tend to generate Ib sites (rather than Ia) since the "tetrahedral Al" Lewis centre generated is stronger than the "octahedral Al" centre and will therefore react preferentially with the $H_2PO_4^-$ ion. At higher loadings of H_3PO_4 these reactions will occur to a lesser extent since firstly, both Al centres may react with phosphoric acid thus leading to a decrease in the number of Ib sites, and secondly, phosphoric acid starts to react with P(OH) groups on the surface in addition to Al(OH) groups. The fact that above around 30 x $10^{13} H_3PO_4$ cm⁻² the number of Ib sites appears to remain constant is difficult to explain. Possibly steric factors come into play at these high loadings so that it is more favourable for H_3PO_4 to react with P(OH) groups than certain Al(OH) groups. Alternatively, a steady state situation may have arisen such that Ib sites do react but they are also formed from the reactions described above.

It should be noted that Peri(171) observed a very intense band at 3800 cm⁻¹ in an $AIPO_4$ aerogel after drying at 600 °C which he assigned to OH groups bonded to tetrahedral aluminium. At high loadings, such OH groups could contribute to the

residual intensity seen in the spectra at 3795 cm⁻¹ (see Fig. 4.2.4(a)). (Recall that at high surface concentrations of H_3PO_4 a surface AlPO₄ phase starts to form.) However, there are many different aluminium orthophosphates, and Mennour <u>et al.(167)</u> observed no bands at all in this region for a commercial, anhydrous AlPO₄ sample. Clearly, the type of AlPO₄ phase formed on the surface of the P/Al₂O₃ samples will have a strong influence on the intensity of the band at 3795 cm⁻¹. In view of the relative intensities of the Al-OH and P-OH bands in the samples in this study containing high loadings of phosphorus we conclude that the AlPO₄ surface phase contains few OH groups attached to tetrahedral aluminium.

4.2.3. Model Compound Reaction Studies

Some catalytic studies were performed to assess the surface acidity of the H_3PO_4/Al_2O_3 surfaces. Three reactions were studied, cumene hydrocracking and 1,3-diisopropylbenzene cracking and hydrocracking. These results are summarized in Tables 4.2.2, 4.2.3 and 4.2.4, respectively. Cumene is a common probe molecule to assess Brønsted acidity since it is cracked to benzene in the presence of these acid sites. Another probe molecule, 1,3-diisopropylbenzene, was also chosen since it is cracked more easily (to cumene) than cumene is to benzene. However, for all of the P/Al₂O₃ catalysts the amount of cracking in both these reactions was low, indicating that any Brønsted acidity developed by the addition of H_3PO_4 to Al_2O_3 is too weak to crack cumene or 1,3-diisopropylbenzene to any great extent. Some tentative conclusions can be drawn from the results; low P loadings leave the surface acidity of γ -alumina unchanged or possibly increase it slightly, while high P loadings decrease the acidity by a small amount.
Catalyst	% Conv. ^a	% Yields				
		Benz. ^b	aMS°	Other		
γ-alumina	0.0	0.0	0.0	0.0		
0.3PA1	1.3	0.3	1.0	0.0		
1.0PA1	1.4	0.3	1.0	0.2		
3.0PA1	1.0	0.0	1.0	0.0		
5.0PA1	0.9	0.0	0.9	0.0		
7.0PA1	-	-	, -	-		

Table 4.2.2: Cumene hydrocracking results over P/Al_2O_3 catalysts

a % conversion after 4h on stream

b Benzene

c α -methylstyrene

Catalyst	% Conv. ^a	Cumene ^b			Other
γ-alumina	18.6	0.4	15.4	1.8	0.9
0.3PA1	17.2	, 0.6	14.6	1.9	-
1.0PA1	19.5	0.4	17.0	2.1	-
3.0PA1	16.8	0.2	14.9	1.7	-
5.0PA1	17.1	trace	14.9	1.9	-
Thermal	15.5	0	14.1	1.4	-

Table 4.2.3: Diisopropylbenzene cracking results over P/Al_2O_3 catalysts

a % conversion after 4h on stream

b Estimated % yield

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Catalyst	% Conv.ª	¥.	
γ-alumina	2.8	0.8	2.0
0.3PA1	2.9	0.8	2.1
1.0PA1	2.0	-	2.0
3.0PA1	1.7	-	1.7
5.0PA1	1.3	-	1.3
7.0PA1	1.3	-	1.3
Thermal	1.9	-	1.9

Table 4.2.4: Diisopropylbenzene hydrocracking over P/Al_2O_3 catalysts

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a % conversion after 4h on stream

4.2.3. Summary of Study of Adsorption of H_3PO_4 on γ -alumina

Inspection of the OH stretching region of the infrared spectra of the P/Al_2O_3 catalysts gives rise to the following conclusions regarding the mechanism for the reaction of H_3PO_4 with γ -alumina. (1) Phosphoric acid reacts with the alumina hydroxyls in an acid-base reaction during the impregnation process; the most basic hydroxyls are expected to react in preference. (2) At higher phosphorus loadings (> 10 x 10^{13} H₃PO₄ cm⁻²) phosphoric acid reacts not only with surface Al-OH but also with P-OH groups to form polyphosphate surface species. (3) Above 51 x 10^{13} H₃PO₄ cm⁻² an AlPO₄-type surface phase starts to form. (4) Ib sites are generated at low phosphorus content by the reaction of H₃PO₄ with Types II and III hydroxyls. Catalytic studies indicate that any Brønsted acidity that may be developed by the addition of H₃PO₄ to γ -alumina is too weak to crack cumene or 1,3-diisopropylbenzene to any great extent. There is some indication, however, that phosphorus may increase the acidity at low loadings and decrease the acidity at higher loadings.

4.3. Influence of P on the MoO₃-Al₂O₃ and NiO-Al₂O₃ Interactions

4.3.1. Introduction

It has been observed that phosphorus, particularly when impregnated first onto γ -alumina, increases the amount of reducible MoO₃ by promoting the formation of small MoO₃ clusters on the surface of alumina(155). This change in the surface distribution of MoO₃ accounted for the increased HDS activities observed for Mo-P/Al₂O₃ compared to Mo/Al₂O₃ catalysts(156).

The interaction between γ -alumina and MoO₃ involves the surface hydroxyl groups of the support. Therefore, any change in the surface distribution of MoO₃ must

also change the surface distribution of the alumina hydroxyls. Therefore, infrared spectroscopy should be useful in studying this interaction also. The $MoO_3-Al_2O_3$ interaction has been studied in some detail by IR spectroscopy (99,173-176), but the MoO_3 -P/Al_2O_3 interaction has received much less attention(168). The work presented in this section examines the influence of phosphorus on the reactivity of surface hydroxyls with molybdena. Also, since it is well known that reduction/sulphidation of Mo results in cleaving of the Al-O-Mo bonds and a regeneration of surface hydroxyls(173), the effect of phosphorus on this sulphiding process is also investigated here. Finally, the influence of phosphorus on the NiO-alumina interaction is also studied in this section.

4.3.2. Compositions and Surface Areas of Catalysts

The compositions and surface areas of the catalysts studied for the $MoO_3-Al_2O_3$ interaction are given in Table 4.3.1 together with their designations and surface areas.

Catalyst	Comp	osition ^a	Surface Area	
-	Wt% P	Wt% MoO3	m ² g ⁻¹	
0MoAl	-	-	193	
1.2MoAl	-	1.2	174	
2.4MoAl	-	2.4	175	
4.7MoAl	-	4.7	177	
0MoPA1	1.0	-	162	
1.2MoPA1	1.0	1.2	153	
2.4MoPA1	1.0	2.4	153	
4.7MoPAl	1.0	4.7	149	

 Table 4.3.1: Composition and surface areas of catalysts

^aRelative to the weight of γ -alumina.

Two support systems were used, γ -alumina and P/alumina, and molybdena loadings of 0-4.7 wt% were studied on each support. These low loadings of molybdena were chosen

so that IR spectra with well defined OH stretching regions could be obtained. The addition of phosphorus to γ -alumina results in a decrease in surface area of about 15%. Further addition of molybdena results in smaller decreases in surface area of between 5-8%. The addition of molybdena to the bare γ -alumina support results in a drop in surface area of about 10% at low loadings, with no further change in surface area occurring at higher loadings.

4.3.3. IR Spectra of Oxides

Figures 4.3.1 and 4.3.2 show the OH stretching region in the IR spectra of the MoAl and MoPAl catalysts, respectively. As discussed in Section 4.2 up to five different OH groups are expected to be present on the surface of γ -alumina(165) and suggested assignments for these have been given by Knözinger and Ratnasamy(166) as: Type Ib - terminal OH bonded to octahedrally-coordinated Al, most basic (3785-3800 cm⁻¹); Type Ia - terminal OH bonded to tetrahedrally-coordinated Al, next basic (3760-3780 cm⁻¹); Types IIa and IIb - doubly bridging hydroxyls (3730-3745 cm⁻¹); and Type III - triply bridging hydroxyls, least basic (3700-3710 cm⁻¹). These are depicted in Fig. 4.2.2 in the previous section. In the spectrum of γ -alumina (Fig. 4.3.1(a)) three OH bands are resolved centred at 3790, 3737 and 3695 cm⁻¹. These are in good agreement with the results reported in Section 4.2, although the Ia and Ib sites have not been resolved for these pretreatment conditions. The bands can be assigned as Types Ib + Ia (unresolved), Types IIb + IIa (unresolved) and Type III respectively. Addition of molybdena (Figs. 4.3.1(b-d)) results in a decrease in intensity of all three bands, indicating that the molybdenum species react with all types of hydroxyls. This is in agreement with the results of other workers(99,173-175).

In the spectrum of 0MoPA1 (Fig. 4.3.2(a)) an additional band is observed at 3676 cm^{-1} which has been assigned to the P(O-H) stretch(167) as discussed previously.



Figure 4.3.1: FT-IR spectra of the oxide forms of: (a) 0MoAl; (b) 1.2MoAl; (c) 2.4MoAl; (d) 4.7MoAl. Spectra were acquired after heating at 600 °C in vacuo and have been offset along the absorbance axis for clarity.



Figure 4.3.2: FT-IR spectra of the oxide forms of: (a) 0MoPAl; (b) 1.2MoPAl; (c) 2.4MoPAl; (d) 4.7MoPAl. Spectra were acquired after the same treatment given to those in Fig. 4.3.1 and have been offset along the absorbance axis for clarity.

All the spectra for the MoPAI catalysts have lower band intensities than those for the MoA1 catalysts since H_3PO_4 also reacts with the alumina hydroxyls, as was shown in Section 4.2. However, in the present study a lower degassing temperature was used (see Chapter 2, Section 2.4.1), and some Type Ia hydroxyls still remain, as shown by the position of the highest wavenumber band in Fig. 2(a) (3790 cm⁻¹). This is lower than would by seen if only Type Ib hydroxyls were present (3795 cm⁻¹). The addition of molybdena results in a decrease in intensity of all bands, but most dramatically for the P(O-H) stretch. Therefore, it is clear that the molybdenum species react preferentially with the P-OH groups on the alumina surface. A similar conclusion was made by van Veen <u>et al.(168)</u> The band at 3790 cm⁻¹ also shifts to 3795 cm⁻¹ for Figures 4.3.2(b-d) indicating that the Ia hydroxyls are removed and only Ib sites remain after the addition of molybdena to P/Al₂O₃.

The eight spectra in Figures 4.3.1 and 4.3.2 were curve-fitted for the different hydroxyl stretches in order to examine the MoO_3 -Al₂O₃ and MoO_3 -P/Al₂O₃ interactions more closely. Figure 4.3.3(a-d) shows the variation in the band areas, normalized with respect to sample weight, as a function of MoO_3 content. Differences between the two interactions are clearly evident: In all cases, low loadings of molybdena react with many of the surface hydroxyls on the P/Al₂O₃ surface. After the addition of 1.2 wt% MoO_3 , a 79% decrease in the area of the P-OH band (Figure 4.3.3(d)), a 54% decrease in the 3790 cm⁻¹ band (Figure 4.3.3(a)), and 31 and 28% decreases in the 3737 and 3695 cm⁻¹ bands, respectively, (Figures 4.3.3(b) and (c)) are observed. Since the P-OH band intensity decreases much more rapidly with increasing molybdenum content compared to that of the Al-OH groups, this implies that the molybdenum species reacts in a bidentate fashion with the -P(OH)₂ groups possibly in the manner similar to that shown in the scheme below, at least to some extent. However, as discussed in the next section, these species





Figure 4.3.3: Effect of the wt% MoO_3 on the OH stretching region of MoAl (+) and MoPAl (o) oxide catalysts. (a) $3795 + 3780 \text{ cm}^{-1}$ bands (Ib and Ia sites); (b) 3737 cm^{-1} band (IIb and IIa sites); (c) 3695 cm^{-1} band (III sites); (d) 3676 cm^{-1} band (P-OH groups). Band areas were obtained from the curve-fitted spectra in Figs. 4.3.1 and 4.3.2, and have been normalized with respect to sample weight.



are sulphided to a greater extent than Mo bonded to other surface hydroxyls suggesting they may be in the form of polymolybdate (Mo_{Oh}) species since Mo_{Oh} is known to be sulphided more readily than $Mo_{Td}(174)$.

The higher area of the 3700 cm⁻¹ band in the MoPAl catalysts compared to the MoAl catalysts probably is just an artifact of the curve fit program used which tends to broaden this band in the former case.

As the molybdenum content increases, the hydroxyls on the surface of γ -alumina react much less than those on the P/alumina surface with increasing molybdenum content. The OH groups associated with the band at 3790 cm⁻¹ are slightly more reactive than those associated with the 3737 and 3695 cm⁻¹ bands, at low molybdena loadings; the decreases in intensities upon addition of 1.2 wt% molybdena are approximately 18, 6 and 5%, respectively. Above 2.4 wt% MoO₃ a greater number of the Type II hydroxyls (3737 cm⁻¹) start to react (Figure 4.3.3(b)); a reduction in band area/g of 48% is observed for this band for the highest Mo loading studied. Other workers have reported simultaneous consumption, by molybdena, of basic and non-basic hydroxyls(99), and preferential reaction of basic hydroxyls with molybdena(168). This work suggests only slight preferential reactivity of the most basic groups with molybdena (and only at low loadings) and similar reactivity of the next most basic hydroxyls at the same loading. The different results of these three studies seem to arise from the various outgassing temperatures and times used, which leads to different OH stretching frequencies and different resolution of the OH group types on the surface. Therefore, comparison of the change in intensities of the same types of alumina hydroxyls for these three studies is not possible.

Some conclusions may be drawn from these results. Firstly, molybdena clearly reacts preferentially with the P-OH groups on the surface of alumina, and secondly, the presence of phosphorus influences the other surface hydroxyls so that they are more reactive towards molybdena. The inference from these conclusions is that phosphorus increases the dispersion of MoO_3 , at least for these low loadings studied. Although no dispersion measurements were made in this study, an increased dispersion of molybdenum in the presence of phosphorus is well established in the literature(154).

4.3.4. IR Spectra of the Sulphides

The IR spectra of the sulphided MoAl and MoPAl catalysts are given in Figures 4.3.4 and 4.3.5 respectively. The reduction/sulphiding process regenerates some of the surface hydroxyls by cleaving the Al-O-Mo(173) and presumably P-O-Mo bonds. Furthermore, the water generated by these processes, or reduction of oxide surface species, may also rehydrate the surface. Therefore, the intensities of the hydroxyl stretches of the sulphided catalysts are higher than those of the corresponding oxide catalysts. The Types Ib and Ia hydroxyls are now resolved at 3795 and 3780 cm⁻¹ respectively; these band positions are in good agreement with those reported in Section 4.2(172). In addition, one other band at 3590 cm⁻¹ is apparent in the spectra of the reduced/sulphided Mo-containing catalysts. This band has been assigned to Al-OH groups(173). However, this band is not present in the spectra of the oxide forms of the catalysts (which were subjected to the same pretreatment conditions, i.e. evacuated at 600 °C overnight), and it also increases in intensity with increasing Mo content in the



Figure 4.3.4: FT-IR spectra of the sulphided forms of: (a) 0MoAl; (b) 1.2MoAl; (c) 2.4MoAl; (d) 4.7MoAl. Spectra were acquired after sulphiding at 500 °C under 200 mmHg 10%H₂S/H₂ mixture, and then heating at 600 °C in vacuo. They have been offset along the absorbance axis for clarity.



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Figure 4.3.5: FT-IR spectra of the sulphided forms of: (a) 0MoPAl; (b) 1.2MoPAl; (c) 2.4MoPAl; (d) 4.7MoPAl. Spectra were acquired after the same treatment given to those in Fig. 4.3.4 and have been offset along the absorbance axis for clarity.

spectra of the reduced/sulphided catalysts. This strongly suggests that this band is associated with the presence of reduced/sulphided Mo.

These spectra were also curve-fitted for the different hydroxyl stretches and it was apparent from these results that certain of the alumina hydroxyls are regenerated to a greater extent than others. Figure 4.3.6 shows the % increase in band area per gram for the MoAl and MoPAl catalysts. An increase in the "% increase in band area per gram" with increasing molybdena content does not mean that there are more sites than on the Al₂O₃ (or P/Al₂O₃) surface, but rather that there are more sites present on the sulphided catalyst compared to the respective oxide surface. For γ -alumina, sulphiding results in a substantial increase in the intensities of Types Ib and Ia hydroxyl stretches and a large increase in the band intensity associated with the Type III hydroxyls, while the number of Type II hydroxyls is unchanged with sulphiding (Figure 4.3.6(a)). These increases in intensity are presumably associated with reduction of surface oxide species, or hydration of coordinatively unsaturated (c.u.s.) Al³⁺ centres. This makes complete interpretation of these figures difficult since increases in intensity for Mo-containing catalysts could be due both to sulphiding of the MoO_3 species, creating surface Al-OH groups, and to rehydration of the y-alumina surface, as described above. In cases where the % increases in intensity are greater for Mo-containing catalysts than for the support alone, then it can be stated unambiguously that sulphidation of the MoO₃ species is occurring. In Figure 4.3.6(a) this is observed only for the band at 3737 cm⁻¹ (Type II) and therefore we may conclude that molybdena which reacts with these hydroxyls can be sulphided to some extent. Interestingly these sites only start to react significantly with molybdena at higher loadings (Figure 4.3.3(b)). This suggests that the molybdenum species impregnated on these sites at lower loadings may be wasted; i.e. may not be convertible to the active form. These findings are in agreement with those of other workers(15) in that at very



Figure 4.3.6: Change in band areas of: (a) $3795 + 3780 \text{ cm}^{-1}$ (+), 3737 cm^{-1} (Δ), and 3695 cm^{-1} (o) bands upon sulphiding of the MoAl catalysts; (b) $3795 + 3780 \text{ cm}^{-1}$ (+), 3737 cm^{-1} (Δ), 3680 cm^{-1} (\bullet), and 3676 cm^{-1} (\blacksquare) bands upon sulphiding of the MoPAl catalysts. Plotted is the % increase in band area (normalized with respect to sample weight) of the sulphided catalyst as compared to the respective oxide catalyst.

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low MoO_3 loadings tetrahedral molybdate species are formed which are difficult to sulphide, while at higher loadings octahedral Mo in polymolybdate is present, which can be converted to the active phase.

Sulphiding of 0MoPAl (Figure 4.3.6(b)) results in an increase in intensity of all but the Type III hydroxyls. Since the number of P-OH groups also increases with sulphiding, the following process is implied:



The possibility that this reaction proceeds further to produce free H_3PO_4 cannot be dismissed on the basis of the IR spectra.

Of particular importance in Figure 4.3.6(b) is that many of the OH groups are regenerated in the MoPAl catalysts to a greater extent than they are for the blank P/Al_2O_3 support. In particular, molybdena which reacted with the P-OH groups is sulphided to a large extent as evidenced by the large % increase in band area upon sulphiding. Similarly, Mo bonded to Type II OH groups is sulphided. The conclusions drawn from the data for the sulphided catalysts are, therefore, that phosphorus clearly increases the sulphidibility/reducibility of molybdenum both directly (Mo bonded to P-OH groups is sulphided) and indirectly (Mo bonded to Type II alumina OH groups is also sulphided more readily). That is, although some of the Mo is still present in a form which is difficult to sulphide, as it is in the MoAl catalysts, some of it, in particular that bonded to phosphorus, is readily sulphided.

4.3.5. Thiophene HDS Studies

The sulphided catalysts were studied in the thiophene HDS reaction and the results are shown in Figure 4.3.7. The thermal conversion in this reaction was around 6% as indicated by the dashed line in Fig. 4.3.7. The activities of the catalysts were quite low (5 - 9 % Conversion, uncorrected for thermal conversion) because of the low loadings of molybdenum present, but nevertheless, differences were apparent. These differences were confirmed to be significant from repeated experiments. The maximum error between repeated experiments is shown by the error bars in Fig. 4.3.7. At very low or zero loadings of molybdenum the % conversion in thiophene HDS is actually less than that obtained thermally. Therefore, it appears that in the absence of catalytic sites a thermal, radical mechanism occurs, but the support provides sites for termination of this mechanism. In agreement with de Beer et al.(16) loadings of above 4 wt% MoO3 were required to see any appreciable activity (above thermal conversion) in thiophene HDS over MoAl catalysts. However, for the phosphorus-containing catalysts, the activity exceeded the thermal % conversion at lower loadings of Mo, i.e. 2.4MoPA1 and 4.7MoPAl catalysts. Also, these catalysts had higher activities than their analogous MoAl counterparts. This demonstrates that in the presence of phosphorus the impregnated molybdenum has a higher activity in this reaction. Clearly, the ability of phosphorus to increase the molybdenum dispersion and reducibility/sulphidability results in catalysts which are more active in thiophene HDS.

4.3.6. IR Spectra of Ni-P and Ni/Al₂O₃ Catalysts

The two support systems, γ -alumina and 1 wt% P/Al₂O₃, were also studied for their interaction with 3 wt% NiO using IR spectroscopy. The infrared spectra of the Ni-P/Al₂O₃ and P/Al₂O₃ catalysts are shown in Fig 4.3.8. No interaction between NiO and the P-OH (or Al-OH) groups is apparent. It has been noted previously that NiO and CoO



Figure 4.3.7: Influence of phosphorus on the thiophene HDS activity of MoAl (+) and MoPAl (o) catalysts. % conversions were after 4 h on stream at 400 ⁰C. Error bars show reproducibility between experiments and the dashed line indicates the thermal % conversion in this reaction.





do not react with surface hydroxyls of γ -alumina(174). The presence of phosphorus does not change this conclusion and it is therefore worth noting that any effect of phosphorus on nickel is an indirect one such as that proposed by Stanislaus <u>et al.(163)</u>; i.e. phosphorus blocks sites on the support on which catalytically inactive NiAl₂O₄ is formed.

4.3.7. Summary of Influence of Phosphorus on the Interactions of Molybdenum and Nickel with Alumina

Phosphorus influences the surface distribution of molybdenum both directly, since molybdena reacts preferentially with P-OH groups, and indirectly, since more alumina OH groups react with molybdena in the presence of P than in its absence. It is suggested that these interactions account for the increased molybdenum dispersion seen in P-Ni-Mo/Al₂O₃ catalysts. In contrast, there is no evidence of any interaction between surface OH groups and NiO. Molybdena in the P-Mo/Al₂O₃ catalysts, particularly that bonded to P-OH groups, is more easily sulphided/reduced compared to Mo/Al₂O₃ catalysts. Both these influences of phosphorus result in improved thiophene HDS activities for P-Mo/Al₂O₃ as compared to Mo/Al₂O₃ catalysts.

4.4. Effect of Preparation Method on Acidity and Activity

4.4.1. Introduction

From the preceding work, and other studies in the literature, it is reasonably expected that the sequence of steps in the preparation of phosphorus-containing catalysts makes an important contribution to the activity of the catalyst. For example, the work in Section 4.3 and that of López Agudo and co-workers(155,156) demonstrates that phosphate interacts with molybdate thus modifying the surface distribution and,

consequently, the hydrogenation and hydrodesulphurisation activities. Also, phosphorus prevents the formation of catalytically inactive nickel or cobalt aluminates, resulting in a greater fraction of the promoter metal in the active phase upon sulphiding(113,154). Furthermore, the use of one impregnating solution containing the metal additives and phosphoric acid has also resulted in more active catalysts(141) and some workers have used this method of preparation while studying phosphorus promotion(113,148,151). Others have used stepwise methods of preparation (149,155,156,163,177). Few studies have made a direct comparison of preparation method and catalytic activity, however, and this was one of the goals of the work in this section. Thus, three series of catalysts, all containing 15.0 wt% MoO₃, 3.0 wt% NiO and 0-7 wt% P were prepared in three different ways: Coimpregnation of γ -alumina with a solution containing all the additives (Method 1); stepwise impregnation, Ni-Mo followed by P additives, with a calcination step before and after the addition of P (Method 2); and a stepwise impregnation of P followed by Ni-Mo additives with a calcination step before and after the addition of the metal additives (Method 3). More details of these preparation procedures are given in Section 2.1.3. These catalysts were studied for their thiophene HDS activities. While this work was in progress, a similar study appeared in the literature(153), although different preparation methods were compared. No difference in HDS activity between the catalysts prepared by different methods was apparent from their work.

As was discussed in the introduction to this chapter, the effect of phosphorus on the surface acidity of alumina-based catalysts, particularly in the sulphided form, remains unanswered. The second aim of the present study, therefore, was to investigate the effect of phosphorus on the surface acidity of the Ni-Mo/Al₂O₃ catalysts using model hydrocracking reactions as a probe. Also, the influence of the different catalyst preparation methods on the surface acidity was explored.

4.4.2. Catalyst Composition and Surface Areas

The compositions and surface areas of the catalysts are given in Table 4.4.1

Table 4.4.1:	Composition	i, surface are	as and thioph	ene HDS	activities
of P-Ni-Mo c	atalysts prep	ared by diffe	rent methods.	•	

Catalyst	NiO	MoO ₃	Pnom	Pmaa	Surface Area m ² g ⁻¹	% Thiophene HDS conversion
NiMoAl MoAl NiAl	3 0 3	15 15 0	0 0 0	-	137 139 189	34.4 14.7 7.1
<u>Method 1</u> 1NiMoP _{0.3} 1NiMoP _{1.0} 1NiMoP _{5.0} 1NiMoP _{5.0}	3 3 3 3 3	15 15 15 15 15	0.3 1 3 5 7	NM NM 2.7 4.1 NM	124 115 79 79 70	39.5 40.8 35.0 33.7 27.6
Method 2 2NiMoP _{0.3} 2NiMoP _{1.0} 2NiMoP _{3.0} 2NiMoP _{5.0} 2NiMoP _{7.0}	3 3 3 3 3	15 15 15 15 15	0.3 1 3 5 7	NM NM 2.6 NM NM	120 121 101 75 57	40.6 41.0 37.8 28.7 25.2
<u>Method 3</u> 3NiMoP _{0.3} 3NiMoP _{1.0} 3NiMoP _{3.0} 3NiMoP _{5.0} 3NiMoP _{7.0}	3 3 3 3 3	15 15 15 15 15	0.3 1 3 5 7	0.4 1.1 3.0 4.6 6.9	143 125 100 75 58	40.4 46.6 40.5 39.1 29.7
Thermal	-		-	-	-	6.0

NM: Not Measured

together with their HDS conversions. All the catalysts contained nominal weight percents of 3.0 wt% NiO and 15.0 wt% MoO_3 and the phosphorus content varied between 0 and 7 wt%. The designations of the catalysts are given by NiMoAl for the catalyst which contains 0 wt% P, and xNiMoP_y where x = 1,2 or 3 and indicates the

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preparation method used (see Chapter 2)) and y = 0.3-7 and gives the wt% P on the catalyst. Some of the catalysts were measured for their phosphorus contents and these are also given in Table 4.4.1. There was good agreement between the nominal and measured weight percents of phosphorus. Two catalysts, MoAl and NiAl containing just 15.0 wt% MoO₃ and 3.0 wt% NiO on alumina, respectively were also prepared for comparison. In addition catalysts containing just phosphorus (0-7 wt%, no metals) were prepared, but were found to have extremely low catalytic activity in all of the reactions studied, and therefore the results for these catalysts are not included here. They are given in Section 4.2.3, however.

The effect of phosphorus on surface area is shown in Figure 4.4.1. A general trend is seen: The surface area decreases approximately linearly as the weight percent phosphorus increases regardless of preparation method. This is consistent with a gradual filling of the pores of alumina with phosphate, eventually forming $AIPO_4(168,172)$. Closer inspection of the surface areas indicates that Method 1 results in an initial rapid decrease in surface area followed by a slower decrease at high P loadings. The reason for this may be associated with the observation that for lower P loadings Method 1 was found to be unreliable; the impregnating solution was unstable leading to the formation of a green/yellow precipitate (probably phosphomolybdates) which would not redissolve. Attempts to stabilize the solution by acidification, which has been suggested by several authors(113,151), were only partially successful. Similar problems with solution stability have been reported by Atanasova and coworkers(148). At higher P loadings the impregnation solutions for Method 1 are stable and the surface areas of the catalysts decrease much more slowly with increasing P content.

Method 3 gives the highest surface areas of the three methods at low phosphorus loadings. This may be a direct result of the phosphorus, when impregnated first,

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Figure 4.4.1: Influence of phosphorus on the surface area of Ni-Mo/Al₂O₃ catalysts prepared by Methods 1 (+), 2 (Δ) and 3 (o).

influencing the impregnation of the metal salts. Several workers have reported that phosphorus affects the nature of the surface nickel species in these types of catalysts(113,150,154,178). Also, it was shown previously (Section 4.3 and reference 179), that low loadings of P strongly influence molybdenum impregnation and seem to increase the dispersion of this metal. Presumably, for catalysts with increased metal dispersion there are fewer pores blocked by the metals and therefore the surface areas remain higher. At higher P loadings Methods 2 and 3 give identical surface areas, perhaps indicating that in the case of Method 3 the effect of phosphorus described above is absent at these high loadings so that, in effect, there is no longer any difference in preparation between methods 2 and 3.

4.4.3. Thiophene HDS Activities

The results of thiophene HDS over these catalysts are also given in Table 4.4.1. The reproducibility of each % Conversion is about \pm 7 % of the value itself, which is much less than the changes observed between different catalysts. This reaction was carried out over the sulphided forms of the catalyst. The activities of MoAl, NiAl, and NiMoAl clearly demonstrate the synergy between nickel and molybdenum sulphides in this reaction. A promotional effect of phosphorus is seen for all three series of catalysts, the maximum promotional effect being around 1.0 wt% P regardless of preparation method. This effect is a true promotional one since the activities of catalysts containing phosphorus only (no metals) are negligible. Therefore, since phosphorus has no inherent activity in this reaction, it is clear that the role of phosphorus is to generate more active sites for thiophene HDS. The results for Method 1 catalysts are in good agreement with those seen previously for coimpregnated Ni-Mo catalysts(148,151), i.e. a maximum promotional effect of phosphorus at approximately 1 wt% P.

The greatest promotional effect is seen for Method 3 (H₃PO₄ impregnated first,

then the metals) which is consistent with the proposal that the presence of low loadings of phosphorus on the alumina surface increases the metal dispersion. It is now quite well established that low loadings of phosphate block Ni adsorption sites on alumina thereby reducing the fraction of Ni forming catalytically inactive nickel aluminate(113,153), and, possibly, allowing more Ni to be incorporated into edge sites of MoS_2 crystallites upon sulphiding(113). Similarly, phosphate also affects favourably both the impregnation of molybdate(148,179) and the ease of reduction(155) and sulphidation(179) of the molybdate. Therefore catalysts prepared by Method 3 (phosphorus followed by Ni-Mo) may be expected to have the largest promotional effect of phosphorus since both of these beneficial effects will be manifested.

It is interesting that a promotional effect is seen for all three preparation methods, even Method 2 in which the phosphorus is impregnated after the metal oxides have been formed. Apparently, even under these circumstances, the phosphorus can influence the sulphiding process. Similar findings were observed by Muralidhar <u>et al.</u>(7) for thiophene HDS over Co-Mo catalysts prepared in a similar way to Method 2 but using $(NH_4)_2HPO_4$ as the source of phosphorus; a slight promotional effect was seen at 0.5 wt% additive, but higher loadings (5.0 wt%) lead to a decrease in the rate of thiophene HDS relative to the catalyst containing no phosphorus.

4.4.4. Diisopropylbenzene Hydrocracking Activities

During hydrocracking, *m*-diisopropylbenzene (DIPB) forms a number of different products depending on the types of sites present on the surface. Dehydrogenation of either one or both of the side chains occurs on the metal sites, particularly in the absence of hydrogen. Different cracked and rearranged products are formed on the acid sites of the catalyst. For example, on F/Al_2O_3 which contains stronger Brønsted acid sites than does alumina itself, only cumene and subsequent cumene-cracked products are observed;

9.1% cumene and 26.3% benzene were seen over 6.5 wt% F/Al_2O_3 . The yield of cumene (and benzene) can therefore be used as a measure of the Brønsted surface acidity, assuming that DIPB dealkylation to cumene occurs by the same mechanism as cumene dealkylation to benzene(180). On the P-promoted Ni-Mo catalysts studied here both cumene and other side-chain cracked and rearranged products are formed.

The results of the DIPB hydrocracking on the reduced and sulphided catalysts are given in Tables 4.4.2 and 4.4.3 respectively. The reproducibility of the % Conversions is better than \pm 5% of the value given. Over P/Al₂O₃ (P = 0 - 7.0 wt%, see Section 4.2) the conversion is very low in this reaction and the major product is due to dehydrogenation of the side chain. In addition, trace amounts of cumene were seen, particularly for γ -alumina and 0.3 wt% P/Al₂O₃. From this it is apparent that H₃PO₄ does not have a strong effect on the surface acidity of γ -alumina. In the presence of the metal phase a number of other products are formed in the hydrocracking of DIPB. These include small amounts of the dehydrogenation product (similar amounts to that seen over the γ -alumina support), a significant amount of cumene, small amounts of the side-chain cracked product, 1-isopropyl-3-ethylbenzene (particularly when the catalysts are in the reduced forms), and two products isomeric with DIPB. One of these is produced in very small amounts and has a mass spectrum consistent with that of p-diisopropylbenzene. The other isomer is one of the major products in this reaction and its identity was confirmed as 1-n-propyl-3-isopropylbenzene by nmr decoupling experiments of the product mixture. If sufficient cumene is formed in the reaction then some α -methylstyrene is also seen in the product mixture.

Similar trends in activity are seen for both the reduced and sulphided catalysts, although the sulphided catalysts have substantially higher activity than their reduced counterparts. This discussion will therefore concentrate on the results for the sulphided

		% Yields					
Catalyst	% Conv. ^a) (j)	¥€			Les la	کیر
NiMoAl MoAl NiAl	17.6 17.8 5.9	4.7 6.1 0.9	- - -	2.2 1.2	1.6 1.7 2.0	-	8.4 7.8 3.0
Method 1 1NiMoP _{0.3} 1NiMoP _{1.0} 1NiMoP _{3.0} 1NiMoP _{5.0} 1NiMoP _{7.0}	23.4 23.7 15.1 13.8 14.2	8.2 7.9 5.6 5.5 3.7	1.2 1.7 1.1	2.3 2.1 1.3 1.1	1.0 1.5 1.6 1.6 1.5	- 0.3 2.6	9.4 9.4 5.1 5.3 6.0
Method 2 2NiMoP _{0.3} 2NiMoP _{1.0} 2NiMoP _{3.0} 2NiMoP _{5.0} 2NiMoP _{7.0}	19.6 20.6 15.6 10.4 7.0	5.5 7.7 7.2 5.0 3.9	1.2 - -	2.9 0.9 1.4 1.0 0.6	2.2 1.3 1.4 1.5 1.7	- - - -	9.0 8.7 5.6 2.9 0.7
Method 3 3NiMoP _{0.3} 3NiMoP _{1.0} 3NiMoP _{3.0} 3NiMoP _{5.0} 3NiMoP _{7.0}	18.1 15.0 16.6 14.2 13.9	5.3 5.5 5.4 5.1 5.8	1.2 - - - -	- - - -	1.7 1.4 1.7 1.7 1.5	- 0.8 1.1	8.4 7.3 8.7 6.6 5.4

 Table 4.4.2:
 Diisopropylbenzene hydrocracking over reduced catalysts

^aAfter 4 h on stream. In cases where the % Conversion does not equal Σ % Yields, one other unidentified minor product was present.

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		% Yields					
Catalyst	% Conv. ^a	¥ ©	¥€		Ĕ _Y	K S K	Č.
NiMoAl MoAl NiAl	25.2 22.6 ⁻ 7.3	8.8 13.5 2.2	1.6 1.4 -	2.0	1.4 1.7 1.6	0.8 -	10.1 3.9 3.4
Method 1 1NiMoP _{0.3} 1NiMoP _{1.0} 1NiMoP _{3.0} 1NiMoP _{5.0} 1NiMoP _{7.0}	29.0 29.5 24.2 17.4 16.1	11.8 11.0 8.8 7.0 6.8	2.2 2.4 1.2 -	1.5 1.7 - -	1.3 1.3 1.0 1.8 1.6	0.9 1.0 1.7 1.1 1.4	9.8 10.5 9.8 7.5 6.2
$\begin{array}{c} \text{Method 2} \\ \text{2NiMoP}_{0.3} \\ \text{2NiMoP}_{1.0} \\ \text{2NiMoP}_{3.0} \\ \text{2NiMoP}_{5.0} \\ \text{2NiMoP}_{7.0} \end{array}$	29.8 30.9 32.5 17.8 15.1	10.2 11.5 13.4 8.1 6.6	2.0 2.4 3.0	1.0 1.0 - -	1.3 1.1 1.3 1.2 1.5	1.0 1.4 1.8 1.7 1.5	12.5 11.9 11.5 6.8 5.5
Method 3 3NiMoP _{0.3} 3NiMoP _{1.0} 3NiMoP _{3.0} 3NiMoP _{5.0} 3NiMoP _{7.0}	34.4 29.3 21.6 17.6 15.4	17.3 13.2 9.5 8.2 7.9	3.6 2.6 1.4 1.3	2.2 2.1	1.4 1.1 1.5 1.7 1.6	0.8 0.8 1.0 1.1 1.2	7.7 8.3 7.3 5.1 4.6

 Table 4.4.3:
 Diisopropylbenzene hydrocracking over sulphided catalysts

^aAfter 4 h on stream. In cases where the % Conversion does not equal Σ % Yields, one other unidentified product was present.

catalysts. Sulphided MoAl is quite acidic producing 13.5 % cumene. The addition of Ni (NiMoAl) reduces the surface acidity but increases the amount of the rearranged product. This in agreement with the findings of Topsøe <u>et al.</u>(116) who observed the development of Brønsted acidity on sulphided Mo/Al₂O₃ at above 300 °C. Furthermore, there was a decrease in Brønsted acidity for the Ni- or Co-promoted catalyst as compared to MoS_2/Al_2O_3 . The rearranged product seems to require the presence of the Ni-Mo phase in the case of the sulphided catalysts, but only the molybdenum for the reduced catalysts. The sites for the rearrangement are not the same sites as those on which HDS occurs, however, since the amount of the isomer produced on the various catalysts bears no relation to its activity in thiophene HDS.

For all preparation methods phosphorus significantly increases the % hydrocracking for this reaction, compared to NiMoAl, up to maximum activities at 0.3 wt% P for Methods 1 and 3, and 3 wt% P for Method 2 (sulphided). At higher phosphorus loadings the activity drops to below that seen for NiMoAl, probably a consequence of the low surface area of these catalysts. The increased activity is, in all cases, due to an increase in the amount of cumene observed in the product mixture; the maximum amount of cumene is produced at phosphorus loadings of 0.3 wt% for Methods 1 and 3, and 3.0 wt% for Method 2. The method which resulted in catalysts producing the most cumene is Method 3, and only by Method 3 did the cumene yield exceed that observed for MoAl. A possible explanation of these trends in acidity assumes that the Brønsted acid sites which produce cumene are associated with reduced/sulphided Mo/Al₂O₃ under reaction conditions. The presence of weak Brønsted acid sites on sulphided Mo, Ni-Mo and Co-Mo alumina catalysts at 400 °C has been observed by Topsøe <u>et al.</u>(116). They postulated that these sites may be generated by the dissociation of H₂S on anion vacancies in MoS₂. The DIPB hydrocracking results over the reduced

catalysts suggest that Brønsted acid sites can also be generated at 400 °C in the absence of H_2S , possibly by the dissociation of H_2 over reduced molybdate. If this is the case then Ni decreases the number (or strength) of the Brønsted acid sites, possibly by impeding the reduction/sulphidation of molybdate. In the presence of low loadings of phosphorus, however, either the presence of P increases the number of Brønsted acid sites or it facilitates the reduction/sulphidation of molybdate. The latter argument is consistent with the work of Cordero <u>et al.</u>(155) who saw that phosphorus increases the amount of easily reduced molybdenum particularly when Mo was impregnated after P. If this is the case then Method 3 allows more complete reduction/sulphidation which is consistent with the higher HDS activity observed for catalysts produced in this way. Alternatively, the presence of low loadings of P may increase the dispersion of the molybdenum thereby creating more sites for the production of cumene. A similar inference was made from the thiophene HDS results over these catalysts.

It is difficult to rationalize the relative amounts of the rearrangement product produced. Method 1 seems to have little effect on these sites, while Method 2 increases the amount of this product and Method 3 decreases the amount. Furthermore, the reduced catalysts all produce quite comparable amounts of this product, so the differences in the number of sites are associated with sulphidation. Possibly this reaction occurs on Brønsted acid sites of a different strength to those on which cumene is formed.

Comparable amounts of the other products are produced over all the catalysts regardless of preparation method, but these are produced in quite small quantities so any differences that may be present are too small to detect.

4.4.5. Summary of Effect of Preparation Method on Acidity and Activity

A promotional effect of phosphorus on Ni-Mo/alumina catalysts in thiophene HDS is observed, regardless of preparation method, with a maximum in activity at 1 wt% P loading. This is most significant when phosphorus is impregnated prior to the metals (Method 3) and leads to the suggestion that the promotional effect of phosphorus is due to (1) blocking by phosphate of sites for Ni adsorption so that more nickel is available for the active phase and (2) influencing favourably both the impregnation and reducibility/sulphidability of molybdate. For catalysts prepared by Method 3 both of these effects may be manifested.

An increase in the formation of cumene in DIPB hydrocracking over reduced and sulphided Ni-Mo-P catalysts is seen at low phosphorus loadings for all preparation Methods, and is indicative of increased Brønsted acidity. This increased Brønsted acidity is not due to any inherent acidity imparted by phosphorus since P/Al_2O_3 catalysts (P = 0 - 7 wt%) have little activity in this reaction. Rather it seems to be associated with reduced/sulphided molybdate and so may be explained by the second promotional effect described above. Thus, the NiMoP_{0.3} catalyst produced by Method 3 manifested the greatest Brønsted acidity.

4.5. Conclusions

Phosphoric acid modifies the surface distribution of OH groups on the surface of alumina and also provides new hydroxyl groups bonded to phosphorus. The interaction of molybdenum species with the phosphorus-modified surface is very different to that with unmodified γ -alumina, and results in molybdenum species which are more easily reduced/sulphided in the former case. There is no direct evidence from the FTIR spectroscopic studies that phosphorus modifies the surface distribution of nickel, but this is perhaps not surprising since the nickel species do not interact with surface OH groups. The role of phosphorus in nickel impregnation may be that it blocks nucleation sites for

 $NiAl_2O_4$ formation as noted by other workers(163).

Because of these effects of phosphorus, the preparation method used for the impregnation of the additives on alumina has an important influence on catalytic properties. Impregnation of phosphorus prior to the metal additives results in catalysts which are more active in hydrodesulphurisation because the molybdenum species are more easily sulphided, and probably because of the favourable influence of phosphorus on nickel impregnation.

Sulphided Mo/Al_2O_3 exhibits sufficient Brønsted acidity to crack diisopropylbenzene to cumene by a significant amount. These Brønsted acid sites are thought to result from the dissociation of H_2S on anion vacancies in MoS_2 crystallites(116). Phosphorus-promoted Ni-Mo/Al_2O_3 (sulphided) is more acidic than unpromoted Ni-Mo/Al_2O_3 (sulphided). Since H_3PO_4 -Al_2O_3 itself is not acidic, the increased acidity of P-Ni-Mo/Al_2O_3 compared to that of Ni-Mo/Al_2O_3 is probably a result of improved sulphidation of MoO_3 in the former case.

Chapter 5: Phosphorus and Fluoride Promotion

5.1. Introduction

In Chapter Three it was demonstrated that fluoride dramatically increases the hydrocracking activity of Ni-Mo/Al₂O₃ catalysts and, as shown later in Chapter Six, this translates into an improvement in many other catalyst properties in the hydroprocessing of a gas oil feed. Also, in Chapter Four the promotional effect of phosphorus in these types of catalysts was studied in some detail. Again, as shown later in Chapter Six, the beneficial properties are also manifested in hydroprocessing reactions. Can the favourable properties of both phosphorus and fluoride be merged in one superior catalyst? This is the question addressed in this chapter, which examines the activity of such catalysts in model compound reaction studies. In Chapter Six this investigation is extended to the study of hydroprocessing of a gas oil feed where comparisons to catalysts containing just phosphorus and just fluoride (and metal additives) are made.

In order to investigate the combined effect of fluoride and phosphorus, two series of catalysts were prepared. These contained 3.6 nominal weight percent fluoride, 15.0 wt% MoO_3 , 3.0 wt% NiO and the phosphorus content varied from 0 to 3.0 wt%. A fluoride loading of 3.6 wt% was chosen since this gave maximum activity in hydrocracking. The two catalyst series were prepared by different routes. In the first series the order of addition of the additives was phosphorus, followed by the metal salts, followed by fluoride. Thus the presence of phosphorus should favourably influence the metal additive impregnation as seen in Chapter 4, and the fluoride may modify the acid strength of any remaining surface hydroxyls. This was the strategy behind the preparation of the first series of catalysts.

In the second series of catalysts, the order of addition was phosphorus, followed by fluoride, followed by metal additives. The strategy behind this method was that perhaps fluoride might replace OH groups bonded to phosphorus as well as those bonded to alumina, as shown in Figure 5.1.1. Such a system would be expected to have strong



Figure 5.1.1: Possible reaction of F⁻ with H₃PO₄/Al₂O₃

acidity, by analogy to fluorosulphuric acid(181), due to the electron-withdrawing effect of fluoride, and this acidity should translate into improved hydrocracking activity.

Both series of catalysts were studied for their cumene cracking (oxide forms) and hydrocracking (sulphided forms) activities as well as their thiophene HDS activities.

5.2. Preparation Method and Catalytic Activity

5.2.1. Composition, Surface Areas and Preparation Method

The compositions and surface areas of the catalysts studied are given in Table 5.2.1. The designations of the catalysts are given by xPMF and xPFM, where x = wt% P and PMF and PFM refer to the order of addition of the phosphorus, fluoride and metal (M) additives. All these catalysts were calcined after the addition of each additive (i.e. three calcination steps per catalyst) as detailed in Chapter Two.
Catalyst		Composition (Wt%) ^a					
	MoO ₃	NiO	Р	F _{nom.}	F _{meas.}	(m ² g ⁻¹)	
0PMF	15.0	3.0	0	3.6	3.4	103	
0.3PMF	15.0	3.0	0.3	3.6	3.1	111	
1.0PMF	15.0	3.0	1.0	3.6	3.4	101	
3.0PMF	15.0	3.0	3.0	3.6	3.4	80	
0PFM	15.0	3.0	0	3.6	2.5	97	
0.3PFM	15.0	3.0	0.3	3.6	2.1	91	
1.0PFM	15.0	3.0	1.0	3.6	2.4	80	
3.0PFM	15.0	3.0	3.0	3.6	2.1	68	

 Table 5.2.1:
 Composition and surface areas of catalysts

^aBoth nominal and measured weight percents fluoride are given

The PMF catalysts all have higher surface areas than the corresponding PFM catalysts indicating that fewer pores of the support are blocked by the additives in the former case. The PMF catalysts also have a greater retention of fluoride than the PFM catalysts. This suggests that, firstly, for the PMF catalysts there are still sufficient hydroxyl (or possibly oxide) groups, even after impregnation of the phosphorus and metal additives, to exchange with fluoride, so that nearly all is retained. Secondly, for the PFM catalysts, the fact that less fluoride is retained suggests loss of fluoride, either by displacement by the metal additives, or during the extra calcination step. A possible route to fluoride loss involving molybdenum oxofluorides or AlF_3 species was discussed in Chapter 3.

In addition, it is seen from Table 5.2.1 that the amount of phosphorus on the catalyst does not influence the amount of fluoride retained by the support for either catalyst series; i.e. phosphorus and fluoride are not in competition with one another for surface hydroxyls. The number of surface OH groups on γ -alumina has been estimated to be between 93-145 x 10^{13} OH cm⁻²(99). Since every fluoride ion displaces one hydroxide ion, 3.6 wt% F accounts for 60 x 10^{13} OH cm⁻² assuming an alumina surface area of 198 m²g⁻¹. Similarly, in the case of phosphoric acid, the number of alumina surface hydroxyls reacting per H₃PO₄ molecule is between one and two for low loadings (up to 1 wt% P), and less than this at higher loadings, where condensation of P-OH groups occurs (see Chapter 4, Section 4.2). The maximum number of Al-OH groups consumed by 3 wt% P (assuming a stoichiometry of 2:1) is calculated as approximately 60 x 10^{13} OH cm⁻²; i.e. assuming there are no steric restrictions there are sufficient surface hydroxyls on γ -alumina to accommodate both H_3PO_4 and $F^{\text{-}}$ at the loadings used in this study. So for the PFM series of catalysts it is perhaps not surprising that increasing phosphorus content does not affect the amount of fluoride retained. This does not rule out the formation of P-F bonds by displacement of P-OH groups by F⁻. Fluoride ions do exchange with P-OH groups in aqueous solution. This was verified by measuring the amount of fluoride exchanged with P/Al₂O₃ samples in aqueous solution(88). The results are shown in Table 5.2.2. Since the total number of exchangeable OH groups increases with increasing H₃PO₄ content some of the P-OH groups must exchange with fluoride. In fact, since H₃PO₄ reacts with (and consumes) Al-OH groups, the stoichiometry for the reaction of H₃PO₄ and Al-OH groups must be close to 1:1 at low loadings of phosphorus, i.e. two (exchangeable) P-OH groups are generated for every Al-OH group consumed so that the total number of fluorideexchangeable OH groups increases overall.

Wt% P	H ₃ PO ₄	Exchangeable	Additional OH/cm ² due to H_3PO_4
	/cm ² alumina	OH/cm ²	⁻ (Column 3 - 25.1x10 ¹³)
0	-	25.1 x 10 ¹³	-
0.3	$3.1 \ge 10^{13}$	$28.4 \ge 10^{13}$	3.3 x 10 ¹³
1.0	$10.2 \ge 10^{13}$	$32.2 \ge 10^{13}$	$7.1 \ge 10^{13}$
3.0	30.1 x 10 ¹³	55.1 x 10 ¹³	$30.0 \ge 10^{13}$
5.0	51.2 x 10 ¹³	Not measured	Not measured
7.0	71.6 x 10 ¹³	76.0 x 10 ¹³	50.9 x 10 ¹³

Table 5.2.2: Exchangeable hydroxyls of P/Al_2O_3 catalysts measured by

fluoride exchange

5.2.2. Model Compound Reaction Studies

The results of cumene cracking over the oxide catalysts and cumene hydrocracking and thiophene HDS over the sulphided catalysts are given in Table 5.2.3. The cumene cracking results after 4 h on stream are not very informative since the Brønsted acid sites on which benzene is formed deactivate rapidly. Figure 5.2.1 shows the product distributions with time for 0.0PMF(a) and 0.0PFM(b) as examples. As discussed in Chapter 3, Section 3.3.3 this deactivation is probably due to polymerization of α -methylstyrene (α MS) over the fluoride associated Brønsted acid sites(137).

The cumene hydrocracking results are much more informative, however, since α MS production is suppressed by the presence of hydrogen. The first thing to notice from these results is that the PFM catalysts have a lower yield of benzene than the

	Cum	Cumene Cracking (oxides)			Cun	Cumene Hydrocracking (sulphides)				
Catalysts	%Conv.	% Yields			% Conv.	% Yields				% Conv.
		Benz. ^a	αMS^b	∑SCC°		Benz. ^a	EtB ^d	αMS^b	nPBe	
0.0PMF	26.6	2.1	20.1	4.1	68.3	65.4	0.2	0.5	2.1	31.3
0.3PMF	20.5	1.2	16.4	2.8	51.9	49.0	0.3	0.7	1.8	32.6
1.0PMF	22.0	1.5	17.7	2.8	49.0	45.5	0.1	0.7	2.7	31.8
3.0PMF	17.9	1.4	14.6	2.0	38.0	31.9	0.2	0.9	4.9	32.2
0.0PFM	19.8	0.8	16.7	2.3	40.2	36.5	0.1	1.4	2.1	33.3
0.3PFM	19.3	0.7	16.5	2.1	38.5	33.7	0.4	1.2	3.2	32.3
1.0PFM	19.2	0.8	16.3	2.1	32.7	28.3	0.8	1.3	2.3	29.4
3.0PFM	16.0	0.6	13.8	1.5	22.4	16.8	0.3	1.3	4.0	-

 Table 5.2.3:
 Model compound reaction studies over the oxide and sulphide forms of the PMF and PFM catalysts

^aBenz. = benzene ^b α MS = α -methylstyrene ^c Σ SCC = sum of the side-chain cracked products (excluding benzene) ^dEtB = ethylbenzene ^enPB = n-propylbenzene



Figure 5.2.1: % Conversion and product distributions with time for (a) 0.0PMF and (b) 0.0PFM in cumene cracking; (+) % conversion, (Δ) % yield benzene, (o) % yield α -methylstyrene, and (+) % yield Σ side-chain cracked products (excluding benzene).

analogous PMF catalysts. This implies that the PFM catalysts have fewer Brønsted acid sites than the PMF catalysts, which is not surprising since the former catalysts contain lower loadings of fluoride (see Section 5.2.1).

The second thing of note from the cumene hydrocracking results is that the addition of phosphoric acid decreases the Brønsted acidity of F-Ni-Mo/Al₂O₃. The acidity does not decrease in the same fashion for the two catalyst series, however, as shown in Figure 5.2.2. For the PMF catalysts there is an initial rapid decrease in benzene production for up to 1 wt% P and a gentler decrease for 1 to 3 wt% P, while for the PFM catalysts there is a linear decrease in benzene formation with increasing phosphorus content. It is possible to speculate on the reason for this. The shape of the curve for the PMF catalysts resembles those seen in Chapter 4, Section 4.2 for the reaction of phosphoric acid with alumina(172), i.e. many Al-OH groups are removed by H₃PO₄ up to 1 wt% P, but fewer Al-OH groups are removed at higher wt% P since H_3PO_4 starts to react with P-OH groups. Also, it was seen in Section 4.3 that MoO_3 reacts with many of the P-OH groups in P/Al₂O₃. Therefore, for the PMF catalysts, fluoride exchanges with remaining Al-OH groups, but there are fewer neighbouring Al-OH groups to develop Brønsted acidity because many have been consumed by H_3PO_4 (and the metal additives).

In the case of the PFM catalysts there is a different situation; fluoride may react with P-OH groups in addition to Al-OH groups since it is added prior to the metal additives. In fact it is apparent from Table 5.2.2 that fluoride can indeed exchange with P-OH groups and also that it readily exchanges with two (P)-OH groups per added H_3PO_4 molecules up to 3 wt% P. If this is the case in the calcined catalysts then the situation may not be that envisaged in Figure 5.1.1 but rather that shown in Figure 5.2.3 may predominate. In this situation the electron-withdrawing effect of fluoride on



Figure 5.2.2: Effect of phosphorus loading on the cumene hydrocracking activities of PMF(+) and $PFM(\Delta)$ catalysts.



Figure 5.2.3: Possible reaction of F⁻ with H_3PO_4/Al_2O_3

neighbouring OH groups may be diminished since it must work through five bonds. Thus, the impregnated fluoride is wasted and a decrease in acidity with increasing phosphorus content (i.e. increasing number of P-OH groups) is expected.

There is some difference in the deactivation characteristics of the catalysts with time as shown in Figures 5.2.4 and 5.2.5. Some deactivation is expected due to polymerization of α MS over Brønsted acid sites(137) as discussed in Chapter 3, Section 3.3.3. However, in all cases the PFM catalysts deactivate more rapidly than the analogous PMF catalysts. A speculative explanation of this is that for the PFM catalysts some acid sites of the type shown in Figure 5.1.1 are formed but they deactivate more quickly because of their stronger acidity.

The thiophene HDS results are also given in Table 5.2.3. Rather surprisingly no promotional effect of phosphorus is apparent for either the PMF or PFM catalyst series. For the PMF catalysts, in particular, it was expected that phosphorus could modify the metals impregnation and generate a greater number of active sites (or sites of greater activity), as was seen in Chapter 4, Section 4.4. However, for both series, and particularly for the PMF series, the catalysts maintain high activity in spite of decreasing surface area. One interpretation of this is that either few active sites are lost from pore-







Figure 5.2.5: Deactivation with time of PMF catalysts in cumene hydrocracking; (+) 0.0PMF, (Δ) 0.3PMF, (o) 1.0PMF and (+) 3.0PMF.

plugging in the support by the additives, or that sites are lost in this manner but are also generated by the presence of phosphorus.

5.3. Conclusions

This preliminary study of catalysts containing both phosphorus and fluoride indicates that good retention of fluoride during the preparation procedure can be obtained, particularly if the fluoride is impregnated in the last step. Regardless of preparation methods, the phosphorus-fluoride-promoted Ni-Mo/Al₂O₃ catalysts have high activity in the cracking of cumene to benzene, demonstrating that they are able to develop Brønsted acidity. This acidity decreases with increasing phosphorus content, probably due to the consumption by H_3PO_4 of surface OH groups, which decreases the number of OH groups adjacent to Al-F species. It is also suggested that for the PFM catalysts -OP(O)F₂ species can form on the surface which renders some of the fluoride ineffective for generating Brønsted acid sites. In addition, it is speculated that some -OP(O)(F)OH groups form on the PFM catalysts but that these stronger acid sites deactivate rapidly.

No beneficial effect of phosphorus in thiophene HDS was apparent for either catalyst series. However, constant % conversion was maintained with increasing phosphorus content despite decreasing surface area.

Chapter 6: Gas Oil Studies

6.1. Introduction

The model compound studies discussed in Chapters 3-5 are very useful for probing the different functionalities on the catalyst surface. However, in the hydroprocessing of real feeds the system is far more complex, with competition between different classes of compounds for the same active sites(182) and thus all the reactions occurring are inter-related. In evaluating catalyst performance it is therefore useful to extend the model compound reaction studies to those involving real feeds.

Synthetic crude oil produced from hydroprocessing is superior to conventional crude oil in some respects (it contains little residue, organometallics, salt, sediment or water and is lower in sulphur content(183)), but inferior in others. In particular, all fractions are higher in aromatics than those of conventional crude. This presents no problem in the upgrading of the naptha fraction (82-177 °C) since it increases the octane number(184) of the resulting gasoline. For the mid-distillates (177-343 °C) however, the high aromaticity lowers both the cetane number(185) and smoke point of resultant diesel and jet fuels. Therefore one catalytic property that it would be useful to improve is hydrogenation, particularly of the heavier fractions such as gas oils (343 °C +), which at present are of little demand in North America(183).

In addition, because of their aromatic nature, the heavier gas oils are also difficult to crack and a second catalytic functionality which it may be useful to improve is the hydrocracking activity. Increasing the hydrocracking properties of a catalyst however, means increasing the Brønsted acidity, which may make it more susceptible to poisoning by basic nitrogen compounds within the feed(182,186,187). Therefore, any catalyst with increased hydrocracking functionality must also have increased HDN ability. It is not clear however if this can be achieved. From model compound HDN studies it has been suggested that increased catalyst acidity would promote C-N bond cleavage, the rate-limiting step in the HDN pathway of some nitrogen compounds(188,189). Other studies suggest hydrogenation may be of more importance(93,190). Increased HDN activity is important in its own right since the basic nitrogen compounds in the lighter fractions act as severe poisons to reforming catalysts used further downstream(191).

Thus, there are three catalytic properties which it would be useful to improve in hydroprocessing catalysts: Hydrogenation and hydrocracking, particularly of heavier fractions; and HDN, which is likely related to the first two properties. Certain of the phosphorus-, fluoride- and phosphorus-fluoride-promoted Ni-Mo/Al₂O₃ catalysts described in Chapters 3-5 were therefore studied in the hydroprocessing of a gas oil feedstock and of the same feedstock spiked with quinoline, a nitrogenous base, and the results are presented in this chapter. Quinoline was chosen as a model compound for HDN firstly because it is basic and therefore a poison for acid sites, and secondly it has low reactivity(192). It is also representative of the class of nitrogen compounds which predominate in heavy oils(186,193).

In addition, very few studies in the literature have compared model reactions and real feed studies(78,138). This comparison is attempted, where possible, in this chapter to assess the validity and usefulness of model compound reaction studies.

6.2. Hydroprocessing of a Gas Oil Feed

The gas oil feed was supplied by the Alberta Research Council and has the properties given in Table 6.2.1. Also given in Table 6.2.1 are the properties of the

Treatment H:C % Aromatic C Density (g/cm^3) Wt% S Wt%N None 0.9921 1.42 36 4.48 0.4 Thermal, H₂ 39 1.44 0.9446 2.95 0.3 γ -alumina, H₂ 1.35 42 0.9529 3.12

Table 6.2.1: Properties of untreated feed, thermally hydroprocessed feed and the product obtained after hydroprocessing over γ -alumina.

thermally hydroprocessed feed, and those of the feed which was hydroprocessed over the blank support, γ -alumina. The reaction conditions and analytical methods are given in Chapter 2.

The H:C ratio and the % aromatic carbon provide an indication of the extent of hydrogenation of the feed. Thermal hydrogenation (in the absence of a catalyst) apparently leads to a slight increase in aromaticity. It should be noted that previously a slight decrease in aromaticity (37 to 34%) upon thermal treatment was observed in this laboratory(138). However, the error in the % aromatic carbon is approximately \pm 2, and so in reality the aromaticity is essentially unchanged upon thermal treatment. The pressure profile during the reaction (Figure 6.2.1) also demonstrates that little hydrogen uptake is occurring - the pressure is virtually constant with time once the reaction temperature has been reached. This is not definitive, however, since other gases will be produced in the reaction which will contribute to the overall pressure. Even so, the pressure profile is very different for reactions over catalysts which promote hydrogenation (Figure 6.2.2) and thus Figure 6.2.1 supports the fact that little







Figure 6.2.2: Typical pressure and temperature profiles during the hydroprocessing of the gas oil feed over a catalyst with hydrogenation functionalities.

hydrogenation of the feed occurs thermally.

The density of the liquid product provides an indication of either hydrogenation or hydrocracking or both. For the thermally processed feed the decrease in density implies thermal cracking since the aromaticity is virtually unchanged. This is perhaps not surprising since a temperature of 410 °C is high enough to effect thermal cracking(194). Also, the large decrease in sulphur content and small decrease in nitrogen content suggests that much of the sulphur is present in easily cracked species (thiols, sulphides etc.(195)) while only a small amount of the nitrogen is easily removed.

Gas oil hydroprocessing over the blank γ -alumina support results in a product with a higher aromaticity (and lower H:C ratio) than the gas oil itself has, and a higher density and sulphur content than that seen under thermal hydrocracking (the nitrogen content was not measured). The mechanism for thermal cracking is a free radical one(196), and it is possible that the alumina provides sites for termination reactions thereby suppressing hydrocracking, and hence an increased product density is observed compared to that after thermal hydrocracking. Presumably much of the sulphur can also be removed by simple hydrocracking (i.e. without the need of hydrogenation) and this reaction too is suppressed. A similar inference was made from the model reaction studies, diisopropylbenzene hydrocracking (Section 4.2.3) and thiophene HDS (Section 4.3.5). It is interesting that the presence of γ -alumina actually increases the aromaticity of the product. This implies that either γ -alumina promotes dehydrogenation (or aromatisation) reactions, or it changes the product distribution dramatically, producing a high fraction of light ends and resulting in a liquid product with apparent increased aromaticity. Since the gaseous products were not analysed in these reactions, either of the two explanations is plausible. The pressure profile (Figure 6.2.3) does indicate some increase in pressure during the reaction but it is not possible to say if this is due to H_2



Figure 6.2.3: Pressure and temperature profiles during the hydroprocessing of the gas oil feed over the bare γ -alumina support.

produced by dehydrogenation or other gases from cracking reactions. γ -alumina possesses some Lewis acidity(197,198) (and possibly Brønsted acidity) which may favour carbocation-mediated hydrocracking reactions. Alternatively, in the absence of hydrogenation functionalities, isomerization, cyclization and dehydrogenation may occur resulting in increased aromaticity.

6.2.1. Fluoride Promoted Catalysts

The results of hydroprocessing the gas oil feed over the sulphided, fluoridepromoted Ni-Mo/Al₂O₃ catalysts are given in Table 6.2.2. In the presence of the

 Table 6.2.2: Properties of liquid products from hydroprocessing gas oil

over fluoride-promoted catalysts

Catalyst	H:C	% Aromatic C	Density (g/cm ³)	Wt% S	Wt% N
Feed ^a	1.42	36	.0.9921	4.48	0.4
NiMoAl	1.59	25	0.9015	0.51	0.3
1.8FNiMoAl	1.61	23	0.9034	0.41	0.2
3.5FNiMoAl	1.61	21	0.8948	0.25	0.1
6.4FNiMoAl	1.61	25	0.9053	0.40	0.2

^aProperties of feed (unreacted)

unpromoted Ni-Mo/Al₂O₃ catalyst the liquid product has a much lower aromaticity, density and sulphur content than that produced under thermal hydroprocessing. This demonstrates the advantages of catalytic hydroprocessing compared to thermal hydroprocessing and also shows the importance of the hydrogenating phase. For large fused ring aromatic sulphur compounds hydrogenation is an important step in sulphur

removal(195). Thus, the presence of the Ni-Mo-S phase improves HDS not just through presenting HDS sites, but also by hydrogenating the feed.

From Table 6.2.2 the beneficial effect of fluoride is also evident. In agreement with Boorman <u>et al.</u>(108) fluoride enhances the HDS properties of the catalysts. These authors explained this enhancement in terms of increased hydrocracking activity (due to increased Brønsted acidity from the presence of fluoride) which, by cleaving C-C bonds, exposes more S atoms to the catalyst.

Interestingly, the presence of fluoride in the catalyst can also result in a product with lower aromaticity than that formed over Ni-Mo/Al₂O₃. A similar argument may be used to explain this; sterically-hindered aromatic structures, such as that shown in Figure 6.2.4 may not be able to adsorb onto hydrogenation sites on the support. However,



Figure 6.2.4: Possible source of fluoride promotion in hydrogenation reactions

cracking of the side chains, which is promoted by fluoride (see Chapter 3), would reduce the steric bulk of such a molecule thus allowing it to access surface sites. It is assumed that the intermediates in hydrogenation reactions are π -complexes between the HOMO of the hydrocarbon (i.e. π -bonding orbital) and an unoccupied d-orbital on molybdenum(199) (e.g. anion vacancies in MoS_2 crystallites), so that the molecule must adsorb flat on the surface. Hence bulky side-chains may well decrease the rate of hydrogenation of the aromatic structure.

The nitrogen content of the liquid products provides a first indication that increased Brønsted acidity improves the HDN activity. This is discussed in more detail in Section 6.3.

It is proposed from these results, therefore, that the promotional effect of fluoride in hydrogenation, hydrocracking and sulphur removal (and possibly nitrogen removal) can all be explained in terms of improved hydrocracking activity which results from the increased Brønsted acidity. In this respect there is good agreement between these results and the cumene hydrocracking results over the sulphided catalysts which were discussed in Chapter 3. A loading of 3.5 wt% F gave the maximum activity for Ni-Mo/Al₂O₃ in cumene hydrocracking. This provides good evidence that hydrogenation and HDS are also dependent on hydrocracking since in the hydroprocessing of the gas oil feed 3.5FNiMoAl gave a liquid product having the lowest sulphur and % aromatic carbon contents. Thiophene HDS does not appear to have been a good model compound for studying HDS over these F-Ni-Mo catalysts. The effect of fluoride in thiophene HDS was actually found to be negative. The difference in the effects of fluoride on sulphur removal from the gas oil and from thiophene may be that thiophene is not hindered and can easily access the surface Ni-Mo-S sites. Therefore there is no advantage in having a catalyst which promotes hydrocracking for the HDS of this molecule.

Since the gas oil hydroprocessing was carried out in a batch reactor for 3 h only, it is not possible to comment on the deactivation properties of the catalysts. Do these more acidic catalysts poison more rapidly than Ni-Mo/Al₂O₃ via coking and adsorption of nitrogenous bases? While this cannot be answered from the properties of the liquid products, some attempts to address this question are made in Section 6.4 which examines the compositions of the spent catalysts.

6.2.2. Phosphorus Promoted Catalysts

The catalysts prepared by Method 3 (see Chapter 2 for an explanation of preparation methods) were chosen to study in the hydroprocessing of the gas oil feed since this method gave catalysts with the most improvement in thiophene HDS and the highest surface acidity as probed by m-diisopropylbenzene hydrocracking (see Chapter 4). The properties of both the feed and the hydroprocessed feeds over the different catalysts are given in Table 6.2.3. The results over NiMoAl are again included as a

 Table 6.2.3: Properties of liquid products from hydroprocessing gas oil over

 phosphorus-promoted catalysts

Catalyst	H:C	% Aromatic C	Density (g/cm ³)	Wt% S	Wt% N
Feed ^a	1.42	36	0.9921	4.48	0.4
NiMoAl	1.59	25	0.9015	0.51	0.3
3NiMoP _{0.3}	1.61	29	0.8983	0.36	0.3
3NiMoP _{1.0}	1.60	26	0.9021	0.30	0.3
3NiMoP _{3.0}	1.58	21	0.8978	0.33	0.2
3NiMoP _{5.0}	1.60	31	0.9034	0.50	0.3
3NiMoP _{7.0}	1.60	31	0.9093	0.58	0.3

^aProperties of feed (unreacted)

comparison although these were discussed in the previous section.

The effect of phosphorus is clearly seen in Table 6.2.3; optimum loadings

increase the hydrogenation and HDS activities of the catalyst. It has been reported previously that phosphorus promotes hydrogenation reactions(144) and also that loadings of > 1.5 wt% are required to see this promotional effect(200). The results presented here agree with this - only for the catalyst containing 3.0 wt% was an improvement in hydrogenation seen, i.e. above that for NiMoAl (0 wt% P).

In this case for the phosphorus-promoted Ni-Mo/Al₂O₃ there is excellent agreement between the model thiophene HDS reactions and the sulphur removal from the gas oil feed. In both cases a maximum in the HDS activity was observed at loadings of 1.0 wt% P. In fact there is a very good correlation between the sulphur removal occurring in the two feed types for all the catalysts studied. This is demonstrated in Figure 6.2.5 which plots the wt% sulphur in the liquid products after hydroprocessing against the % conversion in thiophene HDS using the same catalyst.

It is interesting that thiophene HDS is a good model reaction for sulphur removal over the P-Ni-Mo catalysts but a poor model reaction for the F-Ni-Mo catalysts, even though comparable activities in HDS of the gas oil over catalysts containing optimum F or P loadings were observed. This can be explained as follows. It is well known that phosphorus increases either the activity or the number of HDS sites(45,161). Clearly, both of these possibilities would increase the thiophene HDS activity of the catalyst. Similarly, both these possibilities would increase the amount of HDS of stericallyunhindered sulphur compounds within the gas oil feed. In contrast, fluoride has no affect on the HDS sites as seen by thiophene HDS and so the number of sterically-unhindered sulphur compounds undergoing HDS is unaffected by fluoride on the catalysts. However, in addition to this, as explained in the previous section, fluoride may expose some sterically-hindered sulphur through hydrocracking reactions which can then be removed on the HDS sites.



Figure 6.2.5: Correlation between model compound and real feed HDS reactions over phosphorus-promoted Ni-Mo/Al₂O₃ catalysts.

It is more difficult to comment on the effect of phosphorus in the catalyst on the density of the liquid product, since the values are quite similar for all the catalysts used. The catalyst which gave the lowest density product was $3NiMoP_{3.0}$ which also gave a liquid product with the lowest aromaticity. Since the phosphorus-promoted catalysts are far less Brønsted acidic than the fluoride-promoted catalysts it is possible that the density of the liquid product is a better indication of the hydrogenation properties of the catalyst in the former case. Nonetheless, $3NiMoP_{0.3}$ is the most Brønsted acidic of the catalysts studied in this section (as shown in Chapter 4), and since 0.3 wt% P is insufficient to promote hydrogenation reactions(200), the lower density of the product produced over this catalyst compared to that produced over NiMoAl may be a result of its higher acidity, and concomitant increased hydrocracking activity.

6.2.3. Phosphorus and Fluoride Promoted Catalysts

The PMF catalysts were also studied in the hydroprocessing of the gas oil feed and the results are given in Table 6.2.4. The 0.0PMF catalyst behaves very similarly to 3.5FNiMoAl which is not surprising since these catalysts have a similar composition. No beneficial effect of phosphorus is evident at any of the loadings studied, although comparable HDS activity to the $3NiMoP_x$ catalysts is observed. In fact, the presence of phosphorus on the catalyst seems to nullify the beneficial effect of fluoride in HDS. This may be because phosphorus reacts with surface hydroxyl groups (Chapter 4, Section 4.2) and therefore there are fewer remaining which can develop Brønsted acidity upon addition of fluoride. This was observed indirectly in cumene hydrocracking studies (Chapter 5, Section 5.2.2) where decreasing cracking was seen for increasing phosphorus loadings.

There is no obvious trend in sulphur removal over the different catalysts which is similar to what was observed for the thiophene HDS results (Chapter 5, Section 5.2.2); in

Catalyst ^a	H:C	% Aromatic C	Density (g/cm ³)	Wt% S	Wt% N
Feed ^b	1.42	36	0.9921	4.48	0.4
0.0PMF	1.58	24	0.8899	0.27	0.2
0.3PMF	1.58	25	0.9000	0.38	0.3
1.0PMF	1.58	29	0.8947	0.34	0.3
3.0PMF	1.60	26	0.9044	0.47	0.2

Table 6.2.4: Properties of liquid products from hydroprocessing gas oil over

 phosphorus- and fluoride-promoted catalysts

^aAll PMF catalysts contain 3.1-3.4 wt% F ^bProperties of feed (unreacted)

the latter case, also, there was no consistent trend in % thiophene HDS with increasing phosphorus content.

6.3. Hydroprocessing of a Quinoline-Spiked Gas Oil Feed

The properties of the quinoline-spiked feed are given in Table 6.3.1 together with those of the thermally hydroprocessed feed. The amount of quinoline in the feed was 5 vol% which more than doubles the nitrogen content of the gas oil, and, since quinoline is an aromatic, heterocyclic nitrogen compound its presence also increases the % aromatic carbon (and lowers the H:C ratio) of the feed.

Upon thermal hydroprocessing, decreases in aromaticity, sulphur content and density are evident. The decrease in aromaticity suggests hydrogenation of quinoline since little hydrogenation of the gas oil occurs thermally (Table 6.2.1). Indeed, gas

Treatment	H:C	% Aromatic Carbon	Density (g/cm ³)	Wt% S	Wt% N	% Quinoline HDN
None ^a	1.40	43	0.9973	4.10	0.9	0
Thermal, H ₂	1.48	39	0.9465	2.56	0.9	13.1

 Table 6.3.1: Properties of quinoline-spiked feed and thermally hydroprocessed

 quinoline-spiked feed

^aProperties of Feed (unreacted)

chromatography of the resulting product revealed a large reduction in quinoline content and large amounts of 1,2,3,4-tetrahydroquinoline (1THQ), *o*-propylaniline (OPA) and 5,6,7,8-tetrahydroquinoline (5THQ), which are hydrogenation products in the quinoline HDN network, a simplified version of which is given in Figure 6.3.1.(201) In addition, some HDN of quinoline occurs thermally (13.1 %) resulting in propylbenzene and propylcyclohexane as major products. As was seen for the unspiked feed, substantial sulphur removal also occurs thermally.

6.3.1. Fluoride Promoted Catalysts

The results of hydroprocessing the spiked feed over the fluoride-promoted $Ni-Mo/Al_2O_3$ catalysts are given in Table 6.3.2. By comparison with the results using the unspiked feed (Table 6.2.2), the liquid products from the quinoline-spiked feed all have higher aromaticities and sulphur contents. In fact, the promotional effect of fluoride in hydrogenation and sulphur removal, which was observed for the unspiked feed, is no longer apparent. It was proposed in Section 6.2.1 that the fluoride-associated Brønsted acid sites promote hydrogenation and HDS by promoting cracking of



Figure 6.3.1: Simplified reaction network for quinoline HDN; quinoline(Q), 1,2,3,4tetrahydroquinoline(1THQ), *o*-propylaniline(OPA), propylbenzene(PB), 5,6,7,8-tetrahydroquinoline(5THQ), decahydroquinoline(DHQ) and propylcyclohexane(PCH). [Adapted from reference 201.]

sterically-hindered aromatic and thiophenic structures, resulting in less hindered molecules which can then access surface sites for HDS and hydrogenation. Since this effect is no longer observed for the spiked feed it is probable that many of these Brønsted acid sites are poisoned by the nitrogenous base, quinoline. In addition, it is well documented that quinoline and other basic nitrogen compounds inhibit both hydrogenation(199) and HDS(182,199,202) reactions.

A very significant result of this study, however, is that fluoride promotes quinoline HDN. The product distribution for the quinoline HDN reaction is given in Figure 6.3.2 as a function of fluoride content in the catalyst. Both 1THQ and 5THQ are observed indicating that both reaction pathways in Figure 6.3.1 are occurring. With increasing fluoride content in the catalyst, less OPA, 1THQ and 5THQ are present in the

Treatment	H:C	% Aromatic Carbon	Density (g/cm ³)	Wt% S	Wt% N	% Quinoline HDN
None ^a	1.40	43	0.9973	4.10	0.9	0
NiMoA1	1.59	30	0.9058	0.57	0.4	53.6
1.8FNiMoAl	1.57	29	0.8996	0.56	0.3	59.9
3.5FNiMoAl	1.57	34	0.9017	0.60	0.4	64.5
6.4FNiMoAl	1.53	35	0.9056	0.63	0.4	66.1

Table 6.3.2: Properties of the liquid products from hydroprocessing thequinoline-spiked feed over F-Ni-Mo/Al $_2O_3$ catalysts

^a5 vol% quinoline-spiked gas oil (unreacted)

liquid product. In addition, more propylbenzene (PB) and less propylcyclohexane (PCH) are present, although PCH is still the major HDN product. Since fluoride does not improve the % aromaticity of the liquid product for this feed, and since HDN of propylcylcohexamine to propylcyclohexane is rapid(93), it is likely that the promotional effect of fluoride in HDN is due to an increase in the rate of C-N bond cleavage in OPA to produce PB. This is in agreement with proposals of other workers(188,189) who have suggested that increased Brønsted acidity promotes C-N bond hydrogenolysis.

A discussion on the effect of fluoride on coking and poisoning of these catalysts is given in Section 6.4.

6.3.2. Phosphorus Promoted Catalysts

The properties of the liquid products from hydroprocessing the quinoline-spiked feed over the phosphorus-promoted catalysts prepared by Method 3 are given in Table 6.3.3. Comparison of the results in Table 6.3.3 with those for the unspiked feed (Table



Figure 6.3.2: Distribution of major products in the quinoline HDN reaction pathway in the hydroprocessed quinoline-spiked feed as a function of fluoride content in the catalyst. See Figure 6.3.1 for an explanation of abbreviations.

Treatment	H:C	% Aromatic Carbon	Density (g/cm ³)	Wt% S	Wt% N	% Quinoline HDN
None ^a	1.40	43	0.9973	4.10	0.9	0
NiMoAl	1.59	30	0.9058	0.57	0.4	53.6
3NiMoP _{0.3}	1.69	30	0.8997	0.34	0.4	66.9
3NiMoP _{1.0}	1.64	23	0.8971	0.34	0.4	67.0
3NiMoP _{3.0}	1.66	22	0.8939	0.37	0.4	67.3
3NiMoP _{5.0}	1.65	26	0.9085	0.60	0.5	60.0
3NiMoP _{7.0}	1.57	32	0.9179	0.90	0.5	53.9

Table 6.3.3: Properties of the liquid products from hydroprocessing the quinoline-spiked feed over P-Ni-Mo/Al₂O₃ catalysts

^a5 vol% quinoline-spiked gas oil (unreacted)

6.2.3) indicates that, for these short experiment times, the phosphorus-promoted catalysts cope well with the high nitrogen feed in the majority of reactions. Catalysts with optimum phosphorus loadings for hydrogenation (3.0 wt%, and possibly 1.0 wt%) produce liquid products with low aromaticity despite the presence of quinoline. Similarly, catalysts with optimum loadings for HDS (0.3-3 wt% P) maintain good sulphur removal ability from this spiked feed. In contrast, the catalyst containing 0 wt% P (NiMoAl) exhibits poorer hydrogenation of the spiked feed compared to the unspiked feed suggesting poisoning of these sites by quinoline.

In most cases, slightly more sulphur and nitrogen compounds are present in the hydroprocessed spiked feeds compared to the analogous hydroprocessed unspiked feeds. Basic nitrogen compounds poison the sites for HDS(182). Consequently, quinoline, or

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the basic N-containing intermediates in the quinoline HDN reaction pathway, may adsorb strongly on the Ni-Mo-S sites thereby decreasing the extent of sulphur removal from the feed. The higher nitrogen content of the hydroprocessed quinoline-spiked gas oil may simply be due to the fact that the initial nitrogen content of this feed is higher. Furthermore, hydrogenation may also occur on the Ni-Mo-S sites(162). Since the presence of phosphate appears to increase the number of Ni-Mo-S sites, the poisoning of these hydrogenation (and HDS) sites by basic nitrogen compounds is less apparent for catalysts having optimum phosphorus loadings than for NiMoAl which does not contain phosphorus. Alternatively, if phosphorus promotes the activity (rather than the number) of the active sites as suggested by Eijsbouts <u>et al.(161)</u> these sites may be more able to cope with the basic nitrogen compounds; i.e. these compounds may react on, rather than poison, the active site.

A promotional effect of phosphorus in quinoline HDN is also apparent from Table 6.3.3, the optimum phosphorus loadings being 0.3 to 3.0 wt%. Similarly, Eijsbouts <u>et al.</u>(162) observed an optimum phosphorus loading of approximately 2.1 wt% for Ni-Mo catalysts with similar nickel content. Both C-N bond cleavage and hydrogenation reactions are important in the HDN of quinoline(97). Eijsbouts <u>et al.</u>(162) noted that hydrogenation may take place on anion vacancies in MoS₂(203), while C-N bond cleavage may occur on Brønsted acid sites generated by H₂S dissociation on these sites(116), or on the promoted support. Thus, from the results of diisopropylbenzene hydrocracking over the sulphided catalysts (Chapter 4, Section 4.4.4), which demonstrated an increased Brønsted acidity for 0.3 wt% P, we may expect increased C-N bond cleavage. As discussed earlier, a loading of 0.3 wt% P is too low to see any improvement in hydrogenation activity(200), and therefore, the increased quinoline HDN activity of $3NiMoP_{0.3}$ (compared to NiMoAl) may be a consequence of increased Brønsted acidity of this catalyst. High hydrogenation activity seems to be of more importance in quinoline HDN under these reaction conditions, however, since sulphided $3NiMoP_{3.0}$, which has comparable Brønsted acidity to NiMoAl on the basis of diisopropylbenzene hydrocracking results, and which produces a liquid product with the lowest aromaticity, has the highest % quinoline HDN.

High hydrogenation activity may be of more importance with respect to the lifetime of the catalyst since it may prevent coking of the catalyst(204). Since the experiments performed here were three hour batch reactions, it is impossible to comment on deactivation of the catalyst with time. For example, $3NiMoP_{0.3}$ may have high initial HDN activity but may be poisoned rapidly because of its higher surface acidity. A discussion of the compositions and surface areas of the spent catalysts is given in Section 6.4.

6.3.3. Phosphorus and Fluoride Promoted Catalysts

The properties of the liquid products from hydroprocessing the quinoline-spiked feed over the PMF catalysts are given in Table 6.3.4. Like the phosphorus-promoted catalysts, these catalysts maintain good hydrogenation of the spiked feed (at optimum phosphorus loadings), and allow a sulphur removal intermediate to that for the fluoride-only and phosphorus-only promoted catalysts. In addition, these catalysts have a higher quinoline HDN activity than either the fluoride- or phosphorus-promoted catalysts (all at optimum secondary promoter loadings). This is demonstrated in Figures 6.3.3 and 6.3.4 which show the % aromaticity and % quinoline HDN of the feed, respectively, after hydroprocessing over the three series of catalysts. From Figure 6.3.3 it is clear that the PMF catalysts do have some beneficial effect from the phosphorus in hydrogenation since they are more active in this reaction than the xFNiMoAl catalysts. Phosphorus decreases the Brønsted acidity of 3.5FNiMoAl as seen from the cumene hydrocracking

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Treatment	H:C	% Aromatic Carbon	Density (g/cm ³)	Wt% S	Wt% N	% Quinoline HDN
None ^a	1.40	43	0.9973	4.10	0.9	0
0.0PMF	1.59	24	0.9015	0.44	0.3	68.2
0.3PMF	1.63	24	0.9007	0.41	0.3	71.0
1.0PMF	1.60	25	0.8992	0.40	0.3	73.2
3.0PMF	1.60	27	0.9103	0.60	0.4	65.2

Table 6.3.4: Properties of the liquid products from hydroprocessing the quinoline-spiked feed over P-Ni-Mo-F/Al₂O₃ catalysts

^a5 vol% quinoline-spiked gas oil (unreacted)

results presented in Chapter Five. Therefore, it is possible that the PMF catalysts are less susceptible to poisoning by quinoline as a consequence. In addition, the increased hydrogenation activity of the catalysts due to the presence of phosphorus must certainly contribute to the lower aromaticities of the hydroprocessed feeds also. However, the PMF catalysts are much more acidic than the $3NiMoP_x$ catalysts, as determined by model hydrocracking reactions (Chapters Four and Five). Therefore there is still some poisoning of the PMF catalysts by quinoline, as there was for the xFNiMoAl catalysts, so that the hydrogenation activity is not as high as for the $3NiMoP_x$ catalysts.

From Figure 6.3.4 it is clear that the PMF catalysts are more active in quinoline HDN than either the $3NiMoP_x$ or the FNiMoAl catalysts. This suggests that in the PMF catalysts the advantages of both phosphorus and fluoride have been merged successfully. The better hydrogenation activity from phosphorus may make the catalyst more resistant to coking and more active in hydrogenation of quinoline, while the increased Brønsted



Figure 6.3.3: Effect of phosphorus and fluoride secondary promoters in hydrogenation of the quinoline-spiked gas oil feed; (+) fluoride-promoted Ni-Mo/Al₂O₃, (Δ) phosphorus-promoted Ni-Mo/Al₂O₃ and (o) phosphorus- (varying) and fluoride- (3.4 wt%) promoted Ni-Mo/Al₂O₃.



Figure 6.3.4: Effect of phosphorus and fluoride secondary promoters on quinoline HDN in the quinoline-spiked gas oil feed; (+) fluoride-promoted Ni-Mo/Al₂O₃, (Δ) phosphorus-promoted Ni-Mo/Al₂O₃ and (o) phosphorus- (varying) and fluoride- (3.4 wt%) promoted Ni-Mo/Al₂O₃.
acidity promotes C-N bond cleavage. Both these steps (hydrogenation and C-N bond cleavage) are important in quinoline HDN(93,97,203). In summary, the PMF catalysts have increased acidity due to fluoride, but the addition of phosphorus tempers this acidity and also improves the hydrogenation activity so that the acid sites are less susceptible to coking and poisoning. These properties may make PMF catalysts with optimum phosphorus and fluoride loadings good catalysts for hydroprocessing high nitrogen feeds.

6.4. Characterization of Spent Catalysts

The hydroprocessing reactions discussed in Sections 6.2 and 6.3 were 3 h batch reactions and therefore give very little information with regards to the deactivation of the catalysts. Some indication of the susceptibility of the catalysts to coking and poisoning may be obtained from characterization of the spent catalysts. This is the work discussed in this section. In addition, for catalysts containing fluoride, the work from Chapter 3, Section 3.3.7 is extended to study fluoride retention under conditions more resembling those used industrially.

6.4.1. After Hydroprocessing the Gas Oil Feed

The properties of the spent xFNiMoAl, $3NiMoP_x$ and PMF catalysts after hydroprocessing the gas oil feed (unspiked) are given in Tables 6.4.1, 6.4.2 and 6.4.3, respectively. The catalysts were analysed for their C and N contents (and F content, where applicable) and their surface areas were measured, after they had been washed with CH₂Cl₂ and dried in an oven overnight. For the fluoride-promoted catalysts, decreases in surface area of *circa* 35-50 % were observed but, rather surprisingly the presence of fluoride did not increase the amount of coke deposited. This implies that the

Catalyst	Surface Area (m ² /g)		% Decrease in	Wt% F ^a		Wt% C ^b	Wt% N ^b
	Fresh	Spent	Surface Area	Fresh	Spent		
NiMoAl	137	73	47	0	0	6.2	0.5
1.8FNiMoAl	125	82	34	1.8	1.8	3.8	0.6
3.5FNiMoAl	122	62	49	3.5	2.9	4.9	1.0
6.4FNiMoAl	113	66	42	6.4	4.8	4.6	1.3

 Table 6.4.1: Properties of spent xFNiMoAl catalysts after hydroprocessing the gas oil feed

^aRelative to γ -alumina, i.e. spent catalysts corrected for coke and metal contents assuming metals are present as sulphides

^bWt% C or N present on NiMoAl, i.e. corrected for different Wt% F present

Table 6.4.2: Properties of spent $3NiMoP_x$ catalysts after hydroprocessing the gas oil feed

Catalyst	Surface Area (m ² /g)		% Decrease in	Wt% C ^b	Wt% N ^b
	Fresh	Spent	Surface Area		
NiMoAl	137	73	47	6.2	0.5
3NiMoP _{0.3}	143	86	40	4.6	0.3
3NiMoP _{1.0}	125	84	33	3.7	0.3
3NiMoP _{3.0}	100	70	30	3.0	. 0.6
3NiMoP _{5.0}	75	46	39	4.1	0.4
3NiMoP _{7.0}	57	32	45	3.3	0.4

^bWt% C or N present on NiMoAl, i.e. corrected for different Wt% F present

Catalyst	Surface Area (m ² /g)		% Decrease in	Wt% F ^a		Wt% C ^b	Wt% N ^b
	Fresh	Spent	Surface Area	Fresh	Spent		
0.0PMF	103	78	24	3.4	3.0	2.9	0.5
0.3PMF	111	75	32	3.1	3.0	4.1	0.6
1.0PMF	101	82	19	3.4	3.3	2.7	0.6
3.0PMF	80	60	25	3.4	3.0	2.6	0.8

Table 6.4.3: Properties of spent PMF catalysts after hydroprocessing the gas oil feed

^aRelative to γ -alumina, i.e. spent catalysts corrected for coke and metal contents assuming metals are present as sulphides

^bWt% C or N present on NiMoAl, i.e. corrected for different Wt% F present

accelerated catalyst aging experiments discussed in Section 3.3, which used cyclohexene/ N_2 pyrolysis to coke the catalysts, provided a remarkably good assessment of coking propensity. From this work it was determined that the fluoride-associated Brønsted acid sites did not promote cyclohexene polymerization but rather the metal sites were responsible, possibly metal-associated Lewis acid sites. From the results in Table 6.4.1 it is clear that coking is not increased by the presence of fluoride, rather, the opposite is true; the presence of fluoride on the catalyst decreases the amount of coke deposited. The reason for this may be connected to the improved hydrogenation activity of the fluoride-promoted catalysts compared to NiMoAl (see Table 6.2.2). It is proposed that this improved hydrogenation activity is a result of exposing sterically-hindered large, fused ring aromatic and thiophenic structures by cracking aliphatic side chains on fluoride-associated Brønsted acid sites. These unhindered aromatic or thiophenic structures can then adsorb on hydrogenation and HDS sites. Since these large aromatic

structures are possible coke precursors, hydrogenation of these structures may reduce the amount of coke deposited on the catalysts.

Fluoride does increase the amount of nitrogen in the deposited coke, however. Therefore it is probable that the fluoride-associated Brønsted acid sites are poisoned by basic nitrogen compounds. An alternative explanation of the lower coke content of the fluoride-promoted catalysts compared to NiMoAl follows from this; the mechanism of coke formation may be different for the two types of catalysts, with that on the fluoridecontaining catalysts involving more nitrogen compounds as coke precursors.

The fluoride retention is very similar to that observed under model compound reaction conditions, i.e. all fluoride is retained at the lower loadings while an increasing amount of fluoride is lost at increasingly higher loadings. Suggested mechanisms for fluoride loss were given in Chapter Three, Section 3.3. The amounts of fluoride retained after the model compound and gas oil reactions are so similar that one may speculate that there is a limit to the amount of fluoride which can be lost from the catalyst by these mechanisms. It would be interesting to determine if this is indeed the case, otherwise such rapid loss of fluoride from these catalysts suggests that they would not be viable in a commercial process since they would need frequent regeneration.

Table 6.4.2 gives the properties of the spent phosphorus-promoted catalysts after hydroprocessing the gas oil feed. It is clear that low loadings of phosphorus (0.3 to 3.0 wt%) prevent some deactivation of the catalyst by reducing coke deposition and maintaining high surface area. Fitz and Rase(146) also observed that P-Ni-Mo/Al₂O₃ (P = 1.5 to 2.6 wt%) were more resistant to coking than Ni-Mo/Al₂O₃ catalysts. Furthermore, Hopkins and Meyers(205) saw that phosphorus (1 - 3.5 wt%) prevents sintering, with concomitant loss of surface area, in some commercial Co-Mo catalysts. With the exception of 3NiMoP₇, there is a correlation between % decrease in surface area and wt% carbon on the catalyst (Figure 6.4.1) indicating that the deposited coke plugs pores in the catalyst. Since many of the active sites reside in the pores (Chapter 3, Section 3.3.2) this pore plugging would result in a decrease in catalyst activity. It is interesting that the graph in Figure 6.4.1 does not pass through the origin; this is probably a result of heteroatoms (S, N, O) within the coke which also contribute to the decrease in surface area. There is also a fair correlation between Wt% C deposited on the catalyst and the % aromatic carbon within the hydroprocessed feed (see Table 6.2.3) which indicates that the amount of coke deposited depends to a large extent on the hydrogenation properties of the catalyst, in agreement with the results of other workers(206). $3NiMoP_{3.0}$, which has the highest hydrogenation ability (producing a product with the lowest aromaticity, see Table 6.2.3), has the lowest wt% C. Finally, the wt% N deposited on the phosphorus-promoted catalysts is less than that deposited on the fluoride-promoted catalyst, which is probably a consequence of lower surface acidity in the former case.

The properties of the PMF catalysts after hydroprocessing the gas oil feed are given in Table 6.4.3. In general, the % decreases in surface area of the catalysts after the reaction are less than those for both the xFNiMoAl and $3NiMoP_x$ catalysts, which suggests that the beneficial effect of phosphorus in maintaining high surface area is present in these catalysts also. Of particular note in Table 6.4.3 is that there is very good retention of fluoride in the PMF catalysts. It was suggested previously that fluoride loss may result from volatilization of molybdenum oxofluorides. Since phosphorus modifies the surface distribution of molybdate(and nickel), it is possible that it decreases the amount of these oxofluorides which form thereby increasing fluoride retention. This is an important result from a commercial viewpoint and merits further investigations of these systems.



Figure 6.4.1: Correlation between wt% C on spent phosphorus-promoted catalysts and their % decreases in surface area after hydroprocessing the gas oil feed.

6.4.2. After Hydroprocessing the quinoline-spiked gas oil feed

The properties of the xFNiMoAl, $3NiMP_x$ and PMF catalysts after hydroprocessing the quinoline-spiked feed are given in Tables 6.4.4, 6.4.5 and 6.4.6 respectively. For all catalysts the secondary promoters decrease the amount of coke

Catalyst	Surface Area (m ² /g)		% Decrease in	Wt% F ^a		Wt% C ^b	Wt% N ^b
	Fresh	Spent	Surface Area	Fresh	Spent		
NiMoAl	137	42	69	0	0	9.6	0.7
1.8FNiMoAl	125	76	39	1.8	1.5	6.3	0.8
3.5FNiMoAl	122	77	37	3.5	2.9	4.9	0.8
6.4FNiMoAl	113	70	43	6.4	5.3	6.2	1.0

 Table 6.4.4: Properties of spent xFNiMoAl catalysts after hydroprocessing the

 quinoline-spiked gas oil feed

^aRelative to γ -alumina, i.e. spent catalysts corrected for coke and metal contents assuming metals are present as sulphides

^bWt% C or N present on NiMoAl, i.e. corrected for different Wt% F present

deposited on the catalysts and help maintain high surface area. There is some correlation between surface area decrease and wt% C + N deposited (Figure 6.4.2) indicating that much of the deposited coke blocks the pores of the support. It is not possible to comment on any poisoning of specific sites of the catalyst by the presence of quinoline from this data, however, although some inferences were made in the previous section by comparing the properties of the liquid products obtained after hydroprocessing the two feeds over the same catalyst. In most cases the wt% C and wt% N deposited using the spiked feed are comparable to those observed using the regular feed; the exception is

Catalyst	Surface A	rea (m ² /g)	% Decrease in	Wt% C ^b	Wt% N ^b
	Fresh	Spent	Surface Area		
NiMoAl	137	42	69	9.6	0.7
3NiMoP _{0.3}	143	87	39	4.2	0.3
3NiMoP _{1.0}	125	82	34	4.8	0.4
3NiMoP _{3.0}	100	73	27	4.0	0.6
3NiMoP _{5.0}	75	45	40	3.6	0.7
3NiMoP _{7.0}	57	34	41	3.2	0.7

Table 6.4.5: Properties of spent $3NiMoP_x$ catalysts after hydroprocessingthe quinoline-spiked gas oil feed

^bWt% C or N present on NiMoAl, i.e. corrected for different Wt% F present

 Table 6.4.6:
 Properties of spent PMF catalysts after hydroprocessing the quinoline

 spiked gas oil feed

Catalyst	Surface Area (m ² /g)		% Decrease in	Wt% F ^a		Wt% C ^b	Wt% N ^b
	Fresh	Spent	Surface Area	Fresh	Spent		
0.0PMF	103	85	. 17	3.4	3.0	3.1	0.6
0.3PMF	111	83	25	3.1	3.0	3.4	0.6
1.0PMF	101	70	44	3.4	3.3	4.1	0.7
3.0PMF	80	5 8	27	3.4	3.3	3.0	0.8

^aRelative to γ -alumina, i.e. spent catalysts corrected for coke and metal contents assuming metals are present as sulphides

^bWt% C or N present on NiMoAl, i.e. corrected for different Wt% F present



Figure 6.4.2: Correlation between wt% C + N on spent catalysts and their decreases in surface area after hydroprocessing the quinoline-spiked gas oil feed; (+) fluoride-promoted Ni-Mo/Al₂O₃, (Δ) phosphorus-promoted Ni-Mo/Al₂O₃ and (o) phosphorus-and fluoride-promoted Ni-Mo/Al₂O₃.

NiMoAl which has a higher C (and N) content after hydroprocessing the quinolinespiked feed. Therefore, there is no evidence of selective poisoning of acid sites in the fluoride-containing catalysts by quinoline. However, if this poisoning is occurring then it would lower the activity and therefore, presumably the amount of coking, of the catalyst. A lower activity was definitely observed for the xFNiMoAl catalysts for hydroprocessing the quinoline-spiked feed, so possibly this was the reason for less coking.

6.5. Conclusions

In the hydroprocessing of the unspiked feed, fluoride promotes both the hydrogenation and HDS activities of Ni-Mo/Al₂O₃ with an optimum fluoride loading of approximately 3.5 wt%. An explanation of this is that fluoride promotes the cracking of side-chains of sterically-hindered aromatic and thiophenic molecules by increasing the Brønsted acidity of the support. The cracked molecules are then able to adsorb flat on the hydrogenation or HDS sites in the π -bonded fashion required to undergo reaction. In the quinoline-spiked (higher-nitrogen) feed, however, no such promotional effect is observed and it is proposed that the basic nitrogen compounds poison some of the Brønsted acid sites. Even so, fluoride does promote quinoline HDN, possibly by increasing the rate of C-N bond cleavage, which is thought to occur on Brønsted acid sites. However, there is quite a large loss of fluoride from those catalysts containing higher fluoride loadings which may limit their usefulness in commercial processes.

Phosphorus promotes the hydrogenation and HDS activities of Ni-Mo/Al₂O₃ in the hydroprocessing of both unspiked and quinoline-spiked gas oil feeds, with optimum loadings of 1-3 wt% in hydrogenation and 0.3-3 wt% in HDS. This can be explained in

terms of phosphorus modifying the surface distribution of both Mo and Ni resulting in more HDS (and hydrogenation) sites. Optimum loadings of phosphorus (0.3-3 wt%) also promote quinoline HDN, probably by improving the hydrogenation activity of the catalyst. Catalysts with high hydrogenation activity also undergo less coking than does Ni-Mo/Al₂O₃ which is probably a consequence of hydrogenation of coke precursors. This suggests that the phosphorus-promoted catalysts would have a longer lifetime on stream than unpromoted Ni-Mo/Al₂O₃.

Catalysts containing both phosphorus and fluoride showed no real advantage for hydroprocessing the gas oil feed; phosphorus decreases the acidity of the F-Ni-Mo catalysts so that less promotion in hydrogenation and HDS is observed compared to the fluoride-only promoted catalysts. Also, no promotional effect of phosphorus was evident in hydrogenation and HDS. However, in the case of the quinoline-spiked (highernitrogen) feed, the lower acidity of these catalysts was an advantage: Unlike the fluoride-only-promoted catalysts these catalysts had high HDS and hydrogenation activities (although not as high as the phosphorus-only-promoted catalysts) and were very active in quinoline HDN. It is suggested that this is due to increased hydrogenation activity associated with the presence of phosphorus and increased C-N bond cleavage from fluoride-associated Brønsted acid sites. Catalysts containing both phosphorus and fluoride also have excellent fluoride retention under the conditions of these experiments and lower coking propensity than Ni-Mo/Al₂O₃.

In general, the model compound reactions were useful, not only as an assessment of the catalytic activity in gas oil hydroprocessing reactions, but also in interpreting the results of the hydroprocessing studies and allowing a better understanding of the reactions occurring in the real systems. Thiophene HDS is a very good model reaction for studying the activity of catalysts in the HDS of sterically-unhindered sulphur compounds. Where direct comparisons were possible, the model hydrocracking reactions also provided a good indication of the hydrocracking activity of the catalysts

for the gas oil.

Chapter 7: Conclusions and Future Work

7.1. Conclusions

7.1.1. Fluoride as a Secondary Promoter

Three impregnation methods were studied for the preparation of F-Ni-Mo/Al₂O₃ catalysts. Coimpregnation of all the additives (one calcination step) results in nearly quantitative retention of fluoride after calcination, while impregnation of fluoride prior to or after the metal additives (two calcination steps) leads to substantially lower fluoride content in the final catalysts. The two stepwise preparation methods also result in catalysts with lower surface areas than the coimpregnated catalysts, possibly a result of pore-collapsing during the second calcination step. It is proposed that fluoride loss from the stepwise-prepared catalysts results from the formation of molybdenum oxofluorides, and possibly AlF₃, which are lost from the catalyst upon calcination.

The catalysts were studied for their activities in cumene cracking and hydrocracking and thiophene HDS reactions. For all preparation methods fluoride increases the cumene hydrocracking activities of the catalysts by generating Brønsted acid sites on the γ -alumina surface. Comparison of the activities of catalysts with similar fluoride loadings but prepared in the three different ways described above, indicates that impregnation of fluoride after the metal additives gives a more acidic surface. It is suggested that for catalysts prepared by either coimpregnation or impregnation of fluoride-associated Brønsted acid sites. For the coimpregnated catalysts a maximum activity in cumene hydrocracking is observed for a fluoride loading of 3.5 wt%. Above this loading the activity decreases again indicating the removal of Brønsted acid sites by fluoride,

probably by displacing surface OH groups. The increased Brønsted acidity has little effect on the thiophene HDS activity of Ni-Mo/Al₂O₃ up to loadings of 3.5 wt% F; higher fluoride loadings results in a catalyst with lower thiophene HDS activity.

These catalysts were also investigated in accelerated aging studies involving olefin polymerization over the catalysts in an inert atmosphere, in this case cyclohexene/N₂. Coking of the support material was studied in some detail and it was observed that the coking process follows adsorption isotherm-type behaviour for both γ -alumina and boehmite substrates, with monolayer carbon coverages between 26-31 wt%. Characterization of the coked support material indicated that the deposited coke blocks small pores and converts some cylindrical pores to "ink-bottle" pores. These ink-bottle pores are accessible to fluoride but not to larger species such as cyclohexene and cumene. The deposited carbon has a lower surface area than the substrate material so that the surface area of C/Al₂O₃ decreases with increasing carbon content. In spite of this, the deposited carbon has dehydrogenation-hydrogenation character, suggesting that C/Al₂O₃ merits investigation as an alternative support material. Some studies of this have been performed in this laboratory(65,137,138).

Coking over the F-Ni-Mo/Al₂O₃ catalysts indicated that the metal additives promote cyclohexene polymerization, possibly by increasing the Lewis acidity. In contrast, the fluoride-associated Brønsted acid sites do not promote cyclohexene polymerization, but do promote coke formation from species which polymerize more easily, such as α -methylstyrene. Catalyst characterization also indicates that the additives accumulate in the smaller pores of the support during the preparation procedure, and that these pores are blocked by coking. Model compound reaction studies demonstrated that both fluoride-associated Brønsted acid sites and metal sites are blocked by the deposited coke. Since the coking is promoted by the presence of the metal additives this implies that the fluoride-associated Brønsted acid sites are in close proximity to the metal sites. At very high fluoride loadings the coked catalysts still retained some activity in cumene hydrocracking indicating that for these high loadings some fluoride-associated Brønsted acid sites remain outside of the smaller, coked pores. Good retention of fluoride was observed during the accelerated aging experiments for loadings up to 3.5 wt% F.

Fluoride promotes the hydrogenation and HDS activities of Ni-Mo/Al₂O₃ in the hydroprocessing of a low-nitrogen (i.e. unspiked) gas oil feed with an optimum fluoride loading of 3.5 wt%. An explanation of this is that sterically-hindered aromatic and thiophenic structures are made less hindered by cracking of side-chains over fluoride-associated Brønsted acid sites. These less hindered molecules are then able to adsorb flat on hydrogenation and HDS sites more easily. The accelerated aging studies provided a good assessment of the coking propensity of these catalysts in that fluoride-associated Brønsted acid sites do not promote coke formation in gas oil hydroprocessing reactions. In fact catalysts containing fluoride contained less coke after hydroprocessing than did Ni-Mo/Al₂O₃ and it is proposed that this is because the fluoride-associated Brønsted acid sites promote indirectly the hydrogenation of coke precursor molecules.

In contrast to the results observed for the low-nitrogen feed, in the hydroprocessing of a quinoline-spiked, high-nitrogen gas oil feed no promotional effect of fluoride in hydrogenation or HDS is observed. It is suggested that quinoline or other basic nitrogen compounds in the HDN network of quinoline poison many of the fluoride-associated Brønsted acid sites which are responsible for promoting the hydrogenation and HDS of sterically-hindered structures. These acidic catalysts have higher activity in quinoline HDN than does Ni-Mo/Al₂O₃, probably as a result of increased C-N bond cleavage in o-propylaniline to produce propylbenzene; this reaction

is thought to be catalysed by acid sites(188,189).

During the hydroprocessing of both the low-nitrogen and high-nitrogen feeds there was a large loss of fluoride from catalysts containing > 1.8 wt% F. This may limit the usefulness of this type of catalyst in hydroprocessing, although fluoride may not be lost if lower temperatures are employed (see Section 7.2).

7.1.2. Phosphorus as a Secondary Promoter

Spectroscopic investigations of the H₃PO₄-Al₂O₃ interaction demonstrated that phosphoric acid reacts with the surface hydroxyls of alumina in an acid-base reaction during the preparation procedure. The hydroxyls of alumina react preferentially depending on their basicity. The stoichiometry of the reaction is close to 1:1 (i.e. two P(OH) groups are formed for every Al(OH) group consumed), as determined by fluoride At loadings of > 10 x 10^{13} H₃PO₄ cm⁻² (1 wt% P) exchange measurements. polyphosphate surface species start to form by the condensation of surface P-OH groups. At loadings of > 51 x 10^{13} H₃PO₄ cm⁻² (5 wt% P) an AlPO₄-type surface phase starts to form. Type Ib Al-OH surface hydroxyls (OH bound to an octahedral Al) can be generated by the reaction of bridging (Type II) or triply-bridging (Type III) surface hydroxyls with H₂PO₄. The P-OH groups are expected to be more acidic than the Al-OH groups they replace because of their lower v(OH). However, model cracking and hydrocracking reactions indicate that the P/Al₂O₃ catalysts are not sufficiently Brønsted acidic to crack cumene or 1,3-diisopropylbenzene to any great extent. There is some indication, however that phosphoric acid may increase the acidity of γ -alumina at low loadings and decrease the acidity at higher loadings. Even so, the low acidities of the P/Al₂O₃ catalysts suggest that this is not the major role of phosphorus as a secondary promoter.

Phosphorus does have a large influence on the impregnation of the metal species,

however, especially molybdenum. The interaction of molybdena with the surface hydroxyl groups of γ -alumina and 1.0 wt% P/Al₂O₃ was studied by infrared spectroscopy, and it was found that molybdenum reacts preferentially with surface P-OH groups. In addition, there is an indication that the dispersion of MoO₃ is also increased, although this was not measured directly. It is interesting to note that molybdenum bonded to P-OH groups was also more easily reduced/sulphided than molybdenum bonded to Al-OH groups so that the former are more active in thiophene HDS. It is apparent from this work therefore, that phosphorus decreases the interaction between MoO₃ and alumina so that it is more easily converted to the active form. There was no indication of any interaction between nickel and phosphorus from the IR spectra of the v(OH) region. These results do not preclude the suggestion of other workers(113) that phosphorus may block sites on the alumina support on which catalytically-inactive NiAl₂O₄ is formed.

Three different preparation methods of phosphorus-promoted Ni-Mo/Al₂O₃ were studied in model hydrocracking and HDS reactions; coimpregnation of additives from one impregnating solution (Method 1), stepwise impregnation first of the metal additives and then phosphoric acid (two calcination steps) (Method 2), and stepwise impregnation of phosphoric acid followed by the metal additives (two calcination steps) (Method 3). For all preparation methods a promotional effect of phosphorus in thiophene HDS is observed with an optimum phosphorus loading of 1.0 wt% in all cases. The promotional effect was most significant for catalysts prepared by Method 3 and the reason for this is thought to be as follows. Firstly, phosphorus, particularly when impregnated first, modifies favourably the impregnation of molybdenum on alumina, and the resulting molybdenum species are more easily converted to the active form as seen by IR spectroscopic studies. Secondly, phosphorus may block sites in the support where nickel

aluminate can form; in this way a greater fraction of the impregnated nickel is incorporated into the active phase. This effect is expected to be more pronounced when the phosphorus is impregnated first.

There was also a promotional effect of phosphorus in the hydrocracking of 1,3diisopropylbenzene to cumene for all three catalyst series. This is indicative of Brønsted acidity, and appears to be associated with the presence of reduced/sulphided molybdenum. This Brønsted acidity may result from H₂S dissociation on anion vacancies in MoS₂ crystallites. Since phosphorus influences the molybdenum dispersion and reducibility/sulphidibility it also influences the acidity of the catalysts; for Method 3 catalysts 0.3-1.0 wt% P increases the acidity of the sulphided phosphorus-promoted Ni-Mo/Al₂O₃ compared to that of unpromoted Ni-Mo/Al₂O₃. This is a true promotional effect since P/Al₂O₃ (no metals, P = 0.3-7 wt%) is not sufficiently acidic to give any activity in 1,3-diisopropylbenzene hydrocracking.

Phosphorus promotes the hydrogenation and HDS activities of Ni-Mo/Al₂O₃ in the hydroprocessing of both a low-nitrogen gas oil feed and a quinoline-spiked, highnitrogen gas oil feed. Optimum phosphorus loadings were 1-3 wt% in hydrogenation and 0.3-3 wt% in HDS. Phosphorus loadings of 0.3-3 wt% were also optimum for the promotion of quinoline HDN which provides evidence that HDS and HDN occur on the same sites. The improved activities of these P-Ni-Mo/Al₂O₃ catalysts is suggested to be a consequence of the favourable influence of phosphorus on both the molybdenum dispersion and reducibility/sulphidibility, and on the nickel species present. Optimum loadings of phosphorus also helped maintain high catalyst surface areas and catalysts with high hydrogenation activity also underwent less coking. This suggests that the phosphorus-promoted catalysts would have a longer lifetime on stream than unpromoted Ni-Mo/Al₂O₃.

7.1.3. Fluoride and Phosphorus as Secondary Promoters

The possibility of merging the beneficial properties of both fluoride and phosphorus in Ni-Mo/Al₂O₃ has been examined. In this preliminary study two different preparation methods have been investigated. Both methods utilise three impregnation steps; in the first series the order of addition was phosphorus followed by the metals followed by fluoride (PMF), with a calcination step after each impregnation, while in the second series the order of addition was phosphorus followed by fluoride followed by the metal additives (PFM). The PMF catalysts had nearly quantitative retention of fluoride while some loss of fluoride was apparent for the PFM series. For both preparation methods the catalysts had high activity in the hydrocracking of cumene to benzene indicating that the impregnated fluoride is able to generate Brønsted acid sites, as in the case of the fluoride-only-promoted Ni-Mo/Al₂O₃ catalysts. Also, for both catalyst series the Brønsted acidity decreased with increasing phosphorus content, probably due to consumption of Al-OH groups by H_3PO_4 ; i.e., fewer hydroxyls remain which can develop Brønsted acidity as the phosphorus content increases. It is also proposed that in the case of the PFM catalysts Al-OP(O)F₂ species may form on the catalyst surface which renders some of the impregnated fluoride inactive in developing Brønsted acidity. No beneficial effect of phosphorus in thiophene HDS was apparent for either the PMF or the PFM catalyst series.

In the hydroprocessing of a gas oil feed no advantage was observed using the PMF catalysts as compared to the fluoride-only- or phosphorus-only-promoted catalysts. Phosphorus decreases the acidity of $F-Ni-Mo/Al_2O_3$ so that the promotional effect of fluoride in hydrogenation and HDS does not occur to as great an extent. Also, no promotional effect of phosphorus in hydrogenation or HDS was apparent.

In the hydroprocessing of the quinoline-spiked feed the lower acidity of PMF

compared to fluoride-only promoted Ni-Mo/Al₂O₃ was an advantage; the hydrogenation and HDS activities were comparable to that observed for the unspiked feed, i.e. there was little loss in activity due to poisoning of Brønsted acid sites by nitrogenous bases as there was in the case of the fluoride-only-promoted catalysts. Consequently, for the quinoline-spiked feed, the hydrogenation and HDS activities of the PMF catalysts were better than the fluoride-only-promoted catalysts, but not as good as the phosphorus-only promoted catalysts (with optimum loadings). However, the PMF catalysts were superior to both the fluoride-only- and the phosphorus-only-promoted catalysts in quinoline HDN, with an optimum phosphorus loading of 1.0 wt% (wt% F = 3.4). It is suggested that this is because some promotional effect due to phosphorus is occurring, but in addition to this the Brønsted acidity associated with fluoride is tempered by phosphorus so that they are less susceptible to coking and poisoning. The Brønsted acid sites are important in C-N bond cleavage reactions as discussed in Section 7.1.1. These PMF catalysts also have excellent retention of fluoride under the hydroprocessing reaction conditions used in these studies and have a lower coking propensity than Ni-Mo/Al₂O₃.

7.1.4. Usefulness of Model Compound Reaction Studies

The model compound reaction studies are very useful for probing catalytic functionalities. Thiophene HDS was found to be a very good probe of the catalysts' abilities to promote the hydrodesulphurisation of sterically-unhindered sulphur compounds. Thus, there was very good agreement in the trends observed in thiophene HDS and in the HDS of a gas oil feed over the phosphorus-only- and fluoride-phosphorus-promoted Ni-Mo/Al₂O₃ catalysts. However, thiophene HDS is not a good model reaction for HDS over more acidic catalysts, such as the fluoride-only-promoted catalysts. This is because these acidic catalysts can increase the rate of HDS of sterically-hindered thiophenic molecules by promoting side-chain cracking reactions.

This mechanism is not manifested in the thiophene HDS reaction since thiophene is not sterically-hindered.

Where comparisons were possible there was good agreement between the model cumene and diisopropylbenzene cracking reactions and the cracking of molecules in the gas oil feed. For example, the promotional effect of fluoride in the hydrogenation and HDS of the gas oil feed is attributed to cracking of hindered aromatic structures which can then adsorb on the active sites. A fluoride loading of 3.5 wt% gave the maximum activity in cumene hydrocracking, and also maximum hydrogenation and HDS activities in hydroprocessing.

7.2. Future Work

The results presented in Chapter 4 did not clearly resolve the question as to whether phosphorus increases the number or the activity of the active sites in HDS, although they did suggest that the former situation was the case. An approach to answering this question may be to examine the intensity of NO adsorbed on the promoter atoms in the sulphided P-Ni-Mo/Al₂O₃ catalysts by infrared spectroscopy. NO adsorption Ni-Mo/Al₂O₃ well on has characterized by infrared been spectroscopy(156,207-209) and it has been reported that there is a good correlation between the amount of NO adsorbed on the promoter Ni (or Co) atoms and the thiophene HDS activity(207) indicating that NO adsorbs on catalytically important sites. In addition, it may be worth investigating thiophene adsorption by IR spectroscopy since this is expected to be even more specific for HDS sites; this adsorption process would first need to be characterized, however. A problem with using infrared spectroscopy for studying sulphided Ni-Mo/Al₂O₃ catalysts is that, for the normal metal loadings used. industrially, it is very difficult to get sufficient light through the catalyst samples in order to obtain a good spectrum. Therefore extremely thin catalyst wafers would be required to obtain the spectra of adsorbed NO (or thiophene) by transmission FTIR.

The preliminary investigation of Ni-Mo catalysts containing both phosphorus and fluoride secondary promoters which was discussed in Chapters 5 and 6 indicated that this type of catalyst may be useful in the hydroprocessing of high nitrogen feeds. However, while the HDN activity was very high, the activities in hydrogenation and HDS were not as good as those obtained for phosphorus-only-promoted catalysts. This suggests that it may be possible to improve these characteristics in the catalysts containing both phosphorus and fluoride. By careful investigations of preparation methods and fluoride and phosphorus loadings (only one fluoride loading was studied in this work) it may be possible to optimize the catalyst performance for all the hydroprocessing reactions.

The quinoline HDN studies reported in Chapter 6 were limited to 3 h batch reactions in a very complex reaction mixture (i.e. a gas oil). Therefore it was not possible to examine the activity with time of the three different catalyst series. In particular, it was not possible to determine if the more acidic catalysts were rapidly poisoned by the nitrogenous bases in the product mixture. Investigations of HDN either in a flow reactor or in a batch reactor for different reaction times would provide a better insight into the usefulness of acidic catalysts in HDN.

Finally, many of the reactions which are catalysed in hydroprocessing (such as hydrogenation, HDS and HDN) are exothermic(199). Therefore, if the activity of conventional hydroprocessing catalysts in these reactions is increased, it may be possible to utilize the thermodynamic advantage associated with lower reaction temperature. Therefore temperature studies of hydroprocessing over the secondary-promoted catalyst are warranted, particularly for the acidic catalysts where high cracking activity may be

possible at lower temperatures. Lower temperatures may also allow the retention of fluoride by the catalyst for an increased length of time.

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