Nano-Sized Carbon-Supported Molybdenum Disulphide Particles for Hydrodesulphurization

by

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Abstract

Canadian bitumen is a plentiful source of hydrocarbons. However, to obtain oils which may be sold to consumers, bitumen must be upgraded. Among other processes, bitumen upgrading includes lowering sulphur content and correcting the carbon to hydrogen ratio mostly by carbon rejection, which results in the formation of petroleum coke (PC), a by-product which must be stored or disposed of.

This study’s focus was the preparation of a molybdenum disulphide (MoS$_2$) catalyst for a more facile removal of intercalated sulphur from bitumen, by synthesising nano-sized MoS$_2$ particles. Simultaneously, this study attempted to use PC as a catalyst support.

Carbon-supported MoS$_2$ catalysts were successfully prepared by two methods using ammonium tetrathiomolybdate: reverse micelles using the water/IGEPAL CO-520/cyclohexane system, and incipient wetness impregnation from ultra pure water. MoS$_2$ prepared by impregnation was supported on PC, and MoS$_2$ prepared by reverse micelles was supported on both PC and activated carbon (AC). Catalysts prepared by reverse micelles contained nano-sized MoS$_2$ with low stacking order, and the catalyst prepared by impregnation consisted of long sheets of MoS$_2$ with a higher stacking order. The catalysts were screened for hydrodesulfurization activity in a novel slurry-phase batch microreactor using dibenzothiophene as a model compound.

The overall rate constant for DBT conversion per gram of molybdenum for the MoS$_2$/PC prepared by impregnation was greater than that for the catalysts prepared by reverse micelles.
in the temperature range of 350 – 375 °C. MoS$_2$ supported on AC and PC showed a similar activity toward catalysing the HDS of DBT when the MoS$_2$ was prepared by reverse micelles; therefore, PC is a good alternative support to AC for MoS$_2$/C catalysts prepared by this method.

The rate constant associated with hydrogenation was an order of magnitude greater for the catalyst prepared by impregnation than that for the catalysts prepared by reverse micelles. It was concluded that the larger stacking order in MoS$_2$/PC prepared by impregnation provided more sites for hydrogenation, which resulted in an overall larger rate constant than that for the catalysts prepared by reverse micelles, whose MoS$_2$ stacking orders were minimal due to the small particle size.
Preface

The work presented in this document was conducted in the department of Chemical and Biological Engineering in Vancouver at the University of British Columbia.

The M.A.Sc. work was performed by Lucie Solnickova under the direct supervision of Dr. Kevin J. Smith in the same department. Lucie Solnickova was responsible for the design of experiment and its execution, including catalyst synthesis, characterization, activity testing, data collection, data analysis, kinetic modelling, and preparation of this thesis.

Dr. Ross Kukard commissioned the micro batch reactor used for activity testing. Haiyan Wang prepared the activated petcoke used in this study.
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Nomenclature

**Roman symbols**

A  Pre-exponential factor, used in the Arrhenius equation, in cm$^3$ g$_{Mo}^{-1}$ s$^{-1}$

$E_a$  Activation barrier energy, in kJ mol$^{-1}$

$k_x'$  Rate constant parameter for a catalyst, in cm$^3$ g$_{Mo}^{-1}$ s$^{-1}$

$k_x$  Rate constant parameter for thermal and thermocouple-induced reactions, in s$^{-1}$

$M_n$  Number average molecular weight, in g mol$^{-1}$

mol%  Percentage by moles, a measure of concentration

mol%$_C$ of x  $C_x/\Sigma$, a molar percentage of x in the reaction product mixture

MoS$_2$  Molybdenum disulphide

P  Pressure, in Pa

ppm  Parts per million, a measure of concentration

$\Sigma$  $\Sigma (C_{DBT} + C_{BP} + C_{CHB} + C_{THDBT})$, in µmol mg$^{-1}$

Thiolate  C-S-H functional group

t  Reaction time, in hours or minutes

T  Reaction temperature, in °C
vol.% Percentage by volume, a measure of concentration
wt.% Percentage by weight, a measure of concentration
X Conversion

Greek symbols
β Peak width at half maximum intensity, in radians
θ Angle of reflection, in ° or radians
ω Water to surfactant ratio

Abbreviations
AC Activated Carbon, a support
AOT Aerosol OT, a surfactant
APTM Ammonium Polythiomolybdate, a Mo salt
ATTM Ammonium Tetrathiomolybdate, a Mo salt
BE Binding Energy, in eV
BP Biphenyl
CHB Cyclohexylbenzene
DBT Dibenzothiophene
DDS Direct Desulphurization
Decalin Decahydronaphthalene
DFT Density Functional Theory
DPE 1,1-diphenylethylene
GC-MS Gas Chromatography-Mass Spectrometry
HDS Hydrodesulphurization
HG Hydrogenation
<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>Igepal</td>
<td>IGEPAL CO-520, a surfactant</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide, a strong base</td>
</tr>
<tr>
<td>ODE</td>
<td>Ordinary Differential Equation</td>
</tr>
<tr>
<td>PC</td>
<td>Petroleum Coke</td>
</tr>
<tr>
<td>PDF</td>
<td>Powder Diffraction File</td>
</tr>
<tr>
<td>Petcoke</td>
<td>Petroleum Coke</td>
</tr>
<tr>
<td>RM</td>
<td>Reverse Micelle</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>THDBT</td>
<td>1,2,3,4-tetrahydrodibenzothiophene</td>
</tr>
<tr>
<td>TOF</td>
<td>Tunover Frequency</td>
</tr>
<tr>
<td>WI</td>
<td>Wetness Impregnation</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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Chapter 1

Introduction

1.1 Overview

1.1.1 Introduction to bitumen upgrading

Hydrocarbons and coal are currently the world’s leading source of energy, and extrapolating from the trend in Figure 1.1, the world’s energy supply will remain fossil fuel-based for the foreseeable future. After Venezuela and Saudi Arabia, Canada has the largest oil reserves in the world, with proven reserves totalling 166 billion barrels as of 2014. It is expected that the oil-based fossil fuels will continue to be produced in regions with high reserves. Canadian oil reserves are in the form of bitumen in oil sands [1].

Bitumen is a very complex mixture of hydrocarbons and heteroatoms. Compared with conventional offshore crude oil, bitumen has many more impurities, in the form of heavy metals and intercalated heteroatoms (S, O, N), as well as a higher C:H ratio. Table 1.1 summarises the average atomic content of Canadian bitumen, and Figure 1.2 is an example of a hypothesised typical heteroatom-containing bitumen molecule. The exact bitumen composition highly depends on the bitumen’s source and its processing method. The process of refining bitumen into intermediate crude oil includes the feed separation, upgrading, and
removal of impurities \cite{2-5}. These steps are outlined in more detail below.

Table 1.1: Atomic composition of Canadian bitumen \cite{6}

<table>
<thead>
<tr>
<th>Atom</th>
<th>Average content in bitumen (wt.%)</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>83.0</td>
</tr>
<tr>
<td>H</td>
<td>10.2</td>
</tr>
<tr>
<td>S</td>
<td>5.1</td>
</tr>
<tr>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>N</td>
<td>0.4</td>
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1.1.2 Feed separation and bitumen extraction

Canadian bitumen as mined is a mixture of sand, water, and bitumen. The mixture is first slurried with hot water, causing the bitumen to separate as a froth which includes some
solids and water. The froth is diluted with naphtha which allows the bitumen to be extracted by centrifugation and subsequently be sent for upgrading [4]. Liquid with an intermediate density is processed in smaller centrifuge separation vessels in order to extract bitumen from these middlings, and the bottom dense material is sent to a settling basin [4].

1.1.3 Bitumen upgrading processes

Bitumen containing naphtha diluent is first distilled to remove the naturally-occurring light gas oil components (boiling point of $<535 \, ^\circ C$) as well as the naphtha, which is recycled. Light gas oil is sent directly for hydrotreating, a process which converts the distillate into a feed with the correct specifications for jet fuel, diesel, and kerosene [5]. The heavier components which remain even after vacuum distillation, termed residue or heavy gas oil, need to be upgraded [3, 4].

Upgrading the residue is crucial, since about half the bitumen by volume is not light
gas oil. To convert the heavy gas oil into a mixture with specifications similar to those of offshore crude oil, processes to break the large molecules into components with a low boiling point that allows distillation, are employed [3–5].

The residue stream contains a larger concentration of heteroatoms and metals than freshly extracted bitumen, since only hydrocarbons have been removed thus far. Additionally, the residue contains many compounds with unsaturated hydrocarbons and aromatics which need to have their carbon to hydrogen ratio corrected to reduce the viscosity and boiling point of the feed into the specification range acceptable for diesel and gasoline. The C:H ratio is improved by hydroprocessing, either by C rejection or H addition, also called hydroconversion [5].

Hydroprocessing is performed at high temperatures, where the thermal cracking of large molecules occurs radically − a beneficial side-effect which increases the concentration of light oil products. If enough H₂ is present in the system during hydroprocessing, this process is basically hydroconversion. Light components produced by cracking are combined with light components from the initial distillation for hydrotreating [5].

However, if the system is starved of H₂ during hydroprocessing, the temperature is high enough (above 400 °C), or the residence time is long, a coking reaction significantly competes with hydrogenation and the hydrocarbon radicals condense to petroleum coke. This solid coke by-product is often derived from the very reactive asphaltene components of bitumen, defined as compounds insoluble in n-pentane or n-heptane. Many asphaltene molecules contain at least one heteroatom, so removing asphaltene as coke also reduces the S, O, N content of the residue. The exact characteristics of petcoke depend on the way it was made: delayed coke (made in a coking drum) contains more fixed C than fluid coke (made in a fluidized bed), while fluid coke has a higher weight content of S, O and N [8]. Coke makes up to 20 wt.% of the final products derived from bitumen and is often seen as a low-value by-product which must be stored or disposed of [9].
The bitumen upgrading process outlined above reduces the heteroatom content significantly, with the S content after upgrading at approximately 0.5 wt.% [3]. However, this S concentration is still too large for reasons discussed below, and the bitumen needs further upgrading to remove more S.

1.1.4 Regulations for the sulphur content of fuels

S-containing molecules are corrosive to metals, and high-S containing feeds can cause damage to processing equipment [10, 11]. Additionally, costly noble metal catalysts which are used down-stream in the refinery for hydrotreating have very low resistance to S poisoning [12].

Furthermore, specifications for the maximum allowable S content in fuels sold to consumers have decreased by several orders of magnitude: from 500 ppm to 15 ppm allowable S concentration in the last decade [13]. Recently, the Government of Canada announced that new regulations will allow less than 12 ppm (0.0012 wt.%) S concentration starting in 2020 [14], meaning that further innovation needs to occur in order to implement technology capable of reducing the S content to such low levels.

It should be noted that Canada is not alone in regulating S content of oil — the regulations are similar in many countries. For example, the European Union’s S content regulation allows less than 50 ppm, and fuel with a S content of less than 10 ppm must be available for consumers to purchase [15].

This study focused on preparing a highly active catalyst for a more facile removal of sulphur from bitumen.
1.2 Current processes for more complete sulphur removal from bitumen

1.2.1 Introduction

The S content of bitumen at 0.5 wt.% after initial upgrading is still unacceptably high for the equipment and noble catalysts downstream in the refinery, and for the permissible S content in oil regulations set out by governments. Presently, the technology most-often used to obtain fuels at or below the maximum allowable S-content limit is hyroprocessing, specifically hydrodesulphurization (HDS).

The initial MoS$_2$/Al$_2$O$_3$ catalysts developed for HDS deactivate quickly. However, continued development of the catalyst drove its improvement, and new catalysts have longer life-spans and are able to achieve deeper (more complete) desulphurization [16]. Current research is aimed at deeper HDS at lower temperatures, using more active and more selective catalysts. An improved catalyst would enable refineries to keep their current equipment and simply replace the catalyst for an improved one in the hydrotreater, avoiding the high costs associated with a complete shut-down and refitting to accommodate a different desulphurization technology.

1.2.2 HDS catalysts and mechanism

Industrially, HDS occurs in a dedicated unit, essentially a hydrotreater, by the catalytic addition of hydrogen. During the process, the actual reaction occurs when the feed is passed through a fixed-bed reactor housing a metal sulphide catalyst under a H$_2$ atmosphere.

A process diagram of an HDS unit in a petroleum refinery is pictured in Figure 1.3. To start, a pump delivers the feed which is then combined with a H$_2$ stream. The mixture is preheated, and then further heated in a fired heater to vaporize the components of the
feed. This process is very energy intensive, since many of the molecules in the feed have high molecular weights and therefore have high boiling points. The now-vaporized stream passes through the fixed-bed reactor which itself is heated to 300 – 400 °C and pressurized to 3 – 13 MPa. Much energy is required for this step also, since the reactor must be heated to keep all components vaporized. The hot product stream passes through a heat exchanger to preheat the incoming feed while itself being cooled. The product stream must pass through an additional cooler so that it may be separated in the gas separator into two phases: a H₂ rich gas, and an oil-rich liquid. Most of the unreacted H₂ is separated from the gas stream and recycled into the early part of the cycle. The remaining sour gas, termed so for its high H₂S content, is sent for further treatment. The liquid stream is sent to a distillation column (stripper) where the final bottom products are the desired desulphurized oil products. The top gas stream from the stripper contains light C₁ to C₄ hydrocarbons as well as some S-containing molecules. The gas stream is condensed into sour water, and the still-gaseous stream joins the sour gas for processing [17, 18].

Figure 1.3: Schematic of a typical HDS unit in a petroleum refinery plant. Used under a creative commons license from [19]
Currently the most commonly used HDS catalyst is a NiMoS/Al$_2$O$_3$ catalyst, where Ni is a promoter; Co can be used as a promoter in place of Ni. Although unsupported MoS$_2$ catalysts may be used, unsupported catalysts agglomerate faster than supported catalysts; agglomeration decreases the area on which the reaction occurs and consequently the rate of reaction is reduced. The NiMoS catalyst precursor is prepared by impregnating mesoporous Al$_2$O$_3$ with aqueous Mo and Ni solutions, either sequentially or in tandem, followed by calcining. The procedure yields an oxide which must be sulphided in situ prior to the HDS reaction. This preparation method is fast and easy, an important trait due to frequency with which catalyst is prepared. However, the method provides little control over the size of the catalyst particles [20].

![Proposed mechanism for the hydrodesulphurization of thiophene](image)

Figure 1.4: Proposed mechanism for the hydrodesulphurization of thiophene which is hydrogenated to 2,5-dihydrothiophene before the release of the final product, butadiene. Figure adapted by author from [21]

In the actual HDS reaction, organosulphur molecules are removed by reaction with H$_2$ over an MoS$_2$ catalyst to form H$_2$S and hydrocarbons. A proposed mechanism for HDS is outlined in Figure 1.4. Desulphurization begins when a S atom intercalated in the oil molecule binds to the Mo in the vacancy site where a S would have been, through Mo-S $\sigma$ and $\pi$ bonds. There is electron back-donation into the thiophenic $\pi^*$ antibonding orbitals, which weakens
the C-S bond [22]. Then two H atoms coordinated to S atoms in the catalyst migrate to
the substrate, weakening the S-C bonds which are then cleaved. The desulphurized product
is released, while the S remains coordinated to the metal. The next step is the dissociative
addition of H₂, and subsequent release of S, in the form of H₂S, from the Mo to regenerate
the vacant active site on the metal [23]. To complete the catalytic cycle, the S sites are
rehydrogenated by the catalytic dissociation of H₂.

1.2.3 Particle morphology as an indicator for activity

MoS₂ exists as sheets, pictured in Figure 1.5. However, HDS does not occur at basal sites,
since basal S ions are bonded too strongly to be removed and create a vacancy near the Mo
atom for C-S bond activation to occur [24, 25]. For unpromoted MoS₂, the activity at edge
sites is greater than at the corner sites [26].

Figure 1.5: 3D structure of MoS₂, Mo atoms in purple, S atoms in yellow. Adapted by
permission from Macmillan Publishers Ltd: Nature Communications ([27]), copyright (2014)

1.2.3.1 Rim-edge model

HDS occurs only on rim and edge sites of the MoS₂ particle since that is where the vacancies
are located (Figure 1.6). According to the Daage-Chianelli theory, it is the metal ions in a
tetrahedral site which are more active for HDS, rather than the octahedral sites. By this
reasoning, HDS is a structure-sensitive reaction, and hence turnover frequency is dependent
on particle size, with smaller particles offering more edge and rim sites per mass than larger particles [22, 28]. Therefore, creating nano-sized MoS$_2$ catalyst particles, rather than sheets, introduces more of these edge and rim sites per catalyst mass to catalyse the reactions, allowing the use of a smaller amount of catalyst to maintain the same conversion. When MoS$_2$ crystallites are in the 1 – 10 nm size range, the proportion of surface sites in various coordination numbers and molecular shapes changes noticeably with size and geometry [22].

Furthermore, depending on the shape of the MoS$_2$ nano-crystallite, different selectivities may be accessed. This has also been explained by the rim-edge model which proposes that hydrogenation (HG) occurs exclusively on top and bottom (rim) perimeter sites, while direct desulphurization (DDS) by hydrogenolysis is accessed at the edge sites of the MoS$_2$ crystallite [23, 29]. Therefore, it is theoretically possible to change the shape of the crystallite to favour more edge or rim sites, depending on the treatment necessary: HG for highly aromatic feeds, DDS for very sour feeds.

![Rim/edge model of an MoS$_2$ catalyst particle, some sites omitted for clarity. Figure adapted by author from [30]](image-url)
1.2.3.2 Brim sites

To add on to the rim-edge model and the mechanism outlined above, Topsøe and co-workers suggested that HDS activity can occur on an equilibrium MoS$_2$ edge without the creation of a vacancy at a Mo atom due to a “metallic brim site.” These metallic brim edge sites were observed by Scanning Tunnelling Microscopy (STM) and calculated by Density Functional Theory (DFT) as metallic in contrast to the basal plane of the fully sulphided Mo edge [31, 32]. The brim site is only exposed past the top layer of a multi-stacked particle, and not observed in single-slab structures [33]. The authors claimed that the brim sites could bind thiophene and be involved in HG reactions without the creation of a coordinatively unsaturated Mo site.

However, an earlier publication from the same research group stated that thiophene adsorption on these brim sites was only observed below $-73^\circ$C by DFT, above which the molecules dissociate before finally concluding that the brim sites were likely inconsequential to HDS catalysis [34]. Later, the group claimed that when H is present on sites adjacent to the weakly bound thiophene as S-H, both HG and ring-opening may occur [33]. This publication further claimed that brim sites are free of steric-hindrance effects and allow the adsorption of bulky atoms easier than non-brim sites. Additionally, the researcher claimed that brim sites are poisoned by basic N-containing substrates but unaffected by H$_2$S, explaining why the HG route is not suppressed by high H$_2$S concentrations [33].

Clearly this theory is still in the progress of being developed and tested, and should not be overlooked.
1.3 Role of support in catalysis

1.3.1 Introduction

In general, unsupported catalysts agglomerate faster than supported catalysts. Agglomeration lowers the surface area of the catalyst in the reaction mixture and results in decreased activity [35]. Therefore, supported catalysts offer one less deactivation mechanism to overcome.

Furthermore, the support anchors and stabilises the nano-sized catalyst particles on its surface, and limits sintering at reaction temperatures to ensure that the surface area of the catalyst particles remains high. However, the support is not involved in creating active sites on the particle [26].

1.3.2 Types of support

The selection of a support material for the catalyst is crucial, since the metal-support interaction can impact the activity of the catalyst in several ways, such as the polarity of the support-metal bond, support-precursor interaction, and the sulphidability of the oxidic precursor. These factors are discussed in detail below.

A variety of oxidic supports, such as $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, $\text{TiO}_2$ and zeolites are available; however, a particularly interesting support is carbon. Of special interest in this project is petroleum coke (petcoke), a C source produced in great quantity as a by-product of hydroprocessing of oil sands bitumen – an estimated 77 million tonnes of pet coke were stockpiled in Alberta by 2013, and approximately 4 million tonnes are created each year [8].

Successfully replacing the support for the MoS$_2$ HDS catalyst with petcoke at the site of its creation would reduce the costs associated both with storing the petcoke, and the purchasing and transportation costs of the material it would replace. However, petcoke has very low surface area and porosity, so it would first need to be activated to mesoporous
pet coke before being used as a catalyst support. Mesopores (pores with a diameter between 2 – 50 nm) are essential for an HDS catalyst support in order to accommodate the MoS$_2$ crystallite, and to reduce the diffusion effects related to the large molecules which need to diffuse in to reach the MoS$_2$ in order to be desulphurized [36, 37].

1.3.2.1 Activation of pet coke

The preparation of activated carbon consists of two steps: carbonization (heating in inert gas to $\sim$ 800 °C), followed by either physical or chemical activation. Pet coke can be similarly activated. In physical activation, steam or CO$_2$ increases the porosity of the C material by gasification at $\sim$ 1000 °C [38]. In chemical activation, the coke is combined with a chemical species (usually KOH, though NaOH, HNO$_3$, H$_3$PO$_4$, or ZnCl$_2$ can be used), and heated to 450 – 900 °C followed by subsequent washes to remove and/or neutralize the activating species [8]. Practically chemical activation is faster, but has more costs associated with it due to the waste stream created during washing [8]. On a research laboratory scale, chemical activation is more practical, due to the equipment necessary to inject steam or CO$_2$ into a gasifier needed for physical activation.

Liang and co-workers reported preparing chemically activated pet coke with a surface area of 3234 m$^2$/g and a pore volume of 1.78 cm$^3$/g by mixing coke with an excess of KOH and heating at 900 °C followed by subsequent washing. The average pore size was 2.2 nm; however, the authors do not specify how much of the pore volume was due to mesopores [39].

Chen and co-workers reported activating pet coke also by chemical activation but used microwaves rather than conventional heating. They affected the activation of both delayed and fluid coke, and found that delayed coke activated by this method had a larger surface area (1131 m$^2$/g vs. 440 m$^2$/g), and more total pore volume (0.4795 cm$^3$/g vs. 0.2247 cm$^3$/g) than activated fluid coke. However, the fluid coke yielded a larger proportion of mesopores
(0.0842 cm$^3$/g accounting for 37% of pores), than delayed coke (0.0571 cm$^3$/g, accounting for 12% of total pores) [40]. The authors related the differences in surface area and pore volume to the physical properties of the raw cokes: delayed coke is sponge-like enabling the KOH to spread through the internal pores of the raw coke, whereas fluid coke is more hard and smooth, making it difficult for KOH to penetrate to the core of each coke particle [40].

Rambabu and co-workers reported a successful physical activation of fluid petcoke, affected by carbonizing the coke at 900 °C and subsequently injecting steam. Optimised for activation time of 9 hours and a water flow rate of 15.0 g/h, the method’s yield was 35%. The obtained activated petcoke had a surface area of 482 m$^2$/g and a total pore volume of 0.231 cm$^3$/g of which 45% were mesopores [41].

A combined physical/chemical activation was related by Virala and co-workers whom activated delayed petcoke first by NaOH or KOH at 800 °C and later by humidified N$_2$ again at 800 °C without an intermediate washing of the coke. The activated petcoke with the largest mesopore volume was prepared by heating a coke/KOH mixture for 2 hours in dry N$_2$, followed by heating for 2 hours in humidified N$_2$. The activated petcoke had a surface area of 2449 m$^2$/g, and pore volume of 1.54 cm$^3$/g of which 40% were mesopores; however, the method’s yield was only 2%. The activated petcoke with the best compromise between yield (27%) and mesopore volume (0.61 cm$^3$/g of which 51% were mesopores) was prepared by heating petcoke with NaOH for 2 hours in dry N$_2$, followed by heating for 30 minutes in humidified N$_2$ [42].

1.3.3 Metal-support interaction

It has been demonstrated that one of the parameters which determine the activity of MoS$_2$ toward HDS is the covalent character of the catalyst’s Mo-S bond [43]. When MoS$_2$ is supported on an oxidic material, Mo can bind to O on the support which decreases the electron density at the metal centre. Reduced electron density increases the polarity of the
Mo-S bond, decreasing its covalency and consequently the HDS activity is lowered [43, 44]. The C-Mo bond is less polarized than the corresponding Mo-O-Al interaction on Al₂O₃, or the Mo-O-Si link on SiO₂ [44].

The magnitude of the activity decrease is proportional to the number of OH sites present on the surface of the support: Al₂O₃ has the most, SiO₂ has fewer, and C has very few OH sites [44]. Furthermore, Kibsgaard and co-workers found that the MoS₂ particles supported on oxidic supports are attached to the O through the particle’s edge sites, hence blocking the very sites active for HDS as discussed above [45]. Therefore, supporting MoS₂ on C as opposed to Al₂O₃ or SiO₂ should result in an increase in HDS activity.

The polarity of the support-metal bond determines the oxidation state of the metal. Additionally, the oxidation state of the metal in the oxidic precursor MoO₃ dictates the ease with which the oxide can be sulphided, and since MoS₂ not MoO₃ is active for HDS [30], the ease of sulphidation directly impacts the catalyst’s activity; MoO₃/C is more readily sulphided than MoO₃/Al₂O₃ and MoO₃/SiO₂ [44, 46].

A final point regarding the use of Al₂O₃ for HDS catalyst support to consider is the solubility of Ni and Co (common promoters) in the support. For instance, Arteaga and co-workers reported a decrease of HDS activity during a CoMoS/Al₂O₃ catalysed reaction. They attributed the decrease of activity to the decrease of Co atoms at the surface due to their diffusion into the support and formation of bulk CoAl₂O₄, a catalytically inactive species which is not sulphidable [47]. The diffusion effect is absent when C is used as a support, since C does not solubilize the promoter [48].

1.3.4 Metal loading considerations

Many factors are responsible for effecting catalytic activity, including the metal’s oxidation state, MoS₂ particle size and shape, atom packing, inter-particle metal-metal bonding, and the aforementioned particle-support interaction [35, 49]. Some of these factors (atom pack-
ing, inter-particle metal-metal bonding) are due to metal loading. For example, as the Mo loading increases, the MoS$_2$ particles are inherently more closely spaced, there are more metal-metal bonding interactions, and activity is decreased [50]. For Mo/C catalysts, a maximum conversion exists at approximately 25 wt.% Mo loading [51].

Since HDS is a structure-sensitive reaction, the MoS$_2$ particle size also has interesting implications. As the particle size decreases the shape of the crystallite changes, and the number of corners, edges, and rim sites that its surface offers increases [35]. The particle’s surface appearance impacts the activity directly by the nature of active site offered, which affects the oxidation state of the metal at that site.

1.4 Preparation of nano-sized MoS$_2$ particles

1.4.1 Introduction

For the past three decades, there has been a wide interest in the synthesis of nano-sized metal particles for application to catalysis. These nanoparticles have often been made using the reverse micelle method. The research has tended to focus on making the particles and deducing the variables responsible for the particle’s size. Many research groups have used the synthesised particles to catalyse reactions, after initial reports of nano-sized heterogeneous catalysts being more selective than traditionally prepared catalysts with larger particle sizes [52].

1.4.2 Water-in-oil reverse micelles

As reported extensively since the 1980’s, the size of an MoS$_2$ particle may be controlled by synthesising it in a reverse micelle. Each micelle consists of a small droplet of water surrounded by a layer of surfactant and suspended in an oil phase. The hydrophilic “heads”
of the surfactant molecules point inward to the water pool, while the lipophilic “tails” of
the surfactant are oriented into the oil phase. A water-soluble metal salt may be dissolved
in the internal pool of water, and the micelle can act as a nano-reactor to facilitate the
reduction and/or sulphidation of the salt. A reverse micelle system is an optically-clear,
thermodynamically-stable solution which forms spontaneously.

The micelle size can be controlled by changing the water to surfactant ratio, selection of
the surfactant and oil phase, concentration of the metal salt inside the water pool, reduction
and/or sulphidation conditions, and many other factors [53–59].

1.4.3 Particle nucleation and growth

To isolate the metal particles from the microemulsion, the Mo must be reduced and precip-
itated. The two steps have been demonstrated separately where the metal is first reduced
followed by the addition of a precipitating agent, or can occur simultaneously [57]. The
change of oxidation state either causes the particle to grow beyond its micelle’s size, or
causes its solubility to change such that it is no longer soluble in water. In either case, the
particle precipitates out of solution and may thusly be isolated. Among other factors, the
average particle size is determined by the size of the micelle from which it was precipitated
[53–59].

A mechanism for particle formation from micelles is based on a statistical approach,
rooted in the following assumptions [54, 55, 60, 61]:

1. Metal ions are distributed throughout the micelles of the microemulsion according to
   a Poisson distribution,

2. A micelle must contain a set minimum number of ions in order for a stable nucleus to
   form,

3. Nucleation is much slower than growth,
4. Material exchange between micelles occurs when two water cores coalesce to form a transient dimer which then decoalesces, leaving each core with a randomised solute content.

Upon the introduction of a reducing agent, nucleation occurs only in the micelles which meet the criteria for a stable nucleus. As the reduction proceeds, micelles exchange material amongst themselves by continuously coalescing and decoalescing. The unreduced Mo ions introduced into a micelle containing a reduced nucleus are reduced and incorporated into the nucleus, making it larger (see Figure 1.7). This process continues until either a critical nucleus size with a critical surface tension is reached which prevents further material exchange between micelles, or all Mo ions are reduced. In essence, the number of nuclei formed at the early nucleation stage determines the total number of particles which will form [55].

Figure 1.7: Model for nanoparticle formation and growth in a reverse micelle. Adapted by permission from Macmillan Publishers Ltd: Nature Chemistry ([62]), copyright (2010)

1.5 Effects of water-in-oil emulsion preparation on particle size

1.5.1 Introduction

Microemulsion systems contain many variables, each of which may change the particle’s final size or the particle size distribution. Extensive studies of these variables and their effects on the particle size have been carried out by many groups [53–59]. The average particle size is
a function of the size of the micelles from which the metal was precipitated; however, the exact relationship is a complicated one.

### 1.5.2 Water to surfactant ratio

The size of the micelle can be controlled by changing the ratio of water to surfactant, $\omega$. The larger the $\omega$, the larger the micelles formed, as shown in Figure 1.8 for a reverse micelle system of water, surfactant AOT, and oil phase $n$-heptane. The linear relationship can be explained by the fact that only a certain number of micelles can be formed from a set amount of surfactant. Adding more water molecules to the solution means that each existing micelle must swell in order to accommodate the water since no new micelles can form. The swelling will only continue to a point, the critical micelle concentration, after which if more water is added the microemulsion breaks and two phases form [61, 63].

As discussed above, the critical nucleus size depends on the original size of the micelle, which in turn is set by $\omega$. Therefore, the larger the $\omega$, the larger will be the precipitated particles [56]. However, there are many more factors which influence the final particle size than $\omega$. 
The metal salt concentration inside the water pool is limited by the salt’s solubility in water. Calculating the average salt concentration in the micelle is made more complicated by the fact that one is unable to truly account for all the water inside the water pool, as some water goes toward hydrating the surfactant chains, which is discussed further below [60, 65].

The salt concentration inside the water pool was reported to be a factor which impacts the size of the isolated particles. Fischer and co-workers reported being able to vary the diameter
of Co$_3$O$_4$/Al$_2$O$_3$ particles which maintain their size even after reduction with ammonia; the micelle sizes were changed by varying $\omega$ as well as the salt concentration in the water pool [66]. A lower concentration of metal salt inside the micelle resulted in a smaller average Co$_3$O$_4$ diameter [66].

1.5.4 Microemulsion temperature

The temperature at which the microemulsion is prepared influences the micelle size inversely. At constant water and surfactant concentration, the micellar diameter decreases as temperature increases, with the minimum diameter occurring at $\sim 2{^\circ}C$ below the temperature of phase separation. This effect was argued to be due to hydration of the lipophilic chains of the surfactant, the magnitude of which increases with temperature. At higher temperatures, more water molecules hydrate the surfactant chains, leaving fewer inside the micelle and thus lowering the micellar diameter [65, 67].

However, during the reduction of the salt inside the water pool, the particle size dependence on temperature is reversed. Reductions performed at lower temperatures tend to yield smaller crystallites, if all conditions other than temperature are constant. This was explained by the decreasing oil phase viscosity with increasing temperature – oil phase which is more viscous will result in more nuclei being formed. Thus, fewer nuclei and therefore larger particles are observed when the reduction is affected at higher temperatures, while reductions performed at lower temperatures give smaller crystallites [56, 67].

1.5.5 Precursor reduction and sulphidation

As discussed above, the metal inside the micelle must be reduced and precipitated in order for the particle to be isolated. Furthermore, current industrial HDS catalyst preparation methods use MoO$_3$ precursors which must be sulphided since it is the MoS$_2$ phase which is
active for HDS catalysis [30]. The reduction, precipitation, and sulphidation processes have a large impact on the final MoS$_2$ particle size; some researchers have attempted to combine two or three of these processes to reduce the impact on particle size.

Reduction of the Mo salt in the micelle has been reported by bubbling H$_2$ or N$_2$ through the microemulsion; however, due to particle agglomeration, large and irregularly-sized particles precipitated as a result of this method [53, 68, 69]. Using 5% H$_2$S in H$_2$ to affect the simultaneous in situ reduction and sulphidation at room temperature was also reported to produce large agglomerated bulk particles [70].

Some researchers affected the reduction/sulphidation with liquid agents such as N$_2$H$_4$, LiBH$_4$, NaBH$_4$, Li$_2$S, (NH$_4$)$_2$CO$_3$, or NH$_4$OH instead of the gaseous H$_2$S or H$_2$. It was reported that the amount of liquid reducing agent added to the microemulsion impacted the average particle size [54, 58]. Boutonnet and co-workers reported that the catalyst whose metal was reduced by N$_2$H$_4$ was significantly more active, by an order of magnitude, than the catalyst prepared by reduction using H$_2$ [69].

Other researchers avoid the oxide to sulphide transformation, which can lead to incomplete sulphidation or agglomeration of the particles, by utilising a Mo salt which is already a sulphide. Most often, this salt is ammonium tetrathiomolybdate (ATTM) which contains [MoS$_4$]$^{2-}$. Researchers have reported making a catalyst more active for HDS than a conventional catalyst by using the ATTM salt in place of an oxidic salt [71–73].

1.5.6 Supporting the metal particles

Fischer and co-workers reported several different methods of supporting Co$_3$O$_4$ particles, and the large impact this procedure has on the particle size and its distribution. They found that the smallest particles resulted when the Co salt was first reduced for thirty minutes inside the micelle with an aqueous reducing agent but not isolated from the emulsion, followed by the addition of Al$_2$O$_3$ support and the destabilization of the emulsion [74].
Boutonnet and co-workers reported obtaining nano-sized Pt/pumice particles with a narrow size distribution by initially reducing the Pt salt in the microemulsion with aqueous \( \text{N}_2\text{H}_4 \), and subsequently adding the support into the vessel and heating the solution to 60 or 85 °C to remove the oil phase [52].

1.6 Catalytic activity of MoS\(_2\) nanoparticles

1.6.1 Introduction

While early research focused on the effect of the variables discussed above on the size of the particles isolated from the micelles, much research lately has focused on using these nanoparticles to catalyse reactions.

1.6.2 Effect of surfactant on the catalysis

Some researchers have reported using the catalysts directly after separating them out of the rest of the solution with no adverse effects [52, 57]. However, others related that the surfactant has a poisoning effect on the reaction being catalysed [70, 74–76].

It has been suggested that not only does the surfactant poison the MoS\(_2\) catalyst outright, but that its thermal decomposition products scavenge H atoms from the solvent, reducing the solvent’s efficacy as a hydrogen shuttle [76]. For instance, AOT begins decomposing at 200 °C [77], and the typical HDS reaction temperature is 350 – 400 °C. Furthermore, the proposed mechanism for HDS suggests that the reaction starts by a C-S bond scission, followed by H transfer to a thiolate intermediate; thus, the concentration of H\(_2\) in the reaction mixture effects reactivity [78]. Therefore, it seems that whether or not the surfactant will poison the reaction depends on the reaction mechanism; HDS is poisoned by surfactant remaining in the reaction mixture. To prevent the HDS reaction from being poisoned, it is
best to remove the surfactant and its constituents prior to reaction.

Additionally, the boiling point of the surfactant is such that it begins to sublime under vacuum, precluding characterization methods performed at high vacuum, such as BET, TEM, and XPS.

The drawback to heating metal catalysts is that elevated temperatures enable species to migrate, resulting in particle agglomeration or sintering. It was reported that sulphiding MoS$_2$/Al$_2$O$_3$ at temperatures below 397 °C preserves the catalyst’s dispersion [44].

### 1.6.3 Model compounds

In lieu of using a real oil feed to study the activity of a novel MoS$_2$ catalyst toward HDS, researchers often use thiophene to greatly simplify the reaction mixture. Many groups prefer to use dibenzothiophene (DBT) or its substituted version 4,6-dimethyldibenzothiophene (4,6-DMDBT) as sterically-hindered S-containing molecules resistant to hydroprocessing (see Figure 1.9 for the structures of these compounds). Often these model compounds are used as the feed stock in search for improved HDS catalysts [79–81].

![Figure 1.9: Frequently used model compounds to study HDS. a) Thiophene; b) DBT; c) 4,6-DMDBT](image)

Though a model compound does not accurately display the full variety of complex molecules in an oil feedstock, it is postulated that the catalyst most successful at desulphurizing a model compound will translate to the best candidate for treating a more complex
mixture. Using a model compound eases the deconvolution of the results of catalytic tests, especially in terms of selectivity.

### 1.6.4 Reactors for research laboratory-scale activity testing

Industrially, most hydrotreating processes are either trickle flow or gas-phase processes. These reactor systems are generally too large to be viable in laboratories, and researchers often use the equipment already available in their laboratories for catalyst testing. Some have reported catalytic testing of nanoparticles in batch reactors [82, 83], and some in continuous flow reactors [84, 85].

No matter the regime, microreactors are often used in research to test the activity of novel catalysts, or to deduce mechanisms of reactions. The use of microreactors is advantageous since these small-scale reactors require the use of less catalyst and substrate, and consequently less waste is generated. Furthermore, it is easier to fully control the reaction conditions in a microreactor than in a full scale one. The disadvantages include a large degree of error inherent to any experiment dealing with small volumes, and frequent down-times for cleaning and maintenance [84, 86, 87].

### 1.7 Literature review summary

Fossil fuel-based oils will continue to be prominent in the near future. As the concentration of S in feedstocks continuously increases, improved catalysts with higher HDS activities will need to be implemented to meet S content regulations. Using C as a support increases the activity of supported MoS$_2$ catalysts toward HDS. Utilising pet coke, a low-value by-product of bitumen upgrading, as a catalyst support for bitumen upgrading would help the oilsands be more sustainable. Using reverse micelles to synthesise MoS$_2$ catalysts offers control over particle size by carefully controlling preparation conditions. Control over geometry, and
therefore selectivity, is also possible. Catalysts need to be fully cleansed of surfactant prior to being screened for HDS activity. Microreactors utilising DBT as a model compound are effective to test catalysts for HDS activity.

1.8 Study approach and objectives

This work sought to prepare a highly active, pet coke-supported MoS$_2$ catalyst for the HDS of the model compound DBT. A series of MoS$_2$/C catalysts were prepared and compared quantitatively in terms of their activity toward affecting the HDS of DBT reaction.

Two MoS$_2$/C catalysts were prepared using the reverse micelle method in the hopes of synthesising nano-sized particles – one on activated carbon and one on activated pet coke in order to draw a comparison between the C supports.

A conventional MoS$_2$/C catalyst using incipient wetness impregnation was prepared in order to draw a comparison between the reverse micelle approach and a conventional preparation.
Chapter 2

Experimental

The procedures used to prepare and analyse the catalysts are outlined in this chapter.

2.1 Catalyst preparation

2.1.1 Carbon supports

Two types of carbon were used to support the MoS$_2$: activated carbon (Sigma Aldrich, Darco G-60 high purity powder, referred to as AC), and petroleum coke which was chemically activated by a fellow group member (referred to as PC). The properties of the supports are given in Table 3.1 on page 47, and the petroleum coke activation procedure is detailed in Appendix C.

In all preparations, the Mo loading target was 10% Mo by weight.

2.1.2 MoS$_2$ preparation using reverse micelles

In an attempt to prepare a more active MoS$_2$ catalyst, it was desirable to synthesise particles of small diameters which would provide many edge and rim sites to facilitate the hydrodesulphurization reaction [30]. For this reason, reverse micelles were utilized to syn-
thesise nano-sized MoS$_2$ particles. There are many micelle systems cited in the literature ([88] and references within), and this study utilised two water-in-oil microemulsion systems: water/Igepal/cyclohexane and water/AOT/n-heptane. AOT (Sigma-Aldrich, $\geq$96.0% by TLC) shown in Figure 2.1 is an anionic surfactant, and IGEPAL CO-520 (Sigma-Aldrich, Average M$_n$ 441, referred to as Igepal in this document) shown in Figure 2.2 is a non-ionic surfactant; both surfactants were used as received. Oil phase solvents cyclohexane (Anachemia, 99%), and n-heptane (Fisher, 99.8%) were also used as received. The reasoning for selecting these specific surfactant/oil systems is discussed in section 3.4.

The Mo salt ammonium tetrathiomolybdate (ATTM, discussed in more detail below) was obtained from Strem chemicals and used as received.

![Molecular structure of surfactant AOT](image1)

Figure 2.1: Molecular structure of surfactant AOT

![Molecular structure of surfactant IGEPAL CO-520](image2)

Figure 2.2: Molecular structure of surfactant IGEPAL CO-520
2.1.3 Typical MoS$_2$ preparation via reverse micelles

A preparation for MoS$_2$/PC by the reverse micelle method is presented here for one batch of MoS$_2$/PC catalyst. The calculations to arrive at the masses and volumes of substances used can be found in Appendix A.

In a typical preparation, enough surfactant was added to a certain volume of oil to give a 0.1 or 0.3 M solution of surfactant in oil – for example, 48.6 g of Igepal was added to 367 mL of cyclohexane (a 0.3 M surfactant in oil solution), and the solution was stirred for two hours to achieve thermodynamic equilibrium. During the mixing period, a 5 mM solution of solubilized ATTM was prepared by weighing out enough salt and dissolving it in ultra-pure water (e.g. 0.1912 g of ATTM in 147.04 g of water).

After the surfactant and oil phase had been sufficiently mixed, enough acid (0.5 M H$_2$SO$_4$ in ultra-pure water) was added to the surfactant/oil mixture such that there would be 10 H$^+$ protons for each ATTM molecule (added later), and this solution was mixed for one hour. The acid served as the reducing and precipitating agent [59, 75]. In this preparation, 1.9 mL of 0.5 M H$_2$SO$_4$ was added.

During the mixing period of acid into the oil/surfactant mixture, nano-sized reverse micelles are hypothesised to have formed, indicated by the solution remaining optically transparent. To this solution of nano-sized water pools encapsulated by surfactant and suspended in oil phase, the solubilized Mo salt was added dropwise. Continuing with the preparation outlined thus far, 37.95 mL of the aqueous 5 mM ATTM solution was added dropwise over approximately nine minutes in nine portions of 4.22 mL using a calibrated pipette. This mixture was allowed to stir for thirty minutes, during which some of the ATTM salt would have been reduced to MoS$_3$ (as reported by Wang and co-workers [89]). It should be mentioned that the amount of total water added from the acid and aqueous ATTM solution was carefully calculated so that the molecular water to surfactant ratio, $\omega$, was 20.
After the mixing period, enough C support was added such that the metal loading was 10 wt.% Mo in the final MoS$_2$ catalyst, 0.1516 g of PC in this case, and this mixture was allowed to stir for one more hour. It is hypothesised that during this mixing period, more of the ATTM salt was reduced, and the particles anchored on the support.

Finally, to break the emulsion and separate the solid precursor, 200 mL of acetone was added dropwise over the course of two hours while the solution was being stirred. To complete the separation of the phases, the mixture was allowed to settle overnight. The next day, a black precipitate and a clear and colourless supernatant were completely separate such that much of the supernatant could be decanted. The remaining solution was gravity filtered through Whatman quantitative ashless filter paper, and the collected solid was washed with 250 mL of methanol in several aliquots in an attempt to remove as much supernatant from the catalyst precursor as possible. The solid was isolated and allowed to air-dry. To prevent the oxidation of the metal, at no point during the preparation or subsequent activity testing was the precursor allowed to heat above 65 °C in air.

The final step in the preparation of the catalysts obtained by the reverse micelle method was the annealing step which transformed the catalyst precursor into catalyst. The heating regime removed much of the remaining surfactant by thermolysis, completed the reduction of the Mo salt, and allowed the MoS$_2$ to organize into sheets. The transition of MoS$_4$ to MoS$_2$ is complete at 320 °C [90].

The annealing procedure was performed by transferring the solid into a quartz glass U-tube into which a plug of quartz wool was first inserted. The tube containing the precursor was then positioned into a Barnstead Thermolyne Type 47900 muffle furnace equipped with a temperature controller. The tube was connected to ultra-high purity Ar or N$_2$ gas via a mass flow controller on one end, and directly to building ventilation on the other end. Finally, the gas flow rate was slowly increased until the surface of the powder was visibly moving, indicating that the bed of solid would not rise into the ventilation. The precursor
was flushed with inert gas for ten minutes. After all air was presumably displaced from the powder, the furnace was set to ramp at 10 °C per minute to 350 °C, and to hold at 350 °C for sixty minutes during which inert gas continued to be flushed through the solid. After the hold period, the furnace was shut off, and the furnace door was opened to allow for rapid cooling to ensure that the annealing step was as close to 60 minutes as possible.

Table 2.3 summarises the preparation methods and naming conventions of the catalysts prepared and screened for kinetic parameters in this study.

### 2.1.4 Making a stable micelle

The preparation outlined above was a typical preparation performed during the course of this work, and yielded approximately 100 mg of solid catalyst per preparation. The product mass may seem disproportionate to the volume of solvent used during the preparation; however, the volumes used were strictly calculated to maintain micellar integrity or to keep certain ratios constant between preparations.

The phase diagram for the water/AOT/n-heptane system is presented in Figure 2.3. Stable micelles will form only from solutions whose component concentrations are such that they fall in the L2 region. A molar concentration of surfactant in oil needs to be high enough to accommodate enough water and subsequently metal in the micelle to enable isolation of solid after preparation (some solid is lost during washing and annealing). Throughout much of this project and in the synthesis outlined above, a concentration of 0.3 M of surfactant in oil was used.

The next constraint was the water to surfactant ratio, which was set to 20 to maintain preparations as close to identical as possible. Finally, the concentration of the metal solution and the ratio of acid to Mo salt was kept constant at 5 mM and 10:1, respectively. With these constraints, the mass fraction of each component could be calculated, and is presented in Table 2.1 along with similarly calculated values for a 0.1 M system; the detailed calculations
can be found in Appendix A.

![Phase diagram of the water/AOT/n-heptane system.](image)  
Figure 2.3: Phase diagram of the water/AOT/n-heptane system. Figure adapted from [91], used under a creative commons license

<table>
<thead>
<tr>
<th>Concentration of surfactant in oil (M)</th>
<th>n-heptane mass fraction</th>
<th>AOT mass fraction</th>
<th>Water mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.89</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>0.3</td>
<td>0.74</td>
<td>0.14</td>
<td>0.12</td>
</tr>
</tbody>
</table>
2.1.5 Mo salt selection

Aside from selecting a surfactant/oil system, there was the matter of the Mo-containing salt. As mentioned in the literature review, many researchers begin with MoO$_3$ before sulphiding the oxide to obtain MoS$_2$ – the species active for HDS; however, the sulphidation process leads to the restructuring of the particle, manifesting in large and/or irregularly sized particles [53, 68–70]. To avoid needing to sulphide the oxidic precursor, the catalyst precursor in this study was made from a Mo salt which already contained S; the Mo salts used in this study are summarised in Table 2.2. Ammonium tetrathiomolybdate (ATTM) was chosen as the sulphidic salt containing [MoS$_4$]$^{2-}$. Two batches of ATTM salt were obtained from Strem and used as received (certificates of analysis for the two batches can be found in Appendix D). However, one batch of Mo salt obtained was later determined to be ammonium polythiomolybdate (APTM) with different properties than ATTM. For instance, APTM is only very sparingly soluble in water, whereas the solubility of ATTM is moderate. Needless to say, the solubility impacted the preparation of the micelle-derived catalysts drastically.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATTM</td>
<td>Ammonium tetrathiomolybdate</td>
<td>(NH$_4$)$_2$MoS$_4$</td>
</tr>
<tr>
<td>APTM</td>
<td>Ammonium polythiomolybdate</td>
<td>(NH$_4$)$_2$Mo$<em>3$S$</em>{13}$(H$_2$O)</td>
</tr>
</tbody>
</table>

2.1.6 MoS$_2$ preparation by incipient wetness impregnation

Finally, to be able to compare the micelle-derived MoS$_2$ catalysts to a conventionally-prepared catalyst, an MoS$_2$/PC catalyst was prepared using incipient wetness impregnation. In this preparation method, only enough solvent is added to the solid support such that the liquid is completely taken up by the pores of the support; the salt to be deposited onto the support is dissolved in the liquid. To prepare 0.3 g of the conventional MoS$_2$ catalyst (of
which 0.05 g would be MoS$_2$, calculation in Appendix A) on PC, 0.0814 g of ATTM would need to be added to 0.25 g of the support.

Solubility trials of ATTM in ultra-pure water were performed, and it was found by visual observation that 0.0836 g of ATTM was dissolved in 0.7113 g of ultra-pure water. However, the pore volume of PC is 0.97 cm$^3$/g, so only 0.2425 cm$^3$ of liquid could be added to 0.25 g of the support at once. Therefore, the ATTM salt was added to the support in three additions over three days. On each day, 0.0279 g of ATTM was dissolved in 0.2415 g of ultra-pure water and added dropwise onto the PC support using a Pasteur pipette. The solid was allowed to rest at room temperature for 24 hours after each addition. It was assumed that the pore volume was not changed by the step-wise impregnation, and that all the liquid evaporated between additions.

As in the catalyst preparation by reverse micelles, the solid was never allowed to heat above 65 °C in air. The conventional catalyst’s preparation was completed with the same annealing procedure employed for the reverse micelle-derived catalysts.

Table 2.3 summarises the preparation methods and naming conventions of the catalysts prepared and screened for kinetic parameters in this study.

Table 2.3: Preparation methods and naming of the catalysts screened for kinetic parameters

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo source</th>
<th>Support</th>
<th>Preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/AC-RM</td>
<td>ATTM</td>
<td>AC</td>
<td>Reverse micelles: water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>MoS$_2$/PC-RM</td>
<td>ATTM</td>
<td>PC</td>
<td>Reverse micelles: water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>MoS$_2$/PC-WI</td>
<td>ATTM</td>
<td>PC</td>
<td>Incipient wetness impregnation</td>
</tr>
</tbody>
</table>

2.2 Catalyst characterization

A series of analytical methods were used to characterize the prepared catalysts. It should be noted that all the characterizations listed were performed ex situ due to instrumental
limitations. For more accurate data, in situ characterizations would have been preferable.

2.2.1 X-Ray diffraction

The presence of the desired metal, its oxidation state, and potentially crystallite size may be studied by Powder X-Ray Diffraction (XRD). The spectrum of each catalyst was collected using a Bruker D8 Focus X-Ray diffractometer (equipped with a LynxEye detector) with Co Kα radiation (λ=1.79 Å, 35 kV), and scan range 2θ = 10 to 90° at 0.08°/second. Each sample was spun at 50 RPM during measurement to ensure complete powder averaging.

By analysing the sample supported on a quartz plate, which does not produce an amorphous “bump” in the 15 – 30° 2θ region like glass, the 002 reflection of MoS2 centred at 16° 2θ can be fully visualized, and crystallite size calculated using the Scherrer equation (2.1) using the peak’s line-broadening (provided the crystallites are large enough).

\[ d_c = \frac{0.89 \lambda}{\beta \cos(\theta)} \]  

β is the full width at half the maximum intensity and θ is the angle of reflection.

Since XRD is not performed under vacuum, the method is not sensitive to the presence of surfactant and can be used to compare the structure and chemical identity of species prior to, and after annealing.

2.2.2 X-Ray photoelectron spectroscopy

The presence and concentration of the desired metal on the catalyst surface as well as its oxidation state can be studied by X-Ray Photoelectron Spectroscopy (XPS). XPS spectra were collected using a Leybold MAX200 X-Ray photoelectron spectrometer with an Al Kα source. Survey scans were collected at 192 eV, and narrow scans at 48 eV.

XPS provides the binding energies (BE) of atoms at the solid’s surface. Correcting for
the charging effects by referencing the BE scale to the C 1s signal at 284.8 eV enables the comparison of signal positions between samples. BE can be used to determine a chemical species’ identity by comparing the experimental BE value to those reported by other researchers (see Table 2.4 for binding energies in Mo complexes relevant to this work).

Table 2.4: Binding energies for Mo 3d_{3/2} spectral lines for selected compounds

<table>
<thead>
<tr>
<th>Species</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂</td>
<td>232.3 ± 0.1 [92]</td>
</tr>
<tr>
<td>MoO₃</td>
<td>235.6 ± 0.2 [93]</td>
</tr>
</tbody>
</table>

The collected XPS spectra were deconvoluted into separate contributions by the species present on the sample surface using the open-source program XPS Peak 4.1.

Furthermore, XPS is only able to scan the top ~1 nm of sample [94], so the bulk Mo concentration cannot be measured; however, XPS can give an estimate of surface metal dispersion by comparing the ratios of the signal intensities due to the metal and the support element. In the case of MoS₂/C, particles with low dispersion will have a low Mo:C intensity ratio; however, if particles with high dispersion are successfully prepared, the Mo:C intensity ratio will be higher [95].

XPS is performed under high vacuum, which precludes the analysis of unannealed samples since surfactant sublimes under vacuum and can destroy the equipment.

2.2.3 Surface area measurements

A Micromeritics ASAP 2020 analyser was used to measure the surface area, pore volume, and average pore size using N₂ adsorption-desorption isotherms measured at −196 °C. Each sample was degassed in vacuum at 200 °C for 4 hours prior to analysis.

Surface area of each sample was calculated from the BET N₂ isotherm. Pore volume was calculated based on the total amount of N₂ adsorbed at 0.995 of the relative pressure (P/P°),
where $P^\circ$ is the saturated vapour pressure of $N_2$ at $-196 \, ^\circ C$ (101 kPa), and $P$ is the pressure that is varied for the measurement. Each sample’s desorption isotherm was analyzed by the Barrett-Joyner-Halenda (BJH) method to determine the average pore size.

### 2.2.4 Metal loading analysis

The exact Mo loading of the catalysts was measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Sample preparation involved completely dissolving the pre-weighed sample by boiling it in aqua regia. A set of standards from which a calibration curve may be constructed was used for quantitative analysis. Sample digestion and standard solution preparation procedures can be found in Appendix C.

The samples were analysed using a Varian 725-ES Optical Emission Spectrometer with a 10 ppm solution of Eu in 2 vol.% HNO$_3$ analysed simultaneously to correct for matrix effects. The computer program ICP Expert II was used to calculate the metal concentration in each prepared sample using a calibration curve.

During analysis, the metal ions in solution are excited by argon plasma at a very high temperature ($\sim 9000 \, ^\circ C$). As the ions relax to ground state they emit a unique ultraviolet and visible light spectrum, the intensity of which is proportional to the concentration of the species in solution. The Mo content is measured quantitatively by the use of a calibration curve. In this method, the total amount of Mo in the bulk sample is accounted for.

### 2.2.5 Transmission electron microscopy

The average size of the MoS$_2$ particles and their size distribution were measured using Transmission Electron Microscopy (TEM). Prior to analysis, a drop of MoS$_2$/C catalyst dispersed in acetone was introduced onto a formvar-coated, carbon-stabilized copper grid, and allowed to air dry. Images were captured using an FEI Tecnai G2 electron microscope.
operated at 200 kV, for which source electrons were generated from a LaB$_6$ filament.

The particle size measured by TEM is a more direct measurement than the volume-averaged size measured by XRD; however, the drawback to analysing particle size with TEM is that a large number of images must be captured to obtain a true average particle size, and can introduce operator bias during particle measurements. In this work, several images of each sample were captured, and the open-source program ImageJ was utilized to measure the diameters of many particles per sample from all over the TEM grid, allowing for a distribution of sizes to be calculated.

As in XPS analysis, unannealed samples could not be studied by TEM due to the presence of surfactant which sublimes at high vacuum and obscures the image, in addition to risking damage to the instrument. Therefore, no samples can be analysed by TEM prior to annealing, and the effect of the annealing treatment on MoS$_2$ dispersion and/or particle size cannot be studied by this method.

2.2.6 Thermogravimetric analysis

Thermogravimetric Analysis (TGA) was used to evaluate the progress of surfactant decomposition by thermolysis. By heating a sample under annealing conditions in a TGA instrument, the mass loss from the sample may be monitored. Surfactant thermolysis experiments in a TGA revealed the temperature at which the surfactants decomposed, and the degree of decomposition.

~5 mg of surfactant was placed into an aluminum pan and loaded into a Shimadzu TGA-50 thermogravimetric analyzer. A constant flow of N$_2$ at 40 mL/min purged the system of liberated thermolysis products while the sample was ramped at 10 °C/min to 350 °C, and held at 350 °C for sixty minutes to simulate the annealing process during catalyst preparation.
2.3 Activity measurements

The activity and selectivity of the prepared catalysts toward the hydrodesulphurization and hydrogenation reactions were investigated by using dibenzothiophene (DBT) as a model reactant. The catalyst activity was tested using a novel batch microreactor, pictured in Figure 2.4. The reactor operates isothermally [86], and the temperature was controlled by a 800 W Lindberg 55031 tubular furnace and continuously monitored by an OMEGA type K thermocouple immersed in the reaction mixture. The reactor's small dimensions reduce the heat and mass transfer effects [86].

It was previously found by Kukard that the stainless steel thermocouple and reactor walls of the reactor used in this study are active for cracking reactions [86]. To avoid introducing activity from the walls and also for easier clean-up, a glass insert in which the reaction would proceed was utilised. These inserts were commissioned from CANSCI Glass Products Ltd., and measured 260 mm in length, 6 mm in outer diameter and 4 mm in inner diameter. Between reactions the inserts were cleaned with aqua regia to remove all catalyst and products from the walls, and the thermocouple was wiped with acetone-moistened paper towel until no more black solid was removed.

Prior to testing, the catalyst was ground and sieved to a maximum particle diameter of 63 µm to eliminate internal diffusion effects. To perform a reaction, a known amount of catalyst was suspended in acetone and transferred to a clean and dry glass insert by Pasteur pipette. To remove the acetone without oxidizing the catalyst, the reactor tube was immersed in a water bath maintained at 65 °C with a hotplate for 24 hours. Since the boiling point of acetone is 56 °C, this process removed all the acetone without allowing the catalyst to become oxidized. Additionally, this slow evaporation ensured that all the solid remained at the bottom of the tube instead of being carried upward as might occur with a fast evaporation.
Figure 2.4: Process flow diagram of the batch microreactor used for activity testing. Reprinted with permission from [86]. Copyright (2015) American Chemical Society
Once the acetone was removed from it, the insert was allowed to cool to room temperature before feed containing the model compound was added to it. The volume of liquid feed added to the insert was calculated such that the Mo concentration would be 900 ppm during the reaction. The feed consisted of 2 wt.% DBT and 0.4 wt.% CS$_2$, with the balance composed of decahydronaphthalene (Sigma-Aldrich, $\geq 99\%$, referred to as decalin). The calculations involved with the feed preparation are given in Appendix A. The purpose of the CS$_2$ was to sulphide any MoO$_3$ present in the catalyst, but was also kept low to prevent the poisoning effect of H$_2$S [80]. The liquid volume was sufficient to allow the vortex mixer to agitate the contents at 2000 RPM, approximately 150 $\mu$L [86]. In addition to keeping the contents well-mixed, the use of a vortex mixer at the base of the reactor also minimized external diffusion effects.

The glass insert containing all the components of the reaction was placed inside the steel reactor, the thermocouple was inserted into the tube, and the reactor was hermetically sealed using a stainless steel gasket. The reactor was purged of air by three cycles of adding $\sim 0.7$ MPa of H$_2$ and its subsequent venting. After purging, the system was pressurized to 4.14 MPa and tested for leaks with a PerkinElmer leak detector (N9306089) to ensure it was well-sealed.

With the reactor loaded, well-sealed and pressurized, the reaction could proceed. Reactions were performed at reaction temperatures, $T$, of 350 °C, 365 °C, or 375 °C and at reactions times, $t$, of 60 min, 120 min, or 180 min. The pressure at reaction temperature reached on average 5.08 MPa.

In order for the reaction mixture to achieve reaction temperature, the tubular furnace surrounding the reactor tube was activated and controlled by an OMEGA CN8201 temperature controller. The heating program was composed of a fast temperature ramp to 5 °C below target $T$ followed by a 120 second hold, and a slow ramp to final $T$. This program ensured that the target temperature was not overshot by more than 2 °C. The reaction time
was considered to be $t = 0$ when the temperature first crossed temperature $T$. Regardless of $T$, the time to reach it was $\sim 21$ minutes, and all liquid products include the products produced during this heat-up period.

After $t$ minutes, the furnace control was set to 0, the furnace door opened, and a fan was turned on to help cool the system faster. Once below 30 °C, the system was slowly depressurized by opening the needle valve and directing the gas through a bubbler. Upon reaching atmospheric pressure, the system was opened and the liquid product extracted by a long stainless steel needle attached to a glass syringe to prevent the adsorption of substrates to the walls, which might occur if a plastic syringe was used. The liquid products were stored at $-20$ °C unless being actively diluted for GC-MS analysis.

### 2.3.1 Gas chromatography-mass spectrometry

Gas Chromatography-Mass Spectrometry (GC-MS) was used to quantify the products of the reaction. An Agilent 7890B GC separated the components in each sample, and they were detected by an Agilent 5977A MS.

To quantify the products, a calibration curve was constructed for each analyte, and a known amount of internal standard was added to each calibration sample. Calibration curves of biphenyl (BP), cyclohexylbenzene (CHB), and dibenzothiophene (DBT) were constructed. The internal standard used in this study was 1,1-diphenylethylene (Sigma-Aldrich, 97%, referred to as DPE), a compound with similar chemical characteristics as the analytes. The product 1,2,3,4-tetrahydrodibenzothiophene (THDBT) was quantified by the DBT curve, since pure THDBT is not commercially available. No bicyclohexyl was detected as a product in this study.

Each calibration curve plotted the known concentration ratio of analyte:DPE against the area ratio of analyte:DPE for each analyte diluted from pure reference samples, where the areas were measured by integrating the peak areas of chromatograms obtained by the
Prior to analysis, each sample was diluted with decalin to place the concentrations of the analytes in the linear range of the detector, and a known quantity of internal standard was added. This method enabled the calculation of each analyte’s concentration in the reaction product mixture from the known concentration of internal standard and calculated chromatogram areas of the internal standard and analyte.
Chapter 3

Catalyst Properties and Characterization Results

3.1 Introduction

The results of the catalyst characterization by the methods outlined in the Chapter 2 are presented, summarised, and discussed in this chapter; a comprehensive summary is given at the end of this chapter. The kinetic activity testing results are presented in Chapter 4.

3.2 TGA results

The water/AOT/n-heptane system for nanoparticle preparation using reverse micelles has been extensively studied [49, 59–62, 75, 88, 91, 96–98], and was therefore determined to be a suitable system to use since the effect of many variables (e.g. water:surfactant ratio, metal concentration in the water pool) have been reported. Additionally, using the same system as other researchers would enable comparisons to be drawn between particles prepared by other groups with the particles prepared during this project.
However, the preliminary activity results with catalysts prepared with APTM as a Mo salt in the water/AOT/n-heptane system were poor, and an explanation for these results was sought. It was hypothesised that some of the surfactant from the preparation remained on the catalyst even after annealing, covering the metal and blocking the active sites, which would cause low activity. Studied by Luwang and co-workers, the decomposition of AOT was reported to occur in two stages, the first at 340 °C, and the final decomposition occurring at 550 – 700 °C which corresponds to the evaporation of SO₂ due to the decomposition of the SO₃ group [98].

![Figure 3.1: Thermolytic decomposition of surfactant AOT under N₂ by TGA](image)

The annealing procedure during catalyst preparation was reproduced in a TGA instrument, with the results of AOT thermolysis presented in Figure 3.1. The results indicate that indeed the AOT was not fully burned off after heating at 350 °C for one hour, and that 14.5 wt.% of the surfactant remained on the catalyst surface. However, the decomposition profile was not identical to the one reported by Luwang [98], with the initial decomposition
occurring at a lower temperature.

Since the goal of this project was to make an MoS$_2$ catalyst with high activity toward HDS of DBT, a different system would need to be used to prepare the catalyst if leftover surfactant was causing suppressed activity. AOT is an anionic surfactant, and adding salts into the water pool of a micelle bounded by an ionic surfactant was found to lead to an increase in the micellar size [99], so the search for a different surfactant system was limited to non-ionic surfactants. A non-ionic surfactant often mentioned in the literature is IGEPAL CO-520 (referred to as Igepal in this document), reportedly used as part of the water/Igepal/cyclohexane system. Only 0.7 wt.% of Igepal’s mass remained after thermolysis at annealing conditions, as shown in Figure 3.2, a good improvement over AOT.

![Figure 3.2: Thermolytic decomposition of surfactant Igepal under N$_2$ by TGA](image)

Figure 3.2: Thermolytic decomposition of surfactant Igepal under N$_2$ by TGA
3.3 BET results

Table 3.1 presents the catalyst surface properties measured by BET. AC is used for many purposes because of its high surface area, including as a catalyst support; the surface area of the AC used in this study was measured to be 1136 m$^2$/g, while the surface area of PC was measured to be 2030 m$^2$/g.

Table 3.1: BET surface area, pore volume, and pore size of the prepared catalysts used for activity testing, and of their supports

<table>
<thead>
<tr>
<th>Support or catalyst</th>
<th>BET surface area (m$^2$/g)</th>
<th>Specific pore volume (cm$^3$/g)</th>
<th>Pore size (nm)</th>
<th>Mo content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon (AC)</td>
<td>1136</td>
<td>0.98</td>
<td>3.4</td>
<td>0</td>
</tr>
<tr>
<td>MoS$_2$/AC-RM</td>
<td>464</td>
<td>0.51</td>
<td>4.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Petroleum Coke (PC)</td>
<td>2030</td>
<td>0.97</td>
<td>1.9</td>
<td>0</td>
</tr>
<tr>
<td>MoS$_2$/PC-RM</td>
<td>927</td>
<td>0.49</td>
<td>2.1</td>
<td>7.8</td>
</tr>
<tr>
<td>MoS$_2$/PC-WI</td>
<td>1677</td>
<td>0.85</td>
<td>2.0</td>
<td>8.7</td>
</tr>
</tbody>
</table>

The PC was prepared by chemical activation at 800 °C, so it was assumed that the annealing step at 350 °C during catalysis preparation did not impact the structure of PC much. However, it is possible that some pores collapsed during the annealing step of the MoS$_2$/AC-RM catalyst. Furthermore, since all three catalysts presented in Table 3.1 underwent the same annealing process, it is possible to discuss the effect the catalyst preparations had on the surface of the supports.

Comparing PC to MoS$_2$/PC-WI, it can be seen that the surface area decreased by 17%, pore volume decreased by 12%, and pore size remained statistically unchanged after wet impregnation of the support and subsequent annealing. The small loss of surface area and pore volume was attributed to MoS$_2$ occupying space on the surface of the catalyst.
Comparing PC to MoS\textsubscript{2}/PC-RM, the changes to the C surface are much more drastic: the surface area decreased by 54\%, and the pore volume decreased by 49\%. The pore size remained statistically unchanged.

From the three PC data sets, it was concluded that the reverse micelle preparation method was responsible for surface area and pore volume loss on the surface of the PC support. Since all other factors except the use of surfactant were the same, it is hypothesised that the 0.17 wt.\% of Igepal that remained after annealing somehow decreased the surface area of the PC supported catalyst. The exact mechanism is unknown.

A significant loss in surface area and pore volume was also observed in the MoS\textsubscript{2}/AC-RM catalyst when compared to AC: 60\% of the surface area was lost, and the pore volume decreased by 48\%. The catalyst had a larger pore size than AC before catalyst preparation, suggesting that the MoS\textsubscript{2} filled the smaller pores preferentially over the larger pores. However, AC was not treated at elevated temperatures prior to catalyst preparation, so it is possible that some of the pores collapsed during annealing, resulting in the decreased surface area and pore volume. Conversely, it is possible that a similar mechanism responsible for the loss of surface area on PC during the preparation of MoS\textsubscript{2}/PC-RM may be responsible for the surface area loss in the MoS\textsubscript{2}/AC-RM catalyst as well.

### 3.4 Metal loading results

The preliminary catalyst preparations were plentiful, and it was not practical to fully characterize the kinetic activity of each catalyst. However, the success of the preparations can be partially ascertained by the amount of Mo which was possible to be supported with each preparation method. The results are summarised in Table 3.2. Due to the combined errors associated with the ICP-OES instrument, incomplete metal extraction during digestion prior to analysis and the fact that the sample is not perfectly homogeneous, the error with the
ICP-EOS analysis was calculated to be 4% from performing some digestions and analyses multiple times. The errors for values presented in Table 3.2 include this calculated error.

Table 3.2: Summary of Mo sources, preparation methods, and metal loading of some of the prepared catalysts. Target loading was set to 10 wt.% Mo in all cases. The error associated with this measurement was calculated to be 4%.

<table>
<thead>
<tr>
<th>#</th>
<th>Mo source</th>
<th>Support</th>
<th>Mo content (wt.%)</th>
<th>Reverse micelle system</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>APTM</td>
<td>PC</td>
<td>1.2 ± 0.1</td>
<td>water/AOT/n-heptane</td>
</tr>
<tr>
<td>2</td>
<td>APTM</td>
<td>AC</td>
<td>4.0 ± 0.2</td>
<td>water/AOT/n-heptane</td>
</tr>
<tr>
<td>3</td>
<td>APTM</td>
<td>AC</td>
<td>6.8 ± 0.3</td>
<td>water/AOT/n-heptane</td>
</tr>
<tr>
<td>4</td>
<td>APTM</td>
<td>AC</td>
<td>5.9 ± 0.2</td>
<td>water/AOT/n-heptane</td>
</tr>
<tr>
<td>5</td>
<td>APTM</td>
<td>PC</td>
<td>0.4 ± 0.02</td>
<td>water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>6</td>
<td>ATTM</td>
<td>AC</td>
<td>0.5 ± 0.02</td>
<td>water/AOT/n-heptane</td>
</tr>
<tr>
<td>7</td>
<td>ATTM</td>
<td>AC</td>
<td>9.1 ± 0.4</td>
<td>water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>8</td>
<td>ATTM</td>
<td>AC</td>
<td>9.6 ± 0.4</td>
<td>water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>9</td>
<td>ATTM</td>
<td>PC</td>
<td>8.5 ± 0.3</td>
<td>water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>10</td>
<td>ATTM</td>
<td>PC</td>
<td>7.1 ± 0.3</td>
<td>water/Igepal/cyclohexane</td>
</tr>
</tbody>
</table>

Comparing catalysts # 2, 3, and 4 in Table 3.2 allows for the calculation of error associated with the preparation of MoS$_2$/AC using the water/AOT/n-heptane reverse micelle system, calculated to be 26%. This high error is likely due to the fact that APTM is not very soluble in water, as described in Section 2.1.5, so it was difficult to support the Mo consistently between preparations. However, even the high error does not account for the fact that when APTM was attempted to be supported on PC, only 12% of the intended Mo ended up on the support (# 1); using a different system of water/Igepal/cyclohexane did not yield an improved catalyst (# 5). It was concluded that APTM is a poor choice of Mo
salt for preparing MoS$_2$/C catalysts by either of the two reverse micelle systems used in this study.

When the ATTM salt was used, the preparation using the water/AOT/$n$-heptane reverse micelle system was also not successful in supporting a significant amount of Mo on AC (§ 6). A vast improvement in the amount of Mo supported on C was obtained when the water/Igepal/cyclohexane system was used, with 93% of the Mo added attaching to the AC (§ 7 and 8). Using the same system to prepare MoS$_2$/PC was also successful (§ 9 and 10). It is hypothesised that it is the anionic character of AOT which interferes negatively with the anionic [MoS$_4$]$^{2−}$ salt, though the exact interaction is unknown, and the non-ionic character of Igepal which mediates a successful MoS$_2$/C preparation. Furthermore, the repeated preparations presented in catalysts § 7 and 8 and § 9 and 10 allowed for the calculation of error associated with the preparation of MoS$_2$/C from ATTM using the water/Igepal/cyclohexane reverse micelle system, at 9%.

These findings helped to shape the final selection of catalysts which were fully screened for catalytic activity as discussed in Chapter 4. The final selection of salt was ATTM, and the water/Igepal/cyclohexane system. Of the two reverse micelle systems tested, this one proved more effective and consistent in preparing MoS$_2$/C. The preparation methods of the catalysts synthesised for activity testing are summarised in Table 3.3.

The errors for Mo content values presented in Table 3.3 represent the calculated error associated with both the preparation and the ICP-OES analysis for the RM catalysts, and only the analysis for the WI catalyst because its preparation error cannot be calculated since its preparation was not repeated.

From Table 3.3, it can be observed that all three catalysts contain the statistically same amount of Mo in the bulk: 8.6 ± 1.5 wt.% Mo.
Table 3.3: Mo loading and preparation methods of the catalysts screened for kinetic parameters

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo source</th>
<th>Support</th>
<th>Mo content (wt.%)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/AC-RM</td>
<td>ATTM</td>
<td>AC</td>
<td>9.3 ± 0.8</td>
<td>water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>MoS$_2$/PC-RM</td>
<td>ATTM</td>
<td>PC</td>
<td>7.8 ± 0.7</td>
<td>water/Igepal/cyclohexane</td>
</tr>
<tr>
<td>MoS$_2$/PC-WI</td>
<td>ATTM</td>
<td>PC</td>
<td>8.7 ± 0.3</td>
<td>Impregnation</td>
</tr>
</tbody>
</table>

### 3.5 Surface composition and Mo coverage

Measuring Mo content by ICP-OES quantifies the total metal content in the catalyst bulk; however, some of the Mo measured by this method may be inaccessible to the DBT molecules. XPS analysis is a better method to measure how much Mo is on the surface of the catalyst available to catalyse the HDS reaction.

By comparing the values of Mo content measured by ICP-OES with those measured by XPS, it was possible to obtain a sense of the metal dispersion on the catalyst surface; these results for some of the catalysts prepared and discussed above are summarised in Figure 3.3. All data presented in the figure are for annealed catalysts, prepared from either ATTM or APTM Mo salt (as indicated), supported on AC or PC (also indicated), and prepared either by reverse micelles from the water/Igepal/cyclohexane or water/AOT/\(n\)-heptane system, or by incipient wetness impregnation.

From Figure 3.3 it can be seen that the catalyst with the highest surface concentration of Mo was the one prepared by reverse micelles using the water/Igepal/cyclohexane system and ATTM salt, supported on PC. Additionally, the amount of Mo on the surface of this MoS$_2$/PC catalyst showed a linear correlation between the amount of metal detected on the surface and in the bulk. This indicates that when more Mo was supported on the PC by
In addition to Mo, the quantities of S, C, and O on the catalyst surface can be measured by XPS. The results of these surface concentration measurements for the catalysts screened for activity are given in Table 3.4.

Due to the error associated with the low surface S and Mo concentrations, the error in the S:Mo ratio presented in Table 3.4 is such that no comparisons of this ratio between the catalysts may be made; in all three catalysts the ratio was close to the expected value of 2.
Table 3.4: Surface composition of the prepared catalysts screened for kinetic parameters as measured by XPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>S</td>
</tr>
<tr>
<td>MoS$_2$/AC-RM</td>
<td>4.4</td>
<td>0.9</td>
</tr>
<tr>
<td>MoS$_2$/PC-RM</td>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>MoS$_2$/PC-WI</td>
<td>6.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

It was observed by XRD that AC contained highly crystalline SiO$_2$ and PC did not (XRD data are presented below). However, the surface Si concentration results of the catalysts presented in Table 3.4 do not correlate with the Si observations from XRD. It is likely that the Si observed on the surfaces of MoS$_2$/AC-RM and MoS$_2$/PC-WI were the remnants of quartz wool used during the annealing step of catalysis preparation. The effect of Si on the HDS of DBT was not studied, and the values are included for completeness.

3.6 Deconvoluted narrow XPS scans

All collected XPS spectra were deconvoluted into separate peaks using the open-source program XPS Peak, each of which results from a different chemical species on the surface of the sample.

Two separate batches of MoS$_2$/PC-RM were prepared and analysed by XPS to further quantify the repeatability in the catalyst preparation. Figures 3.4a and 3.4b are the deconvoluted spectra of the Mo scans of these two batches, Figures 3.5a and 3.5b are the deconvoluted S scans. Comparing these figures, it appears that the Mo species composition was very similar, while the S composition differed in the amount of SO$_x$ species present (Table 3.8).

Figures 3.4c and 3.5c show the deconvoluted spectra of Mo and S of the species on
MoS$_2$/AC-RM prepared by the micelle method, respectively. The spectra look similar to their MoS$_2$/PC-RM counterparts. Figures 3.4d and 3.5d show the deconvoluted spectra of Mo and S of the species on the surface of the MoS$_2$/PC-RM catalyst prepared by incipient wetness impregnation, respectively.
Figure 3.4: XPS spectra of Mo 3d energy level for: a) MoS$_2$/PC-RM (batch 1); b) MoS$_2$/PC-RM (batch 2); c) MoS$_2$/AC-RM; d) MoS$_2$/PC-WI
Figure 3.5: XPS spectra of S 2p energy level for: a) MoS$_2$/PC-RM (batch 1); b) MoS$_2$/PC-RM (batch 2); c) MoS$_2$/AC-RM; d) MoS$_2$/PC-WI
Figure 3.6 is the deconvoluted XPS scan in the Mo region of the activated PC support. This scan shows that there was no Mo present on the surface of the support before catalysis preparation, as expected. Additionally, this scan shows that the K-\(\beta\) peak incorporated in the deconvolutions of the Mo spectra above is justified, since this signal is significant above noise. The K-\(\beta\) signal is a satellite of the C 1s peak, and is therefore proportional to the concentration of C in the sample. Since C was the support and accounts for \(~90\%\) of the sample by weight, the K-\(\beta\) peak was large in the Mo region of the scans and needed to be accounted for during peak deconvolution.

![Figure 3.6: XPS spectrum of petcoke before metal addition, presence of a K-\(\beta\) peak at 236.09 eV evident](image)

### 3.7 Chemical states of Mo in the catalysts

The deconvolution of XPS spectra into individual peaks enabled the relative area of each peak to be calculated. The ratio of peak areas corresponds directly to the relative concentrations of those species on the surface of the catalyst.
For Mo, the two species present on the catalyst surface were MoS$_2$ and MoO$_3$ (Tables 3.5 – 3.7). The catalyst prepared by incipient wetness impregnation had a higher proportion of oxide present on the surface than the catalysts prepared by the reverse micelle method, whose proportion of MoS$_2$ to MoO$_3$ on the surface was statistically the same.

Table 3.5: Chemical states and their relative amounts of Mo in MoS$_2$/PC-RM, from the Mo narrow XPS scan

<table>
<thead>
<tr>
<th>State</th>
<th>Mo 3d$_{3/2}$ B.E. (eV)</th>
<th>Mo 3d$_{5/2}$ B.E. (eV)</th>
<th>Area (%)</th>
<th>std error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>232.3 ± 0.2</td>
<td>229.1 ± 0.2</td>
<td>77</td>
<td>3</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>235.4 ± 0.2</td>
<td>232.2 ± 0.2</td>
<td>23</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.6: Chemical states and their relative amounts of Mo in MoS$_2$/AC-RM, from the Mo narrow XPS scan

<table>
<thead>
<tr>
<th>State</th>
<th>Mo 3d$_{3/2}$ B.E. (eV)</th>
<th>Mo 3d$_{5/2}$ B.E. (eV)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>232.0 ± 0.2</td>
<td>228.8 ± 0.2</td>
<td>79</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>235.4 ± 0.2</td>
<td>232.2 ± 0.2</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 3.7: Chemical states and their relative amounts of Mo in MoS$_2$/PC-WI, from the Mo narrow XPS scan

<table>
<thead>
<tr>
<th>State</th>
<th>Mo 3d$_{3/2}$ B.E. (eV)</th>
<th>Mo 3d$_{5/2}$ B.E. (eV)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>232.3 ± 0.2</td>
<td>229.1 ± 0.2</td>
<td>68</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>235.7 ± 0.2</td>
<td>232.5 ± 0.2</td>
<td>32</td>
</tr>
</tbody>
</table>
3.8 Chemical states of S in the catalysts

A similar deconvolution was performed on the collected narrow S XPS scans, and the results are summarised in Tables 3.8 – 3.10. Again, the catalysts prepared from the reverse micelles had a similar surface composition with MoS$_2$ accounting for a total of 78 to 88% and an oxide accounting for the balance, while for the catalyst made by incipient wetness impregnation the MoS$_2$ contributed 65% of the S species and the oxide the balance. It should be noted that the MoS$_2$ in the prepared catalysts had two separate binding energies, and both energies have been attributed to MoS$_2$ [100].

Table 3.8: Chemical states and their relative amounts of S in MoS$_2$/PC-RM from two identically made batches, from the S narrow XPS scan.

<table>
<thead>
<tr>
<th>State</th>
<th>S 2p$_{1/2}$ B.E. (eV)</th>
<th>S 2p$_{3/2}$ B.E. (eV)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>163.1 ± 0.2</td>
<td>161.9 ± 0.2</td>
<td>64</td>
</tr>
<tr>
<td>SO$_x$</td>
<td>169.6 ± 0.2</td>
<td>168.4 ± 0.2</td>
<td>14</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>164.8 ± 0.2</td>
<td>163.6 ± 0.2</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 3.9: Chemical states and their relative amounts of S in MoS$_2$/AC-RM, from the S narrow XPS scan.

<table>
<thead>
<tr>
<th>State</th>
<th>S 2p$_{1/2}$ B.E. (eV)</th>
<th>S 2p$_{3/2}$ B.E. (eV)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>162.7 ± 0.2</td>
<td>161.6 ± 0.2</td>
<td>39</td>
</tr>
<tr>
<td>SO$_x$</td>
<td>169.8 ± 0.2</td>
<td>168.6 ± 0.2</td>
<td>21</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>163.9 ± 0.2</td>
<td>162.8 ± 0.2</td>
<td>40</td>
</tr>
</tbody>
</table>
Table 3.10: Chemical states and their relative amounts of S in MoS$_2$/PC-WI, from the S narrow XPS scan

| State | S 2p$_{1/2}$ B.E. (eV) | S 2p$_{3/2}$ B.E. (eV) | Area (%)
|-------|------------------------|------------------------|-------
| MoS$_2$ | 163.0 ± 0.2 | 161.9 ± 0.2 | 26 |
| SO$_x$ | 169.5 ± 0.2 | 168.4 ± 0.2 | 35 |
| MoS$_2$ | 164.0 ± 0.2 | 162.8 ± 0.2 | 39 |

3.9 XRD results

All XRD data were collected by using a quartz plate to support the samples in order to avoid the large amorphous peak around 15° 2θ, which would result from using a glass plate and obscure the signals resulting from the sample.

The intensity of a peak on an XRD spectrum is directly related to the degree of crystallinity of the sample. Essentially, more crystalline samples give rise to sharp and intense peaks when studied by XRD. In terms of MoS$_2$, several reflections are possible depending on the shape and dimensions of the MoS$_2$ particles which make up the sample, and the intensity of those peaks is indicated by the crystallinity, or degree of structural order, of the MoS$_2$ particles. If there is little long-range order in the crystallites, the peak will be very broad; if there is practically no long-range order, there will be no peak.
Figures 3.7 and 3.8 present the collected XRD spectra of the two batches of Mo salt, aligned with their corresponding Powder Diffraction Files (PDF). Comparing to the PDF, the first batch of ATTM was confirmed to actually be APTM, and the second batch of ATTM was indeed ATTM.
Figure 3.8: a) Collected XRD spectrum of the ATTM salt, compared with b) the corresponding PDF for $(\text{NH}_4)_2\text{MoS}_4$ (PDF # 04-015-4295)
Figure 3.9 presents the collected spectra of the two C supports used in this study. The spectrum for AC shows a very crystalline impurity of SiO$_2$ at $32.5^\circ$ 2θ, and very crystalline graphitic C signal at 24.3 and 25.6$^\circ$ 2θ. The XRD spectrum of PC shows C which was very amorphous, indicated by the broadness of the peak centred at $\sim 25^\circ$ 2θ.

![XRD spectra of the supports prior to Mo addition: a) AC; b) PC](image)

Figure 3.9: XRD spectra of the supports prior to Mo addition: a) AC; b) PC
Figure 3.10 presents the XRD spectra of an MoS$_2$/AC sample prepared from APTM using the reverse micelle method and the catalyst’s precursor prior to annealing. The distinctive double peaks of the Mo salt (compared to Figure 3.7a) are visible in the precursor’s spectrum, indicating that the APTM salt was not impacted by the acid-mediated reduction inside the micelle, likely because the salt was not inside the micelle during the reduction due to its poor solubility in water. After annealing, the catalyst presented a broad peak centred at $\sim 16^\circ$ 2$\theta$ indicative of poorly crystalline MoS$_2$ composed of crystallites with moderate stacking. The average crystallite stack height of this MoS$_2$/AC was estimated to be 2.3 nm from the Sherrer equation (Equation 2.1).
Figure 3.11 presents the XRD spectra of catalyst MoS$_2$/AC-RM and its precursor prior to annealing. In this catalyst, the unannealed sample’s spectrum does not resemble that of its Mo salt (compared with Figure 3.8a), and looks rather like slightly-crystalline MoS$_2$, indicated by a slight “bump” around $16^\circ \theta$. The annealed sample does not show this $16^\circ \theta$ peak, indicating that the annealing process did not cause the particles to agglomerate to larger stack heights, but that the MoS$_2$ was well-dispersed and nano-crystalline. The presence of MoS$_2$ on this sample was confirmed by ICP-OES and XPS (vide supra). While the $16^\circ \theta$ (reflection 002) peak disappeared, a $39^\circ \theta$ (reflection 103) peak appeared. The 103 reflection indicates some interlayer rotation in the crystallites [101, 102], though the degree of this rotation is unknown.

Figure 3.11: XRD spectra of MoS$_2$/AC prepared from ATTM by the reverse micelle method a) before annealing; b) after annealing
Figure 3.12 compares the XRD spectra of the three prepared catalysts which were used for activity screening. In all three samples, the peak around 16° 2θ which is most indicative of stacked crystalline MoS$_2$ is absent, indicating that the MoS$_2$ on the catalyst was well-dispersed and nano-crystalline. The presence of MoS$_2$ in these samples was confirmed by ICP-OES and XPS, vide supra. All three catalysts display a peak related to the 103 reflection of MoS$_2$ to different intensities, indicating some interlayer rotation in all three MoS$_2$ catalysts [101, 102]; however, the degree of this twisting is unknown. Additionally, MoS$_2$/PC-WI displays a peak related to the 105 reflection also indicative of interlayer rotation, which is not present for the catalysts prepared by reverse micelles.

![XRD spectra of the catalysts screened for activity](image)

Figure 3.12: XRD spectra of the catalysts screened for activity a) MoS$_2$/PC-WI; b) MoS$_2$/PC-RM; c) MoS$_2$/AC-RM
Additionally, the peaks present at 24.9, 34.8, and 36.0° 2θ observed in the spectrum of MoS$_2$/PC-RM in Figure 3.12b match the PDF of K$_2$SO$_4$, as presented in Figure 3.13. This K$_2$SO$_4$ is likely a product of the leftover K$^+$ ions from the petcoke’s activation combining with SO$_4^{2-}$ ions from the H$_2$SO$_4$ acid used to reduce the Mo salt. However, no K was detected on the surface of the catalyst by XPS, so it was concluded that the K$_2$SO$_4$ was buried in the pores of the support. The effect of K$_2$SO$_4$, if any, on the HDS reaction was not studied.

Figure 3.13: a) XRD spectrum of MoS$_2$/PC-RM, compared with b) the PDF for K$_2$SO$_4$ (PDF # 04-006-8317)
3.10 TEM results

The three catalysts screened for activity were studied by TEM to compare their MoS$_2$ sheet structures. Each sample was mounted on a TEM grid as outlined in section 2.2.5, and several images ($\sim$15) were captured of each sample. Later, these images were visually searched for discrete particles which were measured using the open-source program ImageJ. Histograms of the particle sizes were constructed from the measurements, and are displayed in Figures 3.14 and 3.16 for MoS$_2$/AC-RM and MoS$_2$/PC-RM, respectively. To obtain a robust measurement of particle size distribution, the aim was to measure at least 100 particles per catalyst from all over the grid. Only several particles were measured per image in an attempt to get a fair distribution by measuring particles from many images, representative of a larger area of the grid. Small sections of TEM images after processing are presented in Figures 3.15, 3.17, and 3.18. Complete images from which the sections were taken can be found in Appendix D.

Catalysts MoS$_2$/AC-RM and MoS$_2$/PC-RM had their MoS$_2$ well-dispersed on the surface, as shown by the narrow particle size distribution which fits a lognormal distribution well. The average diameter for the two catalysts prepared by the micelle method was statistically the same at the 95% confidence interval: 3.8 ± 0.8 nm for MoS$_2$/AC-RM and 4.7 ± 1.0 nm for MoS$_2$/PC-RM, summarised in Table 3.11.

Particles on MoS$_2$/PC-WI were difficult to measure. As can be seen from Figure 3.18, the MoS$_2$ was not arranged in discrete particles, but rather in long sheets which twist and bend, and continue for great lengths. Therefore, it was not possible to measure the long sheets and instead only visible small pieces of MoS$_2$ were measured. Obviously this skews the particle size distribution significantly, and the particle length distribution is not reported here due to its large error. Additionally, from the alternating dark and light lines in the TEM micrographs it can be qualitatively observed that there are more layers of MoS$_2$ on MoS$_2$/PC-WI than on the MoS$_2$/C catalysts prepared by reverse micelles.
Table 3.11: Particle lengths of MoS\textsubscript{2} in the MoS\textsubscript{2}/C catalysts prepared by reverse micelles, determined using TEM

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS\textsubscript{2}/AC-RM</td>
<td>3.8 ± 0.8</td>
</tr>
<tr>
<td>MoS\textsubscript{2}/PC-RM</td>
<td>4.7 ± 1.0</td>
</tr>
</tbody>
</table>

Figure 3.14: Particle length distribution of MoS\textsubscript{2}/AC-RM, from measuring 101 particles imaged using TEM
Figure 3.15: TEM image of MoS$_2$/AC-RM, ellipses drawn around particles counted for the distribution displayed in Figure 3.14

Figure 3.16: Particle length distribution of MoS$_2$/PC-RM, from measuring 100 particles imaged using TEM
Figure 3.17: TEM image of MoS$_2$/PC-RM, ellipses drawn around particles counted for the distribution displayed in Figure 3.16

Figure 3.18: TEM image of MoS$_2$/PC-WI, ellipses drawn around several particles which were able to be distinguished from the otherwise long sheets
3.11 Summary

A summary of the findings and conclusions which can be drawn from the characterization results follows.

From TGA:

- Thermolysis of surfactant AOT was incomplete at \(350^\circ\text{C}\), 14.5 wt.% remained;
- Thermolysis of surfactant Igepal was nearly complete at \(350^\circ\text{C}\), 0.7 wt.% remained.

From BET:

- Both MoS\(_2\)/AC-RM and MoS\(_2\)/PC-RM lost \(57 \pm 3\%\) of surface area and \(\sim 48\%\) of pore volume compared to the respective AC and PC supports;
- MoS\(_2\)/PC-WI lost 17% of surface area and 12% of pore volume compared to PC.

From ICP-OES:

- APTM was a poor choice of Mo salt for both reverse micelle systems studied;
- ATTM was a good choice of Mo salt when used with the water/Igepal/cyclohexane reverse micelle system, or incipient wetness impregnation;
- The water/AOT/\(n\)-heptane reverse micelle system was a poor choice when ATTM or APTM were used, possibly due to the ionic character of AOT;
- The error associated with the Mo loading for MoS\(_2\)/C catalysts prepared from the water/Igepal/cyclohexane reverse micelle system was 9%;
- All three catalysts screened for activity contained 8.6 \(\pm\) 1.5 wt.% Mo.
From XPS:

- MoS2/PC-RM had the largest surface dispersion of MoS2 of the three catalysts screened for activity;
- All three catalysts had a surface S:Mo ratio of ~ 2;
- MoS2/PC-WI had a larger surface MoO3 to MoS2 ratio than the catalysts prepared by reverse micelles.

From XRD:

- The AC used had an SiO2 impurity, PC did not;
- The C in AC was graphitic, C in PC was amorphous;
- MoS2/C prepared by the reverse micelles using APTM did not have its Mo reduced by H+ in the micelle; its crystallite stack height was ~ 2.3 nm by XRD after annealing;
- Annealing completed the transformation of Mo salt to MoS2;
- MoS2/C prepared by the reverse micelle using ATTM did have its Mo reduced by H+ in the micelle; its crystallite stack height was too small to be estimated by XRD;
- The MoS2 of all three catalysts screened for activity was well-dispersed and nano-crystalline;
- MoS2/PC-WI had a K2SO4 impurity, likely buried inside the particle.

From TEM:

- The MoS2 was well-dispersed in MoS2/AC-RM and MoS2/PC-RM, and the particles were small: 3.8 ± 0.8 nm and 4.7 ± 1.0 nm, respectively;
• The MoS\(_2\) in MoS\(_2\)/PC-WI existed as long sheets which twist and bend, rather than small particles;

• The MoS\(_2\) stack heights in MoS\(_2\)/PC-WI were greater than those in the particles of MoS\(_2\)/AC-RM and MoS\(_2\)/PC-RM.
Chapter 4

HDS of DBT Reaction Kinetics

4.1 Introduction

In order to quantitatively compare the three prepared catalysts, their activity toward catalysing the HDS of DBT reaction was tested in a novel batch microreactor. Following the reaction, the liquid products were quantified by GC-MS, and the product concentrations were used for kinetic modelling of the reaction. This allowed for the determination of the rate constant and Arrhenius parameters for each catalyst. The reaction activity data are presented in this chapter; a comprehensive summary is given at the end of this chapter.

Table 4.1 summarises the catalyst preparation methods and naming conventions used in this document.

Table 4.1: Preparation methods for the catalysts whose kinetic activities were studied

<table>
<thead>
<tr>
<th>Name</th>
<th>Support</th>
<th>Preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/AC-RM</td>
<td>AC</td>
<td>Reverse micelles: (water/Igepal/cyclohexane)</td>
</tr>
<tr>
<td>MoS$_2$/PC-RM</td>
<td>PC</td>
<td>Reverse micelles: (water/Igepal/cyclohexane)</td>
</tr>
<tr>
<td>MoS$_2$/PC-WI</td>
<td>PC</td>
<td>Incipient wetness impregnation</td>
</tr>
</tbody>
</table>
4.2 Reaction pathways of HDS

Based on the observed products of the HDS reaction in the microreactor as well as previously published work [30, 32, 80, 83, 85, 103, 104], the HDS of DBT was assumed to follow two routes in parallel, as shown in Figure 4.1.

Figure 4.1: Proposed pathways of the hydrodesulphurization reaction of dibenzothiophene, the dotted arrows indicate reactions assumed to be insignificant. Adapted from [83], with permission from Elsevier Ltd, copyright (2005)

In the Direct Desulphurization route (DDS), S is removed from DBT and proceeds to biphenyl (BP). The rate of hydrogenation of BP to cyclohexylbenzene (CHB) is comparatively slower than the other rates especially in the presence of $\text{H}_2\text{S}$ [80, 83, 103], and was ignored in this study.

In the Hydrogenation route (HG), DBT is first hydrogenated to 1,2,3,4-tetrahydrodibenzothiophene (THDBT) which may later be further hydrodesulphurized by the DS route
to CHB. The reverse of the HG, DS, and DDS reactions are insignificant. CHB can be further hydrogenated to bicyclohexyl; however, that reaction was ignored in this study due to its slow rate similar to the hydrogenation of BP to CHB mentioned above. No bicyclohexyl was observed in the reaction mixture.

4.3 Kinetic model development

Once the concentrations of DBT, BP, CHB, and THDBT were quantified by GC-MS as a function of reaction temperature and time, a MATLAB program was used to estimate the rate constant parameter of each of the reaction components. The codes can be found in Appendix B.

In the present study as in previous studies, [68, 80, 83–85, 105], the HDS of DBT reaction was assumed to be pseudo first-order in the concentration of DBT, and zero-order in the concentration of H\(_2\) since H\(_2\) is in large excess in the reactor and is in good contact with the liquid due to the vigorous mixing by the vortex mixer. Furthermore, it was assumed that the catalyst was not deactivating as the reaction progressed.

The kinetic parameters were estimated by minimizing the sum of squares of the measured reactant concentrations and the concentrations predicted by the model using Levenberg-Marquardt non-linear regression. The errors in the kinetic parameters were estimated from the diagonal of their covariance matrices. The series of MATLAB programs calculated the reactant concentration at each iteration by numerical integration of the 4 ODEs describing the system, presented in Equations 4.1 – 4.4.
\[
\begin{align*}
\frac{dC_{DBT}}{dt} &= -(k'_{DDS}C_{cat} + k_{DDS})C_{DBT} - (k'_{HG}C_{cat} + k_{HG})C_{DBT} \\
\frac{dC_{BP}}{dt} &= (k'_{DDS}C_{cat} + k_{DDS})C_{DBT} \\
\frac{dC_{THDBT}}{dt} &= (k'_{HG}C_{cat} + k_{HG})C_{DBT} - (k'_{DS}C_{cat} + k_{DS})C_{THDBT} \\
\frac{dC_{CHB}}{dt} &= (k'_{DS}C_{cat} + k_{DS})C_{THDBT}
\end{align*}
\]

In Equations 4.1 – 4.4, parameters \( k'_x \) are rate constants for the catalyst for the relevant reaction pathway as defined in Figure 4.1, and parameters \( k_x \) are the rate constant contributions of the thermal and thermocouple-induced reactions.

Due to the small volume and number of moles which are associated with the use of a microreactor, the carbon balance rarely sums to 100%. That is to say that summing the concentrations of products and unreacted DBT in the product mixture rarely equals to the number of moles of DBT added to the reaction in the feed. Therefore, to force the carbon balance, the concentration of each component (DBT, BP, CHB, and THDBT) in the product mixture (in units of \( \mu \text{mol/mg} \)) were summed, and this \textit{sum} was set to be the total number of moles in the reaction. The \textit{sum} was subsequently used to calculate the mole fraction of each component, designated as mol\% \( C \), with mol\% \( C \) of all the components always summing to 100. The raw data in \( \mu \text{mol/mg} \) and converted data in mol\% \( C \) can be found in Appendix D.

The difference between calculated and measured \textit{sum} values was on average 6%. This error could be due to thermal cracking resulting in products other than BP, CHB, and THDBT the concentration of which were not measured. However, due to the low temperatures at which the HDS reaction was studied, this error is more likely due to the small volumes and number of moles used in this microreactor study.

With the mole balance constraint in place, the mol\% \( C \) concentration data for each component were entered into the MATLAB program outlined above.
4.4 Modelling results of reactions without catalyst

In order to calculate the rate constants for each component of the HDS reaction catalysed by MoS$_2$/C as presented in Figure 4.1, a set of reactions was performed in the same manner as a catalytic reaction set, but without the presence of MoS$_2$/C catalyst, to evaluate the contribution to reactivity by the thermal and thermocouple-induced reactions. As with the catalysed reactions, the product mixture was analysed by GC-MS for the concentration of the three main products.

Figure 4.2 presents the measured product concentrations along with the modelled fit obtained from the MATLAB program at various temperatures. As can be seen, the product concentrations were very low. The Arrhenius plot in Figure 4.3 was fit using a line which was within error of the points; therefore, the calculated $k_{DDS}$ and $k_{HG}$ values are robust and were subtracted from the corresponding values obtained for the catalysts, vide infra. $k_{DS}$ could not be calculated due to a very low concentration of THDBT and the subsequent high error associated with $k_{DS}$.

The low concentration of THDBT suggests that the thermal and thermocouple-induced reactions proceeded preferentially through the DDS route, and not the HG route.

The MATLAB program output the rate constant parameters for each component of the HDS reaction based on the concentrations of products, discussed in more detail below, and the $k_x$ parameters due to the thermal and thermocouple-induced reactions are presented in Table 4.2.

From Figure 4.2 it can be seen that the contributions of the thermal and thermocouple-induced reactions were small at all temperatures; the conversion reached a maximum of 7.4% after 3 hours at 375 °C, calculated by summing the mol%$_C$ for BP, CHB and THDBT, or subtracting the mol%$_C$ of DBT from 1.
Figure 4.2: Measured data and modelled fit (line) for product concentrations of the HDS of DBT reaction as a function of time, for the thermal and thermocouple-induced reactions at a) 350 °C; b) 365 °C; c) 375 °C
Table 4.2: Estimated reaction rate constants for HDS of DBT for the thermal and thermocouple-induced reactions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>350 °C</th>
<th>365 °C</th>
<th>375 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{DDS}(s^{-1})$</td>
<td>$(2.44 \pm 0.23) \times 10^{-6}$</td>
<td>$(4.12 \pm 0.16) \times 10^{-6}$</td>
<td>$(6.07 \pm 0.33) \times 10^{-6}$</td>
</tr>
<tr>
<td>$k_{HG}(s^{-1})$</td>
<td>$(1.01 \pm 0.26) \times 10^{-6}$</td>
<td>$(1.18 \pm 0.19) \times 10^{-6}$</td>
<td>$(1.62 \pm 0.38) \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Figure 4.3: HDS of DBT rate as a function of temperature, for the thermal and thermocouple-induced reactions
4.5 Modelling results of the prepared MoS$_2$ catalysts

To calculate the rate constants for each component of the HDS reaction as presented in Figure 4.1, each prepared catalyst’s activity toward the HDS reaction was investigated by using DBT as a model reactant in a batch microreactor. The reactor specifications and loading procedure can be found in section 2.3. Reactions were performed at reaction temperatures, $T$, of 350 °C, 365 °C, or 375 °C and at reactions times, $t$, of 60 min, 120 min, or 180 min. The product mixture of each reaction was analysed by GC-MS for the concentration of the three main products (BP, CHB, and THDBT) as well as the starting material DBT, as outlined in section 2.3.1.

Figures 4.4 − 4.5 and Tables 4.3 − 4.4 present the data for the MoS$_2$/AC-RM catalyst prepared by the reverse micelle method.

Figures 4.6 − 4.7 and Tables 4.5 − 4.6 present the data for the MoS$_2$/PC-RM catalyst prepared by the reverse micelle method.

Figures 4.8 − 4.9 and Tables 4.7 − 4.8 present the data for the MoS$_2$/PC-RM catalyst prepared by incipient wetness impregnation.

It should be mentioned that Figures 4.4, 4.6, and 4.8 represent the product concentrations in the reaction mixture, including the products generated from the thermal and thermocouple-induced reactions discussed above. The modelled fits presented in these figures were generated by the MATLAB program detailed in Appendix B, and the data in tabular format can be found in Appendix D.

Furthermore, it is worth reiterating that the figures present the mol%$_C$ concentrations of products and starting material DBT in the reaction mixture as mole factions of the sum, the total number of moles of DBT, BP, CHB, and THDBT measured in the reaction mixture. This in effect forced the mole balance, and at every point along the abscissa in Figures 4.4, 4.6, and 4.8, the mol%$_C$ concentrations of DBT, BP, CHB, and THDBT always sum to 1.
Furthermore, the MATLAB program outputs the rate constant parameters for each component of the HDS reaction based on the concentrations of products. The rate constant parameters associated with the thermal and thermocouple-induced reactions, $k_x$, presented in Table 4.2 were subtracted from the program’s output for the catalyst’s rate constant parameters. Therefore, the rate constant parameters $k'_x$ presented in Tables 4.3, 4.5, and 4.7 are the parameters associated only with the specified catalyst and reaction pathway; the ratios of $k'_{DDS}$ to $k'_{HG}$ for each catalyst at each $T$ are also presented in those tables, and are discussed below.

Even before using the MATLAB program to deconvolute the rate constants, it was obvious that the desulphurization of the partially hydrogenated intermediate, THDBT, by the DS route was very fast for all catalysts. This conclusion was made based on the low concentration of THDBT, and the fact that all CHB present in the product proceeded through THDBT (the HG of BP to form CHB was assumed to be insignificant, vide supra). Therefore, once the rate constants were separated by the kinetic modelling outlined above, it was not surprising that $k'_{DS}$, compared with $k'_{DDS}$ and $k'_{HG}$, had the largest magnitude for all three catalysts at all temperatures tested.

However, it can be seen from the figures presenting product concentrations as a function of time that CHB concentration was never very high for the catalysts prepared by the reverse micelle method (Figures 4.4 and 4.6), and moderate when prepared by incipient wetness impregnation (Figure 4.8). This is because the HG step needs to precede the DS step, and as presented in Tables 4.3, 4.5, and 4.7, $k'_{HG}$ had the smallest magnitude of the rate constant parameters for all three catalysts at all temperatures tested. Thus, it can be surmised that the direct desulphurization route was the most significant contributor to the desulphurization of DBT for all three catalysts. The degree of the catalyst’s preference for DDS over HG is quantified by the $k'_{DDS}$ to $k'_{HG}$ ratio.

Having the $k'_x$ parameters due only to catalyst, it was then possible to calculate both
the pre-exponential factor, $A$, and the activation barrier energy, $E_a$, from the intercept and slope of $\ln(k')$ plotted against $T^{-1}$, respectively, as factors for the Arrhenius equation (Equation 4.5). These plots are presented in Figures 4.5, 4.7, and 4.9. Calculating the Arrhenius parameters for the HDS reactions catalysed by the three catalysts outlined above allowed for their quantitative comparison, and therefore the comparison of the preparation methods and C supports. The calculation of Arrhenius parameters for the thermal and thermocouple-induced reactions can be calculated in a similar way. However, the $A$ and $E_a$ values for the thermal and thermocouple-induced reactions are not significant outside of this study and are not presented here; they can be found in Appendix D.

$$k = A e^{(-E_a/RT)} \quad (4.5)$$

The catalysts can also be compared qualitatively by examining Figures 4.4, 4.6, and 4.8, since the plotted concentration DBT is directly related to conversion. The mole fraction of DBT (its mol\%$_C$), at $t = 0$ is 1, and decreases as the reaction proceeds; the conversion, $X$, can easily be calculated by:

$$X = 1 - \text{mol\%}_C \text{ of DBT}$$

where $\text{mol\%}_C \text{ of DBT} = \frac{C_{DBT}}{\sum(C_{DBT} + C_{BP} + C_{CHB} + C_{THDBT})}$

For instance, the conversion of DBT catalysed by MoS$_2$/PC-RM (and including the thermal and thermocouple-induced reactions) after 3 hours was 11% at 350 °C, 19% at 365 °C, and 26% at 375 °C. Of the three prepared catalysts, MoS$_2$/PC-WI had the greatest conversion at the times and temperatures tested.
Figure 4.4: Measured data and modelled fit (line) concentrations for the products of the HDS of DBT reaction catalysed by MoS$_2$/AC-RM as a function of time at a) 350 °C; b) 365 °C; c) 375 °C
Table 4.3: Estimated reaction rate constants for HDS of DBT catalysed by MoS$_2$/AC-RM

<table>
<thead>
<tr>
<th>Parameter</th>
<th>350 °C</th>
<th>365 °C</th>
<th>375 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k'<em>{DDS}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</td>
<td>($1.05 \pm 0.06$) E-02</td>
<td>($1.52 \pm 0.04$) E-02</td>
<td>($2.1 \pm 0.05$) E-02</td>
</tr>
<tr>
<td>$k'<em>{HG}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</td>
<td>($4.33 \pm 0.72$) E-03</td>
<td>($5.77 \pm 0.50$) E-03</td>
<td>($6.60 \pm 0.62$) E-03</td>
</tr>
<tr>
<td>$k'<em>{DS}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</td>
<td>($2.07 \pm 0.58$) E-01</td>
<td>($2.90 \pm 0.43$) E-01</td>
<td>($3.64 \pm 0.43$) E-01</td>
</tr>
<tr>
<td>$k'<em>{DDS}/k'</em>{HG}$</td>
<td>2.4 ± 0.4</td>
<td>2.6 ± 0.2</td>
<td>3.2 ± 0.3</td>
</tr>
</tbody>
</table>

Figure 4.5: HDS of DBT rate as a function of temperature, catalysed by MoS$_2$/AC-RM
Table 4.4: Pre-exponential factors, $A$, and activation barrier energies, $E_a$, for the rate constants associated with HDS of DBT catalysed by MoS$_2$/AC-RM. The error associated with $A$ is at least 2 orders of magnitude smaller than $A$ and is omitted here.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A$ (cm$^3$ g$_{Mo}^{-1}$ s$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k'_{DDS}$</td>
<td>5.0 E+05</td>
<td>91.7 ± 8.1</td>
</tr>
<tr>
<td>$k'_{HG}$</td>
<td>2.6 E+02</td>
<td>57.0 ± 4.6</td>
</tr>
<tr>
<td>$k'_{DS}$</td>
<td>4.5 E+05</td>
<td>75.6 ± 1.1</td>
</tr>
</tbody>
</table>
Figure 4.6: Measured data and modelled fit (line) concentrations for the products of the HDS of DBT reaction catalysed by MoS\textsubscript{2}/PC-RM as a function of time at a) 350 °C; b) 365 °C; c) 375 °C.
Table 4.5: Estimated reaction rate constants for HDS of DBT catalysed by MoS$_2$/PC-RM

<table>
<thead>
<tr>
<th>Parameter</th>
<th>350 °C</th>
<th>365 °C</th>
<th>375 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k'_{DDS}$</td>
<td>$(6.84 \pm 0.42) \times 10^{-3}$</td>
<td>$(1.41 \pm 0.06) \times 10^{-2}$</td>
<td>$(1.98 \pm 0.10) \times 10^{-2}$</td>
</tr>
<tr>
<td>$k'_{HG}$</td>
<td>$(1.86 \pm 0.48) \times 10^{-3}$</td>
<td>$(3.85 \pm 0.62) \times 10^{-3}$</td>
<td>$(4.03 \pm 1.12) \times 10^{-3}$</td>
</tr>
<tr>
<td>$k'_{DS}$</td>
<td>$(1.12 \pm 0.37) \times 10^{-1}$</td>
<td>$(1.75 \pm 0.47) \times 10^{-1}$</td>
<td>$(2.20 \pm 0.88) \times 10^{-1}$</td>
</tr>
<tr>
<td>$k'<em>{DDS}/k'</em>{HG}$</td>
<td>$3.7 \pm 1.0$</td>
<td>$3.7 \pm 0.6$</td>
<td>$4.9 \pm 1.4$</td>
</tr>
</tbody>
</table>

Figure 4.7: HDS of DBT rate as a function of temperature, catalysed by MoS$_2$/PC-RM
Table 4.6: Pre-exponential factors, A, and activation barrier energies, \( E_a \), for the rate constants associated with HDS of DBT catalysed by MoS\(_2\)/PC-RM. The error associated with A is at least 3 orders of magnitude smaller than A and is omitted here.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A (cm(^3) g(^{-1}) Mo s(^{-1}))</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k'_{DDS} )</td>
<td>7.4 E+09</td>
<td>143.4 ± 11.4</td>
</tr>
<tr>
<td>( k'_{HG} )</td>
<td>1.6 E+06</td>
<td>106.3 ± 39.1</td>
</tr>
<tr>
<td>( k'_{DS} )</td>
<td>4.4 E+06</td>
<td>90.5 ± 5.8</td>
</tr>
</tbody>
</table>
Figure 4.8: Measured data and modelled fit (line) concentrations for the products of the HDS of DBT reaction catalysed by MoS$_2$/PC-WI as a function of time at a) 350 °C; b) 365 °C; c) 375 °C
Table 4.7: Estimated reaction rate constants for HDS of DBT catalysed by MoS$_2$/PC-WI

<table>
<thead>
<tr>
<th>Parameter</th>
<th>350 °C</th>
<th>365 °C</th>
<th>375 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k'<em>{DDS}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</td>
<td>(3.96 ± 0.03) E-02</td>
<td>(7.01 ± 0.17) E-02</td>
<td>(9.66 ± 0.35) E-02</td>
</tr>
<tr>
<td>$k'<em>{HG}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</td>
<td>(3.31 ± 0.17) E-02</td>
<td>(5.24 ± 0.18) E-02</td>
<td>(6.66 ± 0.36) E-02</td>
</tr>
<tr>
<td>$k'<em>{DS}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</td>
<td>(5.62 ± 0.91) E-01</td>
<td>(7.48 ± 0.99) E-01</td>
<td>(8.45 ± 1.9) E-01</td>
</tr>
<tr>
<td>$k'<em>{DDS}/k'</em>{HG}$</td>
<td>1.2 ± 0.1</td>
<td>1.3 ± 0.1</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 4.9: HDS of DBT rate as a function of temperature, catalysed by MoS$_2$/PC-WI
Table 4.8: Pre-exponential factors, A, and activation barrier energies, E\textsubscript{a}, for the rate constants associated with HDS of DBT catalysed by MoS\textsubscript{2}/PC-WI. The error associated with A is at least 4 orders of magnitude smaller than A and is omitted here

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A (cm\textsuperscript{3} g\textsubscript{Mo}\textsuperscript{−1} s\textsuperscript{−1})</th>
<th>E\textsubscript{a} (kJ mol\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>k\textsubscript{DDS}'</td>
<td>4.2 E+08</td>
<td>119.6 ± 4.6</td>
</tr>
<tr>
<td>k\textsubscript{HG}'</td>
<td>2.6 E+06</td>
<td>94.0 ± 5.0</td>
</tr>
<tr>
<td>k\textsubscript{DS}'</td>
<td>2.0 E+04</td>
<td>54.3 ± 6.3</td>
</tr>
</tbody>
</table>

4.6 Error associated with mol\%\textsubscript{C}

Five reactions were performed twice, which enabled the calculation of the error associated with the graphically-presented mol\%\textsubscript{C} for each of DBT, BT, THDBT, and CHB. The errors are presented in Table 4.9, and were calculated using the following formula:

\[
s_e^2 = \frac{\sum_{i=1}^{k} \frac{1}{2} (Y_{i1} - Y_{i2})^2}{\sum_{i=1}^{k} n_i - k}
\]

Table 4.9: Errors associated with presented mol\%\textsubscript{C}, concentration ratios of observed products or starting material compared to total initial DBT concentration

<table>
<thead>
<tr>
<th>Species</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol%\textsubscript{C} CHB</td>
<td>± 0.3</td>
</tr>
<tr>
<td>mol%\textsubscript{C} BP</td>
<td>± 0.5</td>
</tr>
<tr>
<td>mol%\textsubscript{C} THDBT</td>
<td>± 0.2</td>
</tr>
<tr>
<td>mol%\textsubscript{C} DBT</td>
<td>± 0.8</td>
</tr>
</tbody>
</table>
4.7 Discussion of \( k' \) results

The literature was searched for analogous work (HDS of DBT by unpromoted MoS\(_2\)) in the hopes of comparing \( k' \) values for catalysts prepared in this study to those prepared by other researchers. It was found that there is little convention for reporting \( k' \) values, in terms of the units of the values and the data completeness — some researchers report \( k' \) values at only one temperature without also reporting Arrhenius parameters to enable conversion to other temperatures. Consequently, the data from this study were calculated for two temperatures to enable comparison with other work. All compared data were presented or converted to the units of mol\(_{\text{DBT}}\) s\(^{-1}\) g\(^{-1}\)\(_{\text{catalyst}}\) and are presented in Tables 4.10 and 4.11.

Additionally, some researchers report \( k' \) in units of g\(^{-1}\) for supported catalysts without indicating whether the unit is g\(^{-1}\)\(_{\text{catalyst}}\) or g\(^{-1}\)\(_{\text{metal}}\). It was assumed that the researcher always meant g\(^{-1}\)\(_{\text{catalyst}}\). However, if the reported value was in units of g\(^{-1}\)\(_{\text{metal}}\), the discrepancy would be an order of magnitude for a catalyst with a 10% metal loading. Due to these factors, only loose comparisons between the \( k' \) values observed in this study and those reported by other researchers were drawn.

Table 4.10: Comparison of \( k' \) values at 350 °C. If multiple values were reported by the same researcher, the largest \( k' \) is cited

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Catalyst</th>
<th>( k'<em>{DBT} ) (mol(</em>{\text{DBT}}) s(^{-1}) g(^{-1})(_{\text{catalyst}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camacho-Bragado [106]</td>
<td>Unsupported MoS(_2)</td>
<td>3.7 E-07</td>
</tr>
<tr>
<td>Romero [107]</td>
<td>Unsupported MoS(_2)</td>
<td>1.9 E-06</td>
</tr>
<tr>
<td>Tye [105]</td>
<td>Unsupported MoS(_2)</td>
<td>3.32 E-06</td>
</tr>
<tr>
<td>This work</td>
<td>MoS(_2)/AC-RM</td>
<td>(2.0 ± 0.5) E-06</td>
</tr>
<tr>
<td></td>
<td>MoS(_2)/PC-RM</td>
<td>(9.2 ± 2.8) E-07</td>
</tr>
<tr>
<td></td>
<td>MoS(_2)/PC-WI</td>
<td>(5.4 ± 0.8) E-06</td>
</tr>
</tbody>
</table>

Comparing \( k' \) values for the catalysis of the HDS reaction toward DBT at 350 °C pre-
sented in Table 4.10, it was concluded that the catalysts prepared by reverse micelles in this study catalysed the HDS of DBT at a comparatively similar rate to the unsupported MoS$_2$ catalysts prepared by Camacho-Bragado, Romero, and Tye. The rate constant of the MoS$_2$/AC catalyst was $\sim 2x$ that of the MoS$_2$/PC catalyst prepared by reverse micelles. The rate constant of the catalyst prepared by incipient wetness impregnation had an activity which was $\sim 3$ to $6x$ greater than that for the catalysts prepared by reverse micelles, and was also larger than the $k'$ for unsupported MoS$_2$ reported by the compared groups.

It could be argued that the difference in catalytic activity between the RM and WI catalysts prepared in this study is due to the lower surface area and pore volume of the RM catalysts compared to the WI catalyst. While it is true that MoS$_2$/PC-RM had half the surface area (927 compared with 1677 m$^2$/g) and pore volume (0.49 compared with 0.85 cm$^3$/g) of MoS$_2$/PC-WI, the $k'$ value for MoS$_2$/PC-WI is $\sim 6x$ that of the MoS$_2$/PC-RM catalyst. Therefore, it was concluded that the surface appearance of the support was not wholly responsible for the differences in the magnitudes of $k'$.

Table 4.11: Comparison of $k'$ values at 340 °C. If multiple values were reported by the same researcher, the largest $k'$ is cited

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Catalyst</th>
<th>$k'<em>{DBT}$ (mol$</em>{DBT}$ s$^{-1}$ g$^{-1}$ catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reinhoudt [82]</td>
<td>MoS$_2$/Al$_2$O$_3$</td>
<td>5.56 E-07</td>
</tr>
<tr>
<td>Egorova [80]</td>
<td>MoS$_2$/Al$_2$O$_3$</td>
<td>1.37 E-03</td>
</tr>
<tr>
<td>This work</td>
<td>MoS$_2$/AC-RM</td>
<td>(1.6 ± 0.4) E-06</td>
</tr>
<tr>
<td></td>
<td>MoS$_2$/PC-RM</td>
<td>(6.9 ± 2.1) E-07</td>
</tr>
<tr>
<td></td>
<td>MoS$_2$/PC-WI</td>
<td>(4.5 ± 0.6) E-06</td>
</tr>
</tbody>
</table>

The $k'$ values presented in Table 4.11 for comparison are for the HDS of DBT at 340 °C catalysed by unpromoted and supported MoS$_2$ catalysts. As with the comparison at 350 °C, the $k'$ for MoS$_2$/AC-RM was $\sim 2x$ greater than that for MoS$_2$/PC-RM; the $k'$ for MoS$_2$/PC-
WI was again ∼3x greater than that for MoS$_2$/AC-RM. The $k'$ values for the catalysts prepared in this study were greater than the $k'$ for the MoS$_2$/Al$_2$O$_3$ catalyst prepared by Reinshoudt.

The $k'$ for the MoS$_2$/Al$_2$O$_3$ catalyst presented by Egorova is significantly greater than that for the catalysts prepared in this study, even accounting for the possible order of magnitude inflation due to the fact that the article did not state whether the units for the $k'$ were g$_{\text{catalyst}}^{-1}$ or g$_{\text{metal}}^{-1}$. Even if the $k'$ value presented in [80] was stated in the units of g$_{\text{metal}}^{-1}$, after conversion to g$_{\text{catalyst}}^{-1}$ the $k'$ value was still ∼2 orders of magnitude greater than the most active catalyst prepared in this study, MoS$_2$/PC-WI. However, it should be noted that the regime in Egorova’s study was a fixed bed reactor in a continuous mode [80].

4.8 Comparison of accessed selectivities

While $k'_{\text{DBT}}$ is a measure of the overall rate of the conversion of DBT, selectivity measures how much of each product component – BP, CHB, THDBT – was produced from the converted DBT. Together with TEM and XRD data, insight may be gained into the relationship between the shape of the MoS$_2$ crystallites and product selectivity, and to make a comparison with the expectations from the rim-edge model. The selectivity is governed by the magnitude of the individual $k'_x$ components contributing to the overall $k'_{\text{DBT}}$ rate constant.

Figures 4.10 – 4.12 present the proportion of each compound in the product mixture after reaction at a specific $T$, by catalyst. These figures allow for the comparison of the selectivities accessed at different $T$ by a screened MoS$_2$/C catalyst. Figure 4.13 graphically compares each catalyst’s selectivity toward the DDS route, where only the proportion of BP (the sole product of the DDS route) is plotted, and is effectively a graphical representation of the calculated $k'_{\text{DDS}}/k'_{\text{HG}}$ ratios presented in Tables 4.3, 4.5, and 4.7.

Observing the changes in the $k'_{\text{DDS}}/k'_{\text{HG}}$ ratios presented in Tables 4.3, 4.5, and 4.7, it
was noted that the ratio for the each of the RM catalysts remained approximately constant at 350 °C and 365 °C, and significantly increased at 375 °C. The $k'_{DDS}/k'_{HG}$ ratio remained approximately constant for all $T$ when the reaction was catalysed by MoS$_2$/PC-WI. The cause for this effect is unknown, but a sintering event of the nano-crystalline MoS$_2$ at the highest $T$ which would not effect the MoS$_2$ in longer sheets as in MoS$_2$/PC-WI is put forth as a hypothesis.
Figure 4.10: Selectivity of the HDS of DBT reaction catalysed by MoS$_2$/AC-RM after subtracting the thermal and thermocouple-induced reaction contributions at a) 350 °C, b) 365 °C, c) 375 °C
Figure 4.11: Selectivity of the HDS of DBT reaction catalysed by MoS$_2$/PC-RM after subtracting the thermal and thermocouple-induced reaction contributions at a) 350 °C, b) 365 °C, c) 375 °C
Figure 4.12: Selectivity of the HDS of DBT reaction catalysed by MoS$_2$/PC-WI after subtracting the thermal and thermocouple-induced reaction contributions at a) 350 °C, b) 365 °C, c) 375 °C
Figure 4.13: Comparison between the catalysts MoS$_2$/AC-RM, MoS$_2$/PC-RM and MoS$_2$/PC-WI for selectivity toward the DDS route at a) 350 °C, b) 365 °C, c) 375 °C
From the graphical comparisons, it can be observed that the catalysts prepared by the reverse micelle method showed similar selectivity, one that was more favourable toward DDS, than the catalyst prepared by incipient wetness impregnation which still favoured DDS but not by such a wide margin. Table 4.12 summarises some of the data which were presented above to enable a discussion of the selectivity differences between the catalysts.

Table 4.12: Summary of kinetic parameters of the three catalysts at 350 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k'<em>{DDS}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</th>
<th>$k'<em>{HG}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</th>
<th>$k'<em>{DS}$ (cm$^3$ g$</em>{Mo}^{-1}$ s$^{-1}$)</th>
<th>$k'<em>{DDS}/k'</em>{HG}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$/AC-RM</td>
<td>(1.05 ± 0.06) E-02</td>
<td>(4.33 ± 0.72) E-03</td>
<td>(2.07 ± 0.58) E-01</td>
<td>2.4</td>
</tr>
<tr>
<td>MoS$_2$/PC-RM</td>
<td>(6.84 ± 0.42) E-03</td>
<td>(1.86 ± 0.48) E-03</td>
<td>(1.12 ± 0.37) E-01</td>
<td>3.7</td>
</tr>
<tr>
<td>MoS$_2$/PC-WI</td>
<td>(3.96 ± 0.03) E-02</td>
<td>(3.31 ± 0.17) E-02</td>
<td>(5.62 ± 0.91) E-01</td>
<td>1.2</td>
</tr>
</tbody>
</table>

From the TEM data presented in section 3.10, it was concluded that the MoS$_2$ prepared by the reverse micelle method was significantly smaller than MoS$_2$ made by impregnation whose particle size could not be accurately measured due to the long sheets formed. The rim-edge model predicts that the smaller crystallites would be more active for HDS, since small particles offer more rim and edge sites per catalyst mass to facilitate the reaction. However, from the data presented in this chapter and summarised in Table 4.12, it was concluded that the MoS$_2$/PC-WI catalyst is ∼5 to 8x more active for HDS of DBT than the MoS$_2$/C catalysts prepared by the reverse micelle method, by comparing the $k'_{DBT}$ values (sum of the $k'_{DDS}$ + $k'_{HG}$ components).

Furthermore, the rim-edge model states that HG occurs on the rim sites of MoS$_2$, while DDS is affected at edge sites [30]. By geometry, the small MoS$_2$ crystallites prepared in this study by the reverse micelle method had a larger ratio of rim to edge sites than the long MoS$_2$ sheets made by the impregnation method; however, the $k'_{DDS}/k'_{HG}$ ratio was larger for the smaller MoS$_2$ particles — the opposite of what the rim-edge model predicts. This
point is visualised in Figure 4.13 where the molar proportion of BP in the product mixture produced by MoS$_2$/PC-WI is consistently lower than that by MoS$_2$/PC-RM and MoS$_2$/AC-RM. Clearly, the rim-edge model does not accurately predict the catalytic activity and selectivity of the MoS$_2$/C prepared in this study. The rim-edge model has in fact already been questioned by some researchers who concluded that the activity of very small particles could not be predicted by the rim-edge model [26, 104].

Topsøe and co-workers found that Mo/Al$_2$O$_3$ catalysts prepared with a low metal loading formed small crystallites which were less active (per mass of metal) for HDS than those prepared with a higher loading. They concluded that in small crystallites, more atoms are in a corner position rather than being at a true edge position, and that the corner atoms are not as catalytically active as the edge atoms [26]. This is due to the fact that any S binding to metal atoms at a corner are more weakly bound than if they were bound at an edge site. The weaker bond with a substrate’s S molecule means less electron back-donation which is necessary for the C-S bond scission [26, 104].

Hensen and co-workers related the low stacking degree in small MoS$_2$ crystallites to a low overall catalytic activity of HDS of DBT. The authors concluded that since the sterically-hindered DBT molecule binds to MoS$_2$ in an $\eta^6$ planar geometry through the benzene ring [108], rather than $\eta^1$ through the S atom like thiophene, stacking degree has a large impact on the magnitude of $k'$ for DBT, with $k'$ increasing with stacking order [104]. Furthermore, the article related that $k'_{DDS}/k'_{HG}$ decreases as stacking order increases due to $k'_{HG}$ increasing with stacking degree, even though the larger stacking order means that fewer edge sites are available [104].

The activity trends found in this study mirrored those found by Topsøe and Hensen, and it was concluded that the high proportion of corner sites combined with a low MoS$_2$ stacking order in MoS$_2$/AC-RM and MoS$_2$/PC-RM resulted in a lower activity toward the catalysis of HDS of DBT. The MoS$_2$ stacking order in MoS$_2$/PC-WI was larger, which corresponded
to a greater HDS activity.

Furthermore, the selectivity trends can also be explained by the hypotheses set out by Topsøe and Hensen. Referring to Table 4.12, it can be seen that $k'_{HG}$ of MoS$_2$/PC-WI was $\sim$1 order of magnitude greater than the RM catalysts. While the $k'_{DDS}$ of MoS$_2$/PC-WI was also greater than those of the RM catalysts, it was not by an order of magnitude. Therefore, it was concluded that the larger magnitude of the overall rate constant for HDS of DBT of the MoS$_2$/PC-WI was due to more hydrogenation occurring on the WI catalyst than on the RM catalysts, due to the higher stacking order of the MoS$_2$ in MoS$_2$/PC-WI.

4.9 Summary

A summary of the findings and conclusions which can be drawn from the kinetic modelling results follows.

- The thermal and thermocouple-induced reactions were slow at all $T$ and $t$; their contributions were accounted for;

- $k'_{DBT}$ values of catalysts prepared in this study are comparable to those of unsupported MoS$_2$ prepared by other researchers;

- The proportion of sites available for either DDS or HG depends on the catalyst preparation;

- A similar proportion of DDS and HG sites was elucidated to be present on the catalysts prepared by the RM method, for both the AC and PC supports;

- MoS$_2$ supported on AC and PC showed a similar activity toward catalysing the HDS of DBT when the MoS$_2$ was prepared by the reverse micelles; therefore, PC is a good alternative support to AC in these catalysts;
• Long and stacked sheets of MoS$_2$ were more active toward the HDS of DBT than nanocrystallites, as seen by the higher rate constant for MoS$_2$/PC-WI compared with that for MoS$_2$/PC-RM and MoS$_2$/AC-RM;

• The rim-edge model did not correlate to the activity and selectivity observed for HDS of DBT catalysed by MoS$_2$/C prepared by the reverse micelle method;

• The larger magnitude of $k'_{DBT}$ of MoS$_2$/PC-WI was concluded to result from more HG occurring on the WI catalyst than on the RM catalysts, due to the higher stacking order of the MoS$_2$ in MoS$_2$/PC-WI.
Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Carbon-supported molybdenum disulphide catalysts were successfully prepared by two methods using ammonium tetrathiomolybdate as the molybdenum source: reverse micelles using the water/IGEPAL CO-520/cyclohexane system, and incipient wetness impregnation from ultra pure water. MoS$_2$ prepared by impregnation was supported on activated petroleum coke, and MoS$_2$ prepared by the reverse micelle method was supported on both activated petroleum coke and activated carbon. In this way, comparisons between the two preparation methods and two supports were possible.

All three catalysts were extensively characterized, and it was found that the catalysts prepared by the reverse micelle method contained nano-sized MoS$_2$. When prepared by the reverse micelle method, MoS$_2$/AC was composed of supported particles measuring $3.8 \pm 0.8$ nm and the MoS$_2$/PC catalyst’s particles measured $4.7 \pm 1.0$ nm. The MoS$_2$ in the MoS$_2$/PC catalyst prepared by incipient wetness impregnation consisted of long sheets, rather than small particles.

The three catalysts were compared quantitatively by the use of a batch microreactor in
which the catalysed hydrodesulphurization of model compound dibenzothiophene was affected. The products biphenyl, cyclohexylbenzene, and 1,2,3,4-tetrahydrodibenzothiophene were observed and quantified by Gas Chromatography-Mass Spectrometry. A pseudo first-order model was used to decouple the rate constant parameters of each of the three catalysts into separate components corresponding to two parallel routes (hydrogenation and direct desulphurization) by which the HDS of DBT occurs.

It was found that the rate constant per gram of Mo for the MoS$_2$/PC prepared by impregnation was $\sim$3 to 5x greater than that for the catalysts prepared by reverse micelles in the temperature range of 350 to 375 °C. MoS$_2$ supported on AC and PC showed a similar activity toward catalysing the HDS of DBT when the MoS$_2$ was prepared by reverse micelles; therefore, PC is a good alternative support to AC for the MoS$_2$ prepared by this method.

Additionally, the rate constant component associated with the hydrogenation route was an order of magnitude greater for the catalyst prepared by impregnation than that for the MoS$_2$/C catalysts prepared by reverse micelles. It was concluded that the larger stacking order in MoS$_2$/PC prepared by impregnation provided more sites for hydrogenation to occur, which resulted in an overall larger rate constant than that for the catalysts prepared by reverse micelles whose MoS$_2$ stacking orders were minimal due to the small particle dimensions. These findings contradicted the rim-edge model set out by Daage and Chianelli, and corroborated the hypotheses set out by Topsøe and Hensen.

## 5.2 Recommendations

This section sets out some recommendations for future work which would either improve on, or extend, the research performed in this study.

The three catalysts were extensively characterized and it was concluded that the MoS$_2$/C catalysts prepared by reverse micelles had a higher dispersion than MoS$_2$/PC-WI. However,
O₂ chemisorption could be performed to obtain a quantitative measure of MoS₂ dispersion and the number of catalytic sites present on each catalyst. This would allow the rate constants to be calculated per active site which in turn would allow the turnover frequency (TOF) on each catalyst to be quantified. TOF is a measure of the speed of conversion per active site; therefore, this measurement would help to further elucidate the effect of MoS₂ particle size on catalyst activity toward the HDS of DBT.

The water to surfactant ratio in the preparation of MoS₂/PC-RM should be increased in order to make larger micelles and therefore larger MoS₂ crystallites. The size and product selectivity of a catalyst with larger, but still nano-sized, crystallites would help to further clarify the effect of stacking order on the rate constant. Similarly, different reducing agents should be tested to aid in the synthesis of a more active MoS₂/C catalyst.

It was found that MoS₂/PC-RM contained K₂SO₄, hypothesised to have formed due to K⁺ ions remaining from the activation of the petcoke. The effect of this impurity was not studied. In order to eliminate any effects of the K₂SO₄ in MoS₂/PC-RM, the activated petcoke should be washed more to remove all K⁺ ions, or the effect that K₂SO₄ has on the HDS of DBT reaction should be studied in a controlled manner, for example by adding some K₂SO₄ to a catalytic screen test.

Some HDS occurred during the ~21 minute reactor heat-up period before the system reached reaction temperature. In this study, the products associated with this pre-reaction are counted as part of the products from the catalysed reaction. To obtain more accurate kinetic data, the reactor should be ramped to reaction temperature and then cooled quickly. The conversion from this test represents the reaction during the heat-up phase, and could be subtracted from the reaction conversion to give catalyst activity for the reaction time only.

To elucidate whether cracking of DBT is occurring, the gaseous products of the reaction, which in this study were not studied, should be separated by gas chromatography and identified. If products other than BP, CHB or THDBT are detected, the reaction kinetics
of the cracking should be calculated to improve the kinetic model.

The HG reaction was found to be slow for the catalysts prepared by reverse micelles, so ignoring the hydrogenation of BP to CHB or CHB to bicyclohexane in the kinetic model was acceptable. However, for the MoS$_2$/PC-WI catalyst where HG is very fast, these HG routes should be included to improve the results of the modelling. One way to further discriminate between the HDS and HG activities would be to perform the catalytic tests with toluene or diphenylethylene as the reactant instead of, or in addition to, DBT, and monitor the level of hydrogenation. Another option would be to use BP or CHB as the molecule in the feed instead of DBT to obtain the precise rate constant parameters associated with hydrogenation of these compounds.

Finally, an MoS$_2$/AC-WI catalyst should be prepared by incipient wetness impregnation of activated carbon in a preparation similar to that for MoS$_2$/PC-WI. This would enable another direct comparison of the AC and PC supports. Furthermore, a catalyst prepared by incipient wetness impregnation using the ATTM salt should be prepared on alumina to ascertain the effect of the metal-support interaction.
Bibliography


one-dimensional metallic edge states in MoS$_2$ nanoclusters”. In: *Nanotechnology* 14 (2003), pp. 385–389.


[102] S. K. Jana, P. Mukhopadhyay, S. Ghosh, S. Kabi, A. Bag, R. Kumar, and D. Biswas. “High-resolution X-ray diffraction analysis of Al\textsubscript{x}Ga\textsubscript{1−x}N/ In\textsubscript{x}Ga\textsubscript{1−x}N/GaN on sapphire multilayer structures: Theoretical, simulations, and experimental observations”. In: *Journal of Applied Physics* 115 (2014), pp. 174507-1–174507-13.


Appendix A

Calculations

A.1 Feed calculation

It was desired to prepare a feed which consisted of 2 wt.% DBT, enough CS$_2$ to keep the molybdenum sulphided but not too much since it is a poison to HDS. The feed volume during each run should be 150µL with a Mo concentration of 900 ppm.

Calculating the amount of catalyst is straightforward. Assuming a 10 wt.% Mo content, and that the bulk of the feed is composed of decalin which has a density of 0.9 g/mL:

\[
m_{\text{catalyst}} = \left( \frac{900 \, g_{\text{Mo}}}{10^6 \, g_{\text{feed}}} \right) \left( \frac{0.9 \, g_{\text{feed}}}{mL} \right) \left( \frac{mL}{1000 \, \mu L} \right) \left( \frac{150 \, \mu L}{0.1 \, g_{\text{Mo}}} \right) = 1.215 \, mg
\]

To calculate how much sulphiding agent CS$_2$ should be added, it was decided to use a 0.5% mole fraction of H$_2$S in the system. First, however, the amount of H$_2$ in the system needed to be calculated. The number of moles of hydrogen in the system at average reaction
temperature (636 K) and pressure (5.08 MPa) was estimated using the ideal gas law:

\[ n_{H_2} = \frac{PV}{RT} \]
\[ = \frac{(5.08 \times 10^6 \ Pa)[\pi (2 \times 10^{-3} \ m)^2 (0.25 \ m)]}{(8.314 \ m^3 \ Pa \ K^{-1} \ mol^{-1}) (636 \ K)} \]
\[ = 3.0 \times 10^{-3} \ moles \]

It was decided to use a 0.5% mole fraction of \( H_2S \) in the system:

\[ n_{H_2S} = 0.005 \ n_{H_2} \]
\[ = 1.5 \times 10^{-5} \ moles \]

The amount of liquid \( CS_2 \) this corresponds to:

\[ V_{CS_2} = (1.5 \times 10^{-5} \ mol_{H_2S}) \left( \frac{1 \ mol_{CS_2}}{2 \ mol_{H_2S}} \right) \left( \frac{76.13 \ g_{CS_2}}{mol_{CS_2}} \right) \left( \frac{mL}{1.266 \ g_{CS_2}} \right) \]
\[ = 4.5 \times 10^{-4} \ mL \]
\[ = 0.45 \ \mu L \]

Seeing how small the volume of \( CS_2 \) is to the volume of decalin, the 2 wt.% amount of DBT was calculated purely on the weight of decalin:

\[ m_{DBT} = \left( \frac{0.02 \ g_{DBT}}{1 \ g_{feed}} \right) \left( \frac{0.9 \ g_{feed}}{mL} \right) \left( \frac{mL}{1000 \ \mu L} \right) (150 \ \mu L) \]
\[ = 2.7 \ mg \]

To reduce the error associated with the small volumes, a larger batch of feed was prepared. Table A.1 summarises the feed which was prepared and used during the activity testing described in Chapter 4.
Table A.1: Composition of feed used for activity testing

<table>
<thead>
<tr>
<th></th>
<th>Decalin</th>
<th>CS₂</th>
<th>DBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>13261.7</td>
<td>56</td>
<td>271.9</td>
</tr>
<tr>
<td>wt.%</td>
<td>97.59</td>
<td>0.41</td>
<td>2.00</td>
</tr>
</tbody>
</table>

A.2 Calculations for catalysts prepared by the micelle method

The calculations to prepare a 10 wt.% Mo catalyst on PC using a 0.3 M surfactant in oil solution, water:surfactant ratio of 20, and a 5 mM ATTM solution are outlined here.

First, to prepare a 0.3 M Igepal in cyclohexane solution, the number of moles of Igepal to be added to the already measured 367 mL of cyclohexane:

\[
m_{Igepal} = (0.367 \text{ L}_{oil}) \times \left( \frac{0.3 \text{ mol}_{Igepal}}{\text{L}_{oil}} \right) \times \left( \frac{441 \text{ g}_{Igepal}}{\text{mol}_{Igepal}} \right)
\]

\[= 48.55 \text{ g}_{Igepal}\]

Next, the calculation of the total amount of water to be added, which includes the contributions from the 0.5 M H₂SO₄ and 5 mM ATTM solutions:

\[
m_{water} = (48.55 \text{ g}_{Igepal}) \times \left( \frac{\text{mol}_{Igepal}}{441 \text{ g}_{Igepal}} \right) \times \left( \frac{20 \text{ mol}_{H₂O}}{1 \text{ mol}_{Igepal}} \right) \times \left( \frac{15.015 \text{ g}_{H₂O}}{\text{mol}_{H₂O}} \right)
\]

\[= 39.67 \text{ g}_{H₂O}\]

The constraints of a 5 x 10⁻³ molar solution of ATTM, a 0.5 M H₂SO₄ solution, a ratio of 10 H⁺ ions per molecule of ATTM, and total volume of 39.67 g of water were solved simultaneously to obtain the solutions for the amount of each solution needed. In the
preparation outlined in section 2.1.3, the obtained volumes were 37.95 mL of 5 mM ATTM solution and 1.9 mL of 0.5 M H\textsubscript{2}SO\textsubscript{4} solution, with approximately 0.5% error.

From 37.95 mL of 5 mM ATTM solution, the mass of formed Mo was calculated:

\[ m_{Mo} = \left(5 \times 10^{-3} \frac{mol_{ATTM}}{L}\right)(37.95 \times 10^{-3} \ L)(\frac{1 \ mol_{Mo}}{1 \ mol_{ATTM}})(\frac{95.94 \ g_{Mo}}{mol_{Mo}}) \]

\[ = 0.0182 \ g_{Mo} \]

Then the total mass of catalyst with a 10% Mo loading will be:

\[ m_{catalyst} = (0.0182 \ g_{Mo})(\frac{g_{catalyst}}{0.1 \ g_{Mo}}) \]

\[ = 0.182 \ g_{catalyst} \]

Of that 0.182 g of catalyst, some will be MoS\textsubscript{2} with the balance of C support. To calculate the mass of MoS\textsubscript{2}:

\[ m_{MoS_2} = (0.0182 \ g_{Mo})(\frac{mol_{Mo}}{95.94 \ g_{Mo}})(\frac{mol_{MoS_2}}{mol_{Mo}})(\frac{160.07 \ g_{MoS_2}}{mol_{MoS_2}}) \]

\[ = 0.0304 \ g_{MoS_2} \]

Then to calculate the amount of PC support that needs to be added:

\[ m_{PC} = m_{catalyst} - m_{MoS_2} \]

\[ = 0.182 \ g_{catalyst} - 0.0304 \ g_{MoS_2} \]

\[ = 0.1516 \ g_{PC} \]
A.3 Calculations for catalysts prepared by the incipient wetness impregnation method

The calculations to prepare a 10 wt.% Mo catalyst on PC by incipient wetness impregnation are outlined here. They are similar to the calculations for preparing MoS$_2$/PC by reverse micelles, only simpler.

A 0.3 g amount of catalyst with a 10 wt.% Mo loading contains 0.03 g of Mo. To calculate the mass of MoS$_2$ this corresponds to:

\[
m_{\text{MoS}_2} = (0.03 \text{ g Mo})(\frac{\text{mol Mo}}{95.94 \text{ g Mo}})(\frac{\text{mol MoS}_2}{\text{mol Mo}})(\frac{160.07 \text{ g MoS}_2}{\text{mol MoS}_2})
\]

\[
= 0.050 \text{ g MoS}_2
\]

To calculate the amount of ATTM to be added to the 0.250 g of PC to make the 10 wt.% MoS$_2$/PC by wetness impregnation:

\[
m_{\text{ATTM}} = (0.05 \text{ g MoS}_2)(\frac{\text{mol MoS}_2}{160.07 \text{ g MoS}_2})(\frac{\text{mol ATTM}}{\text{mol MoS}_2})(\frac{260.28 \text{ g MoS}_2}{\text{mol ATTM}})
\]

\[
= 0.0814 \text{ g ATTM}
\]

A.4 Calculation to convert Tye’s k data

Tye reported $k_{\text{DBT}}$ in units of [mL mol Mo$_6^{-1}$s$^{-1}$] [105]. To convert to units of [mol$_{\text{DBT}}$ s$^{-1}$ g$^{-1}$catalyst], the following calculation was performed, shown for the AHM derived MoS$_2$ (Note: the re-
searcher used a 900 ppm feed of DBT in \( n \)-hexadecane, whose density is 0.77 g/mL):

\[
k_{DBT} = \frac{791 \text{ mL}}{\text{mol Mo}_e \text{ s}}
\]

\[
= \left( \frac{791 \text{ mL}}{\text{mol Mo}_e \text{ s}} \right) \left( \frac{0.107 \text{ mol Mo}_e}{\text{mol Mo}} \right) \left( \frac{900 \text{ g DBT}}{10^6 \text{ g feed}} \right) \left( \frac{0.77 \text{ g feed}}{\text{mL}} \right) \left( \frac{\text{mol Mo}}{95.94 \text{ g Mo}} \right) \left( \frac{\text{mol DBT}}{184.26 \text{ g DBT}} \right)
\]

\[
= 3.32 \times 10^{-6} \text{ mol}_{\text{DBT}} \text{ s}^{-1} \text{ g}_{\text{catalyst}}^{-1}
\]
Appendix B

MATLAB Codes

The MATLAB code for a Levenberg-Marquardt Non-Linear Regression was created by R. Shrager and modified by R. Muzic and A. Jutan. The code below has been used by this research group for many years, and was combined with a series of ODEs prepared describing the HDS of DBT reaction by the author. To calculate the rate constants presented in Chapter 4, the model was solved simultaneously using a 4th order Runge–Kutta algorithm.

B.1 Main body

diary MicellePC375Clog.txt
clear all
global nvar nx x0 y0;
global verbose;
global n1 n2 n3 H2;
verbose(1:2) = 1;
% x is the indep variable vector e.g. time measurements
% y is matrix of responses
% Columns of y are responses y1, y2 (e.g. mol frac of component 1 and 2)
% Rows of y are y values at the value of the indep variable (time) in x
% First row of y is initial value of response
% The program uses the Levenberg-Marquardt method to estimate parameters
% and calculate statistics - done in leasqr.m and dfdp.m
% These two matlab m-files are designed for single response
The input data is re-arranged to yield a single response vector \( y \)

The L-M requires the model to be calculated - this is done in `modelmulti.m`

and assumes the model is a series of ODEs, with the number of ODEs equal to the number of responses. The ODEs are calculated in `ODEfunm.m`.

Note that this function must use the correct model for each \( y \) % Also note that the rate constants are in units of per minute

% INPUT
% input number of responses

% Order of reactions:
\( n_1 = 1; \) % order of CA
\( n_2 = 1; \) % order of CB
\( n_3 = 1; \) % order of CC

% Concentration of Hydrogen in liquid.
\( T = [0 \ 3600 \ 7200 \ 10800]'; \) %time in seconds

\( n_t = \text{length} \ (T); \)
\( x(1:nt-1) = T(2:nt); \)
\( nx = \text{length}(x); \)

\( CAX = [1 \ 0.91254 \ 0.83929 \ 0.74013]'; \) % Conc of DBT (mole frac.)
\( CBX = [0 \ 0.07113 \ 0.13033 \ 0.21439]'; \) % Conc of BP (mole frac.)
\( CCX = [0 \ 0 \ 0.01279 \ 0.02719]'; \) % Conc of CHB (mole frac.)
\( CDX = [0 \ 0.01632 \ 0.01758 \ 0.01828]'; \) % Conc of THDBT (mole frac.)

for \( j = 1:nt-1 \)
\( y1(j) = CAX(j+1); \)
\( y2(j) = CBX(j+1); \)
\( y3(j) = CCX(j+1); \)
\( y4(j) = CDX(j+1); \)
end

\( nvar = 4; \)
\( x0 = 0; \)
\( oldx = x; \)
\( nx = \text{length}(x); \)
\( y = [y1' \ y2' \ y3' \ y4']; \)
\( newy = y(:); \)
\( oldy = \text{reshape}(newy, nx, nvar); \)
\( x = x'; \)
\( newx = [x; x; x; x]; \)
\( y01(1:nx) = CAX(1); \)
\( y02(1:nx) = CBX(1); \)
\( y03(1:nx) = CCX(1); \)
\( y04(1:nx) = CDX(1); \)
\( newy0 = [y01'; y02'; y03'; y04']; \)

%INPUT DATA NOW IN CORRECT COLUMN FORMAT
\begin{verbatim}
y0=newy0;
x=newx;
y=newy;

% Provide initial parameter guesses
theta=[0.002 0.002 0.03];
np=length(theta);

% Begin calculation by calling L-M least squares routine
[f,p,kvg,iter,covp,covr,stdresid,Z,r2]=leasqr(x,y,pin\'modelmulti\')
disp('RESPONSE:')
if kvg ==1
    disp ('PROBLEM CONVERGED')
elseif kvg == 0
    disp('PROBLEM DID NOT CONVERGE')
end

format shortEng
oldf=reshape(f,nx,nvar);
oldr=reshape(y-f, nx, nvar);
tspan=0:0.1:180;
C0 = [y0(1);CBX(1);CCX(1);CDX(1)];
[t,Y]=ode45(@ODEfunm,tspan,C0,[],p);
CA=Y(:,1);
CB=Y(:,2);
CC=Y(:,3);
CD=Y(:,4);
disp ('X-values:')
disp (oldx')
disp ('Y-values:')
disp (oldy)
disp ('f-values - i.e. model calculated responses:')
disp (oldf)
disp ('Residuals:')
disp (oldr)
disp ('Standardized residuals:')
disp (stdresid)
disp ('Estimated parameter values are:')
disp (p)
disp ('Covariance of estimated parameters - sqrt of diagonal gives CL')
disp (covp)
disp ('R2 values are:')
disp (r2)
figure
\end{verbatim}
ax1 = gca;
hold on
p1=plot(oldx(:,),oldy(:,1),'bx');
title('T=375C, Micelle/PC')
xlabel('Time (min)')
ylabel('Concentration of DBT (mol frac)')
plot(tspan,CA,'b–')

ax2 = axes('Position',get(ax1,'Position'),...
     'XAxisLocation','top',...
     'YAxisLocation','right',...
     'Color','none',...
     'XColor','none','YColor','k');
ylabel(ax2,'Concentration of BP, CHB, THDBT (mol frac)')
linkaxes([ax1 ax2],'x');
hold on
p2=plot(oldx(:,),oldy(:,2),'k*','Parent',ax2);
p3=plot(oldx(:,),oldy(:,3),'r+','Parent',ax2);
p4=plot(oldx(:,),oldy(:,4),'gd','Parent',ax2);
plot(tspan,CB,'k–','Parent',ax2);
plot(tspan,CC,'r–','Parent',ax2);
plot(tspan,CD,'g–','Parent',ax2);
legend([p1,p2,p3,p4],'DBT','Biphenyl','CyclohexylBenzene','1,2,3,4-THDBT')
diary off

B.2 Modelmulti code

function f = modelmulti (x,pin)
% Solve a simple system of 2 ODE's - 2 response variables
% find the solution at specified x values - corresponding to measured data
% first data point in x corresponds to initial condition

global nvar nx x0 y0
global verbose
global n1 n2 n3 n4 H2
nxx=length(x);
yzero=reshape(y0,nx,nvar);
for i = 1:nx
    xf = x(i);
    xoo=x0;
    yzed=yzero(i,:);
    [xmodel,ymodel] = ode45 (@ODEfunm,[xoo,xf], yzed,[],pin);
yfinal(i,:)=ymodel(end,:);
end
f = yfinal(:);

B.3 ODEfunm code

function yprime=ODEfunm(xatx,yatx,p)
global nvar nx x0 y0 xstep
global verbose
global n1 n2 n3 n4 H2
k1=p(1);
k2=p(2);
k3=p(3);
yp(1)=-k1*yatx(1)-k2*yatx(1);
yp(2)=k1*yatx(1);
yp(3)=k3*yatx(4);
yp(4)=-k3*yatx(4)+k2*yatx(1);
yprime = [yp(1);yp(2)';yp(3)';yp(4)'];

B.4 Calculation of Jacobian matrix

function prt=dfdp(x,f,p,dp,func)
% numerical partial derivatives (Jacobian) df/dp for use with leasqr
% ———INPUT VARIABLES———
% x=vec or matrix of indep var(used as arg to func) x=[x0 x1 ....]
% f=func(x,p) vector initialised by user before each call to dfdp
% p= vec of current parameter values
% dp= fractional increment of p for numerical derivatives
% dp(j)>0 one sided differences calculated
% dp(j)<0 one sided differences calculated
% dp(j)=0 sets corresponding partials to zero; i.e. holds p(j) fixed
% func=string naming the function (.m) file
% e.g. to calc Jacobian for function expsum prt=dfdp(x,f,p,dp,’expsum’)
% ———OUTPUT VARIABLES———
% %prt= Jacobian Matrix prt(i,j)=df(i)/dp(j)
% m=length(x);n=length(p); %dimensions
ps=p;prt=zeros(m,n);del=zeros(n,1); % initialise Jacobian to Zero
for j=1:n
    del(j)=dp(j) .*p(j); %cal delx=fract(dp)*param value(p)
    if p(j)==0
        del(j)=dp(j); %if param=0 delx=fraction
    end
    p(j)=ps(j) + del(j);
    if del(j)~=0, f1=feval(func,x,p);
        if dp(j) < 0, prt(:,j)=(f1-f)./del(j);
        else
            p(j)=ps(j)- del(j);
            prt(:,j)=(f1-feval(func,x,p))./(2 .*del(j));
        end
    end
    p(j)=ps(j); %restore p(j)
end
return

B.5 Least square code

function [f,p,kvg,iter,corp,covp,covr,stdresid,Z,r2]= ...
    leasqr(x,y,pin,F,stol,niter,wt,dp,dFdp,options)
%function[f,p,kvg,iter,corp,covp,covr,stdresid,Z,r2]=
% leasqr(x,y,pin,F,stol,niter,wt,dp,dFdp,options)
% Version 3.beta
% {} = optional parameters
% Levenberg-Marquardt nonlinear regression of f(x,p) to y(x), where:
% x=vec or mat of indep variables, 1 row/observation: x=[x0 x1....xm]
% y=vec of obs values, same no. of rows as x.
% wt=vec(dim=length(x)) of statistical weights. These should be set
% to be proportional to (sqrt of var(y))^\-1; (That is, the covariance
% matrix of the data is assumed to be proportional to diagonal with diagonal
% equal to (wt.^2)^\-1. The constant of proportionality will be estimated.),
% default=ones(length(y),1).
% pin=vector of initial parameters to be adjusted by leasqr.
% dp=fractional incr of p for numerical partials,default= .001*ones(size(pin))
% dp(j)>0 means central differences.
% dp(j)<0 means one-sided differences.
% Note: dp(j)=0 holds p(j) fixed i.e. leasqr wont change initial guess: pin(j)
% F=name of function in quotes, of the form y=f(x,p)
% dFdp=name of partials M-file in quotes default is prt=dfdp(x,f,p,dp,F)
% stol=scalar tolerances on fractional improvement in ss,default stol=.0001
% niter=scalar max no. of iterations, default = 20
% options=matrix of n rows (same number of rows as pin) containing
% column 1: desired fractional precision in parameter estimates.
% Iterations are terminated if change in parameter vector (chg) on two
% consecutive iterations is less than their corresponding elements
% in options(:,1). [ie. all(abs(chg*current parm est) <options(:,1))
% on two consecutive iterations.], default = zeros().
% column 2: maximum fractional step change in parameter vector.
% Fractional change in elements of parameter vector is constrained to be
% at most options(:,2) between successive iterations.
% [ie. abs(chg(i))=abs(min([chg(i) options(i,2)*current param estimate])).],
% default = Inf*ones().
% OUTPUT VARIABLES
% f=vec function values computed in function func.
% p=vec trial or final parameters. i.e, the solution.
% kvg=scalar: =1 if convergence, =0 otherwise.
% iter=scalar no. of iterations used.
% corp= correlation matrix for parameters
% covp= covariance matrix of the parameters
% covr = diag(covariance matrix of the residuals)
% stdresid= standardized residuals
% Z= matrix that defines confidence region
% r2= coefficient of multiple determination
% All Zero guesses not acceptable
% Richard I. Shrager (301)-496-1122
% Modified by A.Jutan (519)-679-2111
% Modified by Ray Muzic 14-Jul-1992
% 1) add maxstep feature for limiting changes in parameter estimates
% at each step.
% 2) remove forced columnization of x (x=x(:)) at beginning. x could be
% a matrix with the ith row of containing values of the
% independent variables at the ith observation.
% 3) add verbose option
% 4) add optional return arguments covp, stdresid, chi2
% 5) revise estimates of corp, stdev
% Modified by Ray Muzic 11-Oct-1992
% 1) revise estimate of Vy. remove chi2, add Z as return values
% Modified by Ray Muzic 7-Jan-1994
% 1) Replace ones(x) with a construct that is compatible with versions
% newer and older than v 4.1.
% 2) Added global declaration of verbose (needed for newer than v4.4)
% 3) Replace return value var, the variance of the residuals with covr,
% the covariance matrix of the residuals.
% 4) Introduce options as 10th input argument. Include
% convergence criteria and maxstep in it.
% 5) Correct calculation of xtx which affects covariance estimate.
% 6) Eliminate stdev (estimate of standard deviation of parameter
% estimates) from the return values. The covp is a much more
% meaningful expression of precision because it specifies a confidence
% region in contrast to a confidence interval. If needed, however,
% stdev may be calculated as stdev=sqrt(diag(covp)).
% 7) Change the order of the return values to a more logical order.
% 8) Change to more efficient algorithm of Bard for selecting epsL.
% 9) Tighten up memory usage by making use of sparse matrices (if
% MATLAB version >= 4.0) in computation of covp, corp, stdresid.
% Modified by Sean Brennan 17-May-1994
% verbose is now a vector:
% verbose(1) controls output of results
% verbose(2) controls plotting intermediate results
% References:
% set default args
% argument processing
plotcmd='plot(x(:,1),y,''+'',x(:,1),f); shg';
if (sscanf(version,'%f') >= 4),
vernum= sscanf(version,'%f');
if vernum(1) >= 4,
  global verbose
  plotcmd='plot(x(:,1),y,''+'',x(:,1),f); figure(gcf);
end;
if (exist('OCTAVE_VERSION'))
  global verbose
end;
if(exist('verbose')~=1), %If verbose undefined, print nothing
  verbose(1)=0 %This will not tell them the results
  verbose(2)=0 %This will not replot each loop
end;
if (nargin <= 8), dFdp='dfdp'; end;
if (nargin <= 7), dp=.001*(pin*0+1); end; %DT
if (nargin <= 6), wt=ones(length(y),1); end; % SMB modification
if (nargin <= 5), niter=20; end;
if (nargin == 4), stol=.0001; end;
y=y(:); wt=wt(:); pin=pin(:); dp=dp(:); % change all vectors to columns
% check data vectors- same length?
m=length(y); n=length(pin); p=pin; [m1,m2]=size(x);
if m1~m, error(‘input(x)/output(y) data must have same number of rows ’), end;
if (nargin <= 9),
    options=[zeros(n,1) Inf*ones(n,1)];
    nor = n; noc = 2;
else
    [nor noc]=size(options);
    if (nor ~ n),
        error(‘options and parameter matrices must have same number of rows’),
    end;
    if (noc ~ 2),
        options=[options(noc,1) Inf*ones(noc,1)];
    end;
end;
pprec=options(:,1);
maxstep=options(:,2);
% set up for iterations
f=feval(F,x,p); fbest=f; pbest=p;
r=wt.*(y-f);
sbest=r'*r;
nrm=zeros(n,1);
chgprev=Inf*ones(n,1);
kvg=0;
epsLlast=1;
epstab=[.1 1 1e2 1e4 1e6];
% do iterations
for iter=1:niter,
    pprev=pbest;
    prt=feval(dFd,x,fbest,pprev,dp,F);
    r=wt.*(y-fbest);
    sprev=sbest;
    sgoal=(1-stol)*sprev;
    for j=1:n,
        if dp(j)==0,
            nrm(j)=0;
        else
            prt(:,j)=wt.*prt(:,j);
            nrm(j)=prt(:,j)'*prt(:,j);
            if nrm(j)>0,
                nrm(j)=1/sqrt(nrm(j));
            end;
        end;
    end;
    pprev=pbest;
    prt=feval(dFd,x,fbest,pprev,dp,F);
    r=wt.*(y-fbest);
    sprev=sbest;
    sgoal=(1-stol)*sprev;
end;
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end;
end
prt(:,j)=nrm(j)*prt(:,j);
end;
% above loop could ? be replaced by:
% prt=prt.*wt(:,ones(1,n));
% nrm=dp./sqrt(diag(prt'*prt));
% prt=prt.*nrm(:,ones(1,m));
[prt,s,v]=svd(prt,0);
s=diag(s);
g=prt*r;
for jji=1:length(epstab),
    epsL = max(epsLlast*epstab(jji),1e-7);
    se=sqrt((s.*s)+epsL);
    gse=g./se;
    chg=((v*gse).*nrm);
% check the change constraints and apply as necessary
    ochg=chg;
for iii=1:n,
    if (maxstep(iii)==Inf), break; end;
    chg(iii)=max(chg(iii),-abs(maxstep(iii)*pprev(iii)));
    chg(iii)=min(chg(iii),abs(maxstep(iii)*pprev(iii)));
end;
if (verbose(1) & any(chg
    disp(['Change in parameter(s): ' ...
        sprintf('%d ',find(chg
    end;
    aprec=abs(pprec.*pbest);
% ss=scalar sum of squares=sum((wt.*(y-f))ˆ2).
    if (any(abs(chg) >0.1*aprec)), % only worth evaluating function if
        p=chg+pprev; % there is some non-miniscule change
        f=feval(F,x,p);
        r=wt.*(y-f);
        ss=r'*r;
        if ss<sbest,
            pbest=p;
            fbest=f;
            sbest=ss;
        end;
        if ss<=sgoal,
            break;
        end;
end;

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end;
end;
epsLlast = epsL;

% if (verbose(2)),
% eval(plotcmd);
% end;
if ss < eps,
    break;
end
aprec = abs(pprec.*pbest);

% [aprec chg chgprev]
if (all(abs(chg) < aprec) & all(abs(chgprev) < aprec)),
    kvg = 1;
    if (verbose(1)),
        fprintf('Parameter changes converged to specified precision\n');
    end;
    break;
else
    chgprev = chg;
end;
if ss > sgoal,
    break;
end;
end;

% set return values
p = pbest;
f = fbest;
ss = sbest;
kvg = ((sbest > sgoal) - (sbest <= eps) - kvg);
if kvg ~= 1, disp(' CONVERGENCE NOT ACHIEVED! '), end;

% CALC VARIANCE COV MATRIX AND CORRELATION MATRIX OF PARAMETERS
% re-evaluate the Jacobian at optimal values
jac = feval(dFdp, x, f, p, dp, F);
msk = dp ~= 0;
n = sum(msk); % reduce n to equal number of estimated parameters
jac = jac(:, msk); % use only fitted parameters

% following section is Ray Muzic’s estimate for covariance and correlation
% assuming covariance of data is a diagonal matrix proportional to
% diag(1/wt.^2).
% cov matrix of data est. from Bard Eq. 7-5-13, and Row 1 Table 5.1
if vernum(1) >= 4,
    Q = sparse(1:m,1:m,(0*wt+1)./(wt.^2)); % save memory
end;
Qinv=inv(Q);
else
    Qinv=diag(wt.*wt);
    Q=diag((0*wt+1)./(wt.^2));
end;
resid=y-f;  % un-weighted residuals
covr=resid'*Qinv*resid*Q/(m-n);  % covariance of residuals
Vy=1/(1-n/m)*covr;  % Eq. 7-13-22, Bard  % covariance of the data
jtgjinv=inv(jac'*Qinv*jac);  % argument of inv may be singular
covp=jtgjinv*jac'*Qinv*Vy*Qinv*jac*jtgjinv;  % Eq. 7-5-13, Bard  % cov of parm est
d=sqrt(abs(diag(covp)));
corp=covp./(d*d');
covr=diag(covr);  % convert returned values to compact storage
stdresid=resid./sqrt(diag(Vy));  % compute then convert for compact storage
Z=((m-n)*jac'*Qinv*jac)/(n*resid'*Qinv*resid);
% if someone has asked for it, let them have it
if (verbose(2)), eval(plotcmd); end,
if (verbose(1)),
    disp('Least Squares Estimates of Parameters')
    disp(p')
    disp('Correlation matrix of parameters estimated')
    disp(corp)
    disp('Covariance matrix of Residuals')
    disp(covr)
    disp('Correlation Coefficient R^2')
    disp(r2)
    sprintf('95%% conf region: F(0.05)(%.0f,%.0f)> = delta_pvec''*Z*delta_pvec',n,m-n)
Z
% runs test according to Bard. p 201.
n1 = sum((f-y)<0);
n2 = sum((f-y)>0);
nrun=sum(abs(diff((f-y)<0)))+1;
if ((n1>10)&(n2>10)), % sufficient data for test?
    zed=(nrun-(2*n1*n2/(n1+n2)+1)+0.5)/(2*n1*n2*(2*n1*n2-n1-n2)...
        /(n1+n2)^2*(n1+n2-1));
    if (zed <0),
        prob = erfc(-zed/sqrt(2))/2*100;
        disp([num2str(prob) '% chance of fewer than ' num2str(nrun) ' runs.']);
    else,
        prob = erfc(zed/sqrt(2))/2*100;
        disp([num2str(prob) '% chance of greater than ' num2str(nrun) ' runs.']);
    end;
end;
end;
% A modified version of Levenberg-Marquardt
% Non-Linear Regression program previously submitted by R.Shrager.
% This version corrects an error in that version and also provides
% an easier to use version with automatic numerical calculation of
% the Jacobian Matrix. In addition, this version calculates statistics
% such as correlation, etc....
% Version 3 Notes
% Errors in the original version submitted by Shrager (now called version 1)
% and the improved version of Jutan (now called version 2) have been corrected.
% Additional features, statistical tests, and documentation have also been
% included along with an example of usage. BEWARE: Some the the input and
% output arguments were changed from the previous version.
% Ray Muzic <rfm2@ds2.uh.cwru.edu>
% Arthur Jutan <jutan@charon.ingga.uwo.ca>
Appendix C

Sample Preparation

C.1 Pet coke activation procedure

The following procedure was developed by Haiyan Wang and used to activate the PC used as a support in this study. The activation procedure has 3 steps and results in activated PC with the physical properties presented in Table 3.1.

C.1.1 Obtaining pet coke with a certain particle size

The first step is to crush the pet coke and sieve it to obtain pet coke within a certain particle diameter range:

1. Add raw pet coke into a mortar, crush until pieces are smaller
2. Use two sieve trays to sieve the pet coke into the desired particle diameter of 106–180µm
3. The larger pieces can be crushed more, the smaller pieces are not used for this activation
C.1.2 Chemical activation

The second step is the actual activation of petcoke with potassium hydroxide. Both the petcoke and KOH should be stored in a desiccator to enable accurate mass measurements:

1. Weigh out $x$ g of crushed petcoke, set aside

2. Weigh out $y$ g of KOH pellets so that $z = x:y \sim 3$ (i.e. 3 parts KOH to 1 part petcoke)

3. Place KOH into a mortar and crush with a pestle to turn KOH into a fine powder (Note: use a powder mask or respirator to avoid inhaling KOH, a very caustic substance)

4. Add the petcoke to the mortar and physically mix the two powders

5. Place the mortar in an oven set to $100^\circ C$ and leave it for two hours to evaporate the moisture from the samples introduced during the mixing process

6. Weight a clean ceramic boat, add the dried sample to it, and obtain the mass of the dried sample

7. From the ratio $z$, calculate the amount of petcoke ($m_1$) present in the ceramic boat

8. Place the ceramic boat into the exact centre of a horizontal furnace and seal the furnace

9. Purge the furnace with $N_2$ for 10 minutes

10. Begin the heating program: ramp at $5^\circ C$/minute to $800^\circ C$, hold for 2 hours

C.1.3 Washing the petcoke

The last step is the removal of excess KOH:

1. Line a Buchner funnel with filter paper and wet it with deionized (DI) water

2. Quantitatively transfer the PC into the funnel, using DI water as needed
3. Add DI water to the funnel and mix the slurry to solubilize KOH

4. Connect a pump to the filter flask and turn it on

5. Disengage the pump and add more water to wash the sample, turn the pump on again

6. Repeat step 5 3 times

7. Rinse the sample alternating 1M HCl with DI water until the runoff water has a neutral pH

8. Transfer the washed sample to a glass dish and dry the sample in an oven set to 100°C overnight

9. Weigh the amount of activated petcoke ($m_2$) obtained

10. The carbon burn-off can be calculated from $\frac{m_1 - m_2}{m_1}$

C.2 ICP-OES sample preparation

The following procedure was developed by Lucie Solnickova and is a guideline for preparing samples for ICP-OES analysis in the EOS lab. The samples discussed below are molybdenum sulphide on carbon; this method can be adapted to suit other samples. Contact for ICP-OES technician: Maureen Soon msoon@eos.ubc.ca

C.2.1 Purpose

Have a $\sim$ 5 wt.% Mo in MoS$_2$/C catalyst. Want a solution containing $\sim$ 25 ppm Mo in 2 vol.% HNO$_3$ and bulk DI water. Need 6 standard solutions: 0, 5, 12.5, 25, 37.5, 50 ppm made using AHM in 2 vol.% HNO$_3$ and bulk DI water.
C.2.2 General cautions

1. When combining acid and water, always add acid to water

2. Always add acid dropwise, no matter what you are adding it to

3. Glassware should either be clean and dry (for solids), or clean and rinsed with the liquid which will make up the bulk of the final volume

C.2.3 Required equipment

1. Fumehood

2. 1 x 100mL beaker per sample

3. 1 x hotplate per 3 samples

4. 1 x 25.00 mL volumetric flask per 1 or 2 samples

5. 1 x 15 mL Falcon tube per samples

6. 1 x 50.00 mL volumetric flask

7. Pasteur pipettes calibrated to 1mL

8. Concentrated nitric acid

9. Concentrated hydrochloric acid

10. Ultrapure water

11. Ammonium heptamolybdate
C.2.4 Making the matrix solution

The ICP OES internal standard is Europeum in 2 vol% HNO$_3$. The instrument is unfit to handle stronger acid. The procedure below outlines the preparation of a 2 vol% HNO$_3$ solution, which must be the matrix for all samples analysed. This preparation will suffice for 10 samples and 6 standards, and should be freshly prepared for every sample analysis.

1. To a 500.00 mL volumetric flask add 250 mL ultra-pure water
2. Add 14.2 mL of 69% HNO$_3$ to the 500.00 mL volumetric flask with swirling, checking that it does not get too hot
3. Make it up to the mark with ultra-pure water to obtain 2 vol.% HNO$_3$ in water solution

C.2.5 Digesting the sample

CAUTION! Boiling acid is very dangerous, exercise caution and use a fume hood!

1. Place ∼ 10 mg of sample into a 100 mL beaker, weighing to at least 3 significant figures
2. Add 10mL conc HNO$_3$ to the solid
   • Bring to a boil and reflux for 10 mins, cool
3. Add 2 mL conc HNO$_3$ and 6 mL conc HCl
   • Bring to a boil and reflux for 10 mins, cool
   • There will be much bubbling here as CO$_2$ is produced
4. Add 2 mL conc HNO$_3$ and 6 mL conc HCl
   • Bring to a boil and reflux for 10 mins, cool
   • Again a lot of bubbling
5. Add 1 mL conc HNO₃ and 3 mL conc HCl
   • Bring to a boil and reflux for 10 mins, cool

6. Add 1 mL conc HNO₃ and 3 mL conc HCl
   • Bring to a boil and reflux for 10 mins, cool

7. Add 1 mL conc HNO₃ and 3 mL conc HCl
   • Bring to a boil and reflux for 10 mins, cool

8. If there are solids, filter the contents through an ashless filter paper into another beaker

9. Boil the solution until it is almost dry

10. Add 2 mL of 2 vol.% HNO₃
    • Boil this to dryness to remove all the acid, cool the beaker
    • The metal will remain in the beaker, but all acid must be removed to be sure that the final solution contains only 2 vol.% HNO₃ solution

11. Using 5mL portions of 2 vol.% HNO₃ solution, dissolve all the solids on the beaker and transfer all to a 25.00 mL volumetric flask

12. Make the solution up to the line with 2 vol.% HNO₃ solution

13. Transfer the solution to a Falcon tube the day of the measurement
    • This solution can be stored for approximately a week in a well-covered glass container to prevent evaporation
C.2.6 Preparing the standards

Measuring mass is more accurate than measuring volume – after preparing the stock, the standards were prepared using a pipette and weighed in order to calculate the true concentration.

Knowing the precise concentrations of the standard solutions before doing the analysis is helpful, because the software can do the regression instantly. Otherwise the metal concentration will need to be calculated manually later.

Fresh standards were always prepared on the day of analysis for the most accurate results.

1. Prepare 50.00 mL of a 50. ppm stock solution:
   - Place 4.333 mg of dry AHM into a small vial
   - In several portions, quantitatively transfer the AHM to a 50.00 mL volumetric flask
   - Dilute up to the mark with 2 vol.% HNO₃ solution
   - Make sure all of the solid is dissolved

2. 0 ppm standard:
   - Pour 15mL of the 2 vol.% HNO₃ solution into a Falcon tube

3. 5 ppm standard:
   - Transfer 2 mL of the stock to a vial
   - Add 18 mL of 2 vol.% HNO₃ solution
   - Transfer 15 mL to a Falcon tube

4. 12.5 ppm standard:
   - Transfer 4 mL of the stock to a vial
• Add 12 mL of 2 vol.% HNO₃ solution
• Transfer 15 mL to a Falcon tube

5. 25.0 ppm standard:

• Transfer 9 mL of the stock to a vial
• Add 9 mL of 2 vol.% HNO₃ solution
• Transfer 15 mL to a Falcon tube

6. 37.5 ppm standard:

• Transfer 12.9 mL of the stock to a vial
• Add 4.3 mL of 2 vol.% HNO₃ solution
• Transfer 15 mL to a Falcon tube

7. 50 ppm standard:

• Pour the rest of the 50 ppm stock into a Falcon tube
Appendix D

Detailed Sample Characterization Data

D.1 TEM micrographs

The TEM images shown in Section 3.10 were taken from the larger images to make the MoS$_2$ particles easier to see. Below are the whole images from which the snips were taken.
Figure D.1: Whole TEM image of the MoS$_2$/AC-RM prepared by the micelle method, ellipses drawn around particles counted for the distribution displayed in Figure 3.14
Figure D.2: Whole TEM image of the MoS$_2$/PC-RM prepared by the micelle method, ellipses drawn around particles counted for the distribution displayed in Figure 3.16
Figure D.3: Whole TEM image of the MoS$_2$/PC-RM prepared by incipient wetness impregnation, ellipses drawn around several particles which were able to be distinguished from the otherwise long sheets which skew the particle size distribution

D.2 ATTM certificates of analysis

As mentioned in the Experimental section, two batches of ATTM were purchased from Strem. The first batch turned out to be APTM, and the second batch was ATTM. Below are the certificates of analysis, claiming that both batches are ATTM.
### Figure D.4: Certificate of analysis for ATTM batch 1 (actually APTM)

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## D.3 Values inputted into the MATLAB model

Table D.1: Measured concentrations of products

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<td>t (h)</td>
<td>DBT μmol at X=0</td>
<td>μmol/mg in original sample</td>
<td>mol%C</td>
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Table D.2: Concentrations of products with forced carbon balance, inputted into the MATLAB code for kinetic modelling

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<th>Catalyst</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Concentration (mol%(C))</th>
<th>Conversion (%)</th>
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<tbody>
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<td>0.607 1.216 0.000 98.177</td>
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<td>t (h)</td>
<td>Concentration (mol%(^{C}))</td>
<td>Conversion (%)</td>
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D.4 Arrhenius parameters for the thermal and thermocouple-induced reactions

Table D.3: Pre-exponential factors, $A$, and activation barrier energies, $E_a$, for the rate constants associated with the thermal and thermocouple-induced reactions. The error associated with $A$ is at least 2 orders of magnitude smaller than $A$ and is omitted here.

<table>
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<tr>
<th>Parameter</th>
<th>$A$ (s$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
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<td>121.9 ± 4.6</td>
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