



Alkanes, Alkenes and Aromatics:

The oxidative dehydrogenation of *n*-octane

using iron molybdate catalysts

Thesis submitted in accordance with the requirements of the
University of Cardiff for the degree of Doctor of Philosophy by

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December 2014

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Summary

The oxidative dehydrogenation (ODH) of *n*-octane to produce octene at atmospheric pressure has been studied using an industrially supplied iron molybdate catalyst from Johnson Matthey (JM). *In situ* X-ray diffraction studies revealed at temperatures ≥ 450 °C the catalyst undergoes a reductive phase transition when reacted with *n*-octane at 450 °C where the phase changes from $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ to $\text{FeMoO}_4\text{-MoO}_2\text{-Mo}_4\text{O}_{11}$. As a result, if the temperature is taken back below this point the catalyst does not revert to the original phase and therefore the same activity and selectivity cannot be achieved. Thus the system can be considered as two different catalysts: i) the oxidised phases at temperatures < 450 °C, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, which is associated with the production of octene and CO_x , and ii) as the reduced phases at temperatures ≥ 450 °C, FeMoO_4 , MoO_2 and Mo_4O_{11} , which led to the formation of CO_x and aromatics.

The catalyst was then pre-reduced resulting in the JM $\text{FeMoO}_4\text{-MoO}_2$ catalyst. The selectivity to octene improved at temperatures < 450 °C and the optimum conditions were found to be a C:O ratio of 8:1 at 4000 h^{-1} at 400 °C, achieving *ca.* 82 % selectivity and 8 % conversion. Temperatures above ≥ 450 °C produced aromatics, including ethyl benzene, benzene and styrene. At 550 °C and 1000 h^{-1} the selectivity to CO_x decreased whilst styrene production in particular increased. The result is associated with a combination of active coke, confirmed by Raman spectroscopy and carbon-hydrogen-nitrogen analysis, on the surface of the catalyst and the consumption of CO_2 , produced *in situ*, to produce styrene from ethylbenzene, which was later investigated.

The separate phases of the JM $\text{FeMoO}_4\text{-MoO}_2$ catalyst, i.e. FeMoO_4 and MoO_2 , were then tested with *n*-octane to determine which phases are associated with octene and aromatic and CO_2 production.

Glossary

C bal. = Carbon mass balance

CHN = Carbon-Hydrogen-Nitrogen

C:O = Carbon to mono-oxygen ratio

Conv. = Conversion

CO_x = Carbon Oxides

DH = Dehydrogenation/anaerobic

EDX = Energy Dispersive X-rays

FID = Flame Ionisation Detector

GC = Gas Chromatograph

GHSV = Gas Hourly Space Velocity

i.d. = Internal Diameter

IR = Infra-red

JM = Johnson Matthey

MS = Mass Spectrometry

MvK = Mars van-Krevelen

ODH = Oxidative Dehydrogenation/aerobic

PACOL = Paraffin activation to olefins

SEM = Scanning Electron Microscopy

TOL = Time on line

TCD = Thermal Conductivity Detector

TGA = Thermal Gravimetric Analysis

TPO = Temperature Programmed Oxidation

TPR = Temperature Programmed Reduction

XRPD = X-Ray Powder Diffraction

Contents

Chapter 1: Introduction

1.1. Introduction to Catalysis.....	1
1.1.1.Heterogenous Catalysis.....	5
1.2. Alkane Activation in the Petrol Chemical Industry.....	6
1.2.1.Steam Cracking of Hydrocarbons.....	6
1.2.2.Catalytic Cracking of Hydrocarbons.....	6
1.2.3.Dehydrogenation Catalysis.....	7
1.2.4.Oxidative Dehydrogenation Catalysis.....	8
1.2.4.1. The Mars-van Krevelen Mechanism.....	9
1.3. Research Objectives.....	10
1.4. Literature Review.....	11
1.4.1. Short Chain Alkane Activation C ₂ -C ₅	11
1.4.1.1. Vanadium Catalysis.....	11
1.4.1.2. Molybdenum Catalysis.....	12
1.4.2. Intermediate Chain Alkane Activation C ₆ -C ₁₂	14
1.4.2.1. Summary.....	17
1.4.3.Iron Molybdate Catalysis.....	18
1.4.3.1. Composition and Properties.....	18
1.4.3.2. Industrial Applications.....	19
1.4.3.3. The Partial Oxidation of Methanol to Formaldehyde.....	20
1.4.3.4. Preparation Techniques and Applications.....	22
1.5. Conclusions.....	24
1.6. Thesis Overview.....	26
1.7. References.....	27

Chapter 2: Catalyst Preparation, Experimental Techniques and Theory

2.1. Introduction.....	33
2.2. Catalyst Synthesis.....	33
2.2.1.The Iron Molybdate Catalyst Supplied by Johnson Matthey.....	33
2.2.2.The Reduced Johnson Matthey Iron Molybdate Catalyst.....	34
2.2.3.The Pure Phase FeMoO ₄ Catalyst.....	34
2.2.4.The Pure Phase MoO ₂ Catalyst.....	34
2.3. Catalyst Preparation.....	34
2.4. Gas Phase Reactions.....	35
2.4.1.Reactor Set-Up.....	35
2.4.2.On-line Product Analysis.....	36
2.4.3. Temperature Programming	39
2.5. Catalyst Characterisation.....	39
2.5.1.X-ray Powder Diffraction.....	39

2.5.1.1.	Determination of Crystallite size <i>via</i> the Debye-Scherrer Equation.....	42
2.5.2.	X-ray Photoelectron Spectroscopy.....	43
2.5.2.1.	Experimental Procedure.....	44
2.5.3.	Scanning Electron Microscopy.....	45
2.5.3.1.	Back Scattered Electron Imaging.....	46
2.5.4.	Energy Dispersive X-Ray Spectroscopy.....	46
2.5.4.1.	Experimental Procedures.....	47
2.5.5.	Ultra-Violet/Visible Spectroscopy.....	47
2.5.5.1.	Luminescence.....	47
2.5.5.2.	Absorption.....	49
2.5.5.3.	Selection Rules.....	51
2.5.5.3.1.	Spin Selection Rule.....	51
2.5.5.3.2.	Leporte Selection Rule.....	51
2.5.5.4.	Experimental Procedures.....	51
2.5.6.	Raman Spectroscopy.....	52
2.5.6.1.	Selection rules.....	53
2.5.6.1.1.	Rotational.....	53
2.5.6.1.2.	Vibrational.....	54
2.5.6.2.	Experimental Procedure.....	55
2.5.7.	Temperature Programming Methods.....	55
2.5.7.1.	Temperature Programmed Reduction and Oxidation.....	55
2.5.7.2.	Thermogravimetric Analysis.....	56
2.5.7.3.	Experimental Procedures.....	56
2.5.8.	Carbon-Hydrogen-Nitrogen Analysis.....	56
2.5.9.	Experimental Procedure.....	54
2.6.	References.....	57

Chapter 3: The Reaction of *n*-Octane with the Johnson Matthey Iron Molybdate Catalyst

3.1.	Introduction.....	59
3.2.	Changing Reaction Parameters.....	59
3.2.1.	Temperature.....	59
3.2.2.	Carbon to Oxygen Ratio and Partial Pressures.....	60
3.2.3.	Gas Hourly Space Velocity.....	60
3.3.	Experimental.....	60
3.4.	Calibration Of <i>n</i> -Octane.....	60
3.5.	Results and Discussion.....	61
3.5.1.	Catalytic Activity of the JM Iron Molybdate Catalyst.....	61
3.5.2.	Temperature Dependence Study.....	61
3.5.2.1.	Summary.....	66
3.5.3.	Catalyst stability at 550 °C:DH and ODH to determine the origin of CO _x	67

3.6. Optimisation of Experimental Parameters to Produce Octene and Aromatics from <i>n</i>-Octane	68
3.6.1.A Temperature, GHSV and C:O Ratio Study	68
3.6.2.The Production of Styrene: A TOL study at 550 °C	70
3.6.2.1. Alternating the GHSV between 4000 h ⁻¹ and 1000 h ⁻¹	70
3.6.3.Increasing the Partial Pressures of <i>n</i> -Octane and Oxygen: Optimisation of Octene	73
3.6.3.1. The UKZN Result: Increased partial pressure of <i>n</i> -octane to 11 %	73
3.6.3.2. Testing the JM iron Molybdate Catalyst with 4 % <i>n</i> -Octane	74
3.6.4.Catalyst Stability at 550 °C: 4 % <i>n</i> -octane with alternating GHSV between 4000 h ⁻¹ and 1000 h ⁻¹	78
3.6.4.1. Summary	79
3.6.5.The Optimisation of the JM Iron Molybdate Catalyst with 4 % <i>n</i> -Octane	80
3.6.5.1. A Temperature, GHSV and C:O Ratio Study	80
3.7. Further Characterisation of the Iron Molybdate Catalysts	87
3.7.1.Diffuse Reflectance UV-Vis Spectroscopy (DR-UV-Vis)	87
3.7.2. Temperature Programmed Reduction (TPR) and Oxidation (TPO)	88
3.7.3.X-Ray Photoelectron Spectroscopy (XPS)	89
3.7.4.Raman Spectroscopy	91
3.7.5. Thermogravimetric Analysis (TGA)	92
3.8. Catalyst Stability	93
3.8.1.Hysteresis: Cycling the JM iron molybdate catalyst	93
3.9. Conclusions	95
3.10. References	96

Chapter 4: The Reduced JM Iron Molybdate Catalyst: Reactivity and Mechanistic Studies

4.1. Introduction	98
4.2. Results and Discussion	98
4.2.1. Catalytic Activity with the Reduced JM Iron Molybdate Catalyst	98
4.3. Optimisation of Experimental Parameters to Produce Octene and Aromatics from <i>n</i>-Octane	103
4.3.1.A Temperature, GHSV and C:O Ratio Study	103
4.3.2.Catalyst Stability	107
4.3.2.1. TOL Study at 400 °C Maximising the production of octene	107
4.3.2.1.1. Elemental Analysis and Spectroscopy	108
4.3.2.2. A TOL Study at 550 °C with Alternating GHSVs: Maximising the production of styrene and the importance of carbon	112
4.3.2.3. Elemental Analysis and Spectroscopy	115
4.3.2.3.1. Summary	116

4.4. Proposed Mechanisms.....	117
4.4.1.Active Carbon in Oxidative Dehydrogenation.....	117
4.4.1.1. Summary.....	120
4.4.2.An Alternative Oxidant: CO ₂ for the ODH of Ethylbenzene to Styrene...	121
4.5. Activation of C-H Bonds in <i>n</i>-Octane and Ethylbenzene Using CO₂ as an Oxidant.....	123
4.5.1.Testing of <i>n</i> -octane with the reduced JM iron molybdate catalyst with 5% ethylbenzene and 10 % CO ₂	124
4.5.2.Testing of <i>n</i> -octane and the reduced JM iron molybdate catalyst at 550 °C using CO ₂ as the oxidant.....	128
4.6. Determining the Source of Aromatic Products.....	131
4.6.1.Using Oct-1-ene and the Reduced JM Iron Molybdate catalyst.....	131
4.6.1.1. Controls: Reactivity of oct-1-ene with no catalyst.....	131
4.6.1.2. Reactivity of Oct-1-ene with the reduced JM Iron Molybdate.....	134
4.6.2.Optimisation of Experimental Parameters to Produce Octadienes and Aromatics from Oct-1-ene.....	136
4.6.2.1. A Temperature, GHSV and C:O Ratio Study.....	133
4.6.2.1.1. Summary.....	139
4.7. Conclusions.....	139
4.8. References.....	140

Chapter 5: Pure Oxide Phase Components of the Reduced JM Iron Molybdate Catalyst

5.1. Introduction.....	143
5.2. Results and Discussion.....	143
5.2.1. Pure Phase FeMoO ₄	143
5.2.1.1. Optimisation for the Production of Octene.....	143
5.2.1.2. Detailed Analysis: Eliminating or Consuming CO ₂	148
5.2.1.3. Summary.....	152
5.2.2.Pure Phase MoO ₂	153
5.2.2.1. Optimisation for the Production of Aromatics.....	153
5.2.2.2. Detailed Analysis: The production of aromatics.....	157
5.3. Conclusions.....	162
5.4. References.....	163

Chapter 6: Conclusions and Future Work

5.1. Conclusions.....	164
5.1.1.The JM Iron Molybdate Catalyst.....	164
5.1.2. The Reduced JM Iron Molybdate Catalyst.....	166

5.1.3. The Pure Reduced Oxide Phase Catalysts: FeMoO_4 and MoO_2	
Catalysts.....	167
5.2. Future Work.....	168
5.3. References.....	169
Appendix.....	171

Abstract

The oxidative dehydrogenation (ODH) of *n*-octane to produce octene at atmospheric pressure has been studied using an industrially supplied iron molybdate catalyst from Johnson Matthey (JM). A temperature dependence study from 350 °C to 550 °C showed that at temperatures ≥ 450 °C aromatic selectivity and *n*-octane conversion increased. The catalyst undergoes a reductive phase transition when reacted with *n*-octane at 450 °C where the phase changes from $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ to $\text{FeMoO}_4\text{-MoO}_2\text{-Mo}_4\text{O}_{11}$. If the temperature is taken back below this point the catalyst does not revert to the original phase and therefore the same activity and selectivity cannot be achieved. Thus the system can be considered as two different catalysts: i) the oxidised phases at temperatures < 450 °C, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, which is associated with the production of octene and CO_x , and ii) as the reduced phases at temperatures ≥ 450 °C, FeMoO_4 , MoO_2 and Mo_4O_{11} , which led to the formation of CO_x and aromatics.

The pre-reduction of the JM iron molybdate catalyst resulting in the $\text{FeMoO}_4\text{-MoO}_2$, improved the selectivity to octene at temperatures < 450 °C; optimum conditions for the production of octene was found using a C:O ratio of 8:1 at 4000 h^{-1} at 400 °C, achieving *ca.* 82 % selectivity and 8 % conversion. Time on line (TOL) studies showed that the catalyst was stable under these operating conditions. A subtle increase in conversion was detected with time whilst a decrease in carbon mass balance was observed suggesting the formation of active coke. Lowering the GHSV to 1000 h^{-1} at this temperature produced CO_2 , due to a re-oxidisation of the catalyst and the removal of coke shown by an increase in the carbon mass balance. Temperatures above ≥ 450 °C produced aromatics, including ethyl benzene, benzene and styrene. The increase in aromatic production and conversion increased with increasing temperature which is consistent with the underlying Mars-van Krevelen (MvK) mechanism, in which lattice oxide ions abstract hydrogen from the adsorbed hydrocarbon. The lattice oxygen are more labile at higher temperatures increasing the probability of further dehydrogenation. At 550 °C and 1000 h^{-1} the selectivity to CO_x decreased to *ca.* 20 % whilst aromatic selectivity increased to *ca.* 58 %, (from *ca.* 35 % and 28 % respectively at 500 °C). Styrene production in particular increased dramatically between 500 and 550 °C. These results are associated with a combination of active coke, confirmed by Raman spectroscopy and carbon-hydrogen-

nitrogen (CHN) analysis, on the surface of the catalyst and the activation of CO₂ to produce styrene from ethylbenzene.

The separate phases of the FeMoO₄-MoO₂ catalyst, i.e. FeMoO₄ and MoO₂, were then tested to understand the significance of each phase in relation to octene and aromatic selectivity. The FeMoO₄ catalyst produces octene with high selectivity. The optimal conditions for the production of octene were a C:O ratio of 12:1 at 4000 h⁻¹ at 400 °C achieving 91 % selectivity at 7 % conversion. Aromatic and CO_x production increased with increasing temperature but no decrease in CO_x selectivity or increase in aromatic selectivity was observed from 500 °C to 550 °C at 1000 h⁻¹ unlike the JM iron molybdate catalyst. MoO₂ was tested as was active for both heavier aromatics (naptha and ethyl-naptha) and ethylbenzene.

1

Chapter 1: Introduction and Literature Review: Alkane activation using molybdate catalysts

1.1 Introduction to Catalysis

The term *catalysis* was coined by a Swedish chemist J. J. Berzelius in 1836 from the Greek word “*kata*” meaning "down" and “*lysis*" meaning loosening or breaking¹. The activation energy (E_{act}) is defined as the minimum energy required to overcome an energy barrier in order for molecules to react. A catalyst, which must have multiple turnovers, is a substance that increases the rate to reach chemical equilibrium by lowering the activation energy. This means that more molecules have Gibbs free energy $\geq$ activation energy and therefore the probability of reactant molecules coming together with sufficient free energy to react increases. This is better described as the Maxwell-Boltzmann distribution. The change in Gibbs free energy is equal to the sum of its enthalpy and the product of temperature and entropy of the system (Equation 1.0)

$$\Delta G = \Delta H - T\Delta S \quad (1.0)$$

Where

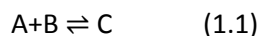
ΔH = Change in enthalpy

T = Temperature

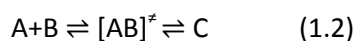
ΔS = Change in entropy

Catalysts are often used to increase the rate of chemical reactions that would otherwise take a long time or need the assistance of higher temperatures and pressures, which can lead to significant costs and engineering issues. The equilibrium constant, K , increases in both directions, which therefore implies that the catalyst only affects the kinetics of a given reaction and not the thermodynamics of the reaction, a phenomenon recognised by Ostwald in 1895¹.

For instance reactants A and B produce product C, where A and B are in equilibrium with C.



In a collisional reaction the conversion of A and B to C proceeds through a high energy state known as the transition state, $[AB]^\ddagger$.



At the transition state the probability of reactants going to products is solely diffusion controlled i.e. the rate k is equal to zero. This transition state stands at the top of the energy profile curve (Figure 1.1).

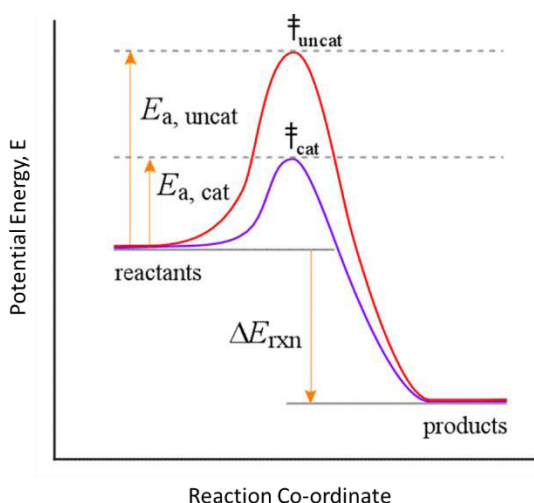


Figure 1.1: Potential energy profile of an exogonic reaction: red line, uncatalysed; purple line, catalysed

Arrhenius observed that the rate of a reaction is temperature dependent and led to the concept of a reaction barrier pathway. The height of the activation barrier is called the activation energy, $\Delta G^\ddagger$, and is the energy required to raise the average energy of one mole of reactant at a given temperature to the energy of the transition state which is also related to the equilibrium constant,

$$\Delta G^\ddagger = -RT \ln K \quad (\text{eq. 1.3})$$

Where

R = Ideal gas constant

T= Absolute temperature

K= Equilibrium constant

The relationship between activation energy and the rate constant of the reaction, k, is given by the Arrhenius equation:

$$k = Ae^{-\Delta G^\ddagger / RT} \quad (1.4)$$

$$\ln k = -(\Delta G^\ddagger / RT) + \text{constant} \quad (1.5)$$

Where A is the Arrhenius constant for a particular reaction and the rate constant:

$$k = k_0 e^{[-\Delta G^\ddagger / RT]} \quad (1.6)$$

Where k_0 is the rate constant when $\Delta G^\ddagger$ is zero i.e. at the top of the barrier (Figure 1.1), and is known as the pre-exponential factor and is a diffusion limited rate constant. Therefore using a catalyst to lower the activation barrier increases the probability of the molecules to reach the transition state and subsequently increase the rate in which to reach chemical equilibrium.

The catalytic cycle is simply described in Figure 1.2 where the reactant or reactants adsorb/adsorbs onto the surface of the catalyst and the products desorb regenerating the catalyst. The intermediate catalyst is often highly reactive and difficult to detect.

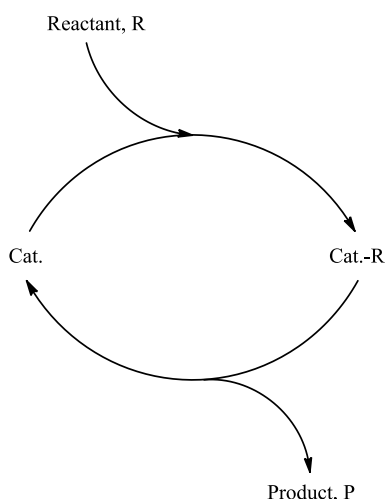


Figure 1.2: The catalytic cycle.

Two mechanisms, the Langmuir–Hinshelwood and Eley–Rideal mechanisms both use the concept of adsorbed species on a catalyst surface². The Langmuir–Hinshelwood model assumes that the reactants must be adsorbed on the catalyst surface before it can react, whereas the Eley–Rideal mechanism requires an adsorbed species on the catalyst surface, and a subsequent species reacts with it and the product desorbs².

In reality competitive reactions and chemical changes can affect catalysts and consequently the catalytic activity resulting in catalyst deactivation. The catalyst therefore must be regenerated or eventually replaced. Poisons are substances that decrease or even deactivate the activity or selectivity of catalysts. Such poisons include coke i.e. a carbonaceous species that inhibits the active site of the catalyst which prevents a reaction from taking place. However catalysts can also be enhanced by adding promoters/dopants, especially in heterogeneous catalysts. A dopant is described as a foreign atom that is introduced into the lattice of the structure. For instance adding potassium, an electropositive atom which donates electron density, to the transition metal (TM) of a TM catalyst promotes the dissociative chemisorption of substrates such as CO. This increases back-bonding into the π^* anti bonding orbital, strengthening the metal-carbon bond and weakening of carbon-oxygen bond.

To conclude, the introduction of catalysts lower the operating conditions that are otherwise required for the direct synthesis of a chemical process. Catalysts improve selectivity and conversion, increase the rate of chemical reactions and enable kinetic

control to attain desired products over thermodynamic products. This provides a more sustainable, greener, and cost effective pathway for both the environment and industry. Some catalysts need activating either by slight elevated temperatures and pressures, however these parameters are considerably lower in energy. Catalysts are able to increase atom efficiency avoiding stoichiometric reagents by direct synthesis.

1.1.1 Heterogeneous Catalysis

The majority of industrial processes are reliant on heterogeneous catalysts, because of the ease of separation and durability^{3, 4}. The manufacture of ammonia, from its elements, for the production of fertilisers is one of the most important catalytic processes known to date; the renowned Haber process⁵. This later led to the development of the Haber-Bosch process, wherein Carl Bosch developed the process for an industrial scale, for which he was awarded the Nobel Prize in 1931. The process significantly increased the agricultural productivity in most regions of the world.

Other advances in catalytic processes include the Fisher-Tropsch (FT) process, which converts syngas (CO and H₂) to alkanes. The syngas is sourced from coal or natural gas and is processed to produce liquid alkane products. SASOL, a South African international integrated chemical and energy company, is one of the world's leading manufacturers of hydrocarbons through the gas-to liquids (GTL) process. For example, the SASOL GTL plant in Louisiana produces 96 000 barrels per day alone in the US, and to date is the largest foreign direct investment in the state⁶.

Most catalysts used in such processes are metal catalysts. Ceramic metal oxides including MgO, Al₂O₃ and SiO₂ are often used as supports for metals. These supports possess desirable properties which include high stability, thermal stability, increase metal dispersion which become important when exposed to vigorous conditions. Supported metal catalysts and metal catalysts are used in wide range of processes including dehydrogenation, hydrogenation and hydrogenolysis. Metal oxides including transition metal oxides (TMO) such as NiO and Cr₂O₃ are used in oxidation, cyclisation and aromatisation processes. Mixed metal oxides M₂MoO_x, where M represents an alternative metal atom, are used in alkane activation and partial oxidation reactions.

These catalysts are versatile because they possess active redox centres, a range of oxidation states and different phases.

1.2 Alkane Activation in the Petrochemical Industry

1.2.1 Steam Cracking of Hydrocarbons

Steam cracking is regarded as one of the most reliable and efficient commercial processes for the production of light alkenes, specifically ethene⁷. Steam cracking is an example of a non-catalytic process which produces light chained alkenes from hydrocarbon feedstocks, such as naphtha in superheated steam⁸. The light alkenes are manufactured into plastics, fibres and other chemicals. At present the process accounts for approximately 180–200 million tons of CO₂ emissions world-wide and is considered to be the world's most energy intensive industrial process⁹. The process typically requires temperatures of 750–950 °C or up to 1100 °C in the presence of oil or gas. Naphtha steam cracking pyrolysis consumes *ca.* 65 % of the total process energy and *ca.* 75 % of the total energy loss⁸. After pyrolysis, which is the thermochemical decomposition of organic material at elevated temperatures, the gas is then quenched by transfer line exchangers (TLE), which slowly dissipate heat, to 550–650 °C followed by a series of heat exchangers decreasing the temperature to *ca.* 300 °C. Products such as gasoline and fuel oils rich in aromatics are condensed and fractionated while the liquids go through series of purification processes. Due to the high temperatures the heat exchangers are prone to degradation and so must be well organised as impromptu shutdowns are often required¹⁰.

1.2.2 Catalytic Cracking of Hydrocarbons

The development of catalysts is significantly influenced by industrial needs. The ability to control reaction efficiency and maintain high selectivities are of utmost importance. Catalytic cracking of hydrocarbons provides an alternative, lower-energy route to the more traditional, energy-intensive steam cracking process and so is a greener and more cost effective solution. Zeolite catalysts for hydrocarbon cracking are known to be the most active^{7, 11}. These solid proton-donor acids, also called Brönsted acids, are complex three dimensional cage aluminosilicates containing aluminium, silicon and

oxygen. They are negatively charged, but are balanced by cations such as sodium or hydrogen^{12, 13}. Fluidised catalytic cracking (FCC) is an acid cracking process that uses acidic ZSM catalysts and heavy feedstocks. FCC currently produces about 30 % of the world's propene by steam cracking of naphtha. The operation temperature is in the range of 450-600 °C compared to the energy intensive steam cracking process at *ca.* 800 °C^{7, 12}. At low temperatures intermediate alkenes can be produced from naphtha in the FCC process. An increase in the carbon chain length of alkanes results in an enhancement in the alkene yield. A decrease in yield and conversion is observed as alkane isomers are formed, i.e. branched alkanes. Using zeolites can avoid isomer production by implementing shape selective catalysis. The decrease in conversion is associated with the increased stability of the carbocation hence n-alkanes > methyl substituted isomers > dimethyl substituted isomers^{12, 14}.

1.2.3 Dehydrogenation Catalysis

The catalytic dehydrogenation (DH) of alkanes is of significant industrial importance, because it represents a route to obtain alkenes from feedstocks of low-cost saturated hydrocarbons^{15,16}. The large volume of patents and technical literature for short-chain hydrocarbon activation far outnumbers the literature on intermediate C₇–C₁₂ alkanes, particularly in the gas phase.

One current industrial process for dehydrogenation of shorter chain alkanes is the CATOFIN dehydrogenation process^{17,18}, licensed and developed by Lummus. The process utilizes a continuous multi-bed flow reactor which cycles to regenerate the CrO_x/Al₂O₃ catalyst¹⁹. The process produces isobutene, propene or isopentene from isobutane, propane or isopentanes respectively with corresponding selectivities > 90 mol %, > 86 mol % and > 75 mol % respectively. However longer chain alkane activation was discovered in the 1940s. The UOP Pacol process²⁰ was based on principles demonstrated by Haensel²¹. It was revealed that Pt-based catalysts had high activity for the dehydrogenation of alkanes to alkenes. In the 1960s, Bloch²² developed and revealed that Pt-based catalysts can dehydrogenate long-chain linear alkanes to mono-alkenes with high activity, selectivity and stability. This was the basis for the UOP Pacol process^{19,23}. The susceptibility of longer chain alkanes to cracking can lead to a range of low-value products which can also result in the formation of an inactive graphitic layer on the catalyst surface triggering deactivation²⁴.

Issues that arise with direct catalytic dehydrogenation process are that the activity and selectivity are restricted by thermodynamics at high temperatures. Elevated temperatures, between 525 – 625 °C , are needed to overcome the activation barrier for the highly endothermic reaction²⁵. Alkane dehydrogenation is limited by chemical equilibrium and, according to Le Chatelier's principle, higher conversion will require either higher temperatures or lower pressures²³. Not only is this an energy intensive process but problems persist in the production of unwanted side products and catalyst deactivation. Regeneration of the catalyst is also required to remove coke that leads to catalyst deactivation and results in downtime.

1.2.4 Oxidative Dehydrogenation Catalysis

Oxidative dehydrogenation (ODH) of alkanes decreases the thermodynamic limitations and avoids the continuous catalytic regeneration that is necessary in dehydrogenation catalysis. Molecular oxygen in the feed also reacts with the hydrogen produced from abstraction and in turn produces water. The removal of hydrogen from the system shifts the equilibrium towards the formation of dehydrogenated products as a result of Le Chatelier's principle. The reaction between oxygen and hydrogen is an exothermic reaction which lowers the overall energy of the system minimising the thermodynamic limitations. Oxygen also inhibits coking by combustion of carbonaceous species that form on the surface or in the pores, and in so doing extends the catalyst lifetime. However, the feed mixture ratio needs to be carefully monitored as the presence of the oxidant can cause the mixture to fall within the flammability range. The presence of oxygen increases the conversion, but selectivity is often a problem due to side reactions, which include partial oxidation products (k_4 - k_7), shown in Figure 1.3 below, and CO_2 . Grasselli *et al.*²⁶ showed that the reaction network for the oxidative dehydrogenation of propane using a cobalt-nickel molybdate catalyst.

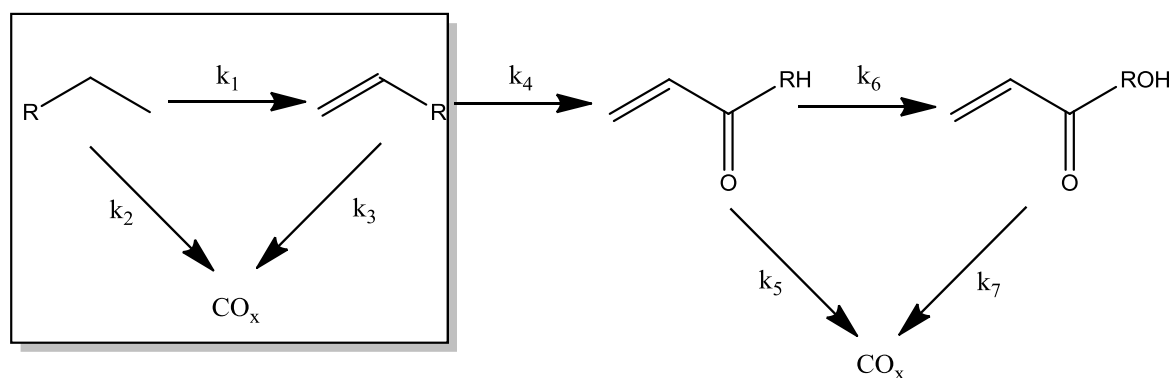


Figure 1.3: Reaction kinetics of propane oxidation²⁶.

However, careful manipulation of reaction parameters including the fuel-to-oxygen ratio (moles of alkane to moles of molecular oxygen) are needed to achieve a high selectivity to the alkene (k_1 - k_3)²⁷.

The partial oxidation of alkanes to alkenes proceeds *via* parallel and sequential oxidation steps (Fig. 1.3, k_1 - k_3). Alkenes are the primary products from ODH however, CO and CO₂ can be produced from the direct combustion of the alkane or secondary oxidation steps from the alkene. The allylic bond of the alkene is significantly stronger than its corresponding alkane²⁸, for example ethane's weakest C-H bond is 419.5 kJmol⁻¹ whereas the weakest C-H bond in ethene is 444 kJ mol⁻¹²⁹. For a more selective reaction the k_2/k_1 ratio is usually low, however with increasing conversion there is usually a decrease in alkene yield corresponding to an increased k_3/k_1 ratio. The stronger allylic bond in the alkene results in a larger k_3/k_1 and is due to the strong bonding interaction between the double bond and the oxide resulting in further oxidation^{27,30}. Literature is sparse on ODH of intermediate alkanes due to these technicalities. However in recent years Friedrich *et al.* have reported ODH reactions of C₆-C₈ alkanes using nickel molybdate^{31, 32} and supported vanadate catalysts³³⁻³⁵. Prior to this many of the processes used to transform hydrocarbons to alkenes and aromatics were reliant on DH^{36,37}.

1.2.4.1 The Mars-van Krevelen Mechanism

It is well documented that mixed metal oxides activating the allylic hydrocarbon bond proceeds through a Mars-van Krevelen mechanism (MvK)³⁸⁻⁴². The oxygen insertion from the lattice induces a redox cycle; the metal reduces and the hydrocarbon is oxidised. The lattice oxygen used in ODH is then replenished by the oxygen from the feed. When the system reaches equilibrium the surface of the catalyst becomes saturated with short lived oxygen species capable of removing the methylene C-H moiety of the alkane molecule. A second hydrogen abstraction occurs before desorption of the alkene molecule resulting in the production of CO_x, and the re-oxidation of the metal centre. Figure 1.4 shows the ODH of propane to propene using a vanadia catalyst⁴³.

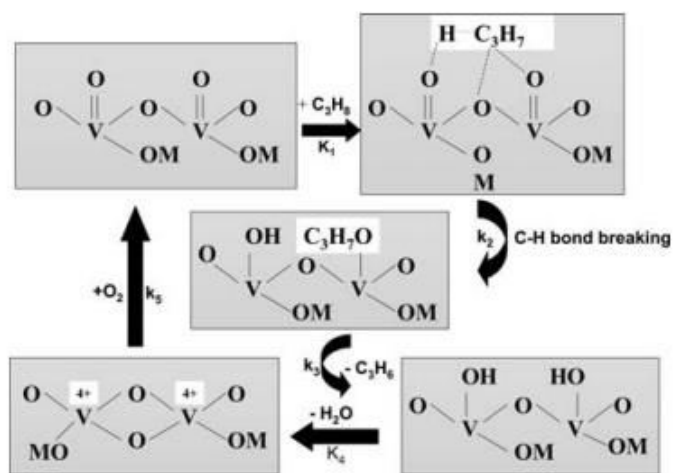


Figure 1.4: The Mars-van Krevelen reaction mechanism for the ODH of propane adapted from Iglesia *et al.*⁴³.

1.3 Research Objectives

The research project is a collaboration between Johnson Matthey, Sasol Technology and the University of Kwazulu Natal. The overall aim of the research is to produce a catalyst capable of selective ODH of intermediate chain length linear alkanes to their corresponding alkenes, modelling on *n*-octane to octene. The project is designed to improve on the existing Honeywell UOP PACOL process. This process is endothermic and requires energy intensive dehydrogenating (DH) conditions using temperatures between 525-625 °C to overcome the thermodynamic limitations. The ODH reaction pathway overcomes the thermodynamic restrictions by providing an alternative route

and shifts the equilibrium to the production of alkenes. This process benefits from increased conversion and extended the catalyst life time by the *in situ* removal of coke, and therefore there is no need to introduce a regeneration step unlike the PACOL process which relies on DH conditions. This may seem ideal, but it has been proved challenging in previous years as unwanted side products are produced. Temperatures ≤ 350 °C often overcome this but at the cost of conversion. Linear alkanes are produced by the Fischer-Tropsch (FT) process at Sasol, using coal or natural gas in the respective gas-to-liquids (GTL) or coal-to-liquids (CTL) technologies. The project concentrates on product upgrading of the intermediate alkanes from the Fischer Tropsch process for gas phase reactions. The project expands on previous investigations within the group using an oxygen free- radical initiator²⁴.

1.4 Literature review

1.4.1 Short Chain Alkane Activation: C₂-C₅

1.4.1.1 Vanadium Catalysis

A substantial volume of research is dedicated to vanadium catalysis for oxidation reactions. The production of maleic anhydride from *n*-butane using vanadium phosphorus oxides (VPOs) was developed in the 1970s to overcome pollution laws from the emission of benzene⁴⁴. VPOs are widely use in *n*-alkane activation and are considered bench mark catalysts for partial oxidisation. The structure of VPO is integral to the working catalyst and is influenced by a range of variables including; the morphology the precursor, V:P ratio, calcination temperature and ramp rate , the gas flow during calcination. The effect of changing parameters produces a variety of crystalline phases observable by X-ray diffraction (XRD) which in turn affect the catalyst performance⁴⁴⁻⁴⁶.

Catalysts containing vanadium oxides on high surface area supports such as alumina, silica, zeolites and their corresponding homologues have proven pivotal in chemical, petroleum and environmental industries.

Supported vanadium pentoxide (V₂O₅) on TiO₂ was instigated to selectively oxidise *o*-xylene to phthalic anhydride, instead of the more traditional reagent naphthalene, which in the 1960s was in ample supply^{47, 48}. The material was considered a

monolayer catalyst consisting of vanadium oxide on the surface that strongly interacts with the support⁴⁹ (Fig.1.5).

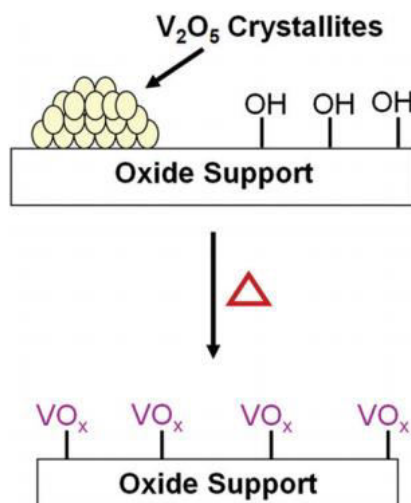


Figure.1.5: Schematic representation adapted from Wachs *et al.*⁴⁷ of the formation of a surface vanadium oxide monolayer.

Vanadium oxide catalysts have been used in a growing number of catalytic processes including the partial oxidation of methanol to formaldehyde⁵⁰, the selective catalytic reduction (SCR) of NO_x ⁵¹, the oxidation of chlorinated aromatics⁵², ammoxidation^{53, 54} of aromatic hydrocarbons. A large volume of literature is obtainable for the oxidative dehydrogenation of alkanes, in particular *n*-propane and *n*-butane, using vanadia-based catalysts⁵⁵⁻⁵⁸. Propene is an essential feed stock produced in the chemical and petrochemical industry and is produced using variety of methods, including dehydrogenation (DH), ODH^{38} , metathesis (MT) and methanol-to-olefins (MTO) producing 80.0 million tonnes annually world-wide⁵⁹.

1.4.1.2 Molybdenum Catalysis

The use of mixed metal molybdate catalysts is well documented for the activation of linear alkanes, especially for low chain alkanes such as propane. Examples include nickel, cobalt, bismuth, vanadium, manganese, magnesium and iron molybdates. However molybdenum has also been investigated in electrochemistry for hydrogen production from water as an alternative to natural gas *via* steam methane reforming,

in which methane and water react to form hydrogen and carbon dioxide⁶⁰. Molybdenite, MoS₂, was used as early as the 1970s for this process but activity was found to be poor⁶¹. The use of inexpensive and relatively abundant transition metal alternatives to Pt, which is currently the best available for the electrochemical generation of hydrogen from water⁶²⁻⁶⁴, would prove beneficial.

Nickel molybdate catalysts have been previously used for the oxidative dehydrogenation (ODH) of lighter alkanes⁶⁵, including C₂^{66, 67}, C₃^{66, 68-71} and C₄⁷² alkanes. Bismuth and vanadium molybdates have been shown to partially oxidise propane to produce acrolein, acrylic acid and acrylonitrile by ammoxidation⁷³.

Studies by Yoon *et al.*⁷⁴ showed that > 80 % selectivity to propene was achieved from a variety of metal molybdate catalyst but their catalytic activities differed greatly. Cobalt molybdate catalysts exhibit high selectivity with moderate conversion to propene from propane, 60 % and 20 % respectively at 450 °C. NiMoO₄ showed the highest activity but was nonselective whereas the MnMoO₄ catalyst revealed poor activity but high selectivity. The corresponding Mg, Ca, Al and Cr molybdate catalysts also showed similar selectivities, however the activities were shown to be relatively low. A magnesium molybdate catalyst produced within the group was found to be the most active at lower temperatures, (400°C) but still with a low maximum conversion of 22 %, and selectivity of 61 %⁷⁵.

Bismuth molybdate has been well studied for the partial oxidation reactions with some of the earliest reported in the 1960s⁷⁶⁻⁷⁹, and more recently for the partial oxidation of propane/ene to acrolein^{73, 80}. It has been proposed that a synergy between different phases of bismuth molybdate exists that increases activity when all phases are present⁸¹. The phases present are the α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆. There are discrepancies between authors for distinguishing which active phases are synergistic. However it has been recently suggested that the gamma phase is the crucial component. The gamma phase is known to be the optimal phase for mobility of lattice oxygen due to its layered structure⁸⁰. However it was found there is not a direct correlation between the rate of production of acrolein with increasing gamma-phase, the opposite was found to be true (Fig.1.6).

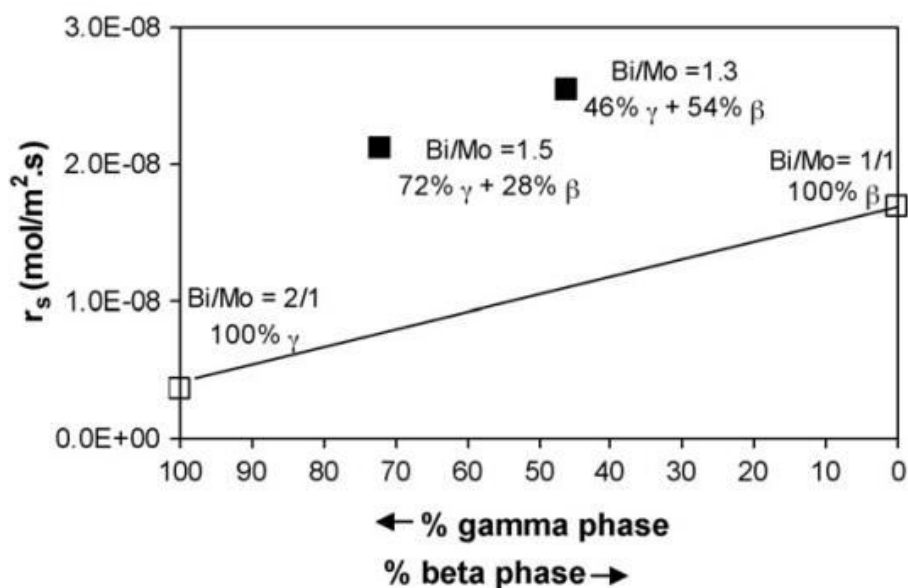


Figure. 1.6: Catalytic activities (reaction rate for propylene consumption) at 425 °C of bismuth molybdate samples with different percentage of gamma or beta phase: □ pure samples, ■ mixed samples⁸¹.

It was postulated that an increase in conductivity (i.e. the increase in lattice oxide mobility) for the pure γ -phase would increase the activity. However Thang *et al.* showed that mixed phases between β and γ increased the activity lowering the conductivity, especially at with a Bi/Mo ratio of 1.3⁸¹.

1.4.2 Intermediate Chain Alkane Activation: C₆-C₁₂

Friedrich *et al.* have reported the ODH of lower chained intermediate alkanes; *n*-hexane^{31, 32} and heptane³⁵ using nickel molybdate and vanadium magnesium oxide catalysts respectively. The oxidation of *n*-heptane over VMgO catalysts with varying amounts of vanadia produced mainly isomers of heptenes, aromatics and oxygenates. The *trans*-hept-2-ene isomer was the dominant isomer where *trans*-hept-2-ene > *trans*-hept-3-ene > hept-3-ene. Toluene was the dominant aromatic produced and was formed *via* the C₁ to C₆ cyclisation mechanism of hept-1-ene³⁵. Heptan-2-ol was the dominant oxygenate produced, suggested to be formed from the partial oxidation of *trans*-hept-2-ene³⁵, proposing that heptene isomers are the precursors for both aromatic and oxygenated products.

Nickel molybdate catalysts play an important role in the catalyst activity and selectivity. It was reported that the pure β -phase is more active than the α -phase for

the production of hexene. The aromatisation to benzene increased with increasing temperatures whilst the selectivity to cyclohexene decreased. It was postulated that the formation of benzene can be produced from the 1, 6 ring closure to form cyclohexane followed by ODH to benzene as shown in Figure.1.7³¹ and 1,5 ring closure followed by ring expansion to cyclohexane and ODH to benzene^{82, 83}.

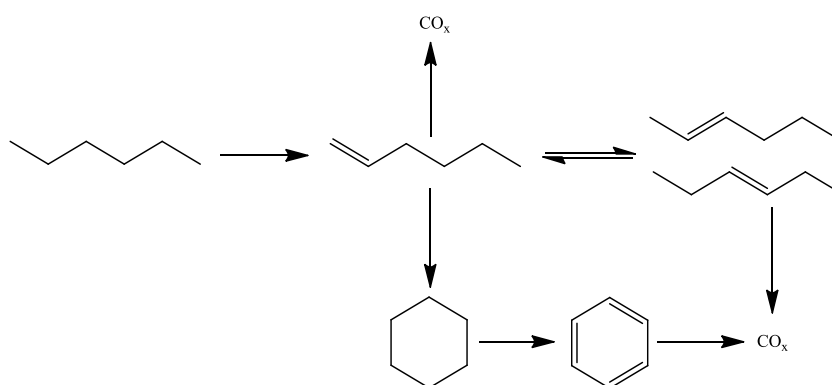


Figure. 1.7: Possible reaction scheme for the ODH of *n*-hexane Adapted from Friedrich *et al*³¹.

The group have also reported the ODH of *n*-octane with doped hydrotalcite catalysts containing a range of alkaline metals and vanadia^{33, 34, 84}. The catalysts produce mainly octenes and aromatics (Fig. 1.8) of which the dominant product was styrene⁸⁴.

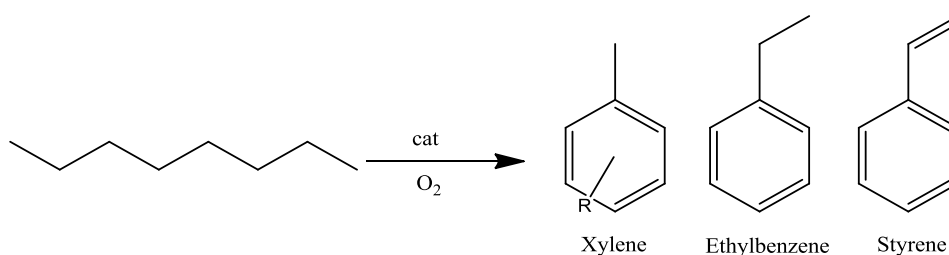


Figure. 1.8: Aromatisation of *n*-octane using doped hydrotalcite catalyst.

It was revealed that styrene selectivity increased with increasing fuel to air ratios, however a decrease in conversion was observed with a decrease in oxygen partial pressure⁸⁴. It was found that an increase in oxygen in the feed beyond a fuel to oxygen ratio of 4 % increased total oxidation and therefore a decrease in styrene was detected. It was postulated that the decrease in selectivity to styrene was due to the decrease in oxygen availability, causing a decrease in the rate of the redox cycle,

because the re-oxidation of the vanadium is less sustainable at lower oxygen concentrations.

It was also reported⁸⁴ that the gas hourly space velocity (GHSV) influenced the selectivity to styrene and activity. A maximum selectivity of 19 % was achieved at 6039 h⁻¹ with a maximum styrene yield of 14 %. Increasing the GHSV up to 11 000 h⁻¹ initially showed a decrease in selectivity but then plateaued at 11 %. The decrease in selectivity to styrene was thought to be due to the increase in alkene and xylene production. Increasing the GHSV decreases the contact time of styrene on the catalyst surface and thus decreases the possibility of further oxidation; the selectivities to CO_x and styrene are most affected by the change in GHSV. It was also found that catalyst precursors possessing more amorphous morphology were superior to those obtained from highly crystalline precursors. Catalysts produced from sodium salts were found to be superior to those obtained from potassium salts⁸⁴.

C₉-C₁₆ hydrocarbons have been studied using aluminium molybdate catalysts as early as the 1960s by Usov *et al.*⁸⁵. It was found that increasing the temperature increased the production of aromatics. Alkyl benzene derivatives were produced with chain lengths < C₁₀, including benzene, toluene and xylenes (BTX) and ethylbenzene. These were also present for carbon numbers ≥ C₁₀. However hydrocarbons ≥ C₁₀ produced alkyl substituted naphthalene homologues due to cyclisation *via* ODH to produce the alkene followed by further ODH to the arene. As the chain number increased the production of naphthalene homologues also increased. It was observed that not all products were *ortho*-substituted, the most thermodynamically stable, but the production of *para*- and *meta*-substituted aromatic hydrocarbons were also present, owing to isomerization and then decomposition or different positioning of ring closure or the initially formed arenes as postulated by Friedrich *et al.*³¹.

Hutchings *et al.*²⁴ also reported similar observations using an iron molybdate catalyst with *n*-decane as the substrate in the production of naphthalene at higher temperatures. The group recently reported that a conventional iron molybdate catalyst can combine oxidative dehydrogenation of *n*-decane with oxygen insertion²⁴. The catalyst is able to produce a mixture of oxygenated aromatics by reacting *n*-decane with an electrophilic oxygen species at temperatures < 460 °C via the Mars–van Krevelen mechanism (Figure 1.9). This in itself is novel in that oxygen insertion

usually takes place with linear alkanes to produce the corresponding linear alcohols, aldehydes, and ketones, not oxygenated aromatics.

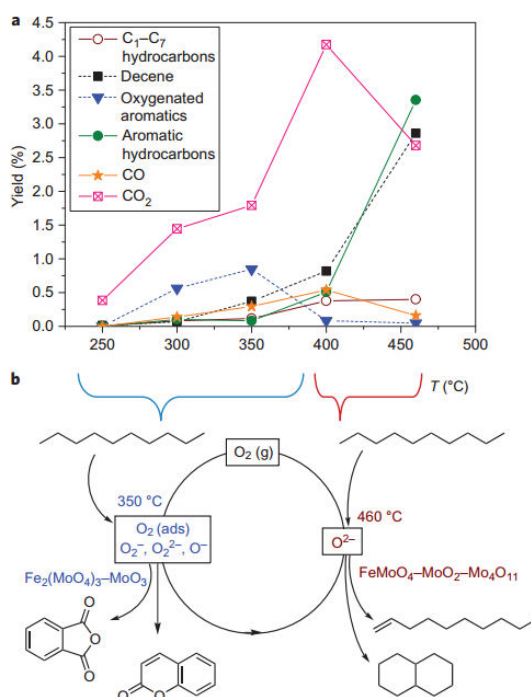


Figure. 1.9: Yields of major products as a function of temperature and state of the catalyst. The two temperature regimes correlate with the different states of the catalyst as shown²⁴.

The oxygen insertion reaction at low temperatures correlates with the oxidised iron molybdate phase, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, in which the MoO_3 enriches the surface of the binary-metal oxide⁸⁶. This however diminishes as a reductive phase change occurs at 460 °C producing the reduced iron molybdate catalyst, $\text{FeMoO}_4\text{-MoO}_2\text{-Mo}_4\text{O}_{11}$. The corresponding reduced iron molybdate phase at temperatures ≥ 460 °C produces non-oxygenated aromatics and decene. However when oxygen is present in the feed the highest yields are obtained which is supported by previous literature⁸⁴.

1.4.2.1 Summary

An extensive amount of research containing molybdenum as the active component for catalysts has been shown. The catalysts are successful for both oxygen insertion to form oxygenated alkanes and the dehydrogenation of alkanes to alkenes via the

Mars-van Krevelen mechanism. The dual functionality iron molybdate catalyst²⁴ will be pivotal in modern chemistry, as the pressures on industry to become more flexible with product distribution will increase. Catalysts that are tuneable will pave the way for industrial processes. The iron molybdate catalyst is already well established for methanol partial oxidation but alkane activation is scarce. Therefore the initial findings from the group will be continued and developed but with the *n*-octane as the reactant model to establish whether or not an array of intermediate chain length alkanes behave in a similar manner with the catalyst. The next part of the literature review will discuss the iron molybdate catalyst and the processes associated with it in significant detail.

1.4.3 Iron Molybdate Catalysis

1.4.3.1 Composition and Properties

Iron molybdate is comprised of a mixture of iron and molybdenum oxides. The catalyst has been used extensively in industry for the partial oxidation of alcohols and hydrocarbons⁸⁷, but primarily in the oxidation of methanol to formaldehyde^{41, 88} after being discovered by Adkins and Peterson in 1931⁸⁹. There are two different structures present for the iron molybdates: the ferric $\text{Fe}_2(\text{MoO}_4)_3$, consisting of Fe^{III} and Mo^{VI} oxidation states, and the ferrous FeMoO_4 consisting of Fe^{II} and mainly Mo^{IV} oxidation state but only the ferric phase is known to be active for the conversion of methanol to formaldehyde. The iron molybdate catalysts with a composition of Mo:Fe >1.5 contain an excess of molybdenum in the form of MoO_3 and is often the case with most commercial catalysts. A composition with Mo:Fe ≤ 1.5 contains both Fe_2O_3 and $\text{Fe}_2(\text{MoO}_4)_3$ phases. A ratio of Mo:Fe=1.5:1 only contains the $\text{Fe}_2(\text{MoO}_4)_3$ phase. It is debatable in some cases whether the active phase is $\text{Fe}_2(\text{MoO}_4)_3$ or if a slight excess of MoO_3 is needed to produce the active catalyst, $\text{Fe}_2(\text{MoO}_4)_3 \cdot x\text{MoO}_3$ ⁹⁰. The industrial methanol oxidation catalyst contains both $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 phases with an Fe:Mo ratio of 1:3⁸⁷. The industrial catalyst is over engineered so that the excess MoO_3 can replenish any lost at high operational temperatures; this procedure prolongs the life time of the catalyst.

Plyasova *et al.*⁹¹ reported that ferric iron molybdate catalyst phase, $\text{Fe}_2(\text{MoO}_4)_3$ consisted of Fe octahedra and Mo tetrahedra sharing corners, and that the stoichiometric structure is monoclinic (Fig.1.10).

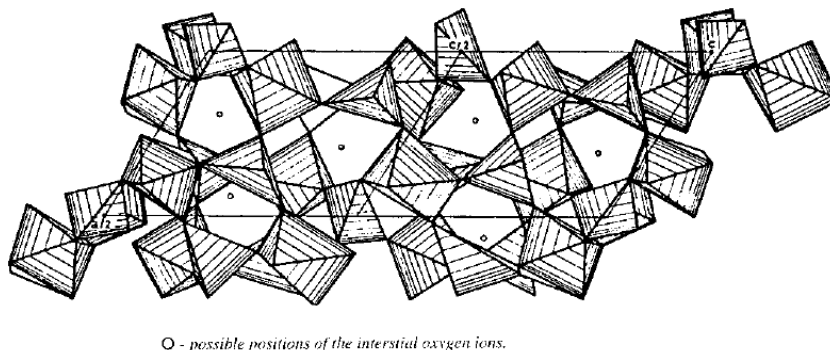


Figure 1.10: Possible interstitial positions of O^{2-} ions in the crystalline structure of $\text{Fe}_2(\text{MoO}_4)_3$.⁹²

Pernicon *et al.*⁹² reported that the unit cells for various iron molybdates have different unit cell parameters due to excess molybdenum. The Mo^{VI} ions replace some of the Fe^{III} in the octahedral coordination sphere, whereupon the oxide ions donated to conserve electroneutrality cause unit cell expansion. It was suggested that these distortions were the active components of the catalyst⁹².

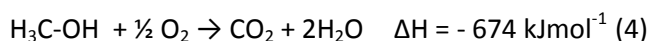
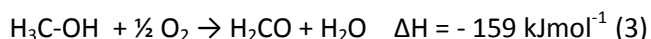
1.4.3.2 Industrial Applications

A vast amount of literature has been reported using iron molybdate catalysts for the partial oxidation of methanol to formaldehyde. Several plants are operational for this process and these plant use silver catalysts for DH and/or iron molybdate catalysts for ODH⁹⁰. The production of formaldehyde using a silver catalyst occurs from either oxidation ($\Delta H = -156 \text{ kJmol}^{-1}$) or dehydrogenation ($\Delta H = +84 \text{ kJmol}^{-1}$) steps^{93, 94}. The industrial process requires a fuel-rich mixture *ca.* 50 % v/v in an inert, and is performed at atmospheric pressure with temperatures between 560 °C – 600 °C. These conditions resulted in a conversion of 65–75 % and ≥ 89 % yield to formaldehyde. The dehydrogenation (DH) reactions are indicated below, however (1) is more thermodynamically favourable than (2).





The iron molybdate catalyst used in the oxidation reaction (ODH), shown by equation (3), overcomes the thermodynamic restrictions of the dehydrogenation process used by the silver catalyst. An excess of air is used with the iron molybdate catalyst to maximise conversion. Operational conditions include 6.7 – 36.5 % v/v in air to avoid the explosive limits, with temperatures ≤ 400 °C to limit side reactions. This catalyst can achieve *ca.* 100 % conversion and 95 % yield to formaldehyde⁹⁰. However the most thermodynamically favoured products are CO₂ and H₂O (4) for total oxidation, so careful monitoring of reaction parameters such as temperature and mixture ratio are required to avoid this⁸⁸.



1.4.3.3 The Partial Oxidation of Methanol to Formaldehyde

Studies by Bowker *et al.*^{41, 88, 90, 95-97} into the partial oxidation of methanol have been of great interest. These studies analysed mixed Mo-Fe oxides, molybdates and hematites using a pulsed reactor and TPD/R/O to determine each of the components' catalytic activity. It was found that the production of formaldehyde was not detected when using a hematite (Fe₂O₃) catalyst. The incorporation of molybdenum oxide species into hematite produced a highly selective catalyst for the partial oxidation of methanol to formaldehyde. Mixed Mo-Fe oxides were found to be more active than Mo oxide alone. It was proposed that the iron molybdate catalyst must have a stronger binding energy to oxygen and a higher concentration of Lewis acid sites than the separate hematite/molybdate solids. TPD experiments helped to describe what each phase of the iron molybdate catalyst was responsible for⁹⁶. It was found that the Fe₂O₃ phases formed a bi-dentate formate adsorbed complex whereas the MoO₃ samples produced a methoxy adsorbed species. It was revealed that a stoichiometric ratio of Mo:Fe was the active phase in the methanol oxidation process, however excess MoO₃ is needed to prevent the formation of iron rich phases on the catalyst surface during the reaction.⁸⁸

Work by Soares,^{90, 98} Grasselli,⁹⁹ and Routray⁸⁶ on methanol oxidation all stated that a small excess of MoO_3 increases catalytic activity in these systems. The excess MoO_3 phase can provide mobile molecular MoO_3 or $\text{MoO}(\text{OH})_2$ for the reduced phase and by doing so, replenishes any lost molybdenum sites. Therefore these excess mobile molybdenum species can restore the interface between the bulk and the surface of the catalyst.

The process of oxidising a hydrocarbon/alcohol undergoes selective oxidation steps as dictated by thermodynamics and kinetics (Fig.1.11).

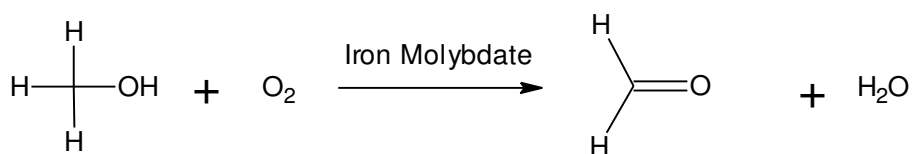
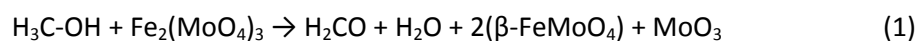


Figure 1.11: The direct route of the partial oxidation of methanol.

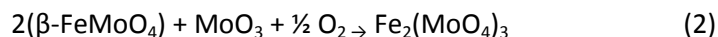
The activation of the C-H bond is the most thermodynamically unfavourable⁹⁴. The first step is the cleavage of the C-H bond which is catalysed by the more basic iron oxide. There are two terminal oxygen atoms double-bonded to the Mo which allow the methanol molecules to bond simultaneously at two points onto the surface.⁹⁸ Hydrogen is then abstracted from the methanol hydroxyl group which produces a methoxy species which is the intermediate for the production of formaldehyde. The insertion of an oxygen atom from the lattice is known as the Mars van Krevelen reaction, and in the process the molybdenum species is reduced from the 6+ to 5+ oxidation state. The reduced molybdenum is then re-oxidised by the oxygen from the feed. Therefore the catalysis of this reaction depends on the ease of the redox cycle of the oxomolybdenum species between its 6+ and 5+ oxidation states.⁸⁶

The redox catalytic process of methanol in presence of a ferric molybdate, $\text{Fe}_2(\text{MoO}_4)_3$, catalyst is well documented^{90, 100}. The individual steps take place during the catalytic process are shown below.

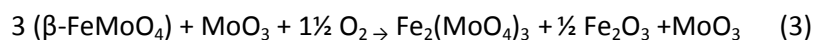
Initial oxidative reaction:



Re-oxidation:



However a deactivation step occurs especially when there is not enough molybdenum present to replenish the ones lost due to sublimation^{100, 101}.



1.4.3.4 Preparation Techniques and Applications

The majority of catalysts reported in the literature and for industrial applications have been prepared using the aqueous co-precipitation method. Other factors can affect the catalyst performance including, but not limited to: calcination temperature, ramp rate of calcination, Fe:Mo ratio, pH and the nature of the precursors^{90, 102}. As a general procedure, iron molybdates are prepared by co-precipitation from an aqueous solution of iron nitrate and ammonium heptamolybdate. The iron nitrate solution is slowly added to the ammonium heptamolybdate solution under vigorous stirring. For a stoichiometric mixed oxide the molybdenum solution is first acidified with nitric acid to a pH of 2. Once complete the precipitates are aged at 80 °C for 3 h under stirring and then filtered and dried at 120 °C overnight. The dried solid is then ground and calcined under flowing air⁹⁸. The industry standard has excess molybdate which maintains activity and selectivity and in so doing provides the active oxidation state at the surface^{97, 98, 102}. Molybdate loss from the surface is often an issue and reduces the catalytic performance by reduction and catalytic deactivation. This is often the case with the stoichiometric catalyst; without a reservoir of molybdate the surface cannot be replenished from sublimation.

The catalyst can also be prepared using the sol-gel¹⁰² and the modified technique^{103, 104}. Typically, under stirring, iron nitrate and molybdenum hexacarbonyl are added into two separate solutions of propionic acid. The solution containing the iron nitrate is added dropwise to the heated molybdenum hexacarbonyl solution under vigorous stirring. On completion the solution was evaporated to dryness where film formation over the vessel wall was established. Liquid nitrogen is then added to give the precursor and dried at 120 °C overnight. The sample is then calcined to give the final catalyst. However it reported that an irreversible reduction occurred during the calcination step decreasing the catalytic performance. The water resulted in the loss

of molybdenum which promotes catalyst surface reduction, and by doing so restricts reoxidation due to surface hydroxylation¹⁰².

More recently, alternative preparation methods have been developed to create specific phases which may determine the nature of the active sites responsible for activation of alcohols and hydrocarbons.

Molybdenum oxide on Fe_2O_3 core shells have been synthesised to probe the structural motifs responsible for methanol oxidation⁹⁷ (Fig. 1.12).

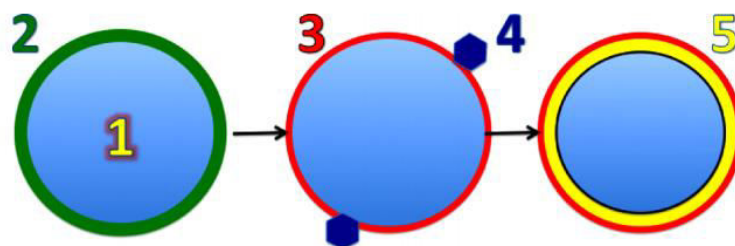


Figure 1.12. The evolution of the surface structure of the 3 monolayers (ML) catalyst as a function of annealing. On the left the low temperature structure is shown. The amorphous surface MoO_x layer (2) is supported on the Fe_2O_3 core (1). In the middle, temperature is at $\sim 400^\circ\text{C}$ showing nano-crystallites of MoO_3 developing (4) at the surface of the catalyst and the surface of MoO_x present. On the right-hand side, after annealing, the MoO_3 have mostly converted to ferric molybdate (yellow layer 5), but with the active monolayer encapsulating it⁹⁷.

It was reported that three monolayers of Mo stay in the surface region, even after annealing to temperatures below 400°C . However above 400°C the Mo reacts with the iron oxide. XAFS data showed that $> 400^\circ\text{C}$, most of the Mo converts to $\text{Fe}_2(\text{MoO}_4)_3$ but below this temperature nanocrystalline MoO_3 is present. The octahedral surface layer is suggested to be responsible for the activity which is present between 300°C and 600°C . The MoO_x layer on the $\text{Fe}_2(\text{MoO}_4)_3$ underlayer is the active component for formaldehyde production, whilst iron oxide aids total oxidation.

Ding *et al.*¹⁰⁵ have produced monoclinic and orthorhombic $\text{Fe}_2(\text{MoO}_4)_3$ micro-sized particles with complex 3D architectures by using template-free hydrothermal processes. It was reported that the pH, reaction time, temperature, and molybdenum

source all have a crucial influence on the phase formation, shape evolution, and microstructures. The pH influences the formation of crystallized iron molybdate resulting at the end of the synthesis, and the temperature affects the crystallization and shape control of the iron molybdate product. To influence size, shape, and dimensionality could prove beneficial in many potential applications throughout catalysis since other nano-materials such as nano-wires have been documented¹⁰⁶.

1.5 Conclusions

From the literature review it is evident that there are many existing industrial processes for the activation of alkanes. The industrial processes such as the Honeywell UOP PACOL process use dehydrogenation (DH) conditions which is an endothermic process. Issues that arise from the process are that the activity and selectivity are restricted by thermodynamics at high temperatures. Elevated temperatures, between 525 °C – 625 °C, are needed to overcome the activation barrier for the highly endothermic reaction²⁵. Alkane dehydrogenation is limited by chemical equilibrium and, according to Le Chatelier's principle, higher conversion will require either higher temperatures or lower pressures²³. The process also requires the regeneration of the catalyst which can lead to downtime.

The alternative method to combat these problems is to use the oxidative dehydrogenation process (ODH). This decreases the thermodynamic limitations and avoids the essential continuous catalytic regeneration that is necessary in dehydrogenation catalysis by introducing oxygen in the feed. According to Le Chatelier's principle the oxygen reacts the hydrogen which shifts the equilibrium towards the formation of dehydrogenated products. This process is also exothermic which will lower the energy needed. Carbonaceous species that form on the surface or in the pores will be combusted *in situ* extending the catalyst lifetime.

Molybdenum containing catalysts have been well researched for this process along with an established background for methanol partial oxidation. The catalysts are successful for both oxygen insertion to form oxygenated alkanes and the dehydrogenation of alkanes to alkenes via the Mars-van Krevelen mechanism. The

dual functionality iron molybdate catalyst discovered by Hutchings *et al.*²⁴ with *n*-decane shows promise for the production of alkanes and aromatics.

1.6 Thesis Overview

The thesis will focus on using an iron molybdate catalyst supplied by Johnson Matthey. The catalyst will be tested for the partial oxidation of *n*-octane using ODH conditions using an array of reaction conditions. The thesis has been separated into six chapters and each results chapter follows on from the previous chapter.

Chapter 1 gives an introduction and literature review about different alkane activation methods that are operational in industry and the use of molybdates for the ODH process.

Chapter 2 describes the preparation of pure phase molybdates and modification of the iron molybdate catalyst supplied by Johnson Matthey. The chapter details characterization techniques used to evaluate the catalysts pre, post and during (*in situ*) reaction(s). Each technique has been described in detail.

Chapter 3 investigates the Johnson Matthey (JM) iron molybdate catalyst with *n*-octane using a wide range of reaction parameters including temperature, carbon to oxygen ratios (C:O), gas hourly space velocity (GHSV) and the partial pressure of *n*-octane and oxygen. The catalyst has been characterised to aid understanding for particular reactions.

Chapter 4 progresses from the conclusions attained in chapter 3. The reduced JM iron molybdate is investigated with *n*-octane along with key experiments to assign possible mechanisms. The use of characterisation is pivotal in this chapter to assign the active components of the catalyst.

Chapter 5 examines the pure oxide phase components of the reduced JM iron molybdate catalyst. The reduced pure oxide phase catalysts were tested with *n*-octane to assign which products are produced as a result of each phase.

Chapter 6 summarises the overall conclusions made throughout the thesis and provides suggestions for further research.

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Chapter 2: Catalyst Preparation, Experimental Techniques and Theory

2.1.Introduction

Catalyst synthesis, testing and characterisation will be discussed in this chapter. The chapter will highlight the importance of the analytical techniques including; X-ray powder diffraction (XRPD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), temperature programmed reduction/oxidation (TPR and TPO), thermogravimetric analysis (TGA) and carbon-hydrogen-nitrogen (CHN) analysis, diffuse reflectance ultra-violet/visible (DR-UV-vis) spectroscopy. The state-of-the-art instrumentation were used to probe the catalysts pre/post reaction to aid the understanding of the nature of the active site(s) by providing information on the atomic structure, oxidation states, phase composition, morphology and crystallinity.

2.2.Catalyst Synthesis

2.2.1. The Iron Molybdate Catalyst Supplied by Johnson Matthey

The *Johnson Matthey* (JM) iron molybdate catalyst, $\text{Fe}_2(\text{MoO}_4)_3\cdot\text{MoO}_3$, with a Mo to Fe atomic ratio of 2.75:1 was synthesised using the adapted co-precipitation method¹. Aqueous solutions of iron nitrate ($\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, BDH, $\geq 98\%$, 27.32 g in 200 ml distilled water) was added dropwise to a solution of ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, BDH, $\geq 99\%$, 26.26 g in 150 ml distilled water) which had been pre-acidified (pH = 2) with nitric acid, under vigorous stirring. The yellow/green slurry was then aged at 80 °C for 3 h under stirring and the slurry containing the precipitate was then filtered without washing, dried in an oven at 120 °C for a duration of 24 h

and then calcined under flowing air at 260 °C 4 h (temperature ramp rate of 10 °C min⁻¹) to produce the final catalyst.

2.2.2. The Reduced Johnson Matthey Iron Molybdate Catalyst

The supplied *Johnson Matthey* (JM) iron molybdate catalyst was reduced under flowing 10 % H₂/Ar for 4 h at 10 °C min⁻¹ producing the reduced JM iron molybdate catalyst.

2.2.3. The Pure Phase FeMoO₄ Catalyst

FeMoO₄ purchased from Sigma Aldrich, was heat treated under flowing helium to 260 °C at 10 °C min⁻¹ for 4 h to produce the final catalyst.

2.2.4. The Pure Phase MoO₂ Catalyst

MoO₂ purchased from Sigma Aldrich, was heat treated under flowing helium to 260 °C at 10 °C min⁻¹ for 4 h to produce the final catalyst.

2.3. Catalyst Preparation

The catalysts were pelleted at 10 tonnes of pressure for 1 minute and sieved to 0.4-0.8 mm. The pelleted catalysts were then packed between quartz wool plugs in the central isothermal zone of the stainless steel reactor tube, with a K-type thermocouple inserted just below the catalyst bed to monitor the catalyst bed temperature. The stainless steel reactor tube was then secured in a Carbolite furnace (220-240 V, 382 W) controlled by Eurotherm controllers with a temperature range from room temperature (RT) to 1000 °C. Blanks of *n*-octane (catalyst subject to reaction conditions at 100 °C and assuming inactive catalyst), and oxygen concentrations were recorded prior to reaction conditions at a particular concentration, typically *c.a.* 1 % and 4%, in the reactor with the catalyst at 100 °C in order to calculate the carbon to oxygen (C:O) ratios and carbon mass balances.

2.4. Gas Phase Reactions

2.4.1. Reactor Set-Up

The gas phase oxidation of *n*-octane was carried out using a multi-bed plug flow reactor (Figure 2.2). The reactors used were stainless steel fixed-bed reactors with inner diameters of 10 mm. Helium and oxygen (BOC Ltd. high purity of $\geq 99.5\%$) were connected to and controlled by mass flow controllers (MFC) (Bronkhorst High Tech). The oxygen and helium lines were joined using a T-piece and connected to a pressure controller (2 bar). The flow was subsequently split, controlled by an individual MFC, to feed the saturators containing the *n*-octane. The saturators were maintained at ca. 10 °C and 40 °C to give *n*-octane concentrations of $\sim 1\%$ and 4% respectively in helium, and if required oxygen.. A knockout flask was connected to the outlet of each of the saturators and was also maintained at the respective temperatures to ensure the concentrations of *n*-octane and oxygen in the helium gas was consistent. All inlet and outlet lines to the reactors (after the saturators) were heated to 130 °C, above the boiling point of octane (125.6 °C), to prevent condensation in the lines. Reaction studies were maintained below the lower explosive limit of *n*-octane. Prior to reaction conditions the system, including the catalyst, was pre-treated for an hour with helium and heated to 100 °C to ensure any fuel and oxygen in the system has been removed to avoid operating outside the explosive limit. The exit of the individual stainless steel reactor tubes were connected to an eight port Valco selector valve, which allowed multiple reactions to be analysed simultaneously online using a Varian CP-3800 gas chromatograph (GC).

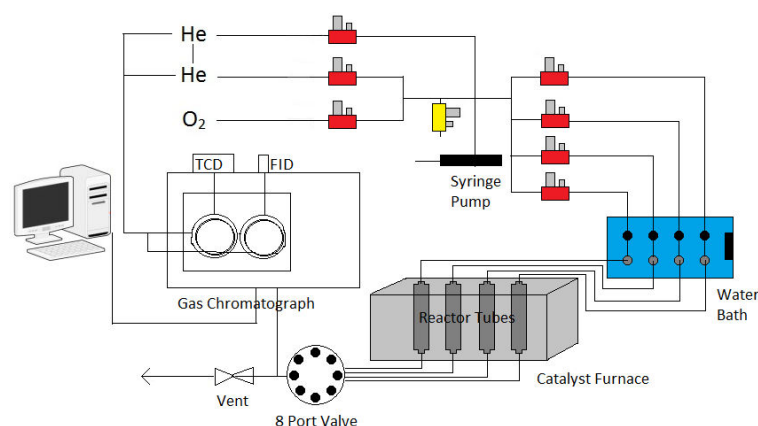


Figure 2.2: Schematic of the gas phase reactor system used in the partial oxidation-dehydrogenation of *n*-octane.

2.4.2. On-line Product Analysis

Hydrocarbons were analysed online using a Varian CP-3800 GC fitted with an Agilent non-polar HP-5 column (30 m, 0.53 mm i.d., 0.5 μ m film of 5 % phenyl-methylpolysiloxane) and equipped with both flame ionization and thermal conductivity detectors. A Molsieve 13X column (to separate CO and O₂) and a Hayesep Q column to detect CO₂ were connected in series and allowed to elute to the TCD. Carbon dioxide adsorbs irreversibly onto the Molsieve 13X column resulting in deactivation. Therefore the Molsieve column needs to be by-passed during the elution of CO₂ to prevent it from entering the column from the complete combustion of hydrocarbons. The HP-5 column separates the hydrocarbons. The retention times and calibrations of the products were determined by gas sampling the reactants using a syringe (5 mL) and syringe pump (0.254 mL/h). The sample injection was controlled using a six port valve, the gas sampling valve (GSV/V3) and allowed the gas flow through the Agilent HP-5 column and to finally to the FID. A second valve, a 10 port valve (V1) controlled gas flow through the Hayesep Q and Molsieve 13X columns. The final valve (V2) controlled whether the Molsieve 13X column was in series or bypass. The columns were fitted in series so that gas flows through both columns, and so a bypass sample line (1/16 inch O.D) was fitted with a restrictor valve in order to maintain equal gas flow throughout the system (Fig. 2.3) The performance of the catalyst was quantified in terms of molar conversion and selectivity along with a carbon mass balance.

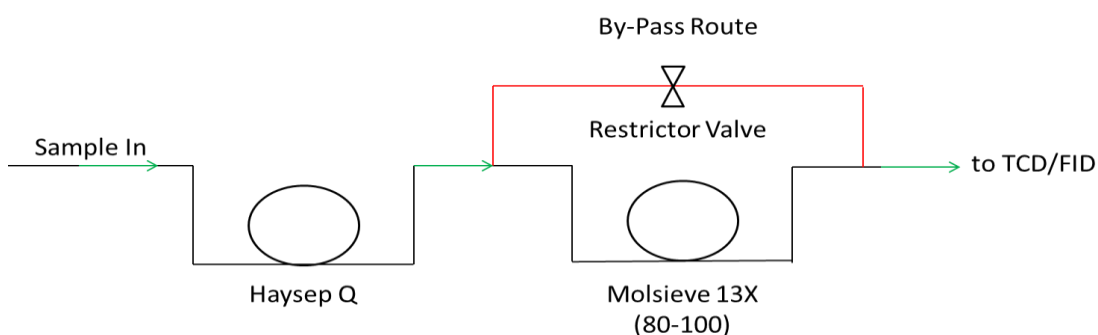


Figure 2.3: Schematic of the column set-up in the Varian CP-3800 GC. Diagram shows that the Molsieve 13X column can be bypassed via a pneumatic valve which described in detail in

Figure 2.6.

The following schematics (Figure 2.4 -2.6) shows in detail the valve configuration for the sample injection to all columns and the more important by-passing of the Molsieve 13X column.

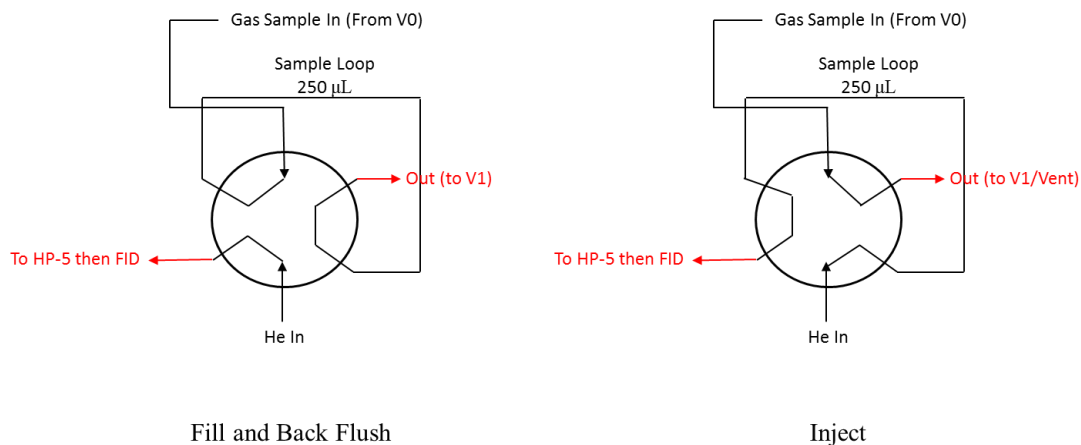


Figure 2.4: Schematic showing the 6 port gas sampling valve (GSV/V3) in the fill and back flush and the inject configurations.

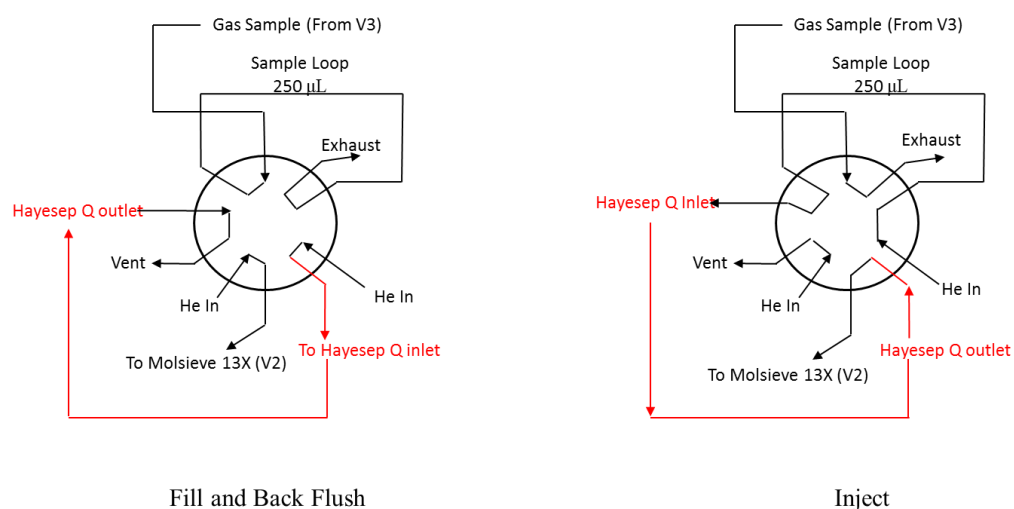


Figure 2.5: Schematic showing the 10 port gas sampling valve control (V1) to the Hayesep Q / Molsieve 13X column in the fill and back flush and inject configurations.

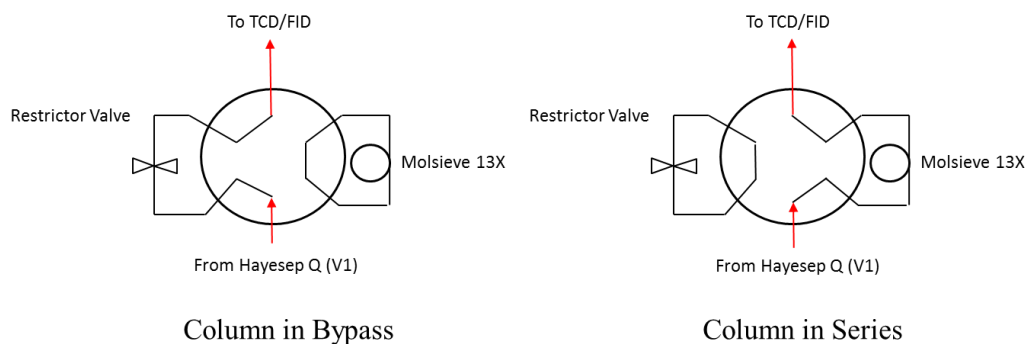


Figure 2.6: Schematic showing the 6 port gas sampling valve column for the Molecular 13X (80-100) in the bypass/series configurations.

Table 2.1 shows in detail the program for valve switching (V2) of the Molsieve 13X column, Hayesep Q column and the HP-5 capillary column.

Table 2.1. Valve switching program for GC runs.

Time (min)	Valve event
Initial	-1, -2, -3
0.01	+1, -2, +3
4.75	+1, +2, +3
8.00	-, -2, +3
60.00	-1, -2, -3

V3= Fill and Back flush (-), Inject (+). Upon injection the gas sample goes to HP-5 capillary column and Haysep Q sampling valve, (V1). V1 = (-) denotes the fill position and (+) the inject position. Once V1 goes to the inject configuration the gas sample goes through the Haysep Q column and then to the Molsieve 13X *via* V2, as these are connected in series. Valve, V2, (+) indicates column in bypass and (-) indicates column in series. The time for carbon dioxide to elute from the Haysep Q column takes *ca.* 6.00-7.75 mins, therefore the column is bypassed just before and after the elution times so that the molsieve column is protected.

2.4.3. Temperature Programme

The GC oven conditions are shown in Table 2.2. The conditions were chosen so that the products eluting from the columns has well defined peak separation from one another allowing detailed quantification of products.

Table 2.2. Temperature program used for GC runs.

	Temperature (°C)	Ramp Rate (°C/min)	Hold (min)	Total Time (min)
Initial	50	N/A	3.00	3.00
1	100	8	20.00	29.25
2	270	8	10.00	60.50

2.5. Catalyst Characterisation

2.5.1. X-ray Powder Diffraction

X-ray powder diffraction (XRPD) is an analytical technique used to classify materials. X-ray diffraction (XRD) probes the bulk of a material and can provide details on; crystal structure, unit-cell dimensions and crystallite size from the analysis of peak broadening.

The technique was first developed by Sir W.H. Bragg and Sir W.L. Bragg, who were awarded the Nobel Prize in 1915². Diffraction patterns are produced and are used to identify the crystallographic phases that are present in the catalysts. The interaction between the incident monochromatic X-rays, usually a Cu K α source, with lattice spacing in a crystalline sample produces an X-ray diffraction pattern.

X-rays can be produced either when, high energy electrons interact with a metal target, usually Cu (Figure 2.8), or by induced X-ray fluorescence (XRF) by primary X-ray radiation, usually a Pb target or by radioactive decay processes.

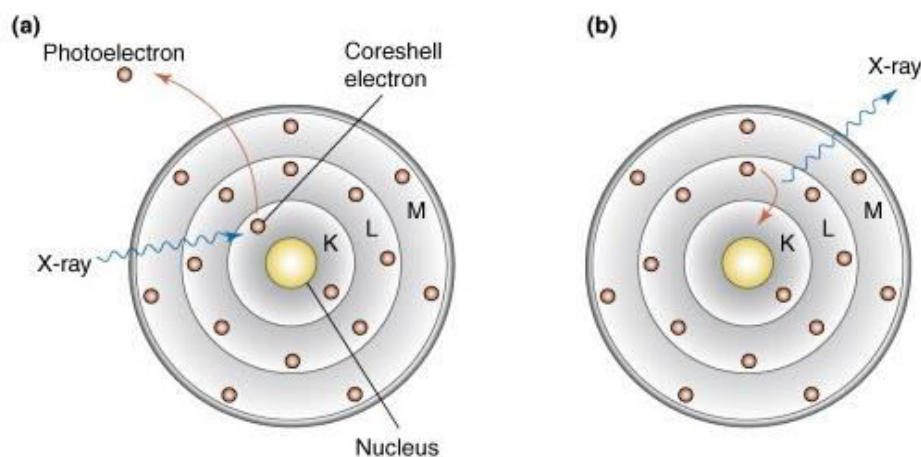


Figure 2.8: Adapted diagram of (a) X-ray excitation leads to the ejection of a core-shell electron from the atom. (b) The vacancy generated by the emission of the electron is filled by an electron in a higher energy orbital. This process results in emission of a photon with energy equal to the difference in binding energies of the two orbitals involved in the transition.³

When a high energy electron interacts with a copper target, an electron is ejected from a core shell orbital. This ejection leaves a vacancy in the orbital, which must be filled, and so an electron transition from a higher energy orbital replaces the electron lost in the lower energy orbital. X-ray photons are then produced with characteristic frequency/wavelength depending on which core shell the electron is ejected, either from a K, L, M shell.

When an X-ray photon interacts with the sample some specific conditions are required for diffraction to occur, these are: the spacing of lattice planes must be a similar wavelength to the incident radiation and the sample must be crystalline i.e. regular spacing of lattice planes. The irradiation of a Cu target emits a photon of specific wavelength from the $K\alpha$ shell which measures $1.54 \text{ \AA}$. The wavelength associated with the separation of two atoms separated by a single bond in a solid material is around this figure.

When X-rays interact with the crystal lattice (Figure 2.9) the X-rays are scattered by the neighbouring atoms which can lead to either constructive or destructive interference. Waves only interfere constructively if the scattered X-rays are arranged symmetrically and so the path difference equals to multiples of the integer wavelength $n\lambda$. In this case the incident beam is deflected by an angle 2θ , producing

a reflection spot in the diffraction pattern.

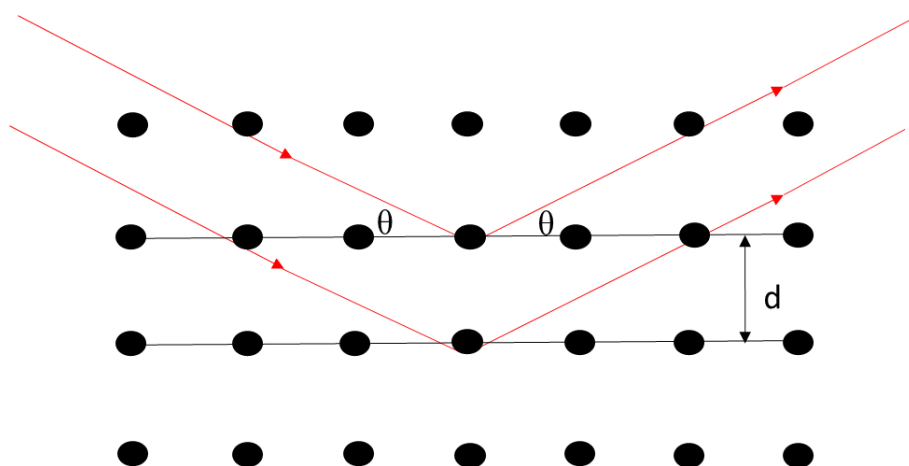


Figure 2.9. Reflection of X-rays in a crystalline solid as defined by Bragg's Law

Destructive interference only occurs when values are not integer. The path difference is calculated as $2d\sin\theta$, where d is the lattice spacing and θ represents the angle from incident radiation to give the Bragg's Law equation (eq. 2.1)

$$n\lambda = 2d\sin\theta \quad (\text{eq. 2.1})$$

Where

n = Order of reflection, an integer number of path length differences between two different X-rays

λ = Wavelength of incident X-ray radiation

d = Inter lattice spacing

θ = Angle of diffraction between incident and scattered radiation

The equation (eq. 2.1) can be applied to both single crystals and for crystalline powders. The random orientation of the crystallites in a powder results in a diffraction cone known as the Debye-Scherrer diffraction ring.

2.5.1.1. Determination of Crystallite Size *via* the Debye-Scherrer Equation

The crystallite size of a particular phase within the powdered material can be quantified using the Debye-Scherrer equation (eq. 2.2)⁴.

$$\beta_K = K\lambda/(d_{hkl} \cos\theta) \quad (\text{eq. 2.2})$$

Where

d_{hkl} = Crystallite size

β_K = Peak width = ($B_{obs} - B_{std}$)

B_{obs} = Overall peak width

B_{std} = Instrument line broadening component

K = Shape factor

λ = Wavelength of radiation used

θ = Position of the peak

The extent of peak broadening is dependent on crystallite size. Sharp peaks represent larger crystallites and broader peaks represent smaller ones. The full width half maximum (FWHM) of broader peaks can be difficult to quantify. The signal to noise ratio can also make this process difficult as well as relying on uniform crystallites throughout the sample. Crystallites are not ideal, i.e. not all the same, and so there are upper and lower limits on the crystallite sizes that can be accurately determine. The lattice strain of the crystallite and instrument contribute to line broadening along with the crystallite size. Instrument broadening can be quantified by using a crystalline silicon standard which is subject to minimal lattice strain and contains large crystallites. Therefore it can be assumed that the resultant peak is only from lattice strain of the sample and not from the instrument. This is calculated using the following equation (eq. 2.3).

$$\text{Lattice Strain} = \sqrt{(B_{\text{obs}}^2 - B_{\text{std}}^2)} / (4 \tan \theta) \quad (\text{eq. 2.3})$$

Where

B_{obs} = Overall peak width

B_{std} = Instrument line broadening component

θ = Position of the peak

2.5.1.2. Experimental Procedure

A PANalytical X'pert Pro diffractometer equipped with a Cu K α X-ray source was used throughout this research project. The conditions used for all experiments used an applied accelerator voltage of 40 kV and a current of 40 mA. Each experimental was performed between the angles of 10 ° – 80 ° 2 θ unless otherwise stated. The patterns produced were compared against reference patterns contained in the international centre for diffraction data (ICDD).

2.5.2. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface technique which is primarily used to gather information regarding the chemical composition and oxidation states of atoms. Emission of photoelectrons in deeper layers is possible > 10 nm, but the mean free energy pathway is too low and only photo-emitted electrons near the surface can escape to the vacuum and be detected⁵. Atoms absorb photons of particular energy and wavelength, $h\nu$, where h is Planck's constant, from an X-ray source. A core or valence shell electron with a binding energy (E_B) is ejected to infinity (i.e. the vacuum) with kinetic energy E_k this is related to the equation below (eq. 2.4).

$$E_k = h\nu - (E_B - \phi) \quad (\text{eq. 2.4})$$

However for the process to take place the excitation/ionisation energy required for a photoelectron emission must be greater or equal to the work function (ϕ). The work function is the energy difference between the vacuum (E_{vac}) and the Fermi energy level (E_F) which is a unique characteristic of each element (Figure 2.10). The Fermi energy level is defined as the energy of an electron in the highest occupied molecular orbital (HOMO) in the valence band at zero Kelvin (K).

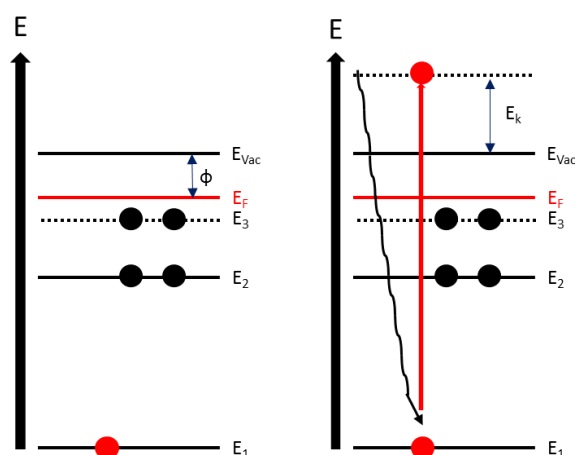


Figure. 2.10: Photoelectron emission diagram; ground state (left) and excitation process (right). E_F = fermi energy, ϕ = work function, E_{vac} = energy to release to vacuum, E_k = kinetic energy of electron.

The intensity of each peak recorded is proportional to the amount of emitting atoms at the surface, while the binding energy of each peak depends on the oxidation state and local environment of the emitting atoms.

2.5.2.1. Experimental Procedure

Throughout this investigation, XPS spectra were obtained using a ESCALAB 220 spectrometer equipped with a chromatic Al $K\alpha$ source and analyser pass energy of 100 eV. The base pressure of the analysis chamber was maintained at 3.9×10^{-8} N/m² and the energy resolution of the spectrometer was determined from the full width at half maximum of metallic gold at pass energy of 20 eV.

2.5.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM) uses high energy electrons to provide information on topology, morphology and composition of a sample. The electrons are generated using a tungsten filament source. Electrons interact with the atoms producing secondary electrons. The secondary electrons are then detected and accumulated to produce the image. Electrons are much smaller than atoms so images high resolution can be achieved as far as the nano scale. Electrons are easily scattered by atoms because they are much larger as so a vacuum is required. The vacuum reduces the amount of gas phase molecules that could interact with the electron beam and disrupt the scattered electrons resulting in a distorted image. When the electron beam interacts with the sample, scattering occurs in the near surface region, known as the interaction volume. Depending on the strength of the electron beam, different effects can be observed when the electron interacts with the material. The magnitude of the interaction volume caused by the electron beam depends on the electron acceleration voltage. The scattered electrons are detected by the detectors within the chamber. When the electron beam interacts with the sample, the collisions can be elastic or inelastic (Figure 2.11).

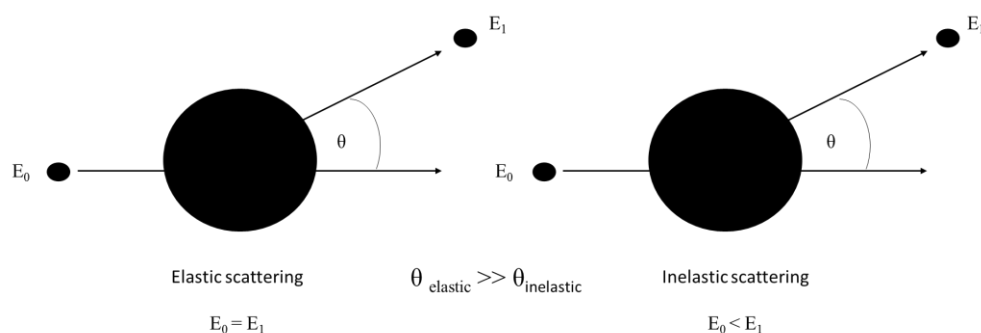


Figure 2.11: Illustrations of elastic (left) and inelastic (right) scattering. E_0 = initial energy of electron, E_1 = final energy of electron, θ = scattering angle.

Elastic scattering occurs when the reflected beam has a negligible energy loss or gain to that of the incident electron beam. Elements with a higher atomic number and lower energy electron beams give rise to elastic scattering. Inelastic collisions occur when there is greater net loss or gain in kinetic energy (E_k) of the reflected beam. Two causes of inelastic scattering are secondary electron emissions and core electron

ejection. Secondary electron emission occurs when the electron in the conduction band are loosely bound and are ejected. These electrons are produced when using higher energy electron beams. Secondly, core electron emission which is a technique used in elemental analysis by the generation of X-rays which will be discussed shortly.

2.5.3.1. Back Scattered Electron Imaging

The generation of back scattered electrons (BSE) is a result of the elastic scattering of the incident electron beam within the interaction volume of material. Therefore elemental composition can be determined and this is dependent on the atomic number, Z . Elements with higher atomic numbers result in a higher quantity of back scattered electrons produced, than an element with a lower atomic number, resulting in brighter spots for heavier element.

2.5.4. Energy Dispersive X-Ray Spectroscopy

Energy dispersive X-ray (EDX) analysis occurs from secondary electron emission of core shell electrons (Figure 2.12). The technique provides quantification on elemental composition of a solid mixture for discrete areas of interest. Therefore the analysis is often used to investigate the elemental composition of material prepared with a desired atomic ratio.

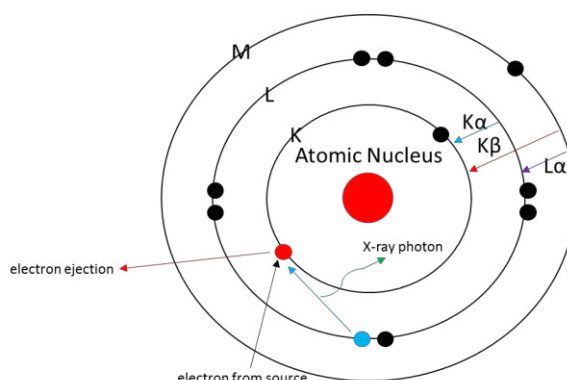


Figure 2.12: Diagram to represent the principles of X-ray generation for EDX spectroscopy.

Elements within the sample are analysed by determining the wavelength/wavelengths of the X-rays produced when the atom of a specific element encounters high energy electrons. Individual elements have a specific set of wavelengths attributed to them,

this is because each element has specific differences between the core and higher energy electron energies. When an atom is irradiated with an electron beam a core electron is emitted from the atom. An electron in a higher energy orbital of the electron that was ejected from the lower core energy orbital will relax into the lower energy orbital in which the core electron was ejected. The kinetic energy lost during this transition process releases a photon as X-ray radiation (i.e. wavelengths of the order of an angstrom, Å). the energy difference between the virtual energy states of an element is specific to each element and therefore specific X-ray wavelengths are emitted.

2.5.4.1. Experimental Procedures

SEM analysis was performed using the Carl Zeiss EVO 40 fitted with backscattered (BS) and secondary electron (SE) detectors. An extra-high tension (EHT) of 25 keV was used for all sample imaging. All samples were mounted on carbon Leit adhesive discs and the images were obtained using both detectors whilst working distances and probe currents were adjusted accordingly to give optimum picture quality and resolution. EDX analysis was performed using the Oxford EDX analyser combined with the Carl Zeiss EVO 40 SEM whilst using the BSD. The working distance was fixed at 9 mm, EHT to 25 keV and the I-probe current, which determines ultimately the size of the spot, and was set to 25 nA to produce the X-rays.

2.5.5. Ultra-Violet/Visible Spectroscopy

2.5.5.1. Luminescence

Ultra-violet/visible (UV-vis) spectroscopy describes the absorption or reflectance in the UV-vis spectral region. Fluorescence and absorption spectroscopy are complementary to each other, in the case of fluorescence electronic transitions occur from the excited state to the ground state. Figure 2.13.

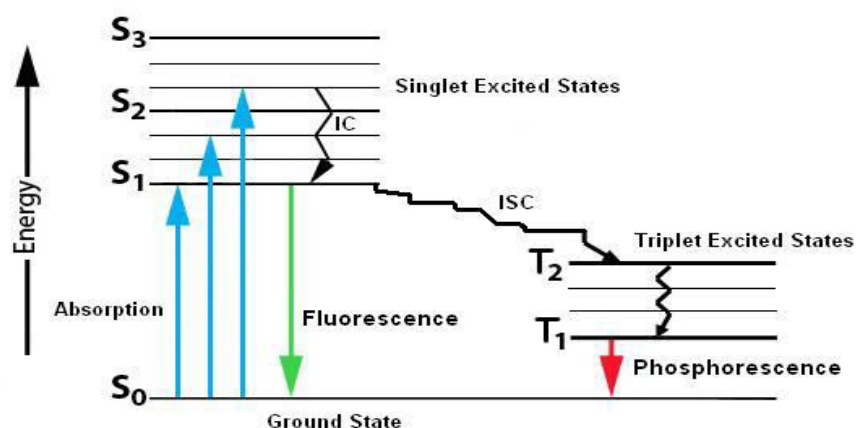


Figure. 2.13: Jablonski diagram showing the difference between absorption and luminescent spectroscopy using ultra-violet/visible radiation. S_0 = singlet ground state (GS), S_{1-3} = Singlet excited vibrational states, IC = internal conversion, ISC = inter system crossing, T_{1-2} = triplet vibrational states.

For luminescence the species in the excited state releases energy when returning to the ground state and can either be released in the form of radiative decay⁶, i.e. a photon, as luminescence, or through non-radiative decay by an energy transfer to another molecule or quencher⁷. The species requires a very specific amount of energy to achieve the excited state which is referred to as the excitation wavelength. Crucially, the molecule must absorb a photon of the correct wavelength for the transition to occur, from a vibrational ground state to a vibrational excited state; which is usually the first vibrational excited state with lowest energy. However electrons can occupy higher vibrational energy levels of the excited state but these will rapidly fall down to the lowest vibrational level, and to the singlet excited state, by colliding with neighbouring species. The spin of the excited electron remains unchanged as it falls to the lowest vibrational level resulting in a spin allowed transition. This process is known as internal conversion, IC. The electron in the first singlet excited state can fall to the ground state by radiative decay which occurs from two different types of luminescence processes known as fluorescence and phosphorescence.

Fluorescence occurs when the electron in the singlet excited state decays directly to ground state with the emission of a photon. The spin of the electron is conserved and

as a result a spin-allowed relaxation process occurs due to the Pauli exclusion principle. This transition is quick and so lifetimes are short⁷ around 10^{-8} – 10^{-9} s.

Phosphorescence occurs when an electron from the singlet excited state decays indirectly to the ground state *via* a vibrational triplet excited state of lower energy to that of the singlet excited state. This process is known as intersystem crossing, ISC. The species in the triplet state changes the spin orientation of the excited electron; therefore this electron has the same spin as the electron in the ground state resulting in a spin-forbidden relaxation process. This transition is therefore slower and so lifetimes are much longer⁷ than fluorescence, around 10^{-6} - 10^1 s.

The emitted light from these two processes, fluorescence and phosphorescence, are lower in energy (longer wavelength) than the absorbed light for excitation due to the energy cost of IC and ISC. This results in a shift in wavelength known as Stoke's shift. (Figure 2.14) which refers to the difference in wavelength between the incident and emitted light⁸.

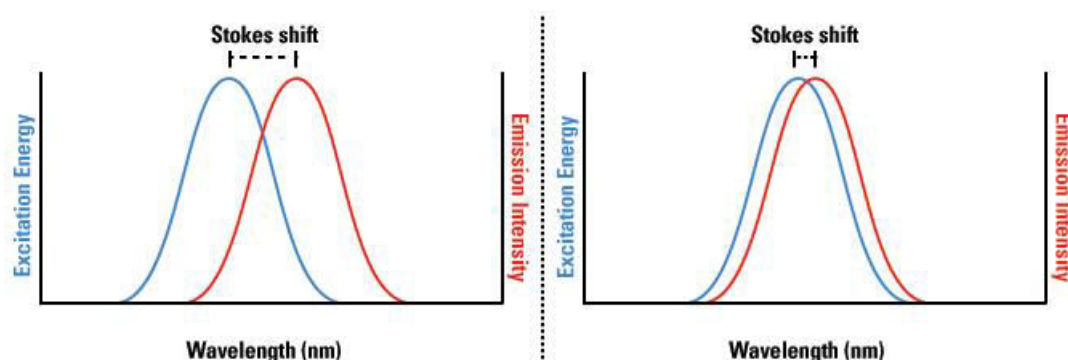


Figure 2.14: A representation of Stokes shift's of different species, large Stoke shift (left) and small Stoke shift (right), which is the difference in wavelength of emitted and absorbed light.

2.5.5.2. Absorption

When a species absorbs a photon of correct wavelength an electronic transition occurs, this process is known as absorption. An electron is promoted from the ground state, usually the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO) as this transition is the lowest in energy, to the excited

state, and only occurs when the excitation energy is greater or equal to the the energy of the electron is the ground state (GS). The energy, E , equals the diffence in the excitation (ES) and grounds state (GS) energy (Figure 2.15)⁹.

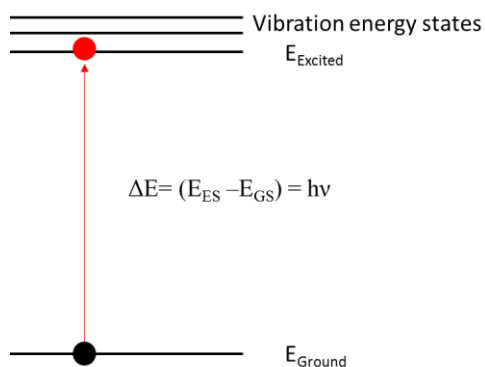


Figure 2.15: The excitation process

The number of molecules capable of absorbing the correct wavelength of light is proportional to the extent of absorption. This is described as the Beer-Lambert Law (Equation.2.5).

$$A = \log_{10} (I_o/I) = \epsilon cl \quad \text{eq. 2.5}$$

Where

A = Absorbance

I_o = Intensity of incident light

I = Intensity of reflected light

ϵ = Molar extinction coefficient

c = Molar concentration

l = Path length of sample

The term $\log (I_o/I)$ is also referred to absorbance. The molar extinction coefficient, ϵ , is a property of the molecule or atom during the electronic transition and is independent of the external variables including, temperature, concentration and pH.

2.5.5.3. Selection Rules

2.5.5.3.1. Spin Selection Rule

The spin selection rule is defined as, the incident electromagnetic field radiation cannot change the relative spin orientation of the electrons in a complex, $\Delta S = 0$, this is known as a spin-allowed transition and occurs between states of same spin multiplicity. When $\Delta S \neq 0$ this is a spin-forbidden transition and occurs between states of different spin multiplicity. The spin selection rule is relaxed by spin-orbit (SO) coupling. The intensities of spin-forbidden transitions relative to spin-allowed transitions increases with increasing SO coupling constants, however these are very weak¹⁰.

2.5.5.3.2. The Laporte Selection rule

In a centrosymmetric molecule or ion (with symmetry element i), the only allowed transitions are those that have a change in parity ($u \rightarrow g$, $g \rightarrow u$). Transitions where there is no change in parity $s-s$, $p-p$, $d-d$, or $f-f$ are orbitally forbidden, this is better known as the Laporte selection rule¹⁰. Transitions should only involve one electron $\Delta L = \pm 1$, and should be vertical, where the species has no time to change in nuclear distance during the transition, known as the Frank Condon Principle¹¹.

2.5.5.4. Experimental Procedures

DR-UV-vis spectra were collected using a Harrick Praying Mantis cell mounted on a Cary 4000 spectrophotometer. The spectra were collected from 900 to 200nm at a scan speed of 60 nm min⁻¹. Background correction was carried out using a fluoropolymer powder (Spectralon). All the powder samples were mounted on a 3 mm diameter diffuse reflectance sampling cup.

2.5.6. Raman Spectroscopy

Raman Spectroscopy is concerned with the change in frequency, $\Delta\nu$, of electromagnetic radiation of scattered by molecules^{12,13}. The technique is used to determine the vibrational, rotational modes in a system. The frequency of the incident light, ν_o , and the reflected light from scattering, ν_r , can cause a raman shift, $\Delta\nu$ (Equation 2.6)

$$\Delta\nu = \nu_o - \nu_r \quad \text{eq 2.6}$$

Where

$\Delta\nu$ = Change in frequency (Raman Shift)

ν_o = frequency of the incident light

ν_r = frequency of the reflected light

The shift can be either positive or negative in sign and the magnitude is referred to as the Raman frequency. The technique relies on the inelastic scattering or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared (NIR), or near ultraviolet (NUV). The light interacts with the bonding electrons and causes vibrations and rotations of the molecule. Not all molecules are Raman active there are selection rules which must be followed. The molecule must be non-centrosymmetric, i.e. does not possess the symmetry element, i , in order to be Raman active. Raman active species must also have a changeable polarisability (α). When a molecule is irradiated the interaction and the consequent scattering can either be elastic and inelastic as shown in Figure 2.16.

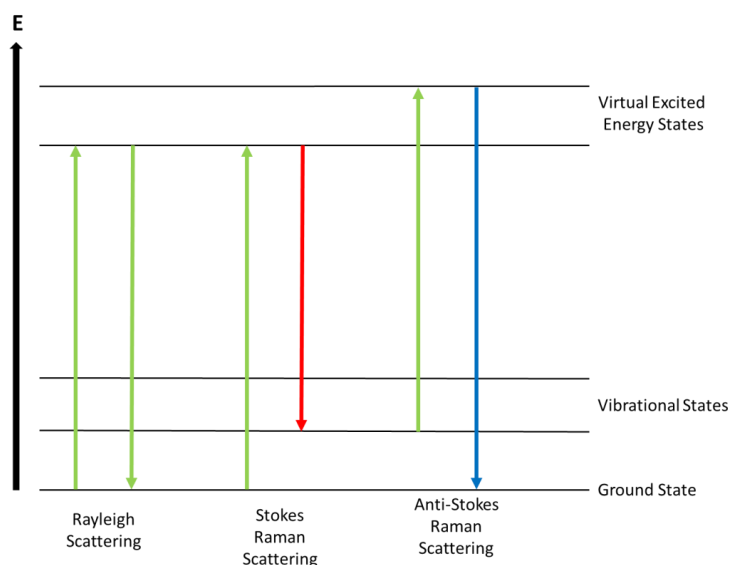


Figure. 2.16: Raman energy level diagram showing Rayleigh, Stokes and Anti-Stokes scattering.

For elastic scattering to occur the kinetic energy (E_k) of the scattered photon must be comparable to the incident radiation and as a result have similar frequencies. This is referred to as Rayleigh scattering. The transition of virtual energy states in this case is contributed to the excitation from the ground state to a higher virtual energy level and a relaxation back to the ground state. If the scattering is inelastic this means that there is a net loss or gain in kinetic energy from the scattered molecule. If the molecule loses energy and therefore the scattered photon gains kinetic energy, then anti-Stokes frequencies are observed. If the molecule gains energy and therefore the molecule losses energy, then Stokes frequencies are observed.

2.5.6.1. Selection Rules

2.5.6.1.1. Rotational

If a molecule is isotopic, pure rotational Raman Effect is not possible. The polarisability (α) needs to change in order to become Raman active. The polarisability of a molecule in an electric field is given as:

$$\mu = \alpha E$$

Where μ is the induced electric moment created by the incident electric field, E . E and μ are both vectors and as long as they are in the same direction α becomes a scalar

quantity. For a linear molecule, $\Delta J = \pm 2$, where J is the rotational quantum number. Classically, by symmetry, a rotation along the axis in line with the nuclei by half a turn produces the identical molecule and a full turn once again, the frequency of change is therefore two and coincides with the quantum model. Therefore of non-linear molecules, $J = \pm 1$ because one full rotation is required to produce the same molecule dipole^{12, 13}.

2.5.6.1.2. Vibrational

The applied energy field will cause a molecule to vibrate in a number of ways known as the vibrational mode. Molecules with a number of atoms, N , which are linear possess $3N - 5$ degrees of vibrational modes, or more commonly known as degrees of freedom. Non-linear molecules have $3N - 6$ degrees of freedom¹⁴ (Figure 2.17).

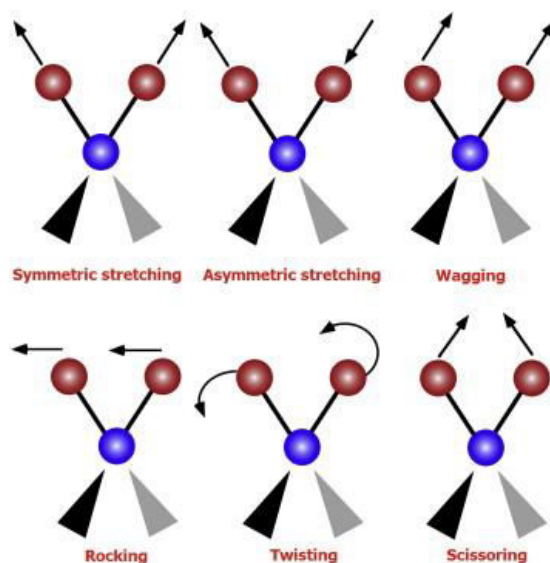


Figure 2.17. Vibrational modes associated to a molecular dipole moment change detectable in an IR absorption spectrum. In addition to the two stretching modes, the four different bending vibrations are showed, adapted from Marcelli *et. al.*¹⁵.

Molecules that absorb specific frequencies that are characteristic to their corresponding structure resonate, this is known as the resonant frequencies, i.e. the frequency of the absorbed radiation is the same as the transition energy of the bond that vibrates. The energy required to make a bond resonate is determined by the masses of the atoms, bond strength and the associated *vibronic* coupling^{14,11}.

2.5.6.2. Experimental Procedure

Raman spectra were obtained using a Renishaw Ramascope fitted with a Spectraphysics argon ion laser ($\lambda = 514 \text{ nm}$) at a power of 20 mW. An Olympus BH2-UMA microscope was utilized for focussing the laser.

2.5.7. Temperature Programming Methods

Temperature programmed methods are used for thermal analysis, but can also be used for kinetic investigations of heterogeneous catalytic reactions by controlling the temperature in the surrounding environment. Techniques based on a controlled temperature program can aid the understanding of interactions of substrates and the catalyst by understanding fundamental properties; such techniques are temperature-programmed reduction (TPR)¹⁶, temperature-programmed oxidation (TPO)¹⁶ and thermogravimetric analysis (TGA).^{17,18,19}

2.5.7.1. Temperature Programmed Reduction and Oxidation

Temperature programme reduction (TPR) measures the reaction of a reductant¹⁶. Throughout this thesis 10 % H_2/Ar was used at various temperatures. The sample must be reducible in order for reduction to take place. The opposite is true for oxidation (TPO), throughout this thesis a mixture of 10% O_2/Ar was used.

The technique operates by flowing the gas while methodically increasing the temperature of the sample. The initial concentration of the gas is known before the start of the experiment and therefore any decrease in the concentration is monitored during the temperature increase. This information can aid the understanding of the catalyst properties and can be valuable when explaining the catalytic activity *i.e.* phase changes and redox reactions.

2.5.7.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measures the physical and reactive properties of material as a function of the temperature using a temperature programmed ramping method.²⁰ The technique is coupled to a Differential scanning calorimetry (DSC) which monitors the phase changes associated with either absorption or evolution of heat, *i.e.* exothermic or endothermic reactions.

In thermogravimetric analysis (TGA) the weight of a heated sample is measured as a function of time and temperature. Volatile products results in mass loss and oxidation or absorption results in weight gain. The derivative of this curve is normally calculated, as the loss of weight can be associated with peaks. The TGA profile provides information on transformation, decomposition or reaction that occur during the temperature ramp.

2.5.7.3. Experimental Procedures

A Quantachrome Thermo TPDRO 1100 was used to collect the temperature programmed reductions/oxidations presented throughout the thesis. Samples were pre-treated in flowing argon (20 ml min^{-1} , $20 \text{ }^{\circ}\text{C min}^{-1}$) at $110 \text{ }^{\circ}\text{C}$ for 40 minutes. After pretreatment the catalysts were analysed using a temperature range, unless otherwise stated, from ambient temperature to $800 \text{ }^{\circ}\text{C}$. A $10\% \text{ H}_2/\text{Ar}$ for TPR or $10\% \text{ O}_2/\text{He}$ for TPO with a flow of 20 ml min^{-1} was used with a heating ramp of $10 \text{ }^{\circ}\text{C min}^{-1}$ unless otherwise stated.

A Perkin Elmer TGA 7 was used for the analyses of the catalysts pre and post reactions. The analysis was performed in air (50 ml min^{-1}) from 30°C to 800°C ($5^{\circ}\text{C min}^{-1}$), unless otherwise stated.

2.5.8. Carbon-Hydrogen-Nitrogen Analysis

Carbon-Hydrogen-Nitrogen (CHN) analysis is used to identify the elemental composition of a material²¹. The technique uses a combustion process using pure oxygen under static conditions. An inert, usually helium, which is chemically inert and has a high coefficient of thermal conductivity used as the reference gas, is used to

carry the combustion products through the system. A reduction tube is fitted to reduce nitrous oxide to nitrogen and the residual oxygen is removed. The gas sample are then homogenized in a mixing chamber at known volume, temperature, and pressure and is analysed using a TCD. An absorption trap removes water from the gas and the differential signal produced pre-and-post trap determines the concentration of water in the sample, and therefore amount of hydrogen in can be calculated. The similar process is used to analysis the carbon content by measuring CO₂. At this point the gas mixture consists of consists helium and nitrogen which is then detected by the TCD and the concentration is calculated²².

2.5.9. Experimental Procedure

Samples were analysed by Exeter Analytical Inc. using the CE-440 Elemental Analyzer. Samples were weighed, typically 1-3 mg, into disposable tin or aluminum capsules. The samples were injected into a high temperature furnace and combusted in pure oxygen under static conditions. An additional amount of oxygen was added at the end to ensure total combustion of all inorganic and organic compounds²².

2.6. References

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Chapter 3: The Reaction of *n*-octane with the Johnson Matthey Iron Molybdate Catalyst

3.1. Introduction

The reaction of *n*-octane with the iron molybdate catalyst, supplied by Johnson Matthey (JM), was investigated in detail in this chapter. The catalyst composition of the mixed metal oxide $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{MoO}_3$ is Mo:Fe 2.75:1. The data was supplied by Johnson Matthey using X-ray fluorescence (XRF) spectroscopy and confirmed using EDX. The chapter also focuses on the subtle manipulation of the reaction parameters to produce products of high commercial value. Those parameters include the change in the temperature of the catalyst bed, the carbon to oxygen (C:O) ratio, which represents the number of carbon atoms to oxygen atoms available in the gas phase, the gas hourly space velocity (GHSV) and the change in partial pressure of octane and oxygen. The chapter also includes detailed characterisation of the JM iron molybdate catalyst pre and post reaction in addition to *in situ* characterisation under reaction conditions to examine the catalyst in depth. The products were identified using GC-*EIMS* and were quantified using on-line gas chromatography (GC) and therefore the activity and selectivity of the catalyst under varying reaction conditions was determined.

3.2. Changing Reaction Parameters

3.2.1. Temperature

Catalytic reactions were carried out between 350 °C and 550 °C, and unless stated otherwise, were increased in 50 °C increments at a ramp rate of 20 °C min⁻¹. The reactor was purged and stabilised under reaction conditions for 1 h before each

temperature ramp and subsequent injection. The catalyst bed temperature was monitored *via* a K-type thermocouple inserted just below the catalyst bed and monitored using data acquisition software, PicoLog TC-08 by Pico Technology.

3.2.2. Carbon to Oxygen Ratio and Partial Pressures

The carbon to oxygen (C:O) ratios used throughout this investigation were, 2:1, 8:1, 12:1 and 8:0, where 8:0 represents anaerobic/dehydrogenation (DH) conditions. These ratios were calculated using the percentage volume (v/v %) of octane in the feed which was *ca.* 1 % and 4 % unless otherwise stated and the oxygen concentration was adjusted to produce the desired ratios.

3.2.3. Gas Hourly Space Velocity

The gas hourly space velocity (GHSV) was investigated throughout this chapter and is explored in more detail in chapters 4 and 5. Throughout all investigations in this thesis 0.2 ml of pelletized catalyst (10 tons, 800-1000 μm) was used in all reaction studies, see Chapter 2 for details, The GHSV was varied by adjusting the flow rates using Bronkhorst mass flow controllers (MFCs) to give 1000 h^{-1} , 4000 h^{-1} and 6000 h^{-1} .

3.3. Experimental

The JM iron molybdate catalyst with a Mo to Fe atomic ratio of 2.75:1 was prepared by a co-precipitation which is detailed in *Chapter 2*.

3.4. Calibration of *n*-Octane

Experiments were carried out below the lower explosive limit of *n*-octane. To prevent the reactant composition entering the flammability range, the system was purged with *n*-octane and helium and then the oxidant was introduced in to the feed. Calibrations of *n*-octane were completed using a syringe and syringe pump and the desired concentrations were produced by adjusting the helium flow. Oxygen was also calibrated by adjusting the flow rates of oxygen and helium MFCs to produce the desired concentrations and corresponding calibration curve (see Appendix Figs.1 and 2).

3.5. Results and Discussion

3.5.1. Catalytic Activity of the JM Iron Molybdate Catalyst

3.5.2. A Temperature Dependence Study

The JM iron molybdate catalyst was tested with *n*-octane (0.2 ml of catalyst, 1 % octane, C:O = 8:1, 1000 h⁻¹) and the temperature was increased from 350 °C to 550 °C as shown in Figure.3.1.

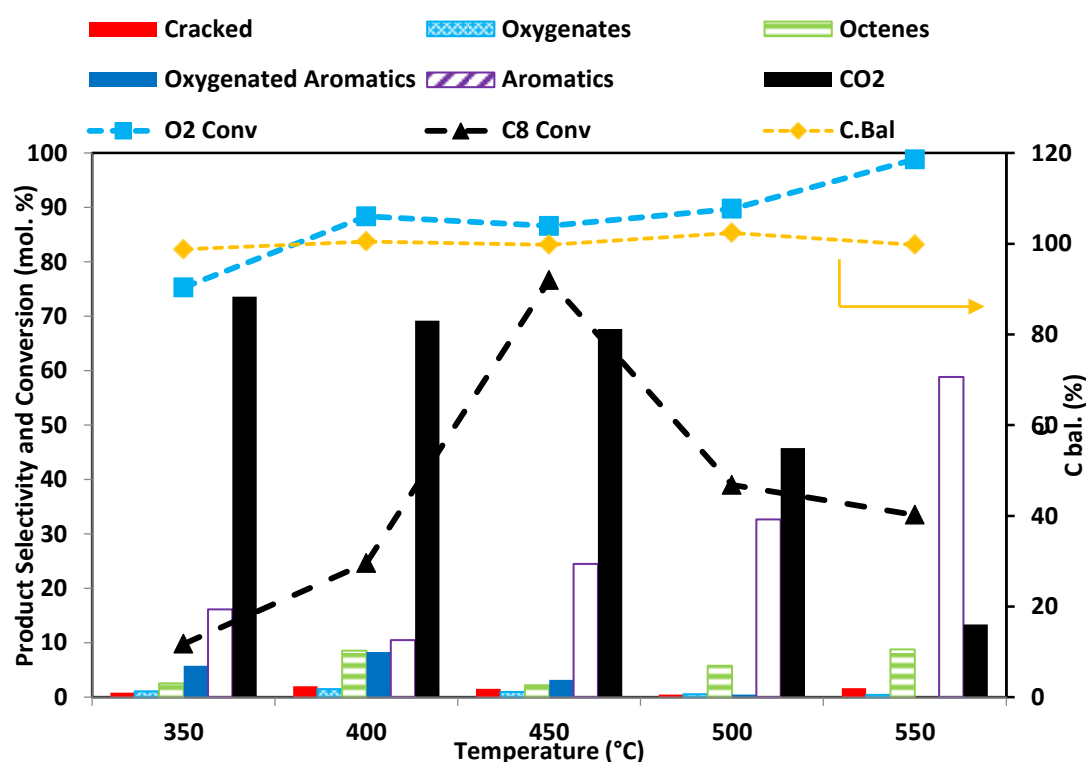


Figure. 3.1: Reaction of 1 % *n*-octane (C:O 8:1, GHSV 1000 h⁻¹) with JM iron molybdate catalyst. Temperature range from 350- 550 °C.

The *n*-octane (-▲-) conversion increased with temperature between 350 °C and 450 °C. However, above 450 °C the conversion of octane decreased, possibly due to the increased consumption of oxygen (-■-) in the gas phase. The system has become oxygen limited and therefore lattice oxygen from the catalyst is no longer replenished. As the reaction is known to proceed through an oxidative dehydrogenation Mars-van Krevelen (ODH-MvK) mechanism^{1,2} the catalyst deactivates when the lattice oxygen are no longer replenished. This process requires

oxygen from the gas phase oxidising the bulk of the catalyst which then reorder to replace surface oxygen lost in the dehydrogenation process. At 450 °C a dramatic increase in conversion to 76 % was observed. This was attributed to the phase change from $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ to $\text{FeMoO}_4\text{-MoO}_2\text{-Mo}_4\text{O}_{11}$, where there are enough lattice oxygens available in the lattice to last an hour before the conversion decreases under the operating conditions used. The phase change is complemented by *in situ* XRPD from previous work with *n*-decane³ and under similar reaction conditions with *n*-octane, shown in Figure 3.2.

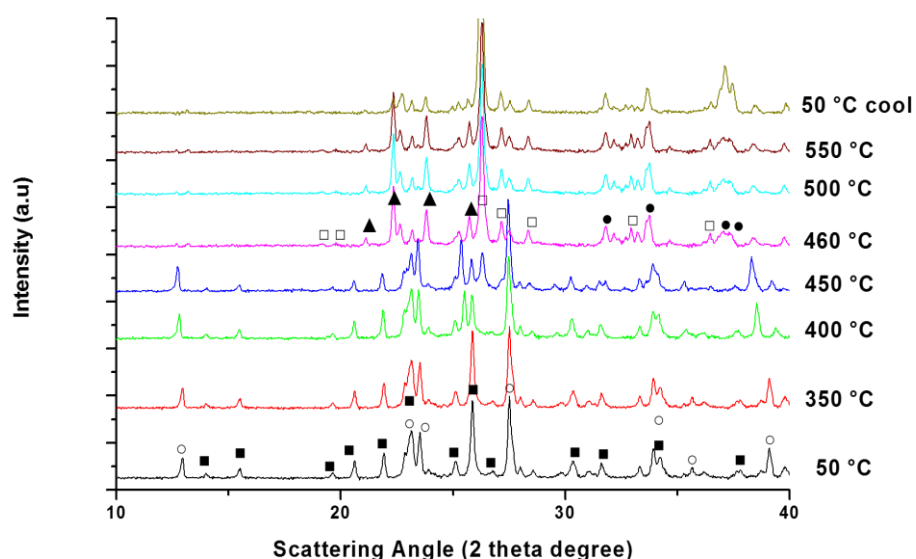


Figure 3.2: *In situ* XRPD of the JM iron molybdate catalyst with *n*-octane under aerobic conditions (C:O ;8:1) up to 550 °C. Phases present: MoO_3 (o), $\text{Fe}_2(\text{MoO}_3)_4$ (■), $\beta\text{-FeMoO}_4$ (□), Mo_4O_{11} (▲), and MoO_2 (●). A fast phase reduction at 460 °C (within 40 min) is observed with conversion of $\alpha\text{-Fe}_2(\text{MoO}_4)_3$ to $\beta\text{-FeMoO}_4$, MoO_2 and Mo_4O_{11} .

The fresh JM iron molybdate catalyst, which is represented by the black line at 50 °C, contains both MoO_3 (o) and $\text{Fe}_2(\text{MoO}_3)_4$ (■) phases. The reflections observed at 12.8° (452 Å) and 33.8° (138 Å) relate to the lattice planes (200) and (111) of the MoO_3 phase. The peaks at 20.5° (410 Å), 21.8° (395 Å), 23.0° (202 Å) and 31.4° (143 Å) correspond to the lattice planes (120), (214), (220), (032) and correspond to the $\text{Fe}_2(\text{MoO}_3)_4$ phase⁴. When the temperature was increased to 460 °C the JM iron molybdate catalyst underwent a reductive phase transition in the presence of *n*-octane. This reductive phase transition seems to be more facile compared with the previous studies with *n*-decane suggesting that *n*-octanes reducing nature is comparatively greater. The phase reduction from $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 to the

reduced β -FeMoO₄ ($\square$) Mo₄O₁₁ ($\blacktriangle$) and MoO₂ ($\bullet$) is shown by the pink line. Figures 3.3 and 3.4, courtesy of Marco Conté, provides the whole diffractogram (10° - 80 °) and a smaller detailed region (10.5 ° - 17.5 °) respectively. The time-on-line (TOL) *in situ* XRPD study used *n*-octane under oxidative conditions (C:O 8:1, GHSV= 3250 h⁻¹) to establish how quickly the reductive transition occurs at 460 °C.

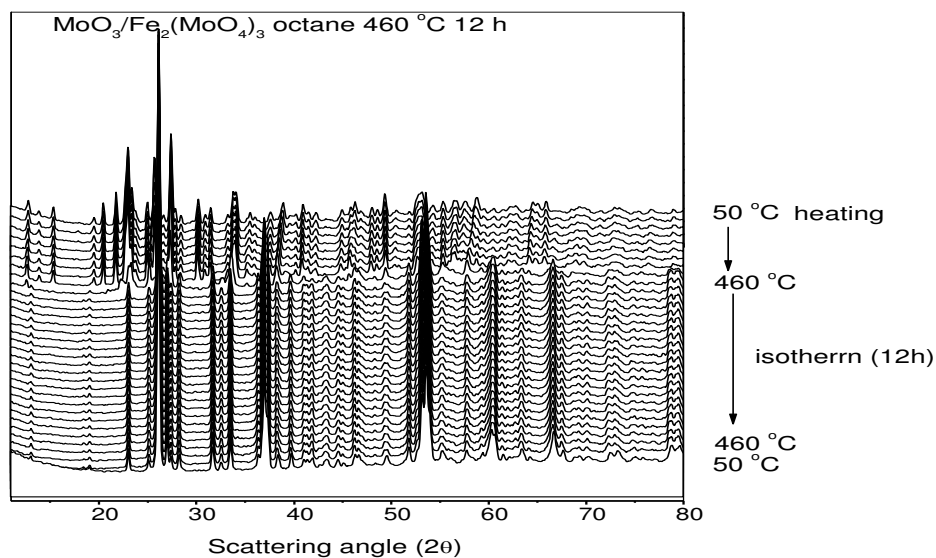


Figure 3.3. The reaction using the JM iron molybdate catalyst with *n*-octane under aerobic conditions (0.3% O₂) up to 460 °C and held for 12h. A fast phase reduction (within 40 min) is observed with conversion of α -Fe₂(MoO₄)₃ to β -FeMoO₄, MoO₂ and Mo₄O₁₁.

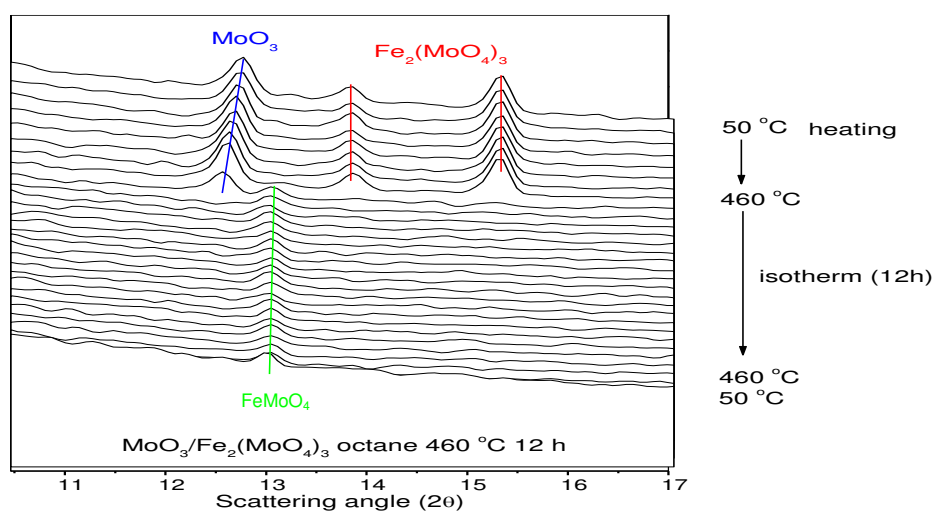


Figure 3.4. Spectral region 10.5-17 ° 2θ during the reaction of the JM iron molybdate catalyst with *n*-octane under aerobic conditions (0.3% O₂) up to 460 °C.

A very fast reduction of bulk $\text{Fe}_2(\text{MoO}_4)_3$ to FeMoO_4 was observed within the first scan when elevated to 460 °C. This showed that the phase transition occurs within the first 40 minutes, and also seems faster than the corresponding *n*-decane reaction data³. However, unlike the experiments in presence of *n*-decane, the MoO_3 phase was not detected suggesting reduction to MoO_2 . The same procedure was used to test the stability of the JM iron molybdate under oxidative reaction conditions, below 460 °C. Figures 3.5(10° - 80 °) and 3.6 (10.5 ° – 17.5 °) shows diffractograms collected by *in situ* XRPD oxidative experiments with *n*-octane at 350 °C.

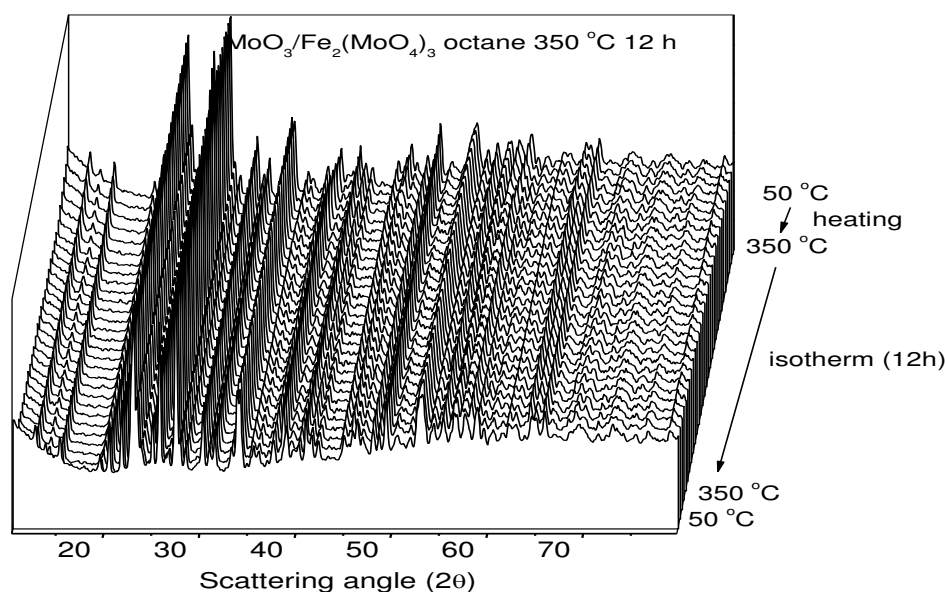


Figure 3.5. The reaction using the JM iron molybdate catalyst with *n*-octane under aerobic conditions (0.3% O_2) up to 350 °C and held for 12h. No apparent phase changes of the $\text{MoO}_3/\text{Fe}_2(\text{MoO}_4)_3$ catalyst is detected.

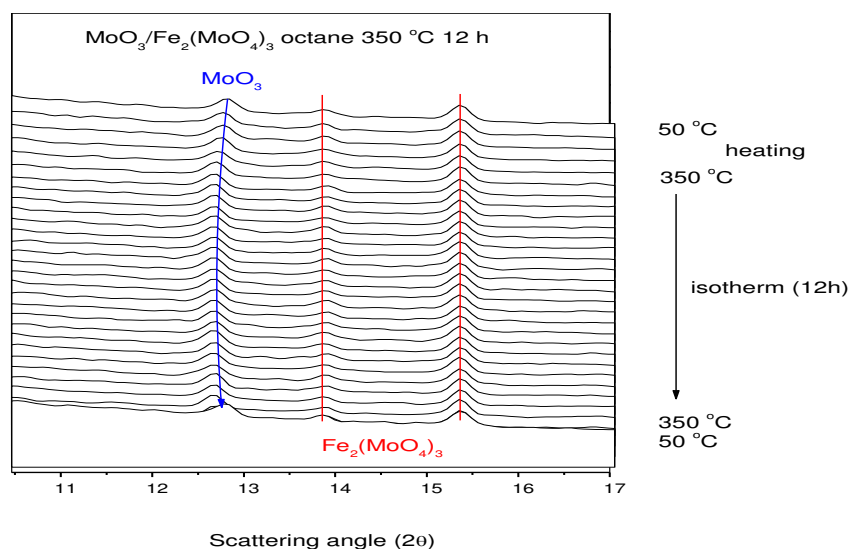


Figure 3.6. Details for the spectral region $10.5\text{--}17^\circ 2\theta$ during the reaction of the JM iron molybdate catalyst with *n*-octane under aerobic conditions ($0.3\% \text{O}_2$) up to 350°C . It is confirmed that no apparent modification of the JM iron molybdate catalyst is detected.

Both diffractograms (Fig. 3.5 and 3.6) showed that the bulk structure of JM iron molybdate remains unchanged during the isothermal treatment for 12 h at 350°C . This observation was also observed when *n*-decane was used, where both $\alpha\text{-Fe}_2(\text{MoO}_4)_3$ and $\alpha\text{-MoO}_3$ phases were preserved³.

The *in situ* XRPD experiments, concerning the bulk reactivity of JM iron molybdate catalyst with *n*-octane, show that there are two distinct phase regions. At temperatures below 460°C the MoO_3 and $\text{Fe}_2(\text{MoO}_4)_3$ phases are preserved and at high temperatures, above 460°C , the catalyst undergoes a reductive phase change to FeMoO_4 , MoO_2 and Mo_4O_{11} . Potentially the latter reduced phases are responsible for the high selectivity towards the non-oxygenated aromatics, especially at 550°C .

The aromatic fraction at temperatures $\leq 450^\circ\text{C}$ (Fig. 3.1) is predominantly comprised of oxygenated aromatics (the aromatic selectivity distribution is shown in Fig. 3.7) which was also shown with the previous studies with *n*-decane³.

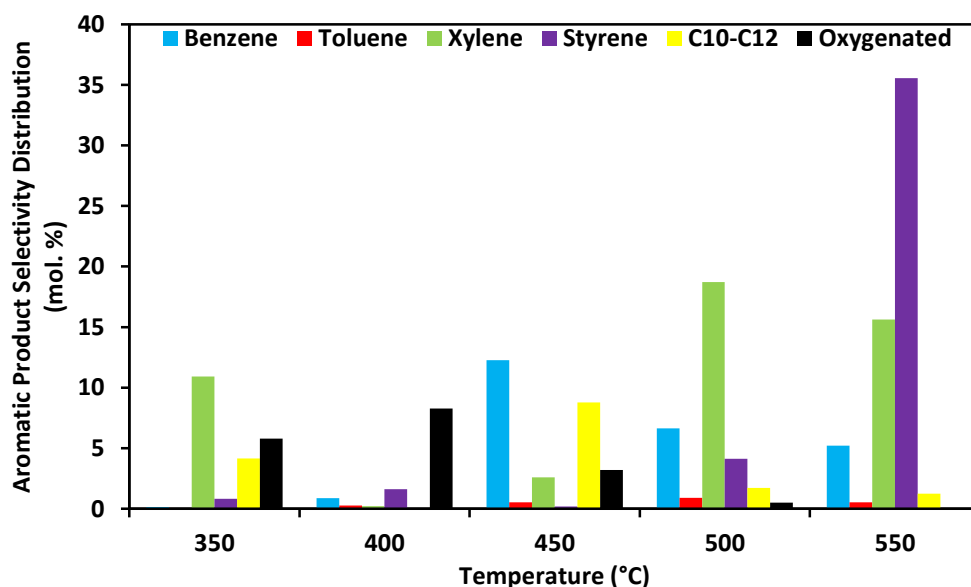


Figure 3.7: Aromatic product selectivity distribution of the reaction of 1 % *n*-octane (C:O 8:1, GHSV 1000 h^{-1}) with the JM iron molybdate catalyst.

The oxygenated aromatics produced from *n*-octane included a mixture of benzaldehyde, methylbenzaldehyde and other trace oxygenated aromatics. When the temperature was increased to 400 °C the selectivity towards the non-oxygenated aromatics increased. The oxygenated aromatics and the non-oxygenated aromatics were identified using GC-MS (Appendix Fig. 3). When the temperature was increased to 500 °C and 550 °C the CO_x selectivity decreased while the selectivity to aromatics increased. The increase in non-oxygenated aromatic selectivity with temperature is suggested to be influenced by the oxygen mobility of the lattice⁵⁻⁷ and therefore facile ODH-MvK.

With increasing temperature an increase in non-oxygenated aromatic selectivity was observed. Holger *et al.*⁵⁻¹³ have also reported similar trends under similar systems, which was also highlighted in Chapter 1. It was thought the alkane molecule dehydrogenates to produce the corresponding alkene. The alkene, depending on the position of the double bond, then cyclises and further dehydrogenates to produce the aromatics^{6,7}.

At 550 °C the selectivity to the aromatics increased to 59 % and the dominant product produced was styrene (36 %), whilst CO_x decreased to *ca.* 13 %. At 550 °C the oxygen in the gas feed was consumed, and as a consequence the reaction has become oxygen limited which resulted in a decrease in *n*-octane conversion. This suggests that the oxygen species responsible for the selectivity to aromatics is the lattice oxygen via the MvK mechanism, and that CO_x is produced from adsorbed oxygen.

3.5.2.1. Summary

The JM iron molybdate catalyst was reacted with *n*-octane under ODH conditions. With increasing temperature the catalyst underwent a reductive phase change at 460 °C from Fe₂(MoO₄)₃-MoO₃ to FeMoO₄-MoO₂-Mo₄O₁₁ which was verified by *in situ* XRPD. The spike in conversion is associated with the reductive phase change. The FeMoO₄-MoO₂-Mo₄O₁₁ phase is thought to be selective to non-oxygenated aromatics, whereas the Fe₂(MoO₄)₃-MoO₃ catalyst is responsible for the production of oxygenated aromatics and CO_x. Similarly this observation was also reported using *n*-decane³. At temperatures ≥ 450 °C the selectivity to CO_x decreased, particularly at 550 °C, due to oxygen consumption. The oxygen in the feed is required to replenish the

oxygen lost from the catalyst during dehydrogenation (DH) *via* the ODH-MvK mechanism. This suggests that the lattice oxygen are required for DH resulting in alkene/aromatic production and the gas phase adsorbed oxygen is responsible for oxygenated aromatics and CO_x.

3.5.3. Catalyst stability at 550 °C: DH and ODH to determine the origin of CO_x

The reaction between *n*-octane and the JM iron molybdate catalyst under ODH conditions (1 ml catalyst, 12.8 ml/min; GHSV = 1000 h⁻¹, C:O = 8:1) was completed for 37 h at 550°C to test the stability of the catalyst.

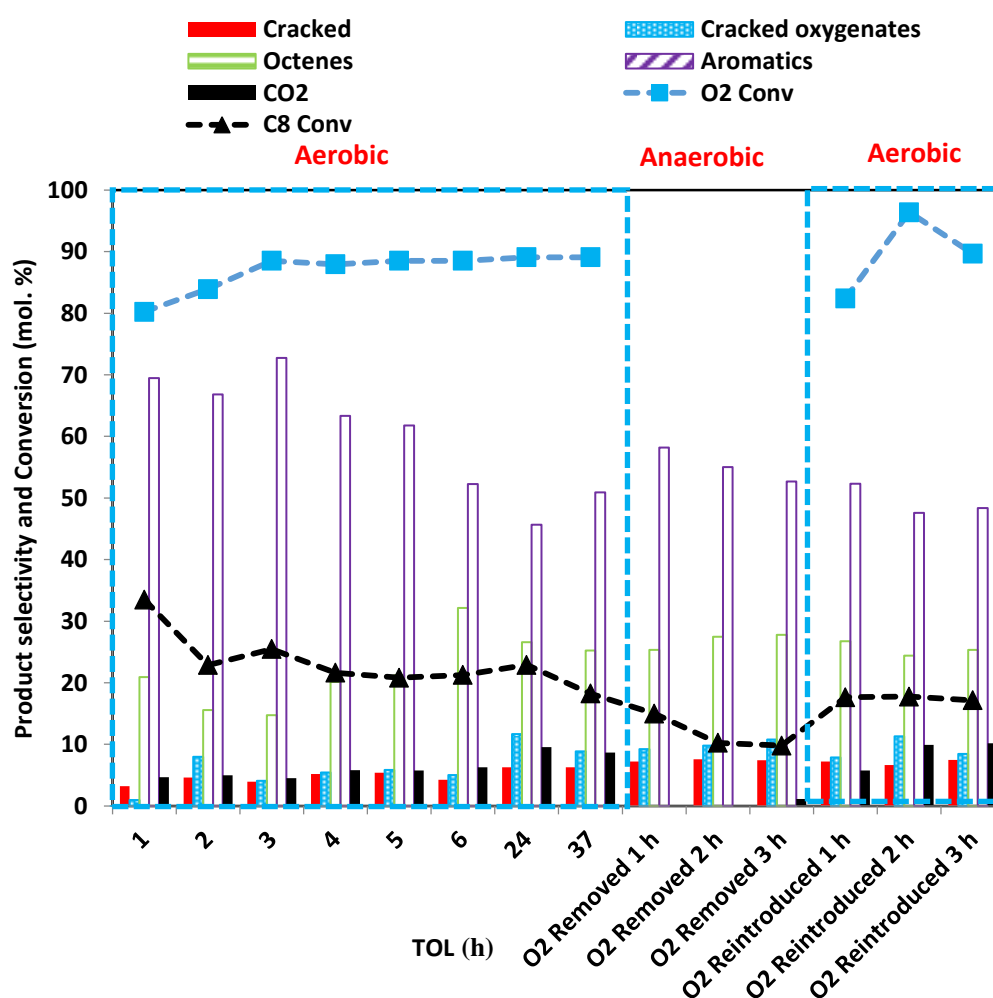


Figure 3.8: TOL analysis at 550 °C. Conditions: 1% *n*-octane (C:O 8:1, 1000 h⁻¹) with JM iron molybdate catalyst. Anaerobic conditions after the 37h period for 3h, and oxygen was reintroduced for 3h after the anaerobic period.

After an initial stabilisation period the *n*-octane conversion was stable at *ca.* 20 % $\pm$ 1.5% over the 37 h aerobic reaction period. The selectivity towards the aromatics decreased with time whilst octene selectivity increased. This suggests blocking of active sites for further ODH to the aromatics. Coke formation is likely to prevent further dehydrogenation from the alkene to the aromatics. It is often reported that coke formation causes catalyst deactivation¹⁴⁻¹⁶. However it has also been reported that coke can be active for alkane dehydrogenation¹⁷, which is discussed in detail in Chapter 4. Octene selectivity increased whilst aromatics decreased due to the lack of active oxygen sites available for aromatisation. The production of CO_x is suppressed at 550 °C as shown in Figure 3.1.

Oxygen was removed from the feed for 3 h which resulted in an immediate decrease in conversion from 15% to 10 %. On switching from aerobic to anaerobic conditions selectivity towards aromatics and octene increased while CO_x decreased to less than 1%. This suggests that the production of CO_x is due to surface oxygen species adsorbing-desorbing from the feed onto the surface of the catalyst, and not from the lattice oxygen from the catalyst through a Mars van Krevelen (MVK) mechanism.

On reintroduction of oxygen the conversion returned to that observed prior to the anaerobic testing (i.e. 18 %). This suggests that at 550°C when the oxygen is removed from the feed the catalyst does not reduce further resulting in deactivation. The selectivities to the aromatics, octene and CO_x returned to similar values before the anaerobic switch. This confirms that this is a reversible change and that the oxygen in the feed is responsible for CO_x production.

3.6. Optimisation of Experimental Parameters to Produce Octene and Aromatics from *n*-Octane

3.6.1. A Temperature, GHSV and C:O Ratio Study

The reaction of *n*-octane with the JM iron molybdate catalyst was tested at different temperatures, from 350 °C to 550 °C in 50 °C increments under a particular set of conditions, e.g. at C:O ratio of 2:1 at 1000 h⁻¹. The two graphs, Figures 3.9 and 3.10, represent the optimum conditions of octene and aromatic production respectively at 400 °C and 550 °C. The following data also showed that adjusting the carbon to

oxygen ratio with the changing of GHSVs can manipulate the product distribution, selectivity and conversion.

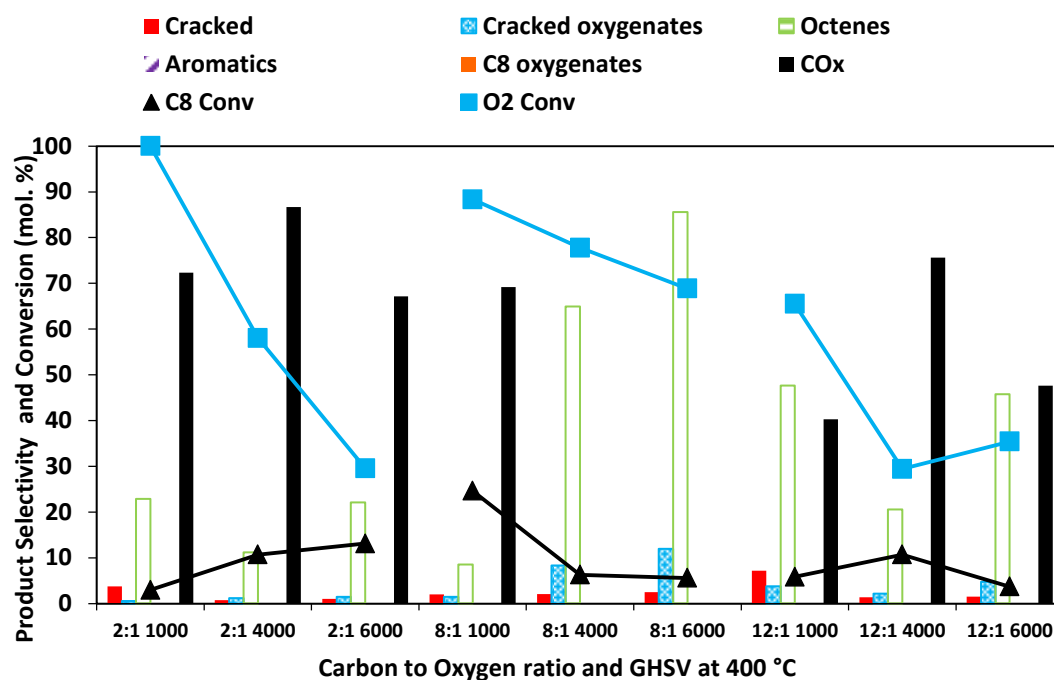


Figure 3.9 Reaction of *n*-octane with the JM iron molybdate catalyst with using various carbon to oxygen ratios between 2:1- 12:1 and GHSVs of 1000 h⁻¹, 4000 h⁻¹ and 6000 h⁻¹ at 400 °C.

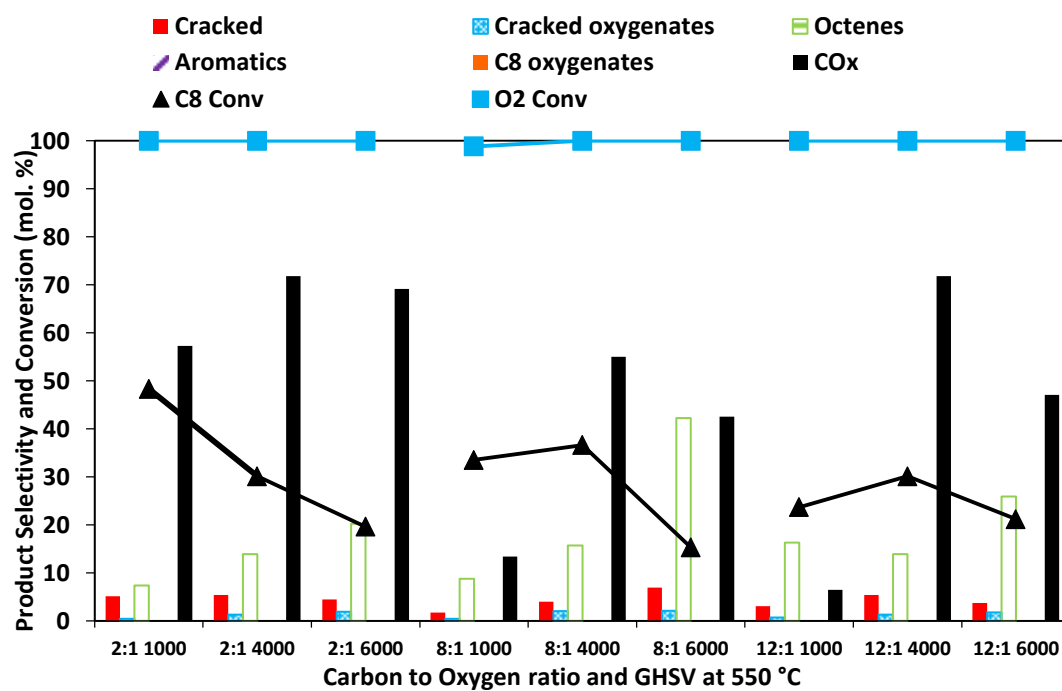


Figure 3.10: Reaction of *n*-octane with the JM iron molybdate catalyst with using various carbon to oxygen ratios between 2:1- 12:1 and GHSVs of 1000 h⁻¹, 4000 h⁻¹ and 6000 h⁻¹ at **550 °C**.

The optimum conditions for the production of octene from *n*-octane was at 400 °C 8:1 6000 h⁻¹. This gave a conversion of *ca.* 5 % with 85 % selectivity. The optimum conditions for the production of aromatics were 550 °C at 8:1 and 12:1 at 1000 h⁻¹. At 12:1 the selectivity reached 74 % which was greater than at 8:1 where the selectivity reached 60 %. However the conversion of *n*-octane was lower, 23.6 % at 12:1 and 33.5 at 8:1, which is probably due to the decrease in the amount of oxygen in the feed. The selectivity to the CO_x decreased significantly at 1000 h⁻¹ compared to that of 4000 h⁻¹. This is counterintuitive because longer contact times often produce the more thermodynamically stable product CO₂. This suggests that CO₂ is being consumed in the reaction as discussed in detail in Chapter 4.

3.6.2. The Production of Styrene : A TOL study at 550 °C

3.6.2.1. Alternating the GHSV between 4000 h⁻¹ and 1000 h⁻¹

The following experiment (Fig.3.11) was designed to suppress the production of CO_x and achieve greater selectivities towards the aromatics, in particular styrene. It was previously shown that at 550 °C if the GHSV was lowered to 1000 h⁻¹ then the selectivity towards styrene increased whilst the selectivity towards CO_x decreased, however this observation is reversed if the GHSV is increased to 4000 h⁻¹. This is counterintuitive as longer contact times often give the most thermodynamically stable product, in this case CO₂ and of course H₂O. Therefore the reaction between the JM iron molybdate catalyst (0.2 ml, 12.8 ml/min; GHSV = 4000 h⁻¹ and 3.4 ml/min; GHSV = 1000h⁻¹, C:O = 8:1), *n*-octane and oxygen under alternating GHSVs was investigated. This experiment established that the change in product distribution is reversible under these operating conditions.

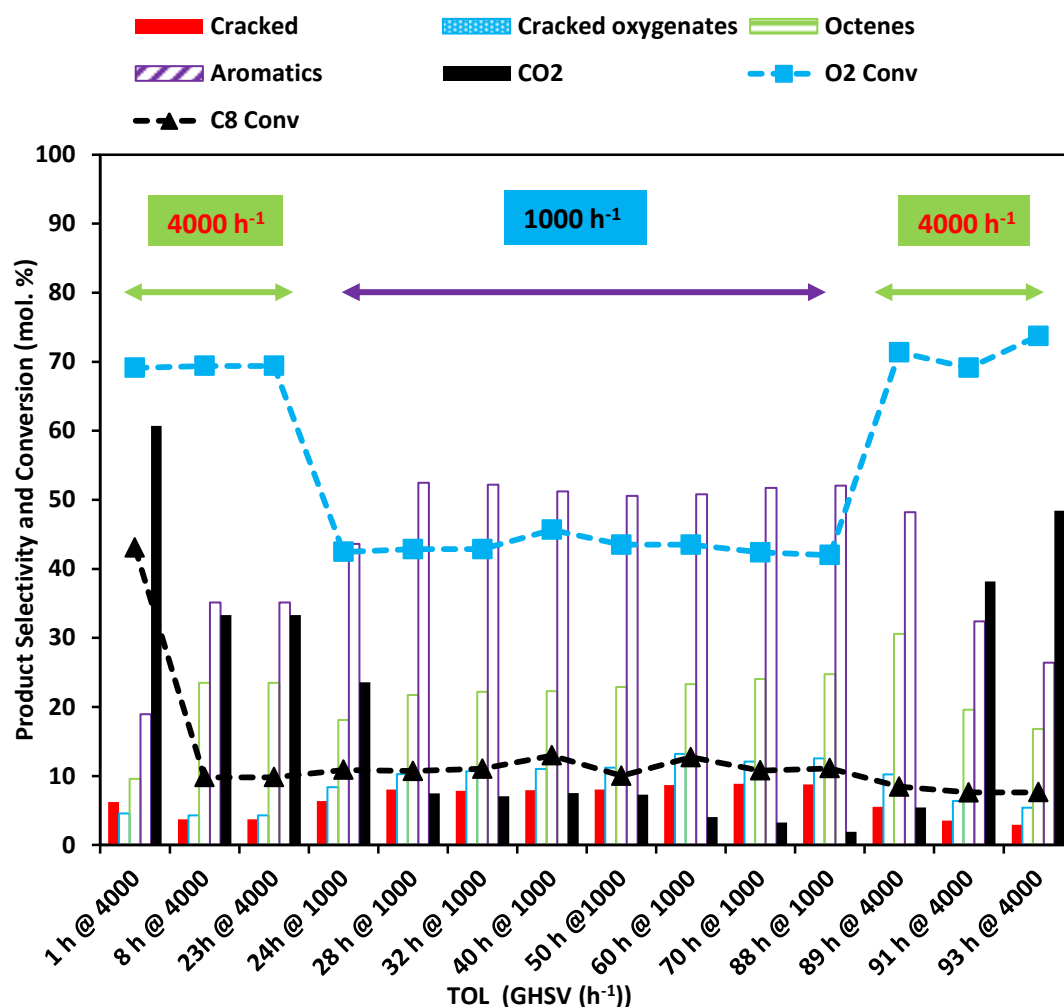


Figure 3.11: Reaction of 1 % *n*-octane (C:O 8:1) with the JM Fe₂(MoO₄)₃-MoO₃ catalyst.

Temperature at 550 °C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹ at 550 °C.

When the GHSV was lowered from 4000 h⁻¹ to 1000 h⁻¹ at 550 °C the conversion of octane increased slightly from *ca.* 8 % to 10 % ± 0.7 %. Note, Switching is not instantaneous and takes one to two hours for the system to stabilise. The oxygen consumption is high when the reaction is at 4000 h⁻¹ (*ca.* 70 %). However at 1000 h⁻¹ the consumption of oxygen decreased to *ca.* 43 %. So the production of CO_x is suppressed at a lower GHSV (*ca.* 4 % after 60 h). This suggests that excess gas phase oxygen is used for total oxidation and the remaining oxygen (43%) is used in production of aromatics and octene *via* the MVK-ODH mechanism and to subsequently replenish the lattice oxygen. This is similar to the aerobic-anaerobic treatment of the catalyst with octane which showed that CO₂ “switched off” when no oxygen is present which was shown in Figure 3.8. When the GHSV was increased again at 89 h, the conversion decreased to *ca.* 7.5 % due to the decrease in contact

time. However, it is shown once again that CO₂ becomes the dominant product reaching selectivities of about 45%.

Figure 3.12 shows the aromatic selectivity product distribution with the alternating GHSVs (4000 h⁻¹ to 1000 h⁻¹) at 550 °C. Over the first 8 h period at 4000 h⁻¹ the selectivity to toluene is the most dominant product (*ca.* 12 %) with benzene (*ca.* 5 %), xylene (*ca.* 8 %), and styrene (*ca.* 9 %) being produced in lower quantities. The production of ethylbenzene has the lowest selectivity (*ca.* 2.5 %) as the production of styrene is favoured in this reaction from the dehydrogenation step of the ethyl group of ethylbenzene. As the GHSV is decreased to 1000 h⁻¹ after 24 h, the production of styrene significantly increases (*ca.* 28 %) whilst all the other aromatic products remain consistent with the GHSV at 4000 h⁻¹. This suggests that CO₂ could be consumed or blocking the active site for the production of styrene. When the GHSV is then increased back to 4000 h⁻¹ at 80 h the selectivity towards styrene starts to decrease back to the original selectivity when the reaction was previously at 4000 h⁻¹. CO₂ therefore must be competing or blocking the site for production of styrene.

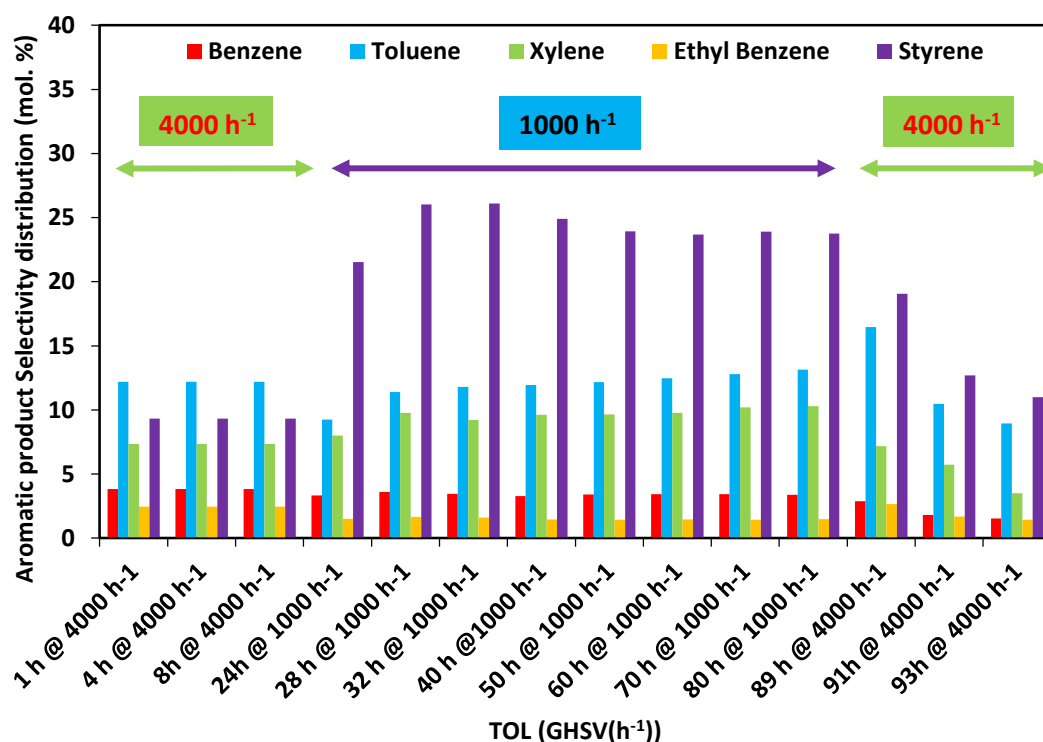


Figure 3.12: The aromatic selectivity profile of the reaction of 1 % *n*-octane (C:O 8:1) with the JM Fe₂(MoO₄)₃-MoO₃ catalyst. Temperature 550°C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹

3.6.3. Increasing the Partial Pressures of *n*-Octane and Oxygen: Optimisation of Octene

3.6.3.1. The UKZN Result: Increased partial pressure of *n*-octane to 11 %

The project extends across two industrial collaborators and an academic institution, Johnson Matthey (JM), Sasol Technology (SASOL) and the University Kwazulu-Natal (UKZN) respectively. The experiment (Fig.3.13) performed in UKZN used 11 % octane C:O; 8:1 4000 h⁻¹ with the same JM Iron molybdate catalyst, to determine the effects of altering the partial pressures of octane and oxygen.

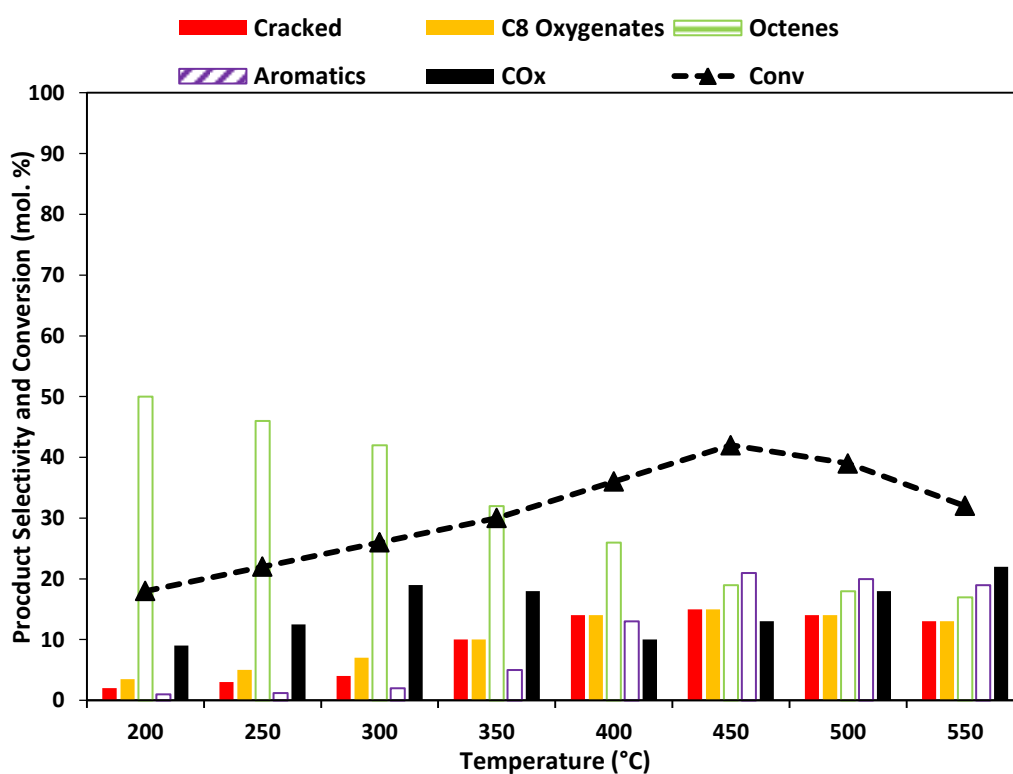


Figure. 3.13: UKZN- Reaction of 11 % *n*-octane (C:O 8:1, GHSV 4000 h⁻¹) with JM iron molybdate catalyst. Temperature range from 200- 550°C.

The data collected shows that the catalyst is active at much lower temperatures than the data which has been previously shown. It is also evident that at higher partial pressures C₈ oxygenates which include octanol and octanones are also present in the product distribution.

3.6.3.2. Testing the JM Iron Molybdate Catalyst with 4 % *n*-Octane

This next section assesses the increasing partial pressure of *n*-octane with the JM iron molybdate catalyst to improve the selectivity to octene. Unlike the research currently held in UKZN, due to differences in reactor design, the experiments used a feed containing 4 % (v/v %) *n*-octane.

Figure 3.14 shows a comparative test using the same conditions as UKZN (4000 h⁻¹ C: O 8:1). The only way in which they differ is that UKZN are using an 11 % octane feed.

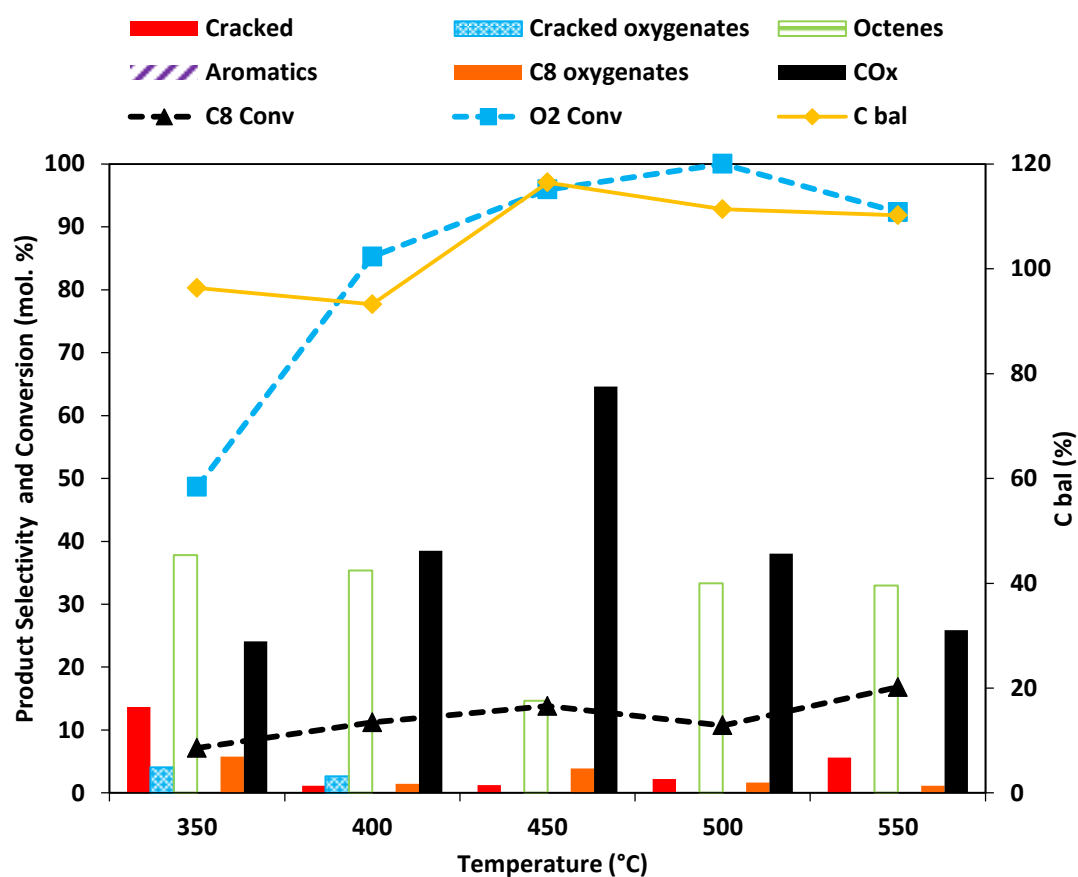


Figure 3.14: Reaction of 4 % *n*-octane (C:O 8:1, GHSV 4000 h⁻¹) with JM iron molybdate catalyst. Temperature range from 350- 550°C.

Figure 3.14 shows that increasing the feed concentration from previous studies from 1 % to 4 % increased the selectivity towards the octene especially at lower

temperatures i.e. 350 °C. Increasing the temperature from 350 °C to 550 °C increased the selectivity to the aromatics. Increasing the partial pressure of octane from 1 % to 4% increases the selectivity to the octene, and decreasing the partial pressure increases the aromatic selectivity. Higher partial pressures of *n*-octane decreases the availability of the oxygen sites available for further dehydrogenation of the same octene molecule at the surface. This suggests that less of the surface is exposed decreasing the relative number active sites available to achieve aromatisation. Therefore fewer sites are available resulting in limited secondary MvK-ODH due to the saturation of the occupied catalyst surface. C₈ oxygenates are also present as an effect of the increased octane feed. However selectivities are not to the same extent presented by UKZN because of the higher partial pressure (11 %) of octane feed that is used.

Figure 3.15 shows as the temperature was increased from 350 °C to 550 °C the selectivity to xylenes and styrene increased, particularly at 500 °C and 550 °C. At 350 °C the most selective aromatic formed was ethylbenzene (12 %). However with increasing temperature the selectivity decreased and xylenes increased which was also observed when using a 1 % octane feed.

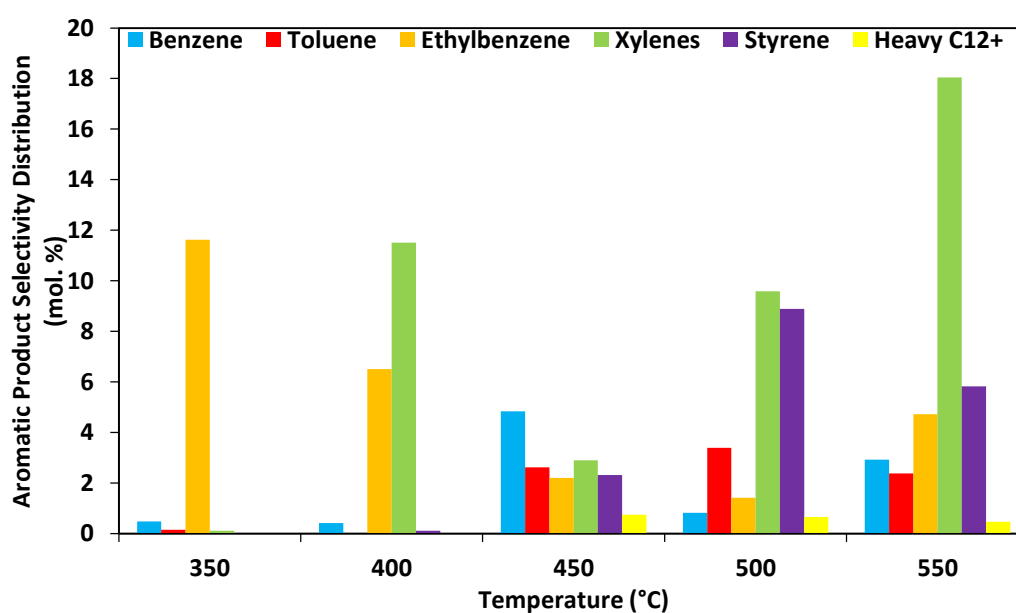


Figure 3.15: The aromatic product selectivity distribution when using the JM iron molybdate catalyst with *n*-octane (4 % vol, C:O; 8:1, 4000h⁻¹) from 350 °C – 550 °C.

When the GHSV was lowered from 4000 h⁻¹ to 1000 h⁻¹ (Figure 3.16.) the production of CO_x increased between 350-500 °C, due to an increase in contact time. However CO_x selectivity decreased significantly at 550 °C, which was also observed for the reaction using 1 % *n*-octane in the feed, whilst the aromatics increased to *ca.* 63 %. Octene selectivity was high at 350 °C and decreased with increasing temperature due to cyclisation and further ODH to aromatics¹². Figure 3.17 shows the aromatic selectivity breakdown to all products.

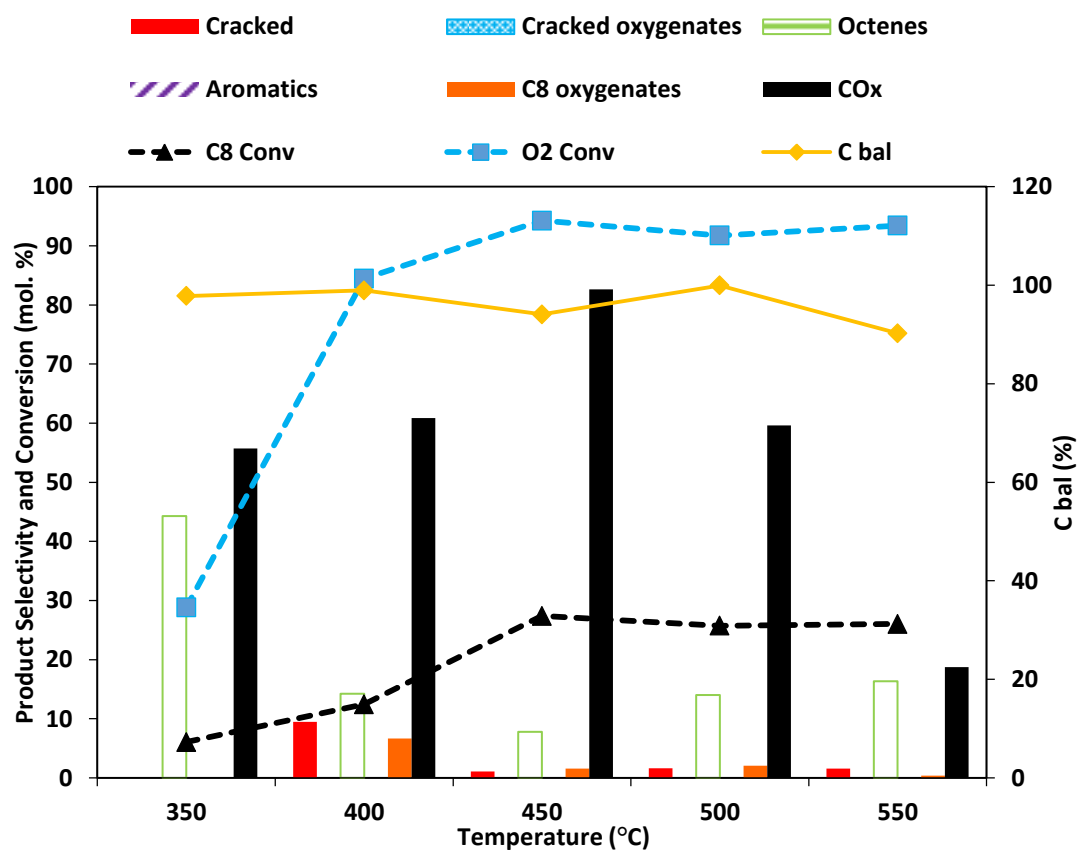


Figure. 3.16: Reaction of 4 % *n*-octane (C:O 8:1, GHSV 1000 h⁻¹) with JM iron catalyst. Temperature range from 350- 550°C.

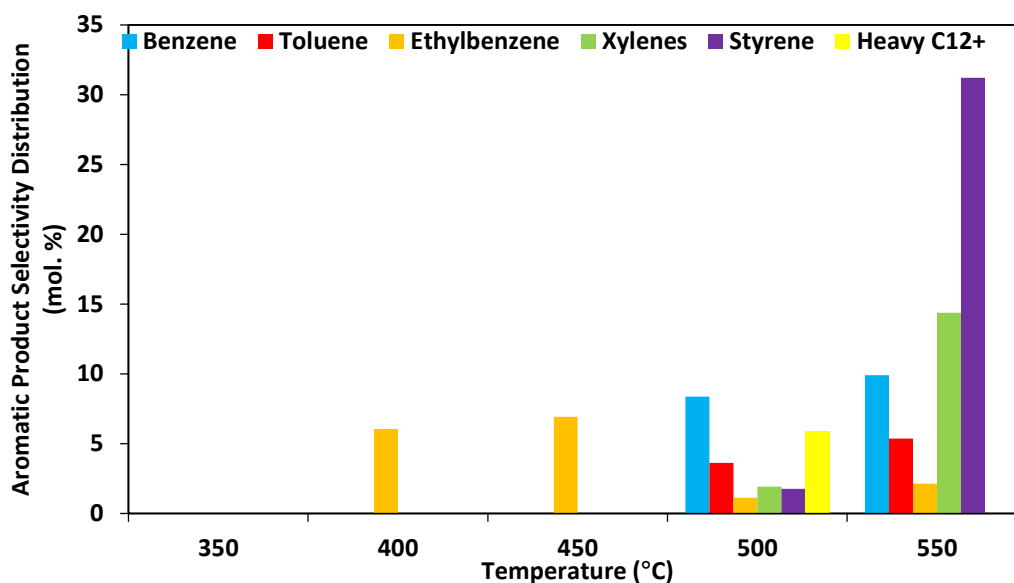


Figure 3.17: The selectivity profile for the aromatic production using the JM iron molybdate catalyst reacted with octane (4% vol, C:O; 8:1, 1000h⁻¹) from 350 °C – 550 °C.

The selectivity to styrene was the most dominant product at 550 °C, which was also seen for the 1 % octane feed. This relationship therefore is not driven by a change in partial pressure but rather a mechanism that operates at 550 °C. At 350 °C and 400 °C the only aromatic produced was ethylbenzene. When the temperature increased the formation of BTX products, and in particular styrene at 550 °C, were produced. The selectivity to ethylbenzene decreased suggesting possible cracking of ethylbenzene to benzene or toluene. However the selectivity to cracked products does not increase which would have resulted in the production of methane and ethane. CO_x does increase at may have been generated from the combustion of methane and ethane.

However, the production of styrene can be produced from the dehydrogenation of the ethyl moiety of the ethylbenzene molecule and would account for the decrease in the amount of ethylbenzene produced and the increase in styrene¹⁸⁻²⁰. The decrease in selectivity to CO_x suggests consumption and it has been reported that CO₂ can activate ethylbenzene to styrene²¹, this will be discussed in detail in Chapter 4.

3.6.4. Catalyst Stability at 550 °C: 4% *n*-octane with alternating GHSV between 4000 h⁻¹ and 1000 h⁻¹

The catalyst was further investigated using TOL studies to obtain information on stability and also alternating the GHSV between 4000 and 1000 h⁻¹ at 550 °C (Fig. 3.18).

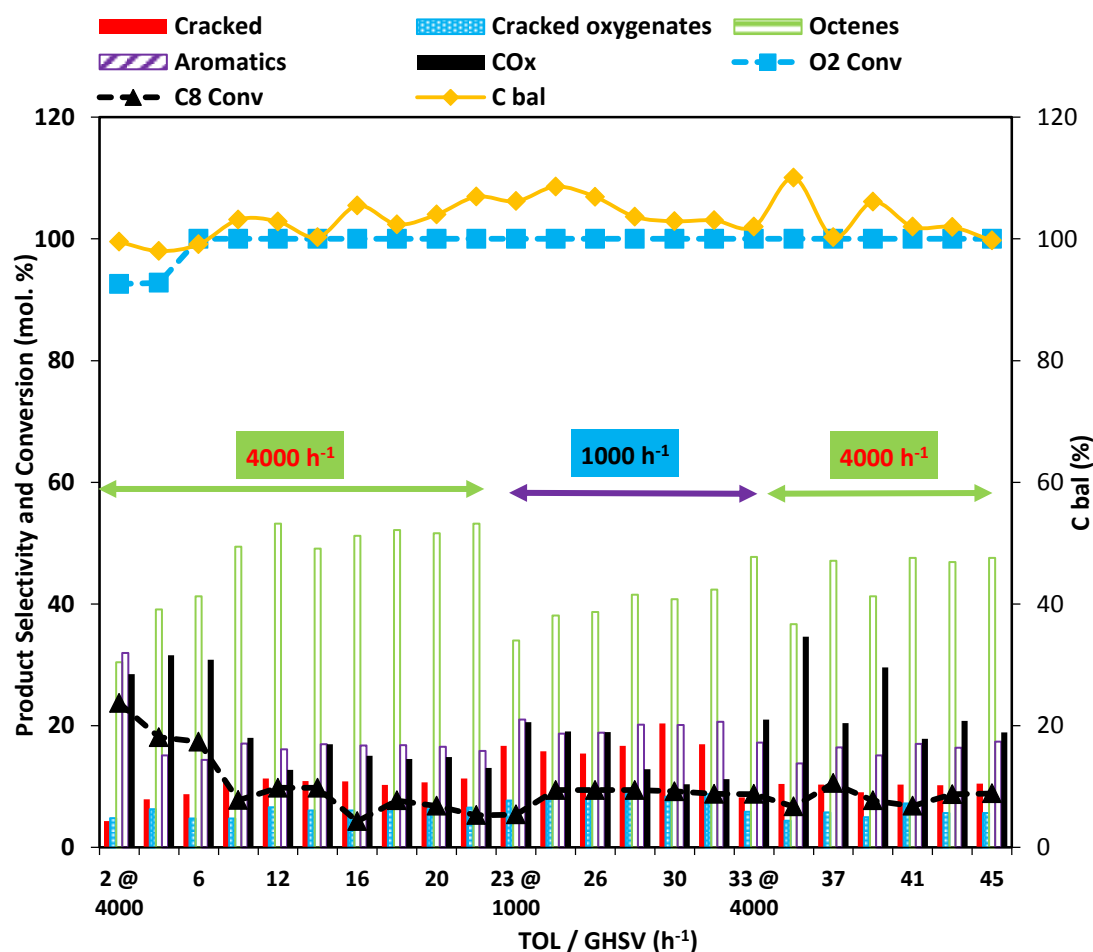


Figure 3.18: TOL study of the JM iron molybdate catalyst with octane (4% vol, C:O; 8:1, 1000 h⁻¹ and 4000h⁻¹) at 550 °C.

The TOL study (Fig. 3.18) shows that the catalyst takes 20 h to stabilise with the conversion fluctuating between 7 % at 4000 h⁻¹ and 10 % at 1000 h⁻¹. Initially, within the first 2 hours at 4000 h⁻¹ aromatics, octene and CO_x are produced in equal quantities with little cracked and cracked oxygenates produced. However, when the conditions stabilised (20 h) the most dominate product was octene (52 %) followed by aromatics (17 %) and carbon oxides (15 %).

Upon switching to 1000 h⁻¹ carbon oxides increased (21 %) due to the increase in contact time. The rise in carbon mass balance suggests that coke has been deposited onto the surface and has undergone total oxidation. When the catalyst stabilises (28th h) and the removal of coke is complete, shown from the stabilisation of the mass balance, the selectivity to carbon oxides decreased to 10 % whilst cracked and cracked oxygenates increased. This is comparable with the results obtained from UKZN. The aromatic selectivity slightly increased due to longer contact times which allows for further ODH. The surface is more saturated at higher partial pressures resulting in a decrease in accessibility to the active sites. This results in a decrease in further dehydrogenation of octane and therefore aromatic production decreased, unlike the experiments with 1 % octane in the feed (Fig. 3.8). Octene selectivity decreased when changing to 1000 h⁻¹ to *ca.* 40 %. This suggests at high temperatures with higher partial pressures the chain begins to crack represented by an increase in cracked products.

The octene selectivity starts to increase with time at 1000 h⁻¹. The carbon balance decreased suggesting carbonaceous species (coke) was deposited onto the surface. Coke and carbides according to Schloegl *et al.*^{17, 22} can promote dehydrogenation of alkanes through dehydrogenation (DH) and depending on the nature of coke and reaction conditions it is also possible to oxidatively dehydrogenate alkanes.

When the GHSV was increased to 4000 h⁻¹ (33 h) the CO_x then increased and the carbon mass balanced increased. After a stabilisation period of a few hours, the CO_x decreased to *ca.* 17 % - 20 % but is still higher than when the GHSV was at 1000 h⁻¹. Octene selectivity slightly increased, but could not achieve the initial high selectivities that were produced before the first GHSV switch from 4000 h⁻¹ to 1000 h⁻¹. The aromatics decreased with increasing GHSV and this confirms that increasing the GHSV decreases the selectivity of the aromatics.

3.6.4.1. Summary

Increasing the partial pressures of octane from 1 % to 4 % increased the selectivity to the octene rather than the aromatics. This emphasises the importance of the partial pressure of *n*-octane used in the feed and as a result the product distribution can be manipulated. UKZN have shown when using a partial pressure of *n*-octane of 11 % at lower temperatures in particular, the selectivity to octene is dominant. The saturation

of the surface suggests that less active sites are accessible on the catalyst surface therefore a decrease in further ODH to aromatics was detected. Carbon deposited onto the surface is suggested to be active in alkane dehydrogenation^{17, 22} and this will be explored in greater detail in Chapter 4.

3.6.5. The Optimisation of the JM iron molybdate catalyst with 4 % *n*-octane

3.6.5.1. A Temperature, GHSV and C:O Ratio Study

The reaction of *n*-octane with the JM iron molybdate catalyst was tested with a higher partial pressure of 4% (v/v %) at different temperatures, from 350 °C to 550 °C in 50 °C increments under a particular set of conditions. The conditions used in the investigation uses C:O ratios of 2:1 and 12:1 at both 4000 h⁻¹ and 1000 h⁻¹. The data showed that adjusting the carbon to oxygen ratio with the changing of GHSVs can manipulate the product distribution, and catalyst performance.

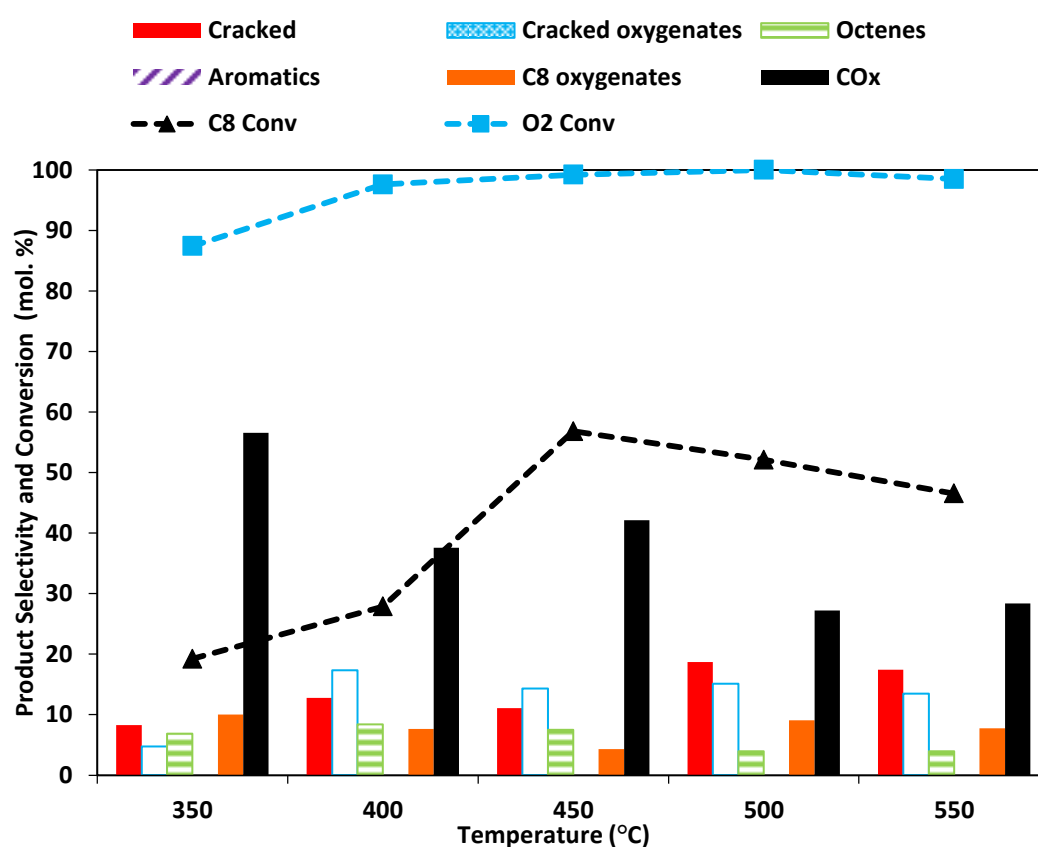


Figure 3.19: The JM iron molybdate catalyst was reacted with octane (4 % vol, C:O; 2:1, 4000 h⁻¹) from 350 °C – 550 °C.

Figure 3.19 shows when the temperature was increased from 350 °C to 550 °C the conversion of octane increased from 19 % to 46 %, with a sharp increase at 450 °C (56.8 %) due to the reductive phase change that is associated with the catalyst (Fig. 3.2). The cracked products increased from 8 % to 17 % from 350 °C to 550 °C respectively due to thermal cracking, while the cracked oxygenated products and C₈ oxygenates increased up to 400 °C and then slightly decrease from 450 °C due to the phase transition which facilitates aromatisation. Gas phase oxygen was present at 350 °C accounting for CO_x (57 %) production. With increasing temperature CO_x decreased when the system became oxygen limited. The oxygen in the gas feed is used to replenish the lattice oxygen lost when used in the ODH of the octane². For the production of aromatics more oxygen is required to aromatise octane and therefore oxygen consumption increased. Aromatisation increased with increasing temperature *via* the ODH-MVK mechanism due to the increased mobility of lattice oxygen^{15, 23}. Figure 3.20 shows the selectivity profile for the aromatic production.

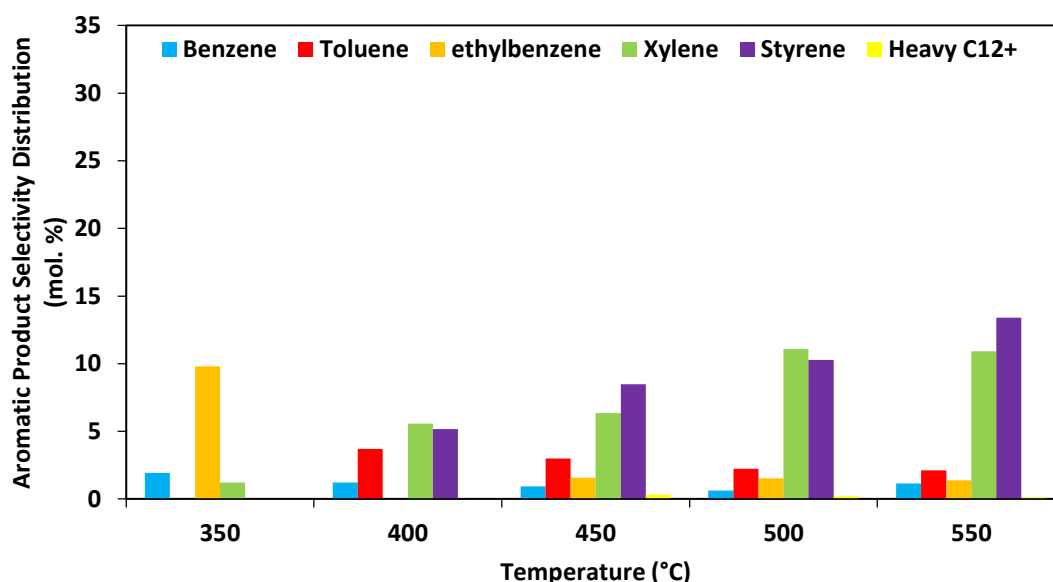


Figure 3.20 The selectivity profile for the aromatic production using the JM iron molybdate catalyst reacted with octane (4 % vol, C:O; 2:1, 4000h⁻¹) from 350 °C – 550 °C.

Figure 3.20 shows as the temperature was increased from 350 °C to 550 °C the selectivity to xylenes and styrene increased. Ethylbenzene is the dominant product at

350 °C, however at higher temperatures the selectivity decreased to *ca.* 1.3 %, likely due to dehydrogenation to styrene^{7, 18}. A 1, 6 ring closure to form ethylbenzene²⁴ followed by ODH to styrene adapted from Holger *et al.*¹². Xylene could be produced from a 2,7 ring closure followed by ODH to xylene²⁴. The production of benzene and toluene could be a result of slight thermal cracking of the *n*-octane chain to give methane and ethane, *ca.* 1.5 % and 2 % respectively at 550 °C. The hexane and heptane chains can then cyclise and aromatise in a similar manner to give benzene and toluene respectively.

When the GHSV was lowered from 4000 h⁻¹ to 1000 h⁻¹ (Fig. 3.21) the selectivity to CO_x increased as a result of a longer contact time. However at 550 °C CO_x is still suppressed suggesting consumption of CO₂. It is evident from the phase change from Fe₂(MoO₄)₃-MoO₃ to FeMoO₄-MoO₂-Mo₄O₁₁ that the reduced phase, along with high temperatures, is responsible for the aromatics produced. Figure 3.22 shows the selectivity profile for the aromatic production from 350 °C to 550 °C.

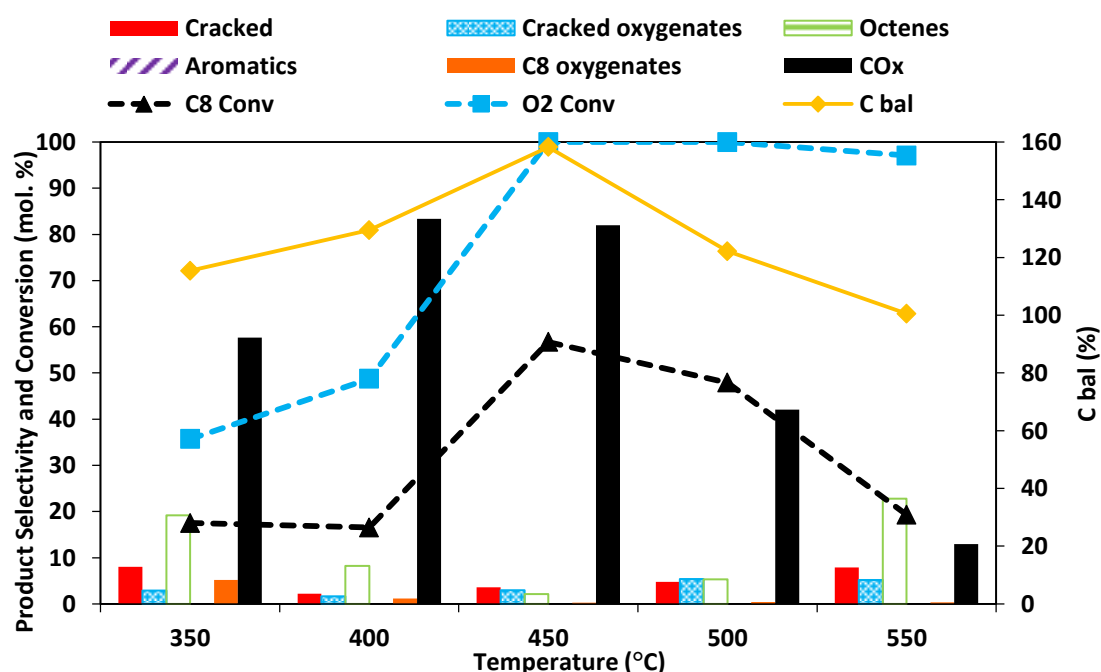


Figure 3.21: The JM iron molybdate catalyst was reacted with octane (4 % vol, C:O; 2:1, 1000 h⁻¹) from 350 °C – 550 °C.

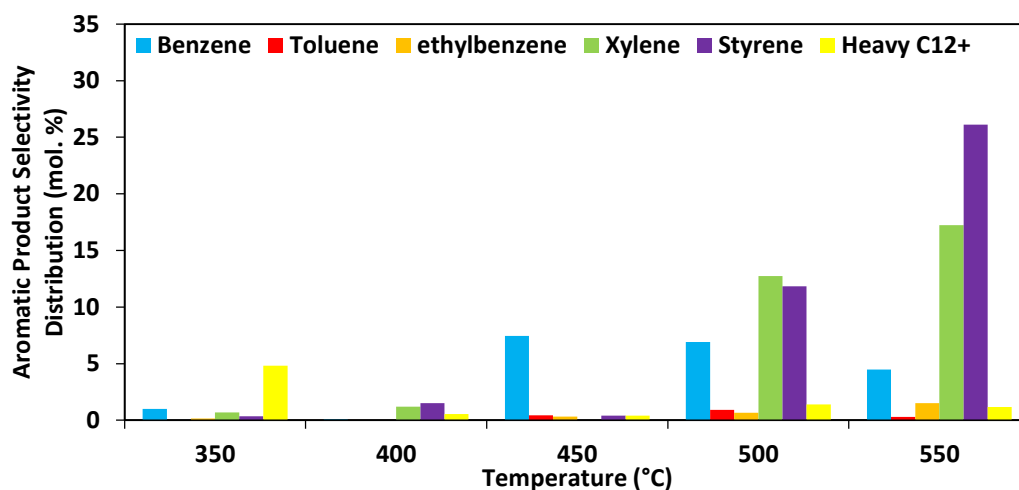


Figure 3.22: The selectivity profile for the aromatic production using the JM iron molybdate catalyst reacted with octane (4% vol, C:O; 2:1, 1000h⁻¹) from 350 °C – 550 °C.

At longer contact times less aromatics are produced at temperatures < 500 °C relative to 4000 h⁻¹ as a result of combustion. However at 500 °C and 550 °C xylene and styrene are both produced with styrene dominant at 550 °C.

The C:O ratio was then changed to 12:1. Figure 3.23 shows that CO_x decreased with respect to 2:1 across the temperature range 350 °C to 550 °C. Less oxygen is available for total oxidation suggesting that adsorbed oxygen species are responsible for total oxidation and the lattice oxygen dehydrogenate the alkane.

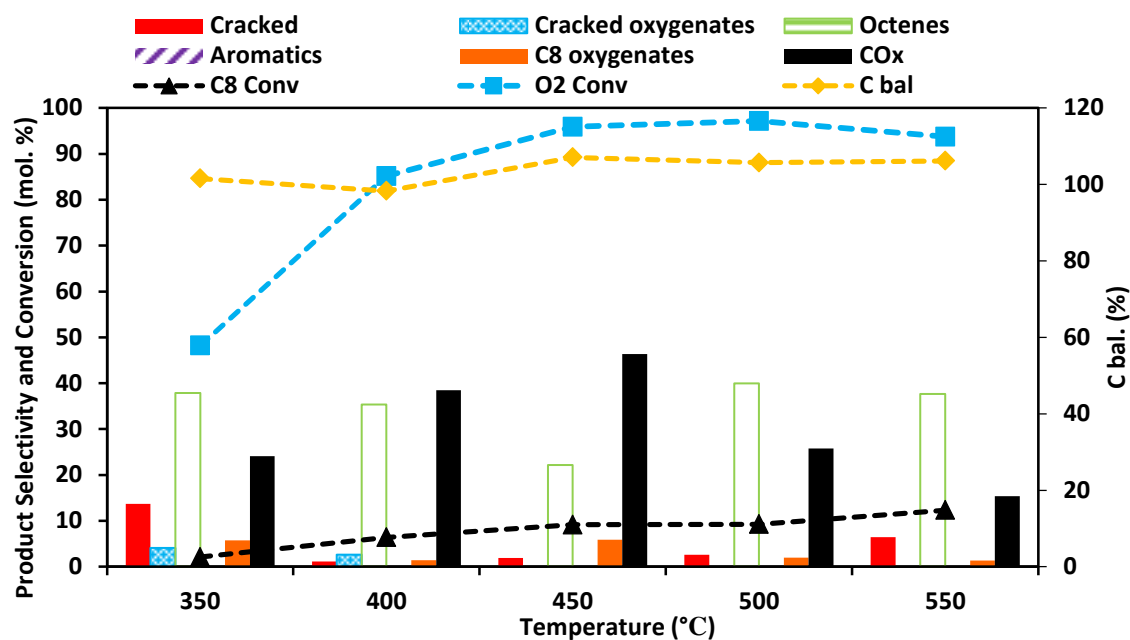


Figure 3.23: The JM iron molybdate catalyst was reacted with octane (4% vol, C:O; 12:1, 4000h⁻¹) from 350 °C – 550 °C.

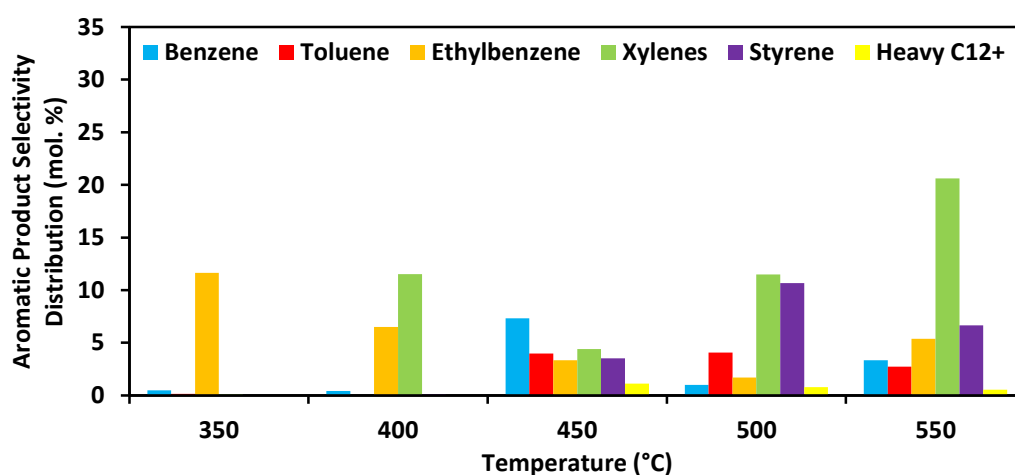


Figure 3.24: The selectivity profile for the aromatic production using the JM iron molybdate catalyst reacted with octane (4% vol, C:O; 12:1, 4000 h⁻¹) from 350 °C – 550 °C.

Figure. 3.34 shows that ethylbenzene is the dominant product at low temperatures. However as the temperature is increased the selectivity towards styrene and xylenes increased with the dominant product of xylene at 500 °C and 550 °C.

When the GHSV was lowered to 1000 h⁻¹ (Fig. 3.23) CO_x increased at temperatures ≤ 450 °C as a result of residence time at temperatures ≥ 450 °C the selectivity to aromatics increased while octene decreased relative to 4000 h⁻¹.

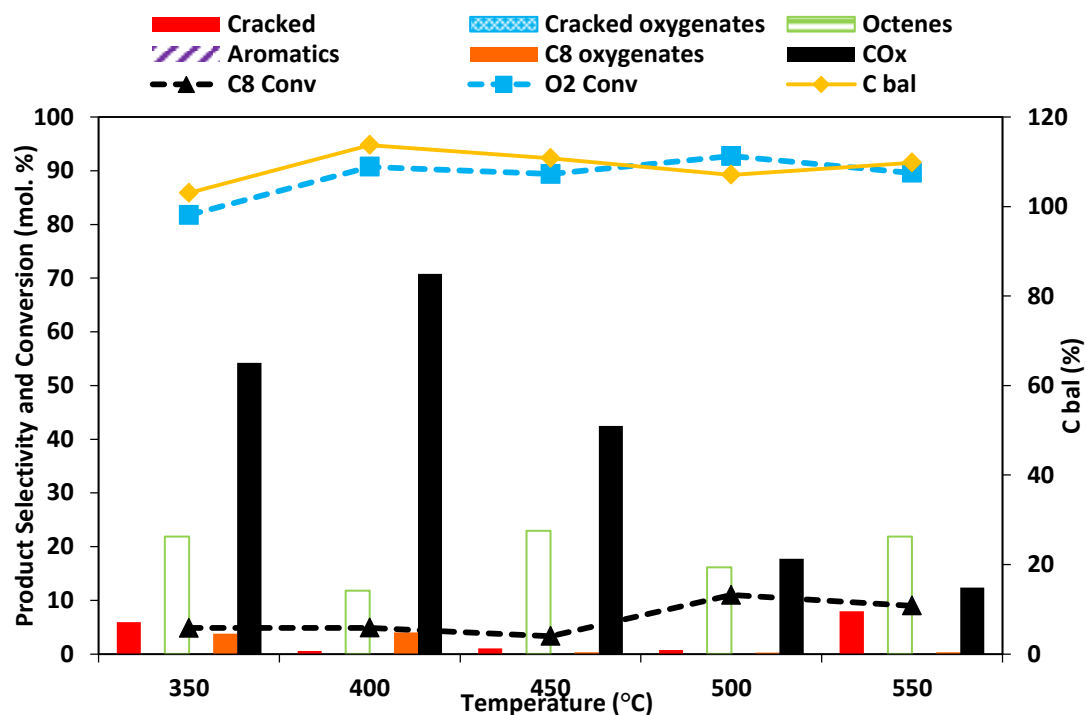


Figure 3.25: The JM iron molybdate catalyst was reacted with octane (4% vol, C:O; 12:1, 1000 h⁻¹) from 350 °C – 550 °C.

When the temperature was increased from 350 °C to 550 °C the conversion of octane increased from *ca.* 5% to 10% respectively, especially at 500 °C and 550 °C where the catalyst produces the aromatics. As the temperature increased CO_x production decreased, however the selectivity towards the octene and aromatics increased, especially at 550 °C. The graph shows at lower space velocities aromatics are more selective compared to higher space velocities, in particular at higher temperatures, where the reduced catalyst is responsible for the production of these aromatics. This is because the octane substrate has a longer contact time with the active sites of the catalyst. This assists in the aromatisation process. It is not clear whether the octane cyclises first then dehydrogenates the terminal ethyl bond in the case of styrene or that octane is dehydrogenated then aromatises to styrene. Figure 3.26 shows the aromatic selectivity breakdown for the temperature range

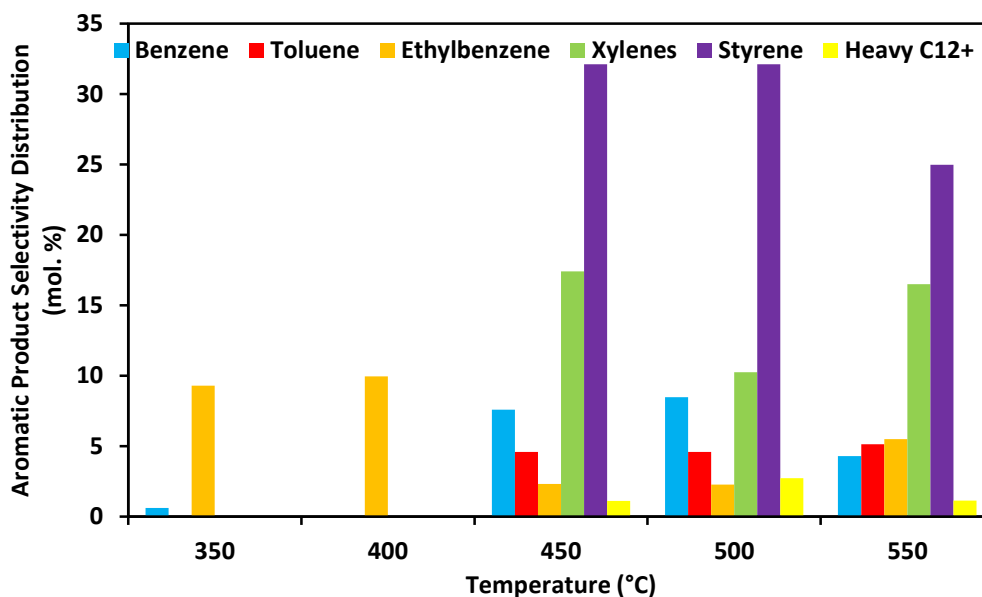


Figure 3.26: The selectivity profile for the aromatic production using the JM iron molybdate catalyst reacted with octane (4% vol, C:O; 12:1, 1000h⁻¹) from 350 °C – 550 °C.

The aromatic breakdown at C:O 12:1 using a GHSV of 1000 h⁻¹ (Fig. 3.26) shows that ethylbenzene is the dominant product at low temperatures. However as the temperature is increased the selectivity towards styrene and xylenes increased with the dominant product being styrene at 550 °C degrees, because of the longer contact time with the catalyst to aid the dehydrogenation (ODH) and cyclisation of octane.

3.7. Further Characterisation of the Iron Molybdate Catalysts

3.7.1. Diffuse Reflectance UV-Vis Spectroscopy (DR-UV-Vis)

A UV-Vis diffuse reflectance spectrum (Fig. 3.27) was collected using a Harrick Praying Mantis cell mounted on a Cary 4000 spectrophotometer. The spectrum was collected from 900 to 200 nm at a scan speed of 60 nm min⁻¹. Background correction was carried out using a fluoropolymer powder (Spectralon). All the powder samples were mounted on a 3 mm diameter diffuse reflectance sampling cup.

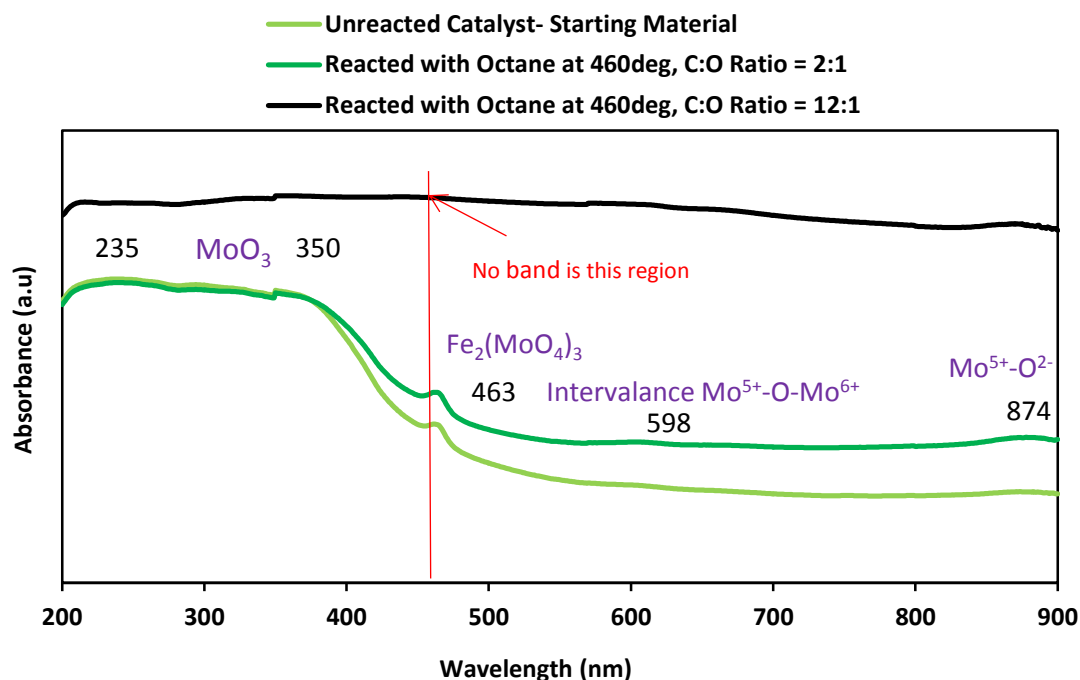
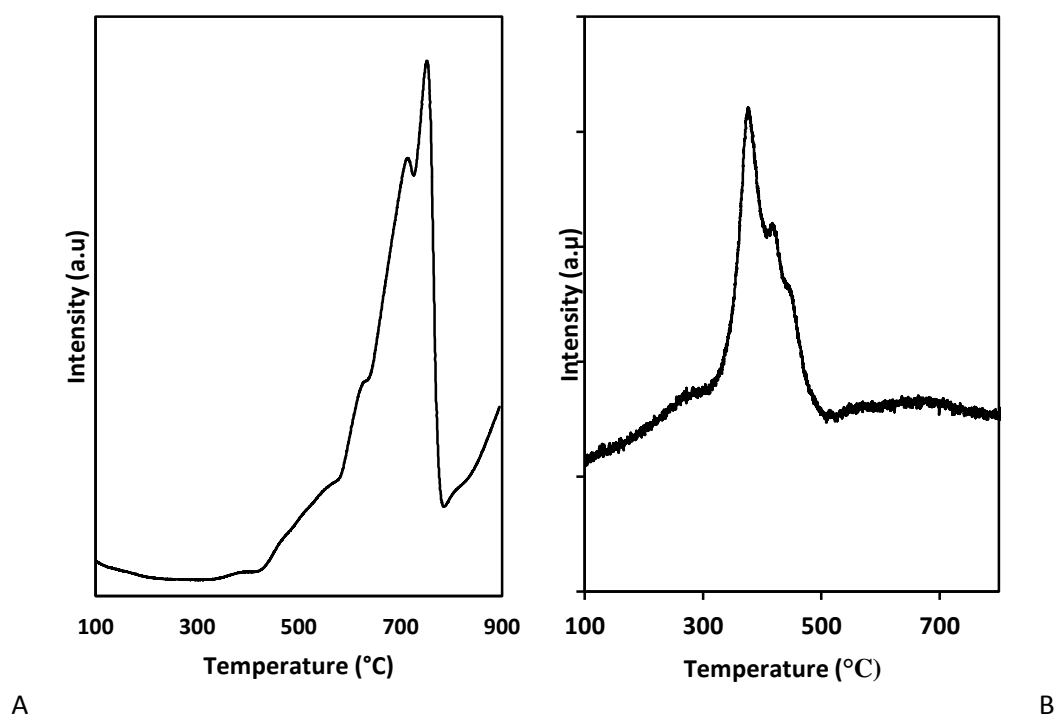


Figure 3.27: DR-UV-Vis spectrum of the JM iron molybdate before and after reaction with octane (C:O = 2:1 and 12:1).

The spectroscopy is consistent with the *in situ* XRPD analysis that was obtained for the iron molybdate samples. This spectrum shows that increasing the carbon to oxygen ratio (12:1) resulted in a reduction of the Fe(III) (~463nm.), with the DR-UV-Vis spectrum dominated by MoO₂.

3.7.2. Temperature Programmed Reduction (TPR) and Oxidation (TPO)

The TPR of the iron molybdate catalyst (Figure 3.28 a) showed a total of five reduction peaks within the temperature range from 300°C to 780°C, including a low temperature reduction peak at ~370°C. Zhang *et al.*²⁵ also reported five reduction peaks (Figure 3.28 b) for the TPR of iron molybdate catalyst having both $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 phases. The reduction peaks and the phases identified by XRD are shown in Table 3.1.



Figures 3.28: (A) TPR of fresh JM iron molybdate catalyst and (B) TPO of the TPR JM iron molybdate catalyst.

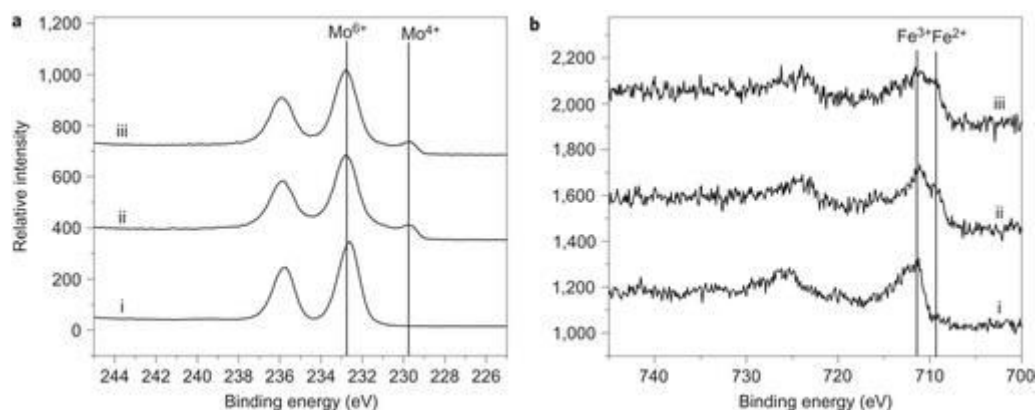
The TPR profile (Fig. 3.28 a) showed 5 reduction peaks. These peaks were identified using XRD. The peaks are listed and identified in Table 3.1²⁵.

Peak	Peak Temperature (°C)	Phase detected by XRD
Before reduction	N/A	$\text{Fe}_2(\text{MoO}_4)_3$, MoO_3
1 st Peak	580	MoO_3 , $\alpha\text{-FeMoO}_4$, $\beta\text{-FeMoO}_4$, Mo_4O_{11}
2 nd Peak	637	MoO_2 , $\alpha\text{-FeMoO}_4$, $\beta\text{-FeMoO}_4$, Mo_4O_{11}
3 rd Peak	679	MoO_2 , Fe_3O_4 , $\text{Fe}_2\text{Mo}_3\text{O}_8$, $\alpha\text{-FeMoO}_4$, $\beta\text{-FeMoO}_4$, Mo_4O_{11}
4 th Peak	741	MoO_2 , Fe_3O_4 , $\text{Fe}_2\text{Mo}_3\text{O}_8$, Fe_3Mo (a little)
5 th Peak	960	Mo^0 , Fe_3Mo alloy

The reduction of JM iron molybdate catalyst proceeds through different phases when the temperature is increased. The temperature of the experiments reported throughout this chapter have a maximum temperature of 550 °C, and therefore the phases that will be formed are β -FeMoO₄, MoO₂ and MoO₄O₁₁. The results reported by Zhang *et al.*²⁵ also support the previous *in situ* XRPD study with octane (Fig. 3.2). The phase change revealed by *in situ* XRPD showed that the reductive phase transition occurred at a far lower temperature (450 °C - 460 °C) than that of the reduction by TPR (580 °C). This could be a result of different catalysts and flow conditions used in the reactor. This was also shown experimentally when the production of the aromatics increased at 450 °C (Fig. 3.1). This suggests the conditions during the reaction when using octane are more reducing. Zhang *et al.* proposed that the reduced phases, Mo₄O₁₁, β -FeMoO₄ and Fe₃O₄ are produced from the reduction of iron^{III} molybdate. However, the phases are detected from the *in situ* XRPD with the exception of the haematite phase. The haematite phase could still be present but in low quantities and/or in the form of small crystallites which are below the detection limit or could be amorphous.

3.7.3. X-Ray Photoelectron Spectroscopy (XPS)

The following XPS spectra of iron and molybdenum (Fig. 3.29a and b respectively) were utilized to help identify phases that are present at the surface. The binding energies of interest are the iron Fe2p and molybdenum Mo3d and were measured for the iron molybdenum catalysts pre and post reaction with *n*-octane. Zhang *et al.*²⁵ proposed that during the reduction of the iron molybdate that an Fe₃O₄ phase was present. However XRPD analysis showed that this phase was not present in the bulk, but it may be present at the surface. The Mo 3d 5/2 binding energy at 232.7 eV is assigned to the Mo^{VI} molybdate species. XPS was obtained from Hutchings *et al.*³ when reacting *n*-decane, which is similar to *n*-octane, with an iron molybdate catalyst at 350 °C. The spectra revealed two observable oxidation states for Mo 3d and Fe2p, Mo 6+/4+ and Fe 3+/ 2+ respectively.



Figures 3.29 XPS of iron molybdate catalyst: (i) as prepared, (ii) after 12 h testing at 350 °C under oxidative conditions followed by 12 h testing at 350 °C in the absence of O_2 , and (iii) after a further 12 h testing at 350 °C with O_2 restored to the feed. Mo(3d) spectra (a) and Fe(2p) spectra (b) indicate that the surface of the catalyst is left in an irreversibly reduced state after exposure to decane in the absence of O_2 at this temperature³.

The XPS shows that at the surface there is reduction of both the molybdenum and iron at 350 °C. The molybdenum was reduced from 6+ to 4+ which corresponds to the MoO_3 to the MoO_2 phase. The reduction of iron, which is indicated with a broadening shoulder, from 3+ to 2+ is representative of iron(III) molybdate to Fe(II)molybdate respectively. The phases reported by Zhang *et al.*²⁵ agree with the XPS data shown here. However when the temperature was ≥ 450 °C it was shown by *in situ* XRPD (Fig. 3.2), XPS³, and TPR²⁵ that the Mo_4O_{11} , i.e. Mo^{5+} , was also present. The XPS spectrum (Fig. 3.30) with the reaction of *n*-octane with the iron molybdate catalyst agrees with the literature reported above and the *in situ* XRPD.

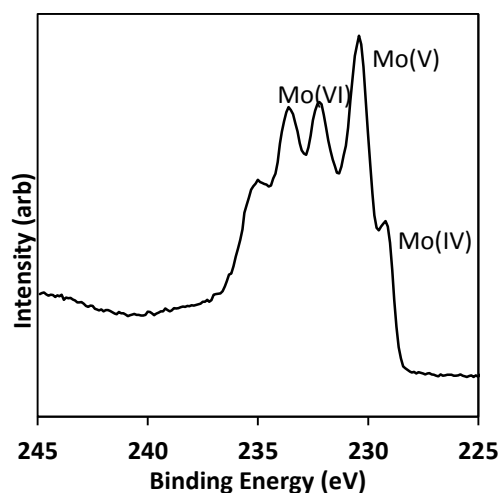


Figure.3.30: XPS of iron molybdate catalyst focusing on the Mo 3d 5/2 region after the reaction with *n*-octane (C:O 8:1, 1000 h^{-1} , 550 °C).

The peaks at 229.4 eV and 230.6 eV is representative of $\text{Mo}^{\text{IV}}\text{O}_2$ and 0.3 $\text{Mo}^{\text{VI}}\text{O}_3$ with Fe_2O_3 which represents the $\text{Fe}_2(\text{MoO}_4)_3$ phase respectively. The peak at 230.6 eV is indicative of MoO_x , more specifically the Mo_4O_{11} which is the Mo 5+ species. The multiple oxidation states established at temperatures $\geq 450^\circ\text{C}$ demonstrates that the molybdenum is extremely sensitive to reaction conditions at the surface, and the Mo^{V} species may account for the high selectivity to the aromatics after the reductive phase transition.

3.7.4. Raman Spectroscopy

Raman spectroscopy (Fig. 3.31) was used to characterize the fresh JM Iron molybdate catalyst and the catalyst post reaction. The Raman spectrum shows absorption bands which represent the $\text{Fe}_2(\text{MoO}_4)_3$ and the MoO_3 phases.

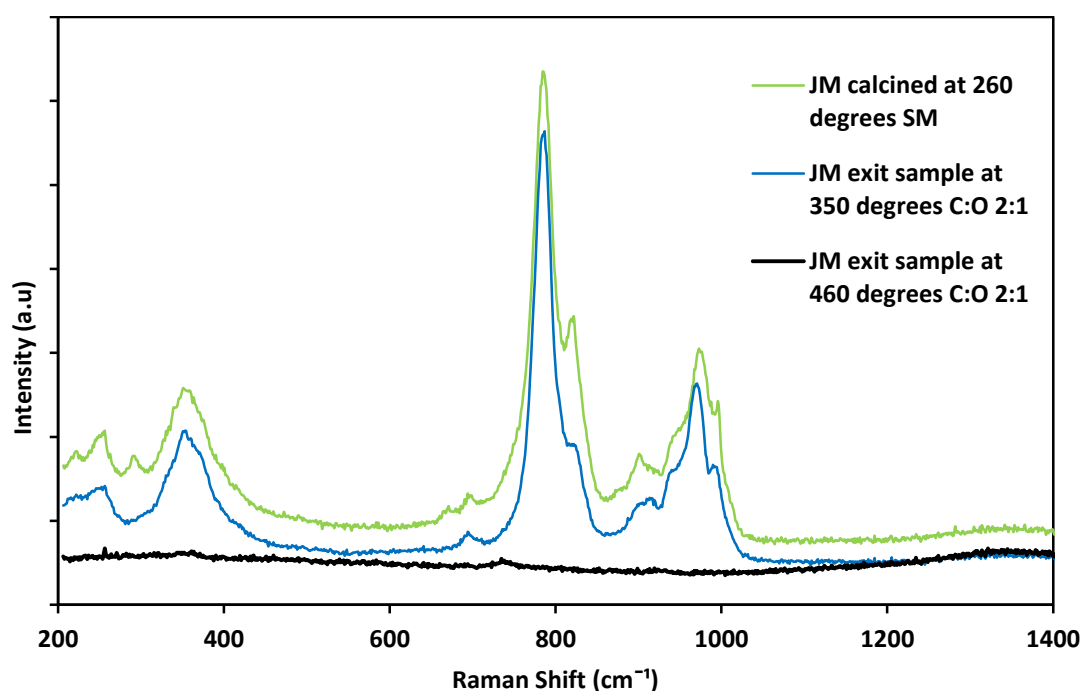


Figure. 3.31: Raman spectroscopy of the JM iron molybdate catalyst starting material (green line), reacted at 350 (blue line) and 460 (black line). C:O ; 2:1, GHSV, 1000h⁻¹.

Molybdenum trioxide (MoO_3) peaks appeared at 996 and 667 cm^{-1} . The bands at 996 and 971 cm^{-1} are from the $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 respectively. These arise from the Mo=O terminal stretching modes. The bands at 785 cm^{-1} and 817 cm^{-1} are the Mo-O-Mo vibrations

within the $\text{Fe}_2(\text{MoO}_4)_3$ phase and the MoO_3 phase respectively. The Raman spectra compliments the previous *in situ* XRPD data for the JM iron molybdate catalyst confirming the presence of both the $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 phases. The spectra obtained under reaction conditions at 350 °C (blue line) and the starting material (green line) showed that both materials are similar suggesting that under the operating conditions the catalyst does not reduce. Reaction with octane (C:O =2:1) at 460 °C the (black line) material has become reduced, which also coincides with the XRPD studies (Fig 3.2), and the sample appears to be Raman inactive. No bands were observed even with repeatedly long scan times and multiple accumulations. Therefore it is suggested that using temperatures < 450 °C preserves the oxidised phase i.e. $\text{Fe}_2(\text{MoO}_4)_3$ - MoO_3 and is responsible for the oxidative dehydrogenation of *n*-octane to octene and oxygenated aromatics via the MVK-ODH process; and at temperatures ≥ 450 °C the reduced catalyst, FeMoO_4 - MoO_2 - Mo_4O_{11} , is responsible for the non-oxygenated aromatics.

3.7.5. Thermogravimetric Analysis (TGA)

Thermal gravimetric analysis of the JM iron molybdate catalyst was performed (Fig. 3.32) before ('fresh catalyst') and after the reaction at 460 °C using C:O 12:1 at 4000 h⁻¹. The weight gain observed from the reacted catalyst is attributed to be the replacement of labile lattice oxygen and has resulted in the re-oxidation of the catalyst.

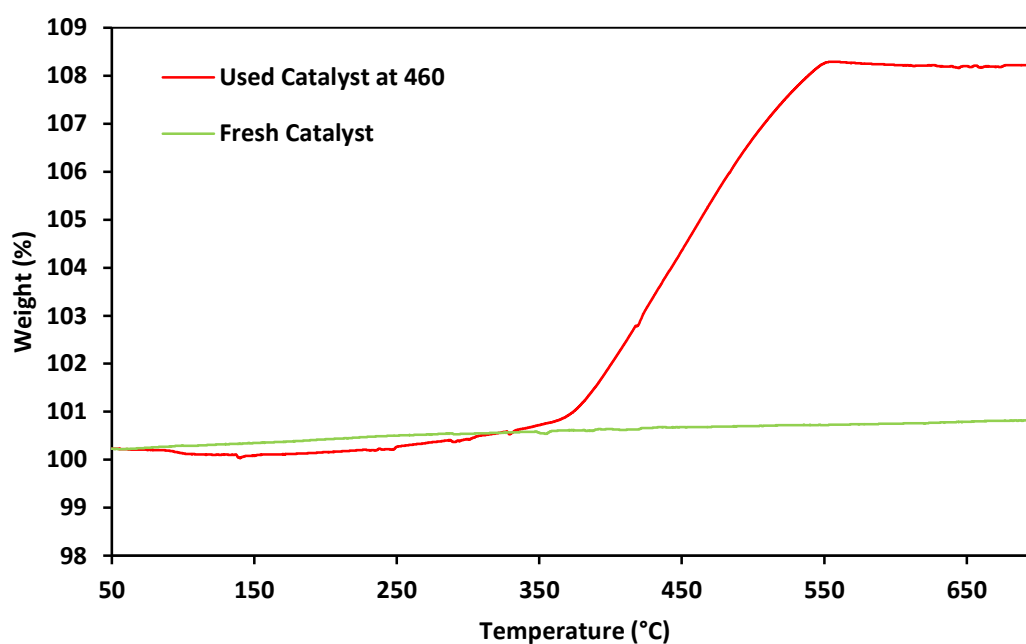


Figure. 3.32: TGA of the JM iron molybdate catalyst starting material (green line) and reacted at 460 (red line) and 460 (black line). C:O ; 12:1, GHSV, 1000h⁻¹.

It was already shown from XRPD that the JM iron molybdate catalyst under reaction conditions at 460°C undergoes a reductive phase change from $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ to $\text{FeMoO}_4\text{-MoO}_2\text{-Mo}_4\text{O}_{11}$. A theoretical calculation has been carried out to estimate how much oxygen is being removed when the catalyst is reduced during reaction based on the ratio of phases measured by XRD of the fresh catalyst. The weight gain from Figure 3.32 is 7.7 % and the theoretical calculated oxygen removed is 9.6 wt. %. The small difference could be due to the re-oxidation of the used iron molybdate catalyst before analysis.

3.8. Catalyst Stability

3.8.1. Hysteresis: Cycling the JM iron molybdate catalyst

The *in situ* XRPD study (Fig. 3.2) of the JM iron molybdate catalyst along with experimental testing showed that the catalyst undergoes a reductive phase transition. Once the catalyst has been reduced it does not go back to the original oxidised form, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ and maintains the $\text{FeMoO}_4\text{-MoO}_2\text{-Mo}_4\text{O}_{11}$ phases. Figure 3.33 shows how a temperature dependence study was used to establish whether the catalyst exhibits hysteresis. The JM Iron molybdate catalyst was tested using the conditions, C:O 8:1 at 4000 h^{-1} .

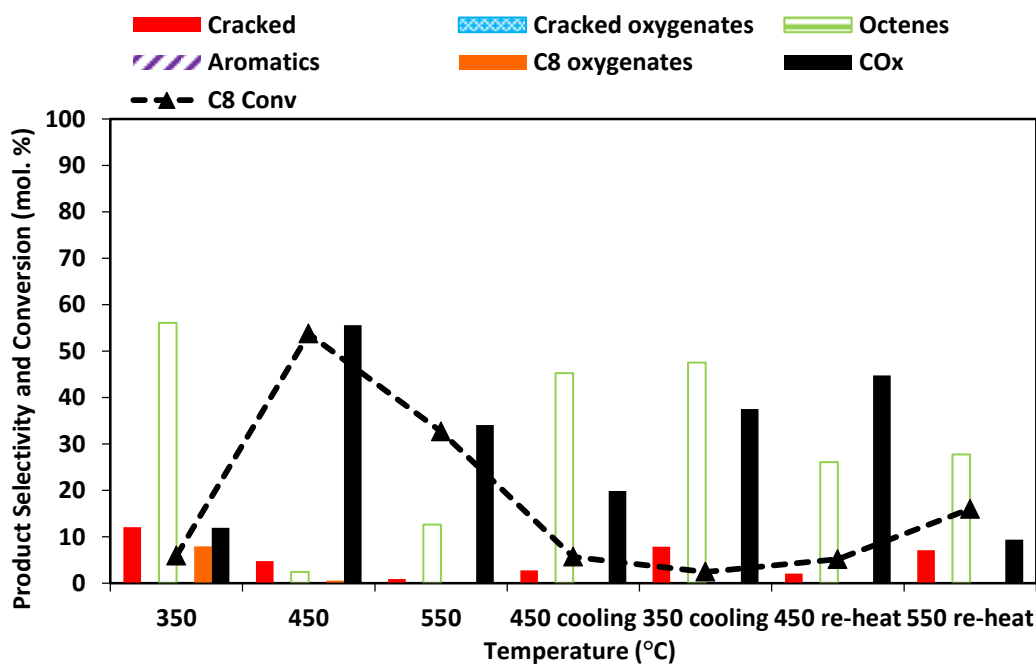


Figure 3.33. Hysteresis test of the JM iron molybdate catalyst with *n*-octane (1 % v/v %, C:O; 8:1, 4000 h^{-1}) from 350 to 550 °C.

The catalyst does not exhibit hysteresis. The catalyst, as predicted, undergoes a reductive phase transition when reacted at 450 °C where the phase changed from $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ to $\text{FeMoO}_4\text{-MoO}_2$. Once the catalyst has gone through the phase change this a permanent transition and the original low temperature selectivities (Fig. 3.34) cannot be achieved.

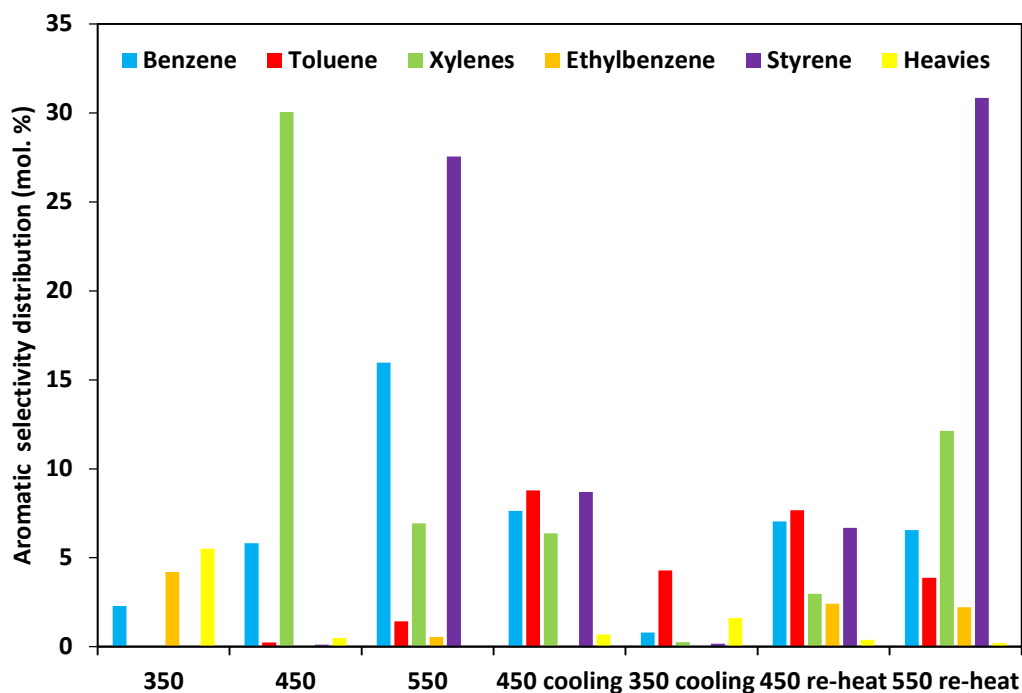


Figure 3.34. Aromatic product selectivity distribution of the hysteresis test of the JM iron molybdate catalyst with *n*-octane (1 % v/v %, C:O; 8:1, 4000h⁻¹) from 350 to 550 °C.

However once the catalyst is reduced both the '550' and '550' re-heat show comparable selectivity and this shows that the catalyst is now more stable. This is also represented by the '450 cooling' and '450 re-heat' cycles.

Therefore the next logical step would be to use the reduced form of the catalyst. The aromatics are produced after the phase transition so it could be possible to produce these aromatics at lower temperatures. It is shown that octene is also produced at lower temperatures but often competes with CO_x formation. So using a pre-reduced catalyst would lower the oxygen capacity and may therefore result in a decrease in CO_x selectivity and increased octene selectivity. When the temperature increases the lattice oxygen mobility increases, and so the production of aromatics increases. Restricting the aromatisation process by operating at lower temperatures would therefore increase octene selectivity.

3.9. Conclusions

The C-H bond activation of *n*-octane using gas phase oxidation with the JM iron molybdate catalyst resulted in the production of octene, aromatics and CO_x. The change in activity and selectivity of the catalyst can be attributed to the phases present at particular temperatures. Temperatures below 450 °C maintains the catalyst bulk integrity of Fe₂(MoO₄)₃-MoO₃ but subtly reduces at the surface which was shown by *in situ* XRPD and XPS respectively. When the temperature increases, ≥ 450 °C, under operating conditions, the bulk of the catalyst reduces along with the surface resulting in FeMoO₄, MoO₂ and Mo₄O₁₁. Lower temperatures, < 450 °C, produce a high selectivity mainly to CO_x and octene, whilst higher temperatures, ≥ 450 °C where the catalyst is reduced, produces CO_x and aromatics. At 550 °C when the catalyst is exposed to dehydrogenating (DH)/anaerobic conditions, CO_x is suppressed suggesting the formation of CO_x is produced from oxygen species in the gas phase through an Eley-Rideal or Langmuir-Hinshelwood style mechanism and not through the MvK-ODH mechanism. When the oxygen was reintroduced into the feed then CO_x selectivity increased. It was also observed that using particular operating conditions, i.e. in the production of styrene at 550 °C at a C:O 8:1, adjusting the GHSV from 4000 h⁻¹ and 1000 h⁻¹ can enhance the selectivity to styrene and decrease the selectivity to CO_x. This is counterintuitive because increasing the contact time would result in the production of more thermodynamically favourable products, CO₂. This will be investigated in more depth in Chapter 4, where CO₂ could be consumed in the reaction under these very specific set of conditions.

Adjusting the partial pressure of *n*-octane also affects the activity and selectivity. Higher partial pressures resulted in a greater selectivity to octene which was comparable with the results obtained from UKZN in Durban.

It appears that adjusting the carbon to oxygen (C:O) ratios can manipulate what products can be produced. Lower C:O ratios i.e. 2:1 often give higher conversions but the major products produced were CO_x. When the C:O ratio increased aromatics and octane selectivity increased. Adjusting the GHSV can also alter the selectivity and conversion. Lower GHSVs often produce CO_x and higher conversions, with exceptions as mentioned above, whilst higher GHSVs produced octene but at a cost with lower conversions.

The catalytic performance of the catalyst is therefore very sensitive to specific conditions. In addition initial catalytic performance is lost when performing hysteresis tests. The

catalyst undergoes a reductive phase transition when reacted at 450 °C where the phase changes from $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ to $\text{FeMoO}_4\text{-MoO}_2$. Once the catalyst has gone through the phase change this is a permanent transition and the original low temperature selectivities and conversions cannot be achieved. So it can be considered that the catalyst is two separate catalysts, i) as the oxidised form, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, at temperatures < 450 °C, and ii) as the reduced form in FeMoO_4 , MoO_2 and Mo_4O_{11} , where the latter is superior at producing octene and aromatics.

It is therefore logical to continue these studies using the reduced phases of the JM iron molybdate catalyst as this phase is responsible for the production of octene and aromatics. Using a pre-reduced catalyst would lower the oxygen capacity and may result in greater selectivities to octene and aromatics at lower temperatures. When the temperature increases the lattice oxygen mobility increases, and so the production of aromatics increases. Restricting the aromatisation process by operating at lower temperatures one would presume an increase in octene selectivity.

3.10. References

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4

Chapter 4: The Reduced JM Iron Molybdate Catalyst: Reactivity, and Mechanistic Studies.

4.1. Introduction

The chapter investigates the reaction of *n*-octane with the reduced JM iron molybdate catalyst. This progresses from Chapter 3, where the $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalyst was discussed. It was shown in the previous chapter and in previous studies¹ that an irreversible phase change occurs when proceeding through the reductive barrier, at 450 °C - 460 °C, effecting the activity, selectivity and the stability of the catalyst. The oxidative dehydrogenation of hydrocarbons and aromatisation have been previously reported using different metal 2+ molybdates such as NiMoO_4 ² and CoMoO_4 ³. Therefore reducing the JM iron molybdate catalyst, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, to produce the FeMoO_4 , MoO_2 and Mo_4O_{11} will be used as a comparison. The JM $\text{FeMoO}_4\text{-MoO}_2$ catalyst will be tested below < 450 °C where in Chapter 3 the $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ phases were present.

4.2. Results and Discussion

4.2.1. Catalyst Activity with the Reduced JM Iron Molybdate

The supplied iron molybdate catalyst from Johnson Matthey was reduced under flowing hydrogen at 500 °C. The catalyst was tested (1 % octane, C:O ; 8:1) by increasing the temperature from 350 °C to 550 °C, in 50 °C increments, at 1000 h⁻¹, 4000 h⁻¹, 6000 h⁻¹ shown by Figures 4.1- 4.3 respectively.

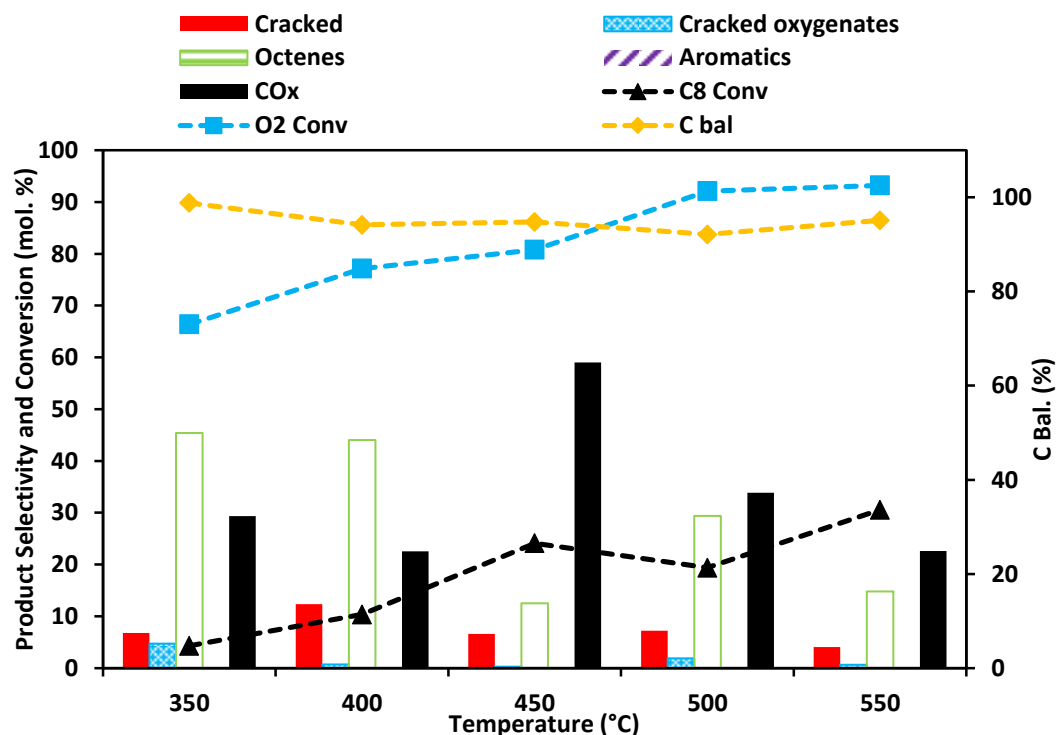


Figure 4.1a: JM reduced iron molybdate catalyst reacted with octane (1%, C:O; 8:1, 1000 h^{-1}). Temperature range 350-550 °C.

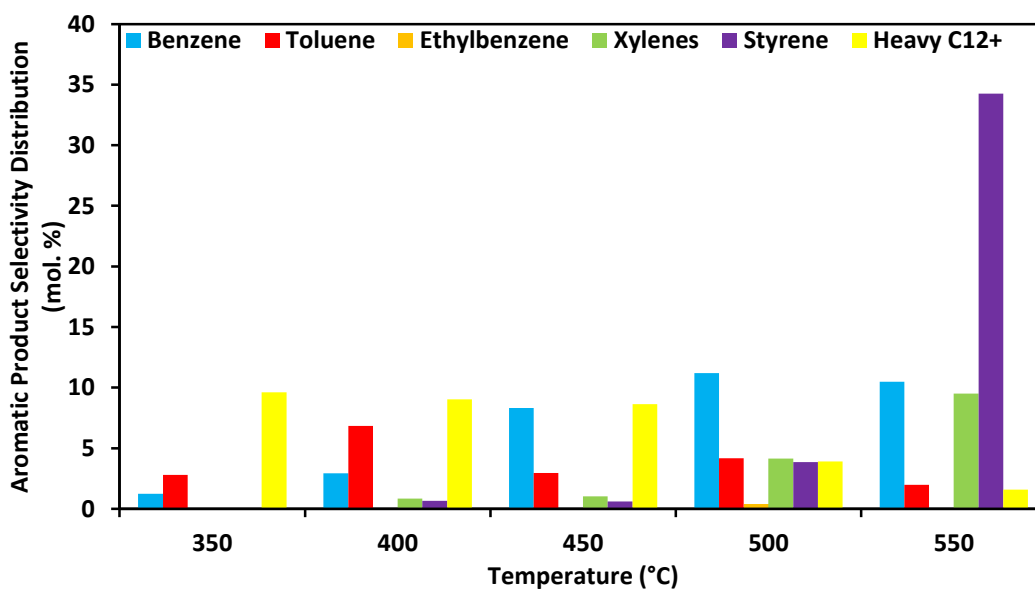


Figure 4.1b: JM reduced iron molybdate catalyst with octane (1%, C:O; 8:1, 1000 h^{-1}). Aromatic product selectivity distribution

Figure 4.11a showed that increasing the temperature from 350 °C to 550 °C the conversion of octane increased from *ca.* 4% to 31%. Oxygen conversion also increased with increasing temperature, from 66 % to 93% at 350 °C and 550 °C respectively.

Within the lower temperature regime ($< 450\text{ }^{\circ}\text{C}$) octene is the dominant product with selectivities reaching *ca.* 45% at both $350\text{ }^{\circ}\text{C}$ and $400\text{ }^{\circ}\text{C}$. At $450\text{ }^{\circ}\text{C}$ the conversion increased to *ca.* 24 % which resulted in an increase selectively to CO_x . The sharp rise in conversion which was seen in chapter 3, due to the phase change from MoO_3 to $\text{FeMoO}_4\text{-MoO}_2$ has been avoided due to reduction treatment of the catalyst. At $500\text{ }^{\circ}\text{C}$ the *n*-octane conversion decreased to *ca.* 20 % which may be attributed to the increase in dehydrogenation necessary to produce the aromatics and octene, which is shown with an increase in oxygen consumption. The selectivity to octene and aromatics increased to *ca.* 30 % and *ca.* 28 % respectively while CO_x selectivity decreased to *ca.* 34 %. At $550\text{ }^{\circ}\text{C}$ the selectivity towards aromatics increased to *ca.* 54 % whilst CO_x and octene decreased significantly to *ca.* 23 % and 15 % respectively. The decrease in octene selectivity observed is associated with aromatic formation, *via* aromatisation of the octene, using these particular set of conditions the dominant product styrene (ST) is produced (Fig. 4.1b).

The reduced JM iron molybdate catalyst was then investigated using a higher GHSV of 4000 h^{-1} (Figs. 4.2).

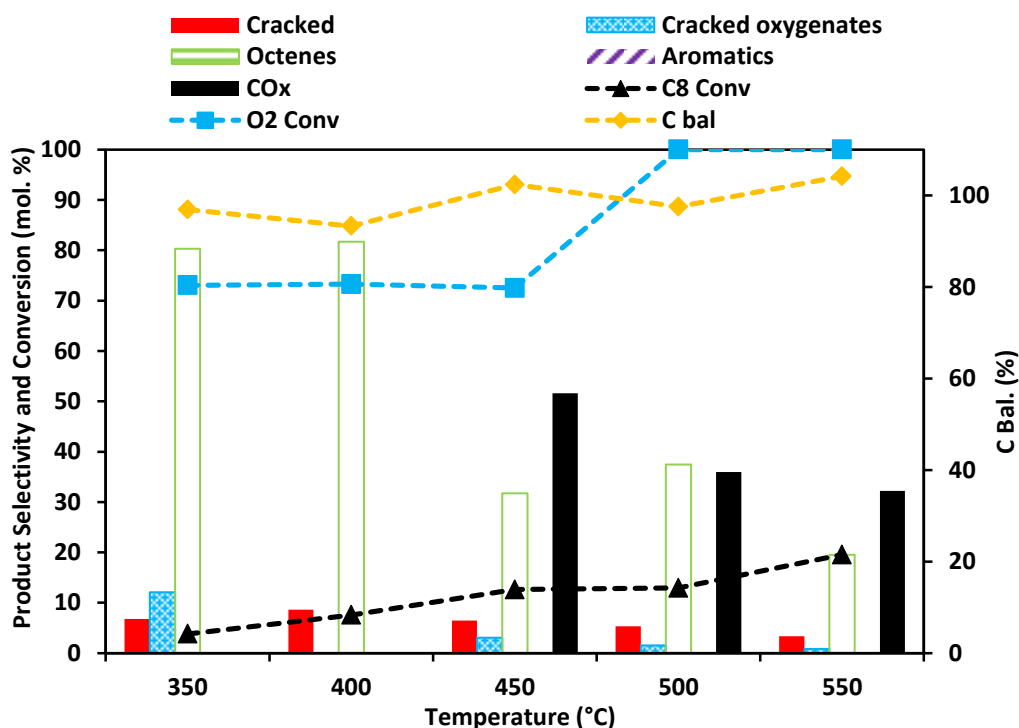


Figure 4.2a: JM reduced iron molybdate catalyst reacted with octane (1%, C:O; 8:1, 4000 h^{-1}). Temperature range $350\text{-}550\text{ }^{\circ}\text{C}$.

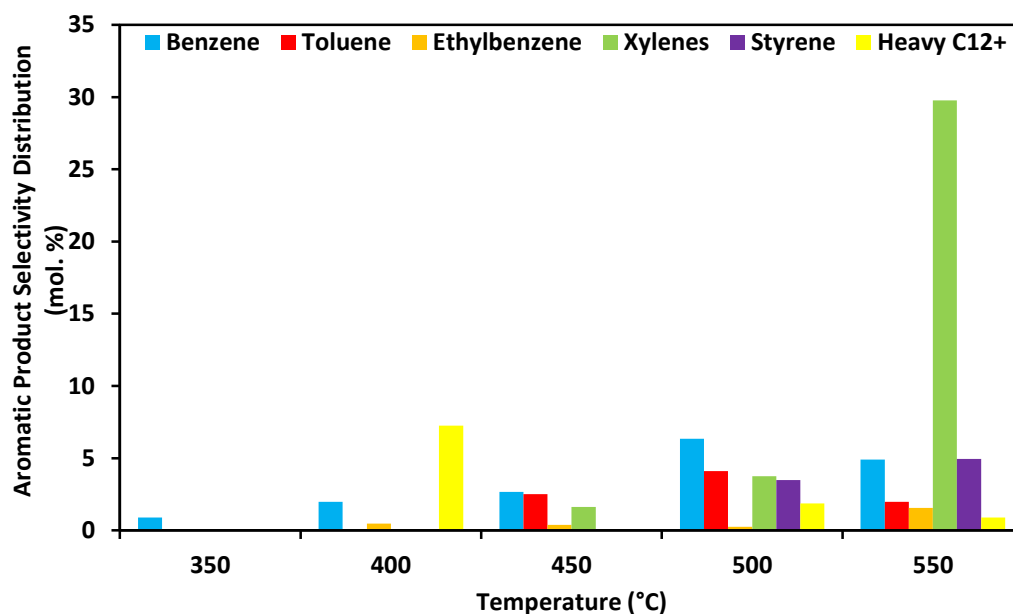


Figure 4.2b: JM reduced iron molybdate catalyst with octane (1%, C:O; 8:1, 4000 h⁻¹). Aromatic product selectivity distribution

Figure 4.2a showed as the temperature was increased from 350 °C to 550 °C the conversion of octane increased from 3.7 % to 19.5 %. However these conversions are lower than the 1000 h⁻¹ study (Fig. 4.1a) due to decrease in contact time, resulting in a lower conversion. This effect is more prominent at higher temperatures, *i.e.* 550 °C. However at lower temperatures (< 450 °C) octene is the dominant product with selectivities reaching *ca.* 80.2 % at 350 °C and 400 °C with no CO_x produced. At 450 °C the octene selectivity decreased to *ca.* 32% whilst the CO_x selectivity increased to *ca.* 52%. At higher temperatures, in particular at 550 °C, the selectivity towards aromatics increased and CO_x decreased (44 % and 32 % respectively) and octene decreased substantially to *ca.* 20 %. The decrease in aromatic selectivity at 550 °C compared to 1000 h⁻¹ (Fig. 4.1a) is due to a decrease in residence time and therefore the formation of aromatics is suppressed. What is also noteworthy is that operating at higher GHSVs less ST is produced and the selectivity towards xylenes increased (Fig. 4.2b). This is consistent with results obtained in chapter 3 with the oxidised JM iron molybdate catalyst, Fe₂(MoO₄)₃-MoO₃, especially when temperatures are ≥ 450 °C. To summarise, alkene selectivity was initially high and decreased with increasing temperature, while aromatic selectivity increased with increasing temperature due to aromatisation of the octene. The production of CO_x emerges at 450 °C but then gradually decreased with increasing temperature.

Increasing the GHSV to 6000 h^{-1} improved the selectivity towards octene at 350°C to 87.9 % (Fig. 4.3a), with no CO_x being produced, but as a result the conversion decreased to 1.1 % because of the decreased residence time. The production of aromatics was also suppressed and little is present at 550°C (1.6 %) due to the decrease in residence time. The residence time seems to influence the aromatisation mechanism, possibly the lack of dehydrogenation of the *n*-octane to produce octadienes inhibits the cyclisation process, and this is shown from the increase in selectivity to octene (ca. 32.6 %) when the GHSV was increased.

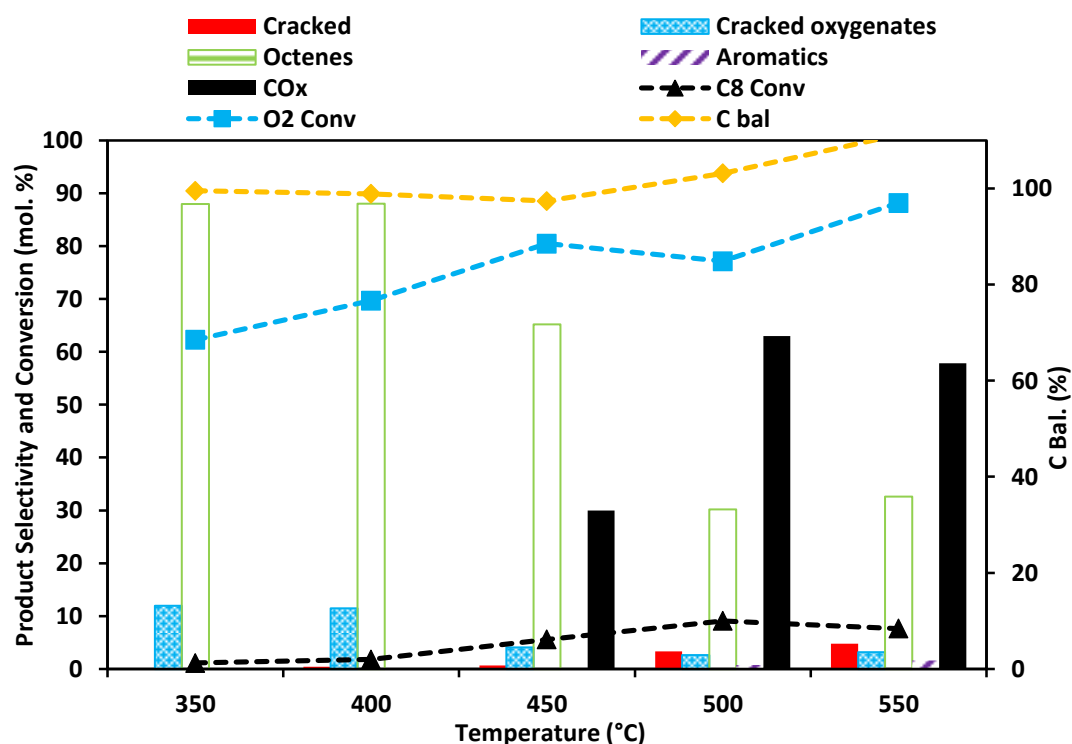


Figure 4.3a: JM reduced iron molybdate catalyst reacted with octane (1%, C:O; 8:1, 6000 h^{-1}). Temperatures range $350\text{--}550^\circ\text{C}$.

4.2.1.1. Summary of the initial testing of the reduced JM iron molybdate catalyst

As a result of the reduction of the catalyst, when the temperature was increased to 450°C under operating conditions the sharp rise in the conversion due to the associated phase change anticipated with the, $\text{Fe}_2(\text{MoO}_4)_3\text{--MoO}_3$ catalyst has been removed. Therefore the $\text{FeMoO}_4\text{--MoO}_2$ catalysts produces less CO_x . At low GHSVs, (Fig.4.1a) there was a slight increase in conversion at 450°C but this is associated with an increase in temperature,

At lower temperatures (< 450 °C) it was evident that selectivity towards octene results in the alkene being the dominant product. As the temperature increased the selectivity towards the aromatics increases which has also been reported in similar studies³⁻⁵. It is noticeable that increasing the GHSV results in an increase in selectivity to octene. While decreasing the GHSV increased the selectivity towards aromatics, this suggests that longer residence times are needed to cyclise the 'intermediate' octene. The dominance in selectivity towards either xylenes or ST is dependent on the residence time and will be discussed in more detail later in the chapter.

4.3. Optimisation of Experimental Parameters to Produce Octene and Aromatics from *n*-Octane

4.3.1. A Temperature, GHSV and C:O Ratio Study

The graphs below (Figs. 4.4- 4.7) show that changing the C:O ratios and GHSV can optimise selectivity towards octene and aromatics. Each graph from Figure 4.4 - 4.7 displays these changes at 350 °C, 400 °C, 450 °C and 550 °C respectively.

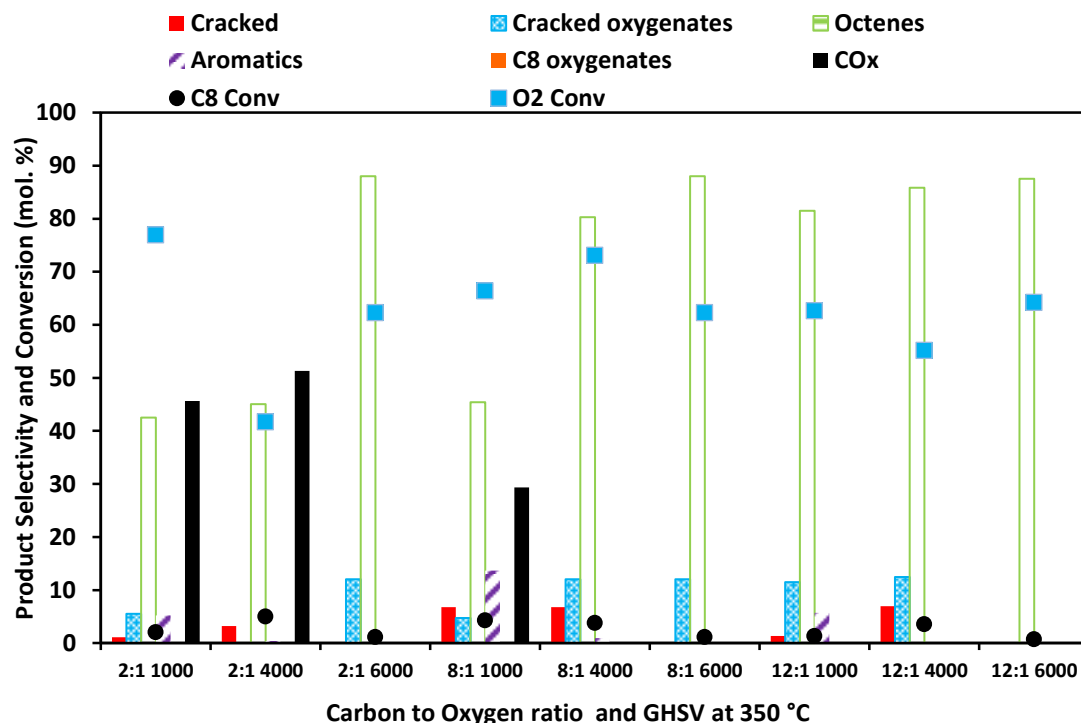


Figure 4.4: Reaction of *n*-octane (1 %) with the reduced JM iron molybdate catalyst using various carbon to oxygen ratios between 1:1- 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at **350 °C**

At 350 °C (Fig. 4.4) using moderate oxidative conditions (C:O ; 2:1), the results show the primary product produced was CO_x along with the octene at GHSVs of 1000 h⁻¹ and 4000 h⁻¹. However at 6000 h⁻¹ CO_x was not produced and so the octene selectivity increased to *ca.* 87 %. The shorter contact time at 6000 h⁻¹ resulted in a low conversion *ca.* 1 %. The C:O ratio was increased to 8:1 and at 1000 h⁻¹ the octene selectivity remained the same, however CO_x decreased to *ca.* 29 % and the aromatics increased to *ca.* 14 %. This suggests that there is a competing reaction between CO_x production and aromatic production which was observed in the previous chapter seen at higher temperatures with the Fe₂(MoO₄)₃-MoO₃ catalyst. As the GHSV increased to 4000 h⁻¹ and 6000 h⁻¹, the conversion further decreased, and the production of CO_x fell to zero. The C:O ratio was then increased to 12:1 and resulted in no CO_x production across the GHSV testing range. This may be due to the decrease in oxygen available in the gas feed, however the oxygen conversion did not increase.

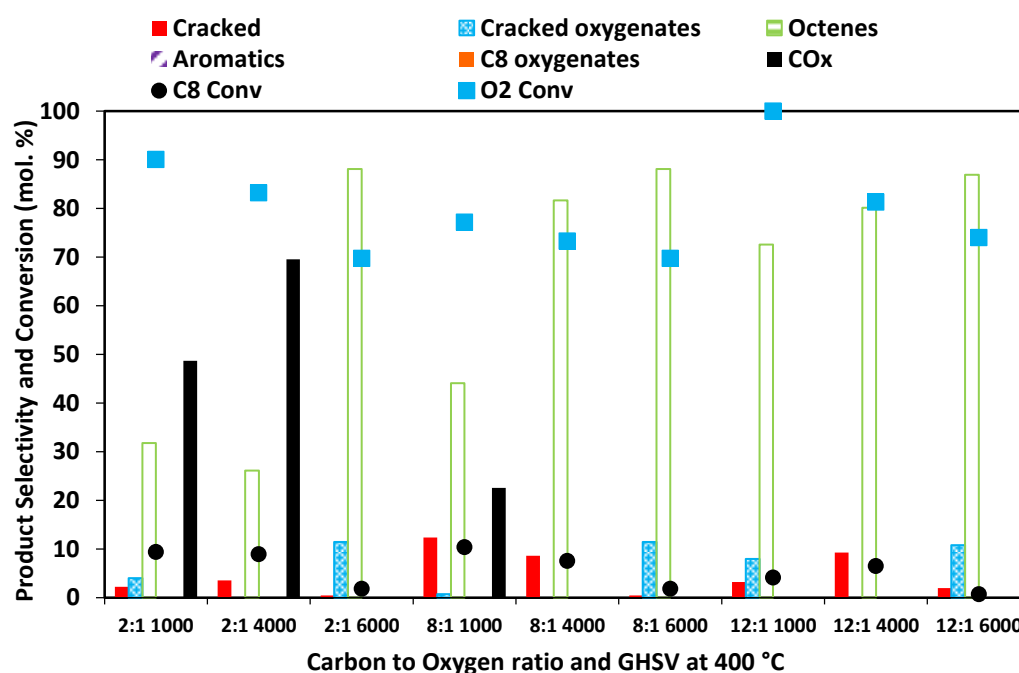


Figure 4.5: Reaction of *n*-octane (1 %) with the reduced JM iron molybdate catalyst using various carbon to oxygen ratios between 1:1- 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at 400 °C.

When the temperature increased to 400 °C (Fig. 4.5) the results were similar to that at 350 °C. CO_x production increased at C:O 2:1 from 350 °C to 400 °C, however CO_x was not produced at 6000 h⁻¹. At 1000 h⁻¹ the aromatic selectivity increased with temperature from 350 °C to 400 °C which is expected as lattice oxygen within the iron

molybdate lattice becomes more labile with increasing temperature¹. When the C:O ratio increased to 8:1 the aromatic selectivity increased compared to that of 350 °C at both 1000 h⁻¹ and 4000 h⁻¹. At 6000 h⁻¹ no aromatics were produced but the octene selectivity remained high at *ca.* 88 %. The octane conversion decreased with increasing space velocity and the production of CO_x decreased to zero when the space velocity was increased from 1000 h⁻¹. The optimum conditions for the production of octene are using a C:O ratio of 8:1 at 4000 h⁻¹ as this gives reasonable conversion, *ca.* 8 % with high selectivities *ca.* 82 %. When the C:O ratio increased to 12:1 the aromatic selectivity increased especially at 1000 h⁻¹ and 4000 h⁻¹. At 6000 h⁻¹ conversion was low, < 1 % which resulted in the high selectivity towards octene.

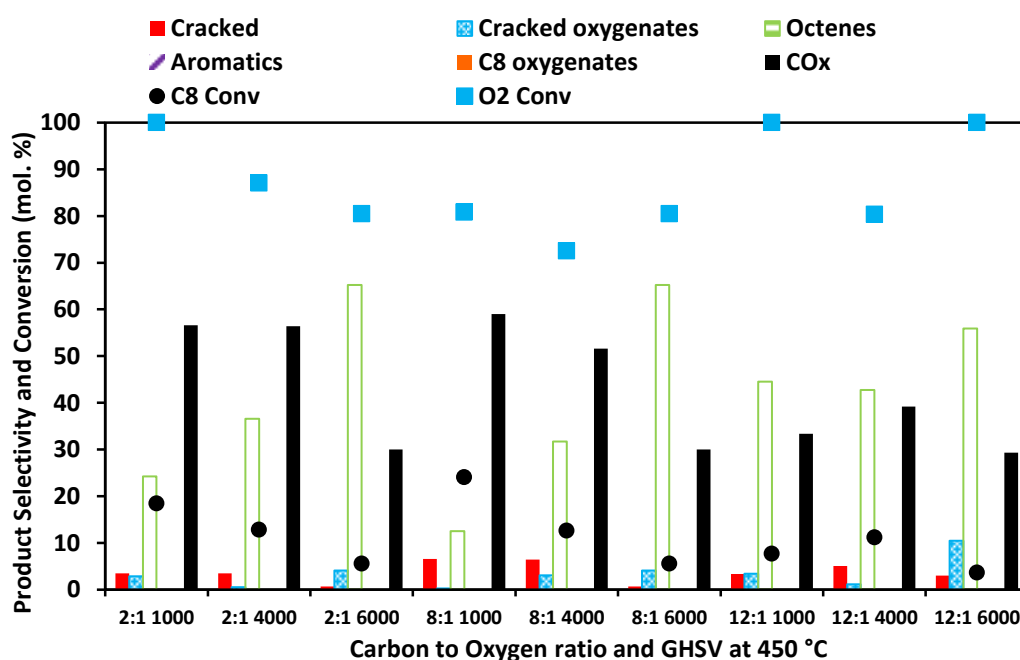


Figure 4.6: Reaction of *n*-octane (1 %) with the reduced JM iron molybdate catalyst using various carbon to oxygen ratios between 1:1- 12:1 and GSVs of 1000 h⁻¹ to 6000 h⁻¹ at 450 °C.

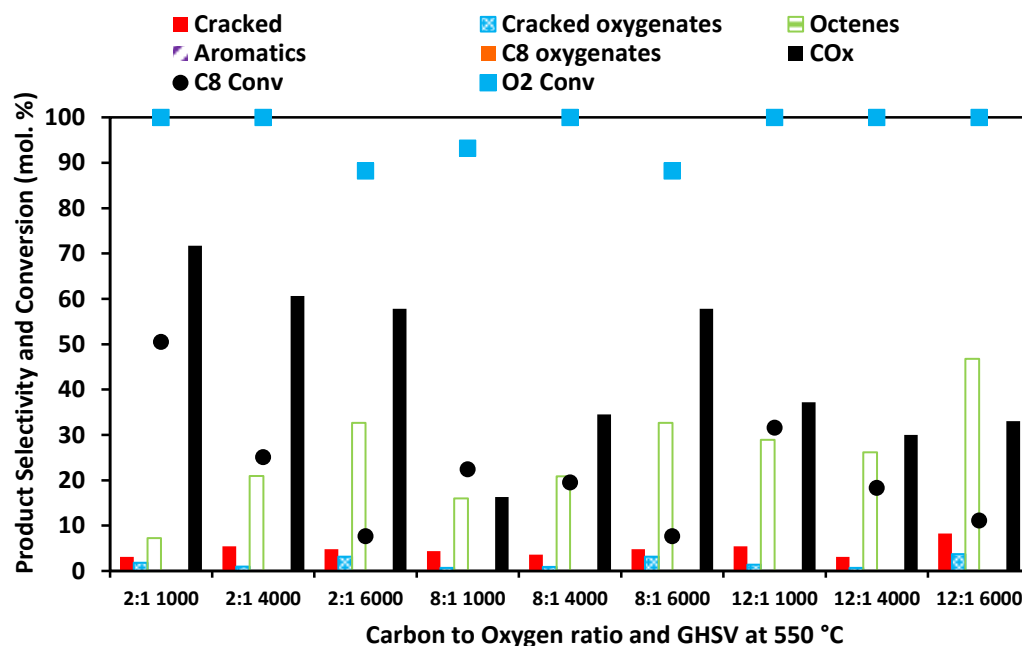


Figure 4.7: Reaction of *n*-octane (1 %) with the reduced JM iron molybdate catalyst using various carbon to oxygen ratios between 1:1- 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at 550 °C.

When the temperature was increased to 450 °C (Fig. 4.6) CO_x production generally increased across all C:O ratios and GHSVs. At 6000 h⁻¹ the selectivity to octene increased relative to the other GHSVs, and the selectivity towards aromatics increased with lower GHSVs. The conversion of *n*-octane decreased with increasing GHSVs due to a decrease in the residence time.

At 550 °C (Fig. 4.7) the conversion increased with the increase in temperature. At C:O ; 2:1 the dominant product produced was CO_x because of the more oxidising conditions. Increasing the GHSV increased the production of octene whilst the production of aromatics decreased. When the C:O ratio was increased to 12:1 the aromatic production increased. With increasing space velocities octene replaced aromatics as the dominant product. At 8:1 with lower space velocities produced aromatics with high selectivity and the CO_x decreased. Only at higher space velocities the CO_x increased. At 8:1 when the GHSV was lowered from 4000 h⁻¹ to 1000 h⁻¹ a drop in CO_x was observed, which was seen when using these conditions with the JM Fe₂(MoO₄)₃-MoO₃ catalyst. This is because the Fe₂(MoO₄)₃-MoO₃ catalyst used in Chapter 3 at temperatures ≥ 460 °C undergoes the reductive phase change to the FeMoO₄-MoO₂, and therefore under the same operating conditions the same material is produced.

4.3.2. Catalyst Stability

4.3.2.1. A TOL Study at 400 °C: Maximising the production of octene

The reduced JM iron molybdate catalyst was tested (Fig. 4.8) using the optimum conditions for the production of octene which used a C:O ratio 8:1 at 4000 h⁻¹ which is seen in Figure 4.5.

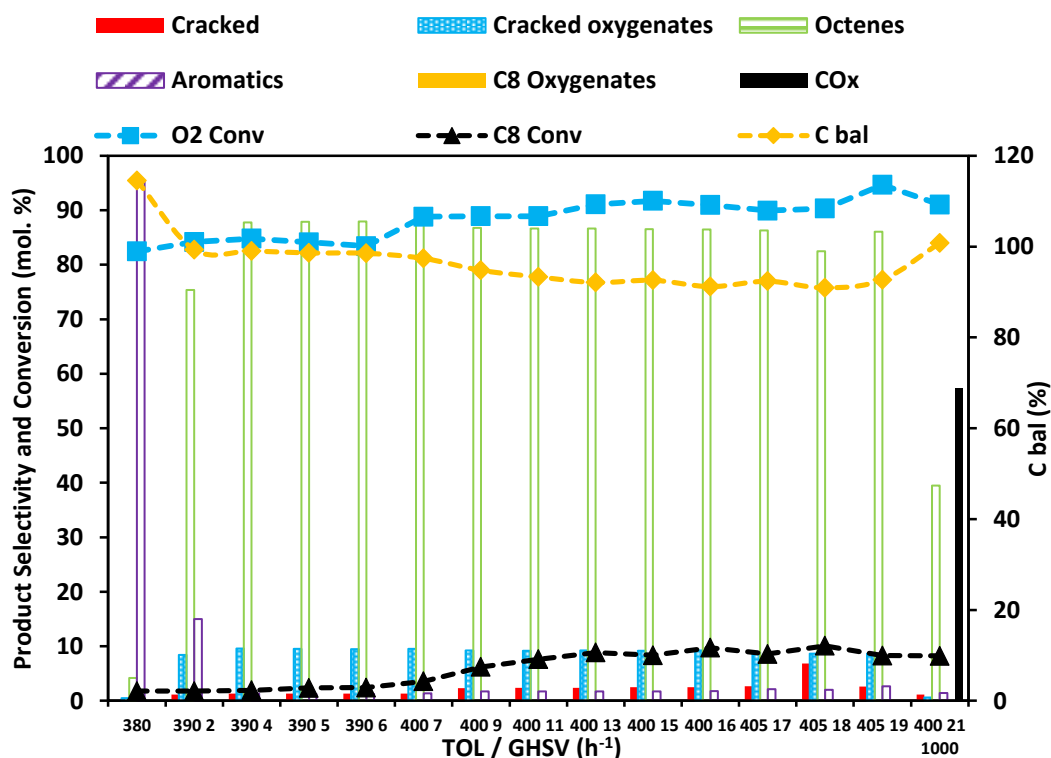


Figure 4.8: Time on line (TOL) reaction of octane with the reduced JM iron molybdate catalyst at a C:O 8:1 at 400-405 °C.

At 380 °C to 390 °C (2 h) a high selectivity to an aromatic product (95.2 %), which was assigned as benzaldehyde was produced but rapidly decreased with time, possibly due to an unsaturated initial exposed catalytic surface that could lead to multiple dehydrogenation along the *n*-octane chain. The system was then stabilised for several hours before reaching 400 °C. The time on line (TOL) data showed that the catalyst was stable from the 11th hour to the 21th hour at 4000 h⁻¹ and maintained a high selectivity towards octene *ca.* 86 %. The experiment also confirms that no CO₂ was produced under the operating conditions. The temperature was then increased to 405 °C to confirm that CO₂ production is not being assisted by a narrow range in

temperature. When the GHSV was reduced to 1000 h^{-1} CO_2 was produced, which is in agreement with earlier results (Fig. 4.1a).

From literature it has been shown that *n*-butane/propane dehydrogenation reactions (DH) over $\text{VO}_x/\text{Al}_2\text{O}_3$ form coke at higher temperatures and that ODH reactions have lower yields in comparison⁶. This could explain the increase in conversion with time as more coke is deposited onto the surface. It was also reported as the temperature increased the more aromatic in nature the coke became⁶.

Wu *et al.* also showed that networks of polyaromatic hydrocarbons can form on the surface of the polymeric VO_x species⁷. *In situ* XRPD (Chapter 3, Fig. 3.2) previously showed that Mo_4O_{11} species are formed at high temperatures which suggests that the phase assists in the production of aromatics.

4.3.2.1.1. Elemental Analysis and Spectroscopy

CHN elemental Analysis (Table 4.1) was used to determine, if any, what carbonaceous species were deposited onto the catalyst because of the observed decrease in carbon mass balance with time shown in Figure. 4.8.

Table 4.1: CHN elemental results for the reaction between *n*-octane and the JM iron molybdate catalyst at 400°C , 4000 h^{-1} .

Sample	Carbon (%wt/wt)	Hydrogen (%wt/wt)	Nitrogen (%wt/wt)
JM Iron molybdate reduced in H_2 SM	0.04	0.00	0.01
JM Iron molybdate reduced in H_2 : 1 % octane at 400°C , 4000 h^{-1}	0.00	0.00	0.00

No carbon was observed by CHN analysis using the optimum conditions (1 % octane at 400°C , 4000 h^{-1}), but was detected for the starting material. This suggests an error of $\pm 0.04 \%$. However using *in situ* Raman spectroscopy (Fig. 4.9) it was shown that

possible carbonaceous species are present. The peak at 1123.02 cm^{-1} suggests that a sp^3 hybridized carbon species is present which is characteristic of nano crystalline diamond. This result suggests that the 'coke' is formed from the pre-existing aromatics that are formed in the initial stages of the reaction as shown and is in agreement with the literature^{8,9}

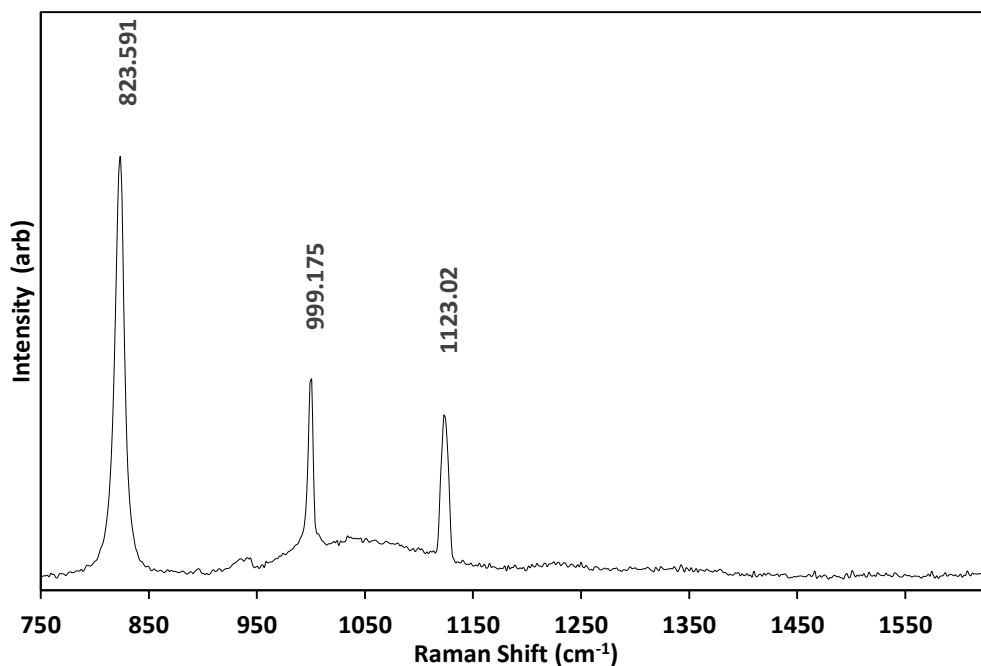


Figure 4.9: *In situ* Raman scan of the reaction of octane with the reduced JM iron molybdate with 5% H_2 catalyst at a C:O 8:1 at 400 at 4000 h^{-1} .

The peaks visible at 823 cm^{-1} and 999 cm^{-1} are assigned to the MoO_x stretching modes. What is worth noting here is that there is no sp^2 hybridized carbon at 1602 cm^{-1} . This peak is characteristic of crystalline graphite, usually at 1582 cm^{-1} , but shifts to higher frequencies in dehydrogenation catalysts⁹, which is possibly related to the conjugated olefinic species or polycyclic aromatic hydrocarbons (PAHs) which is seen at 550°C , which will be discussed later in this chapter.

When the GHSV was lowered to 1000 h^{-1} CO_x was then produced. The carbon mass balance increased to 100 % and the selectivity to CO_x increased from 0 % to 57.2 %. This indicates that the carbon on the surface is being combusted as a consequence of a shorter contact time. The catalyst also undergoes an oxidation process during the change in GHSV which is shown by Raman spectroscopy and complemented by UV-vis spectroscopy (Fig.4.10 and 4.11).

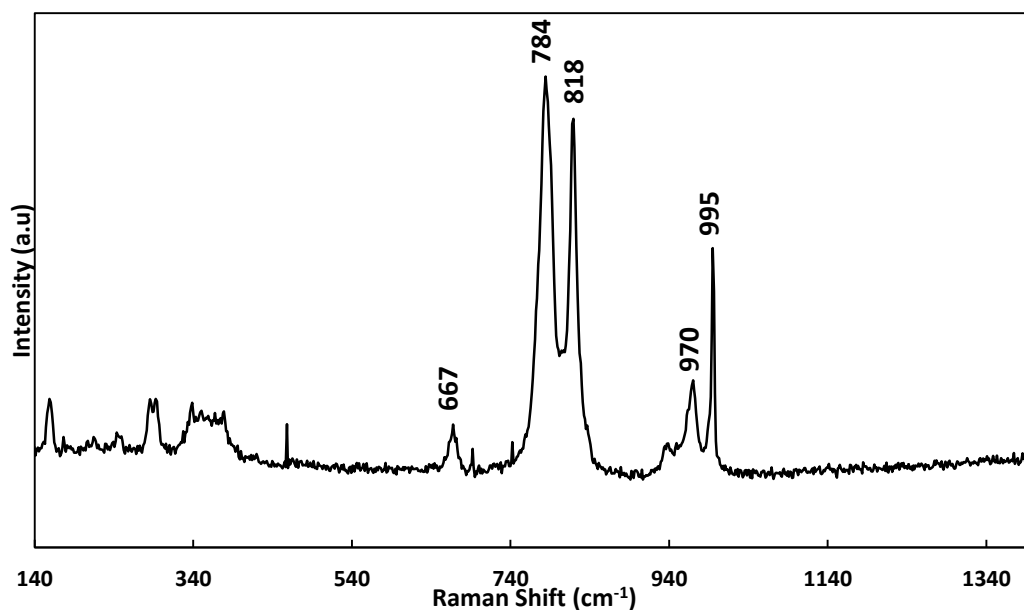


Figure 4.10: Raman scan of the catalyst post reaction (reduced JM iron molybdate catalyst at a C:O 8:1 at 400 °C) after lowering the GHSV to 1000 h⁻¹ from 4000 h⁻¹.

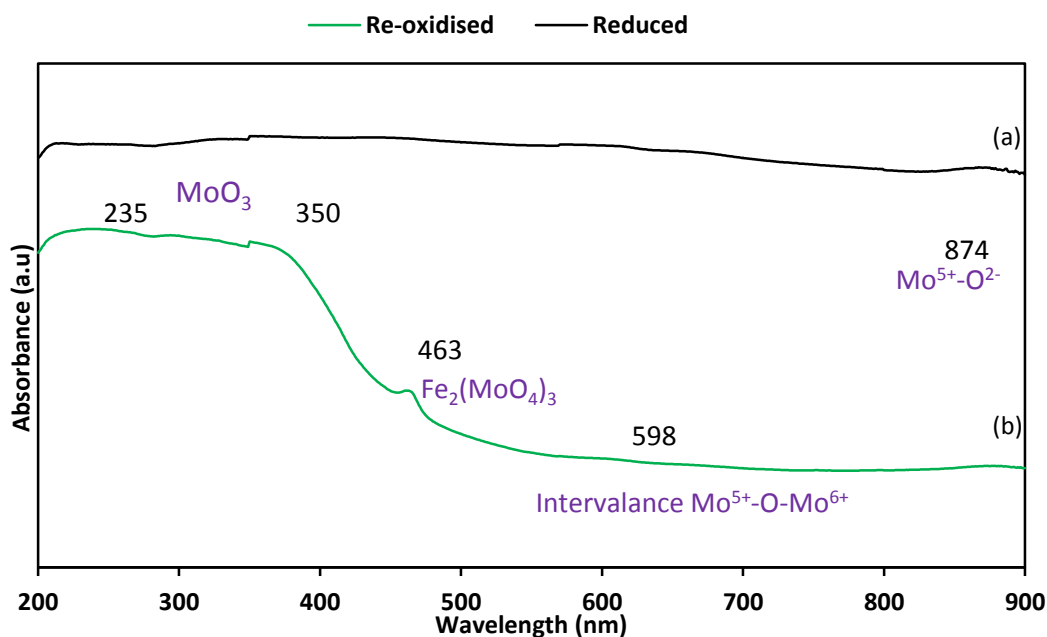


Figure 4.11: UV-vis spectrum of the reduced JM iron molybdate at C:O 8:1 at 400 °C. (a) black line shows catalyst is still reduced when the GHSV remains at 4000 h⁻¹; (b) Green line is representing the catalyst is re-oxidised after the GHSV is lowered to 1000h⁻¹.

The Raman spectrum (Fig. 4.10) shows the presence of molybdenum (VI) oxide (MoO₃) peaks which appeared at 996 and 667 cm⁻¹. The molybdenum (IV) oxide band is unobservable because the molecule is Raman inactive and determines that the

catalyst has re-oxidised. The bands at 996 cm^{-1} and 971 cm^{-1} are indicative of the $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 phases respectively and arise from the Mo=O terminal stretching. The bands visible at 785 cm^{-1} and 817 cm^{-1} correspond to the Mo-O-Mo vibrations in the $\text{Fe}_2(\text{MoO}_4)_3$ phase and the MoO_3 phase respectively^{10, 11, 12} These bands are also unobservable for the FeMoO_4 phase present in the reduced catalyst which confirms that the sample has undergone a re-oxidation process when the GHSV was lowered to 1000 h^{-1} . The Raman spectrum compliments previous XRPD data for the JM $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalyst confirming the presence of both the $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 phases. Therefore after reaction with octane at $400\text{ }^\circ\text{C}$ and 4000 h^{-1} the catalyst is still reduced and the sample appears to be Raman inactive. No bands were observed even with repeatedly long scan times and accumulations.

UV-vis spectroscopy (Fig. 4.11) also confirms the re-oxidation step when the pre-reduced catalyst was tested using a GHSV of 1000 h^{-1} at $400\text{ }^\circ\text{C}$ (C:O 8:1). The band at 463 nm is associated with Fe^{3+} and not Fe^{2+} and confirms that the iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) phase is present¹³.

4.3.2.2.A TOL Study at 550 °C with Alternating GHSVs: Maximising the production of styrene and the importance of carbon

The optimum conditions for the production of ST with high selectivity was shown to be at a C:O ; 8:1 at 1000 h⁻¹ at 550 °C (Chapter 3 Fig. 3.13). The TOL at 550 °C whilst varying the GHSV between 4000 h⁻¹ and 1000 h⁻¹ was discussed in detail in Chapter 3 Figure 3.11, and is shown below (Figs. 4.12a and 4.12b).

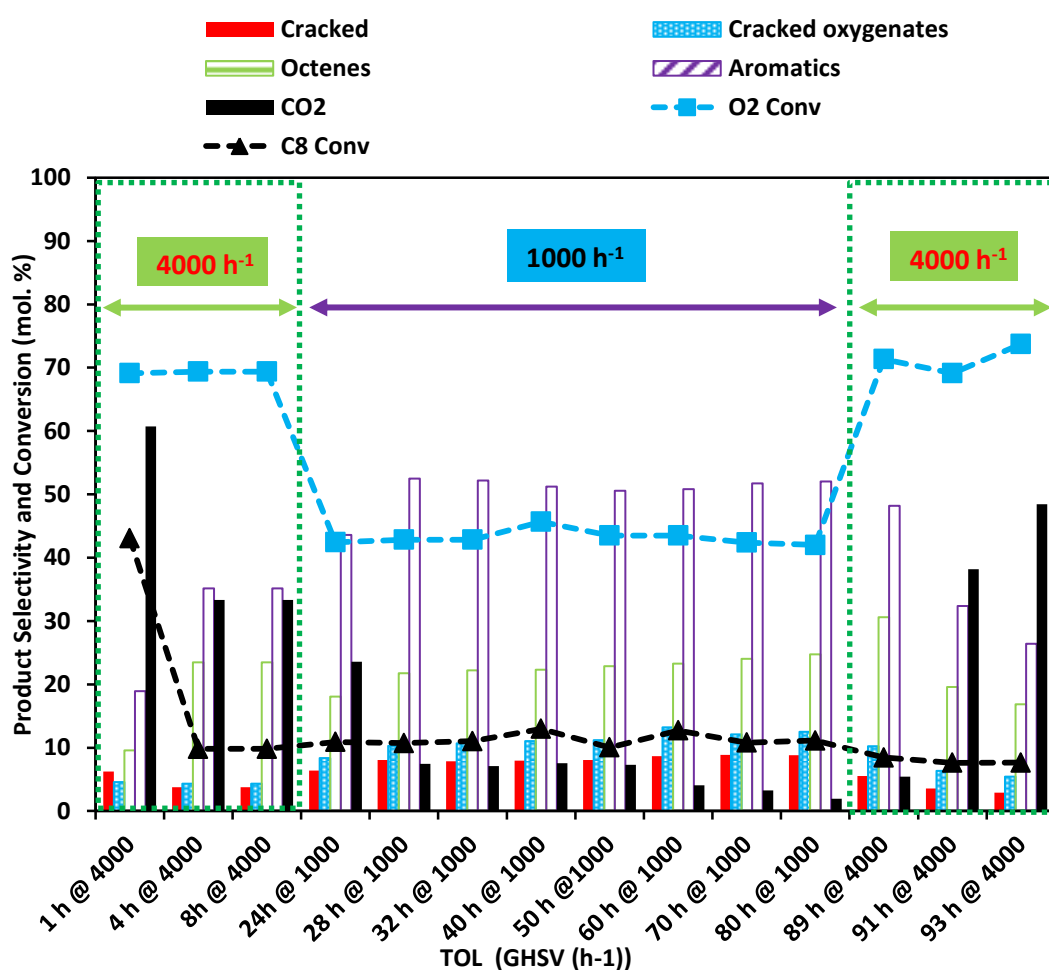


Figure. 4.12a: Reaction of 1 % *n*-octane (C:O 8:1) with the JM Fe₂(MoO₄)₃-MoO₃ catalyst. Temperature at 550°C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹ at 550 °C.

It is kinetically favourable that at lower space velocities more CO_x should be produced, along with water, and this was shown experimentally by using lower C:O ratios of 2:1. However it is not the case under this specific set of conditions. Similar systems in the literature shows at higher temperatures (550 °C) the temperature programmed reduction carburization (TPRC) experiment, a heat treatment with CH₄/H₂, revealed that surface oxygen is stripped and this resulted in 'pure carbon' leading to a loss in

dehydrogenation sites⁶. This is not the case when the reaction temperature is below 500 °C, and so oxygen interacts with the carbon (going back to the 400 °C scenario). It was suggested in the literature that a molybdenum carbide system requires a delicate control of reaction parameters as surface carbon deposits cannot be removed by facile combustion in air¹⁴. So if similar carbon species, not necessarily carbide, are present on the surface of the JM iron molybdate catalyst CO₂ may not be produced at high temperatures from surface adsorbed oxygen species which was shown from the anaerobic/aerobic experiments in Chapter 3.

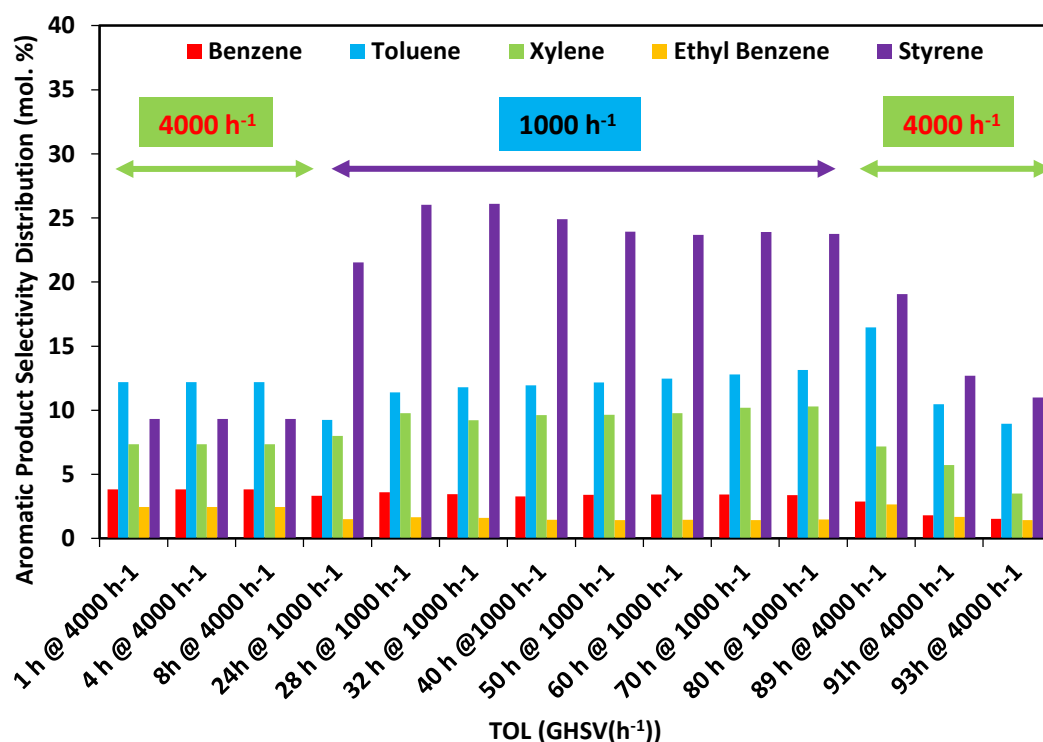


Figure. 4.12b: The aromatic selectivity profile of the reaction of 1% *n*-octane (C:O 8:1) with the JM Fe₂(MoO₄)₃-MoO₃ catalyst. Temperature 550°C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹.

Figures 4.12a and b show clearly that CO₂ decreasing whilst ST selectivity increased at 1000 h⁻¹. It has been shown in literature that coke (polyaromatic coke) on the surface of the catalyst can participate in aromatisation catalysis^{6, 14, 15}, and that Mo₂C containing catalysts assist the production of ethylbenzene (EB) and xylenes¹⁶. So the ODH reaction between *n*-octane and the reduced iron molybdate catalyst above 500 °C may result in carbon leading to aromatisation and temperatures below 500 °C may produce carbon deposits with oxygen resulting in alkene production.

4.3.2.3. Elemental Analysis and Spectroscopy

CHN elemental Analysis (Table 4.2) was performed on the reduced JM iron molybdate catalyst at 550 °C using the optimum conditions of the production of aromatics.

Table 4.2: CHN elemental results for the reaction between *n*-octane and the reduced JM iron molybdate catalyst at 550 °C, 4000 h⁻¹.

Sample	Carbon (%wt/wt)	Hydrogen (%wt/wt)	Nitrogen (%wt/wt)
JM Iron molybdate reduced in H ₂ SM	0.04	0.00	0.01
JM Iron molybdate reduced in H ₂ : 1 % octane at 550 °C, 4000 h ⁻¹	0.26	0.00	0.03
JM Iron molybdate reduced in H ₂ : 1 % octane at 550 °C, 1000 h ⁻¹	1.17	0.00	0.04

Table 4.2 shows that there was more coke at the lower GHSV, the equivalent to *ca.* 30 monolayers. This suggests when the GHSV was increased from 1000 h⁻¹ to 4000 h⁻¹ that the carbon was removed which was observed experimentally with an increase in CO₂ selectivity and increase in O₂ consumption (Figure. 4.12a).

It was shown using Raman spectroscopy (Fig. 4.13) that several Raman bands appear at 1141, 1355, 1401 and 1602 cm⁻¹.

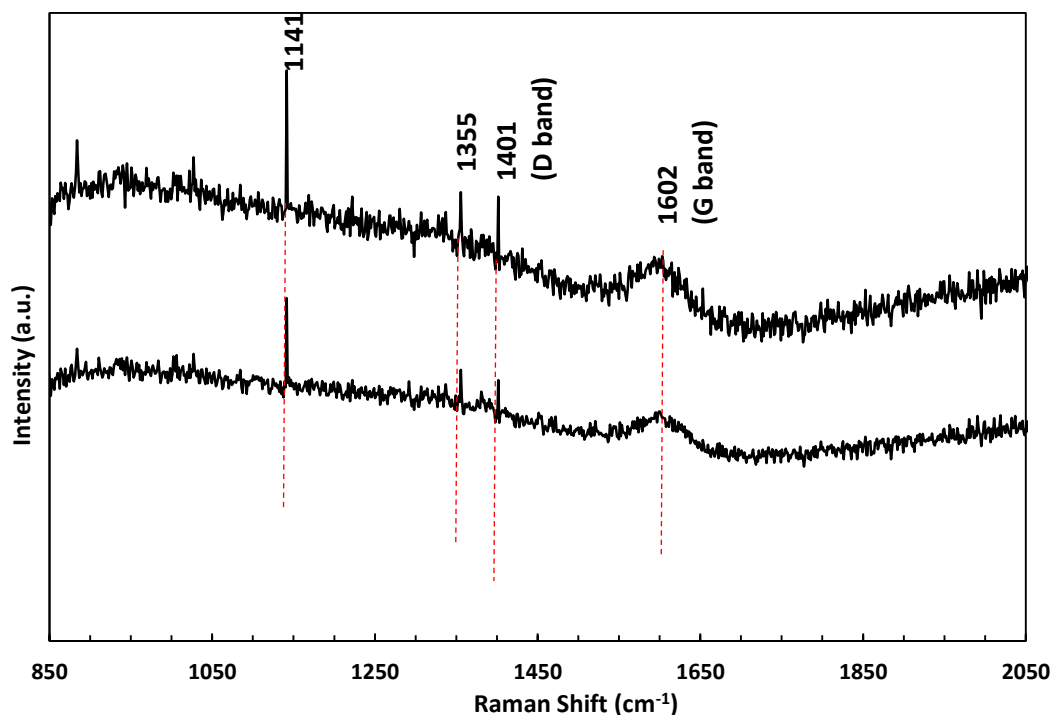


Figure 4.13: Raman scan of the reaction of octane with the reduced JM iron molybdate with 5% H₂ catalyst at a C:O 8:1 at 550 °C at 1000 h⁻¹.

The band at 1355 cm⁻¹ is assigned to the high crystalline quality of the carbon deposited onto the catalyst and the sharp peak at 1141 cm⁻¹ originates from a co-existing sp² phase which has been suggested by Ferrari *et al.* to be a transpolyacetylene/nano-diamond material⁶. The stretching modes at 1401 cm⁻¹ and 1602 cm⁻¹ are due to sp² carbon species. The G band is due to the bond stretching of sp² atoms in both the rings and chains, and the D band is due to the breathing modes of sp² atoms in rings. These two peaks are common for various forms of disordered, noncrystalline, and amorphous carbons in the Raman spectra. It was observed that the band at 1582 cm⁻¹ (G band) of the crystalline graphite shifts to higher frequencies, 1602 cm⁻¹, in dehydrogenation catalysts, which is possibly related to the conjugated olefinic species or polycyclic aromatic hydrocarbons (PAHs)^{8,9}.

The XPS (Fig. 4.14) spectrum of the C 1s region showed a peak at 284.5 eV which displayed a slight tailing to a higher binding energy which is characteristic of graphitic carbon. This complements the Raman and CHN data previously shown at 550 °C at 1000 h⁻¹.

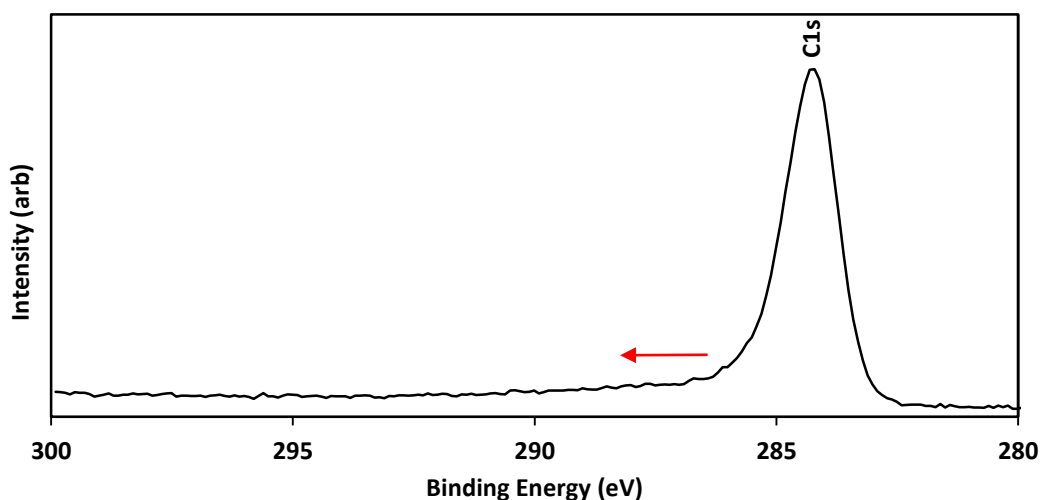


Figure. 4.14: XPS spectra of the Mo 3d region of the iron molybdate catalyst starting material and under reaction conditions at 400 °C and 550 °C.

4.3.2.3.1. Summary

It was shown that reacting *n*-octane under ODH conditions with the JM reduced iron molybdate catalyst (C:O ; 8:1 at 4000 h⁻¹) resulted in high selectivity to octene with no CO_x produced at 400 °C and a high selectivity to aromatics and a decrease in CO_x was observed at 550 °C at 1000 h⁻¹.

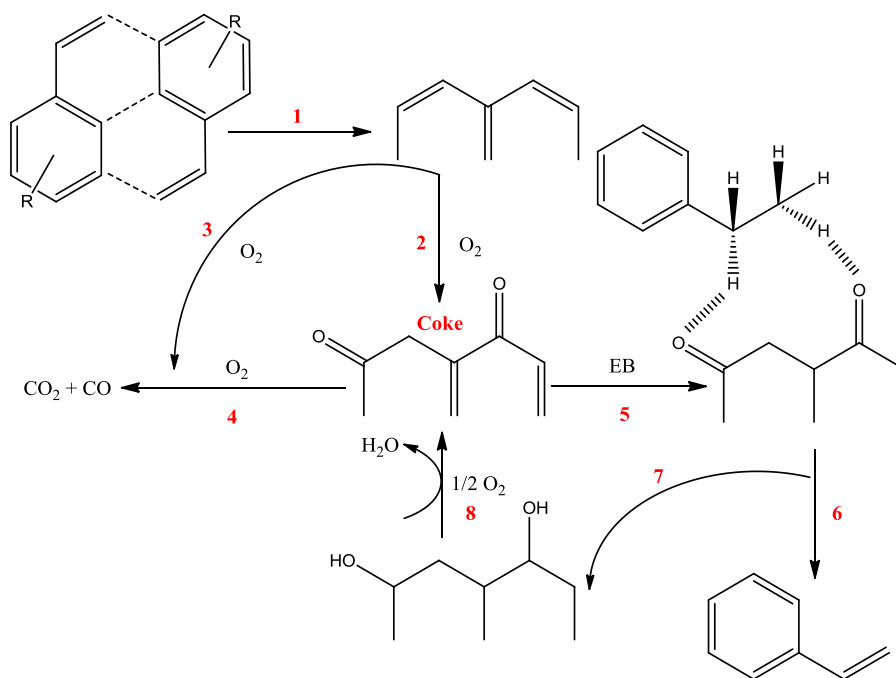
At 400 °C the conversion of octane increased with time whilst the carbon mass balance decreased suggesting that the carbon is deposited onto the surface. However CHN analysis did not show this, but conflicting Raman spectrum showed crystalline carbon species in the form of nano-diamonds were present on the surface of the catalyst. It has been shown that carbonaceous species, not necessarily sp² hybridised carbon, deposited on catalytic surfaces are active for alkane activation¹⁴ so perhaps a similar mechanism is in operation.

At 550 °C CHN analysis showed that 1.17 wt. % carbon was deposited onto the surface of the catalyst and that the complementary Raman spectrum showed that the carbon was sp² hybridised in the form of PAHs.

4.4. Proposed Mechanisms

4.4.1. Active Carbon in Oxidative Dehydrogenation

Cavani *et al.*^{17,18} report that the ODH reaction from EB to ST is exothermic, producing 129 kJ/mol. Catalysts that have greater acidic properties in metal oxides or carbon materials are found to be active and selective. It has been well documented that carbonaceous species (coke) formed on the surface of the catalysts are catalytically active and the catalyst itself may not be required^{6, 11, 15, 17, 18}. The active sites that are formed from the coke are suggested to be quinone/hydroquinone (PAHs) in nature. Conversions of 70-80% with selectivity of > 90% were achieved. The mechanism below (Scheme 4.1) reveals how the coke maybe formed from PAHs and the oxygen forms the catalytically active sites for the ODH reaction.

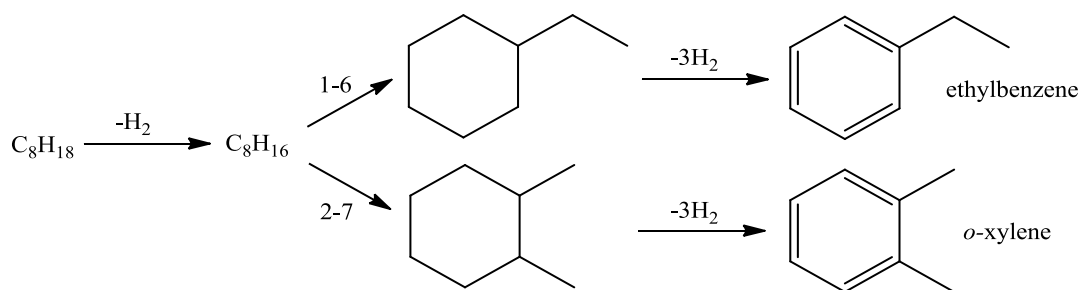


Scheme 4.1: Adapted reaction mechanism for the oxidative dehydrogenation (ODH) of EB to ST using aromatics for coke production^{19,20}.

The reaction mechanism²⁰ (Scheme 4.1) shows one possible route in the production of ST from EB using coke as a catalyst via an oxidative dehydrogenation (ODH) mechanism. Step 1 illustrates the aromatic moieties produced from the reaction with the reduced JM iron molybdate catalyst and 1 % octane (C:O ; 8:1) at 550 °C (Figs. 4.12a and b). In step 2 the oxygen from the gas phase partially oxidises the surface of

the coke to produce the active coke catalyst. If the coke comes from a polyaromatic species it will either combust when oxygen is present (step 4) which is representative of the 4000 h^{-1} data, or it can create active oxygen sites for oxydehydrogenation (step 5) which is representative of the 1000 h^{-1} data. This suggests, along with the experimental data, at 1000 h^{-1} less carbon dioxide is produced, which is unexpected because with longer contact times the production of CO_x increases due to thermodynamics. This hypothesis has been proven at lower temperatures (Fig. 4.8) because when the GHSV was changed from 4000 h^{-1} to 1000 h^{-1} the selectivity to CO_x increased. The CO_2 must therefore have been consumed during the reaction to produce ST from EB. The selectivity to ST (Fig. 4.12b) increased whilst the selectivity to CO_2 (Fig. 4.12a) decreased therefore CO_2 must have been used as an oxidant. It has been reported that CO_2 can be used as an oxidant to activate EB to ST^{21} and with both metal oxide-carbon²¹ and iron-oxide catalysis¹⁵.

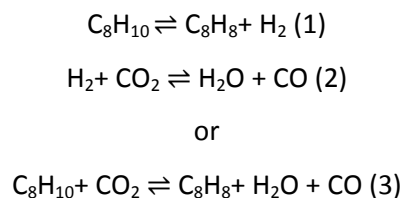
As mentioned earlier, it was also found that molybdenum carbide containing catalysts also assist in the production of aromatics from *n*-octane¹⁶ (Scheme 4.2).



Scheme 4.2: Reaction mechanism for the aromatisation of *n*-octane to EB and *o*-xylene.¹⁶

Wachs *et al.*¹¹ suggested that the molybdate catalysts with excess molybdenum form a monolayer at high temperatures. If carbon is deposited onto the surface it is possible that a similar mechanism can operate with the PAH coke that was formed on the catalyst, and this would be consistent with the experimental studies.

A possible mechanism utilizes the dehydrogenation process. CO₂ can be used in two consecutive reactions: a dehydrogenation (1) followed by the reverse water gas shift (RWGS) (2); or as a direct dehydrogenation by CO₂ (3)²¹.



However it was suggested that that the dominant routes are a redox mechanism (Fig. 4.15), which was also supported by Xiao *et al.*²² for the RWGS reaction, and the two-step pathway for the dehydrogenation in CO₂ (Fig. 4.16).

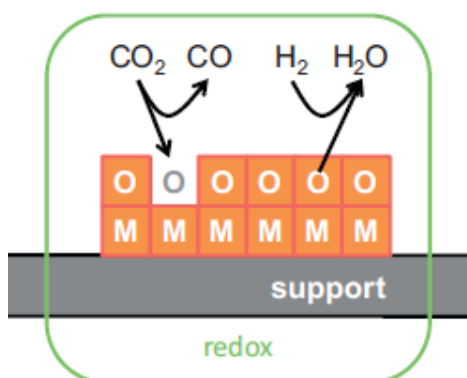


Figure 4.15: Simplified scheme for the redox and associative mechanism of RWGS (only showing the forward reaction).²¹

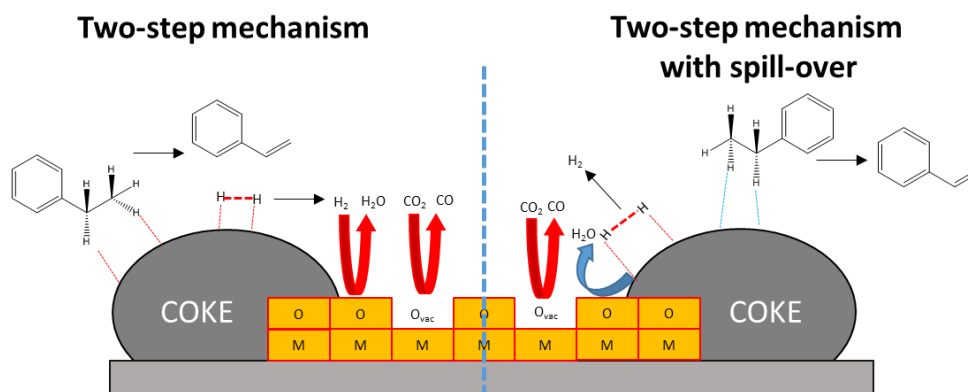
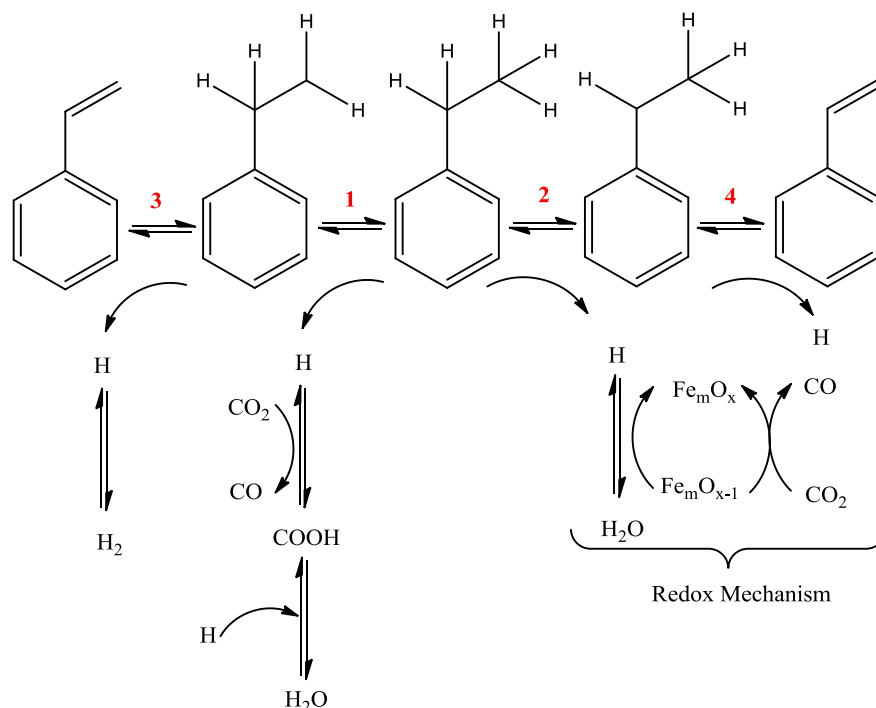


Figure. 4.16: Adapted Schematic with the original two-step mechanism (*left*) and the proposed two-step Mechanism with spill over of hydrogen (*right*).²¹

Depending on the catalyst, coke along with the dehydrogenation reaction can influence the RWGS reaction. Hydrogen is formed from two adsorbed hydrogen atoms generated in the dehydrogenation reaction. The hydrogen can then proceed through the original two-step mechanism (Fig. 4.16 left) where the hydrogen atoms combine and desorb, and is oxidised to water by the metal oxide resulting in a vacant oxygen (O_{vac}). This is then replenished by CO₂ and as a result CO is produced. However it was also postulated that the hydrogen can also spill over (right) from the coke to the RWGS catalyst which then causes a reduction in the catalyst.

4.4.1.1. Summary

A number of potential mechanisms for the ODH and DH of EB to ST using coke as the active component of a catalyst have been reported^{17, 18, 20, 21, 23}. It has been revealed that different carbonaceous species, including PAHs, carbides and quinone/hydroquinone can promote the dehydrogenation of an alkane. This suggests that the coke observed on the catalyst at 550 °C (1000 h⁻¹ C:O ; 8:1) produces ST and no EB. It has also been reported²¹ that CO₂ can be used as the oxidising agent for the DH of alkanes, particularly EB to ST. If CO₂ can be used to dehydrogenate EB to ST this could provide information on why the decrease in CO₂ is observed at 550 °C at 1000 h⁻¹. The following section explains the possibility of using CO₂ produced *in situ* as an oxidising agent for the DH of EB to ST.

4.4.2. An Alternative Oxidant: CO₂ for the ODH of Ethylbenzene to Styrene

Scheme 4.3: Reaction mechanism for the ODH of EB to ST using CO₂.²²

The redox mechanism to the right (Scheme 4.3) shows that a metal oxide redox couple (steps 2 and 4), in this case iron oxide, can be used to activate CO₂. As mentioned, Wachs *et al.*¹¹ suggested that the molybdate catalysts with excess molybdenum forms a monolayer at high temperatures and a molybdenum carbide species can be generated at the surface. It has been shown from XPS¹³ that an excess of molybdenum prevents the inactive iron oxide phase being produced for methanol oxidation²⁴⁻²⁶. However CO₂ may become activated in the presence of an iron molybdate redox couple which is present at the surface so the mechanism could still operate. The carbon could produce EB shown in similar studies with carbides¹⁶ and the exposed iron molybdate could activate the ethyl moiety to produce ST using CO₂. The mechanism to the left (steps 1 and 3) shows hydrogen extraction using CO₂ to produce hydroxycarbonated species and in turn water. It is well documented in the literature that metal oxide redox chemistry is well established for the reaction of EB to ST using CO₂ as the oxidising agent.

Under reaction conditions 550 °C C:O ; 8:1 1000h⁻¹ the XPS of Mo 3d (Fig. 4.17) of the reduced JM iron molybdate catalyst showed various oxidation states of molybdenum on the surface,

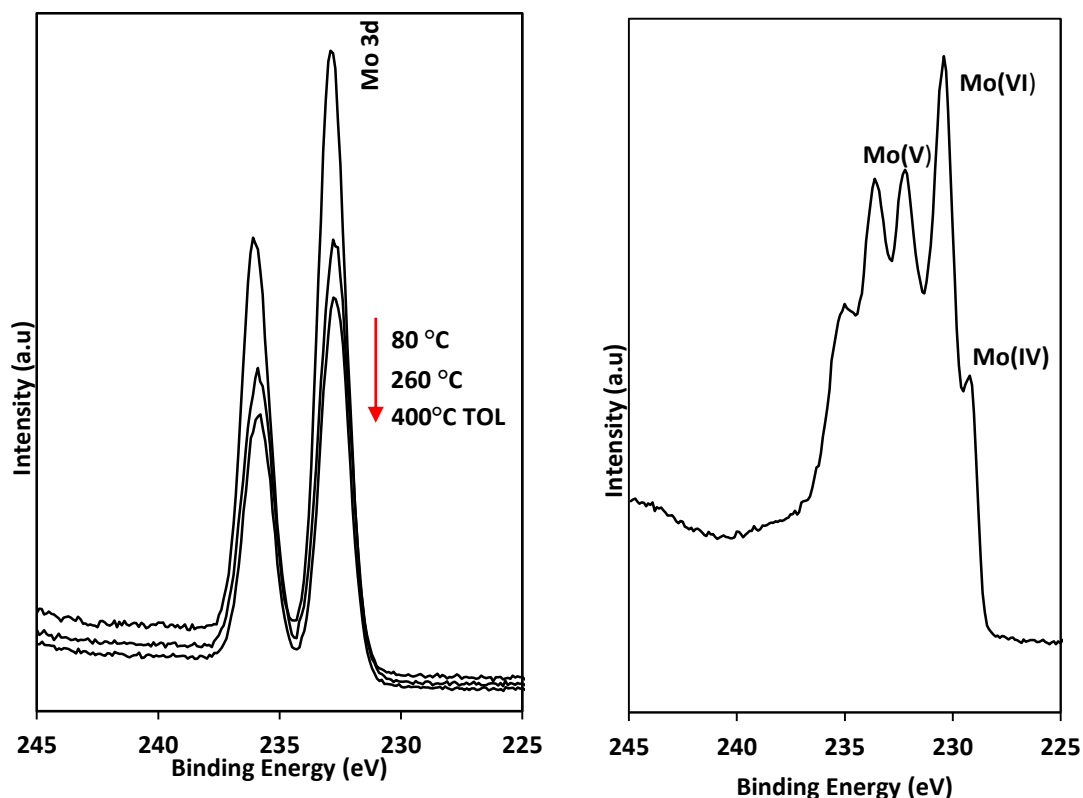


Figure. 4.17: XPS spectra of the Mo 3d region of the iron molybdate catalyst starting material and under reaction conditions at 400 °C and 550 °C.

The peak at 229.4 eV is indicative of MoO_2 and therefore the surface molybdenum has been reduced. There is also a peak at 230.6 eV which represents the MoO_3 bonded to a Fe_2O_3 which confirms the presence of the $\text{Fe}_2(\text{MoO}_4)_3$ phase²⁷. This species is detected on the surface and not in the bulk (from XRPD) due to the ODH conditions, suggesting facile oxidation of the surface. The molybdenum 3d spectrum to the right showed a peak at 232.1 eV which is indicative of a MoO_x species which is likely to be the Mo_4O_{11} phase (Mo^{5+})²⁸. The redox couple between $\text{Mo}^{5+/6+}$ is arguably the active centre^{29, 30} for the production of formaldehyde from methanol, and therefore this species could be the reactive redox couple in the activation of alkanes to alkenes using CO_2 . This shows that the molybdenum is extremely sensitive to reactive conditions at the surface.

4.5. Activation of C-H Bonds in *n*-Octane and Ethylbenzene Using CO₂ as an Oxidant

This section tested the mechanisms hypothesised in accordance with literature and experimentally that were discussed previously. CO₂ was used as the oxidant for the dehydrogenation of *n*-octane to octene and EB to ST.

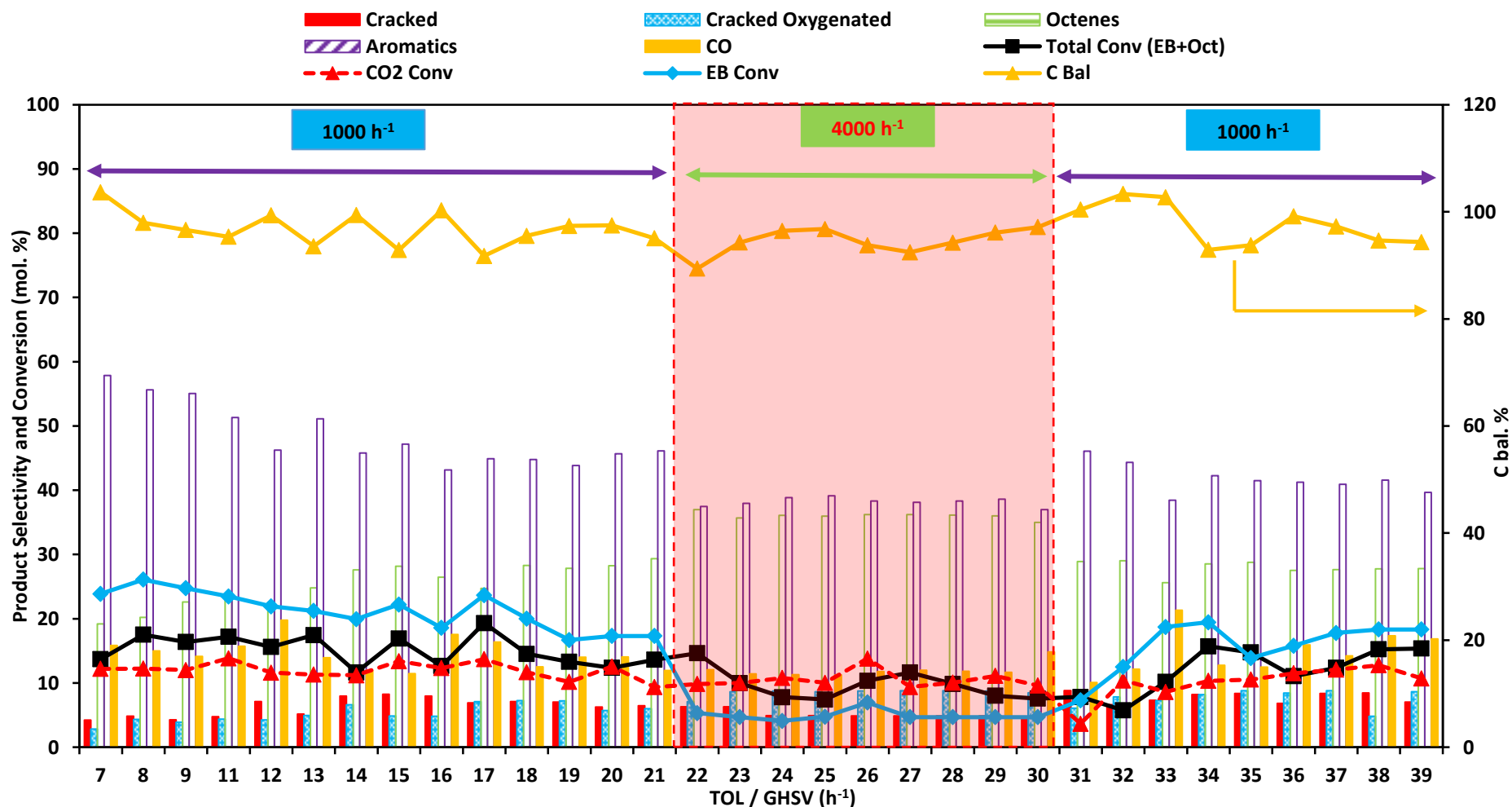
4.5.1. Testing of *n*-octane with the reduced JM iron molybdate catalyst with 5% ethylbenzene and 10 % CO₂

Figure. 4.18a: Reaction of 5 % EB in pure *n*-octane with 10 % CO₂ with the reduced JM iron molybdate catalyst. Temperature at 550°C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹ at 550 °C.

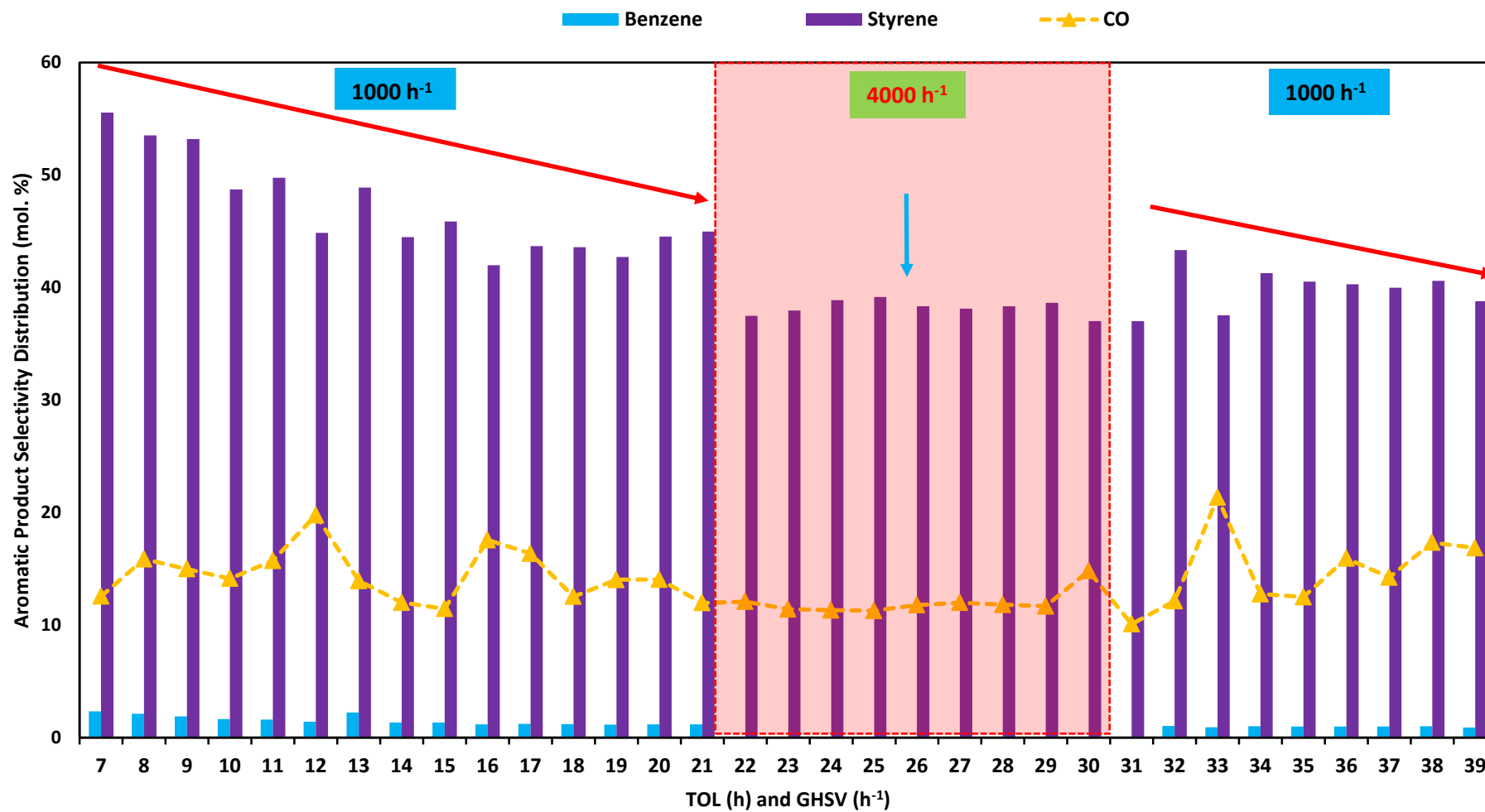


Figure. 4.18b: Aromatic product distribution for the reaction of 5 % EB in *n*-octane with 10 % CO₂ with the reduced JM iron molybdate catalyst. Temperature at 550°C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹ at 550 °C.

The TOL at 550 °C (Figs. 4.18 a and b) showed the reaction between *n*-octane with the reduced JM iron molybdate catalyst with 5% EB and 10 % CO₂ whilst subject to alternating GHSVs between 1000h⁻¹ and 4000 h⁻¹. After the stabilisation period of several hours the total conversion, which includes both octane and EB, remains stable at *ca.* 15 % - 18 % at 1000 h⁻¹. The selectivity to the aromatics was the dominant process, at 57.8 % and 46.1 % after the 7th hour and 21st hour respectively. The decrease in selectivity, between 7 and 21 hours, can be attributed the carbon that is building on the surface forming PAHs on the surface which was shown previously (Table 4.2), and by the overall subtle decrease in carbon mass balance. The carbon aids the dehydrogenation process^{6, 14} and therefore the octene selectivity increased from 19 % to 30 % from the 7th hour to the 21st hour respectively. The aromatic selectivity decreased because more oxygen surface species are required to produce aromatics, and with increasing coke less CO₂ can be activated and therefore the DH increases. To confirm this H₂/H₂O analysis would have been needed but this was unavailable. The CO₂ conversion remained at a constant (*ca.*11 %) along with total conversion, however, the EB conversion decreased with time along with aromatic selectivity and ST production (Fig. 4.18b). Therefore the CO₂ must be activating octane to octene because the production of CO remains consistent at 14 % - 17 % over time.

When the GHSV was increased to 4000 h⁻¹ the total conversion decreased to *ca.* 5 % - 7 % as a result of a shorter contact time with the catalyst. It was observed that CO₂ conversion remained consistent whilst the change in GHSV was introduced. The octene selectivity increased during this period (*ca.* 35 %) and the aromatic selectivity decreased (*ca.* 37 %) and as a result the selectivity towards ST decreased and benzene decreased to zero. The carbon mass balance increased during this period, and this suggests that the carbon was removed from the surface but doesn't account for the CO₂, as no oxygen is present in the feed.

When the GHSV was returned to 1000 h⁻¹, after an initial stabilisation period (31 h – 35 h), the EB conversion and total conversion returned. The selectivity to octene decreased and aromatic selectivity. The selectivity to ST decreased with time as the carbon re-deposited onto the surface of the catalyst, as shown by the decrease in carbon mass balance. What was shown here is the selectivity to aromatics and octene can be tuned even at higher temperatures, but as the octene selectivity decreased with longer contact time aromatic production increased in the form of ST. This

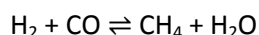
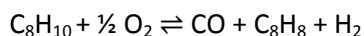
suggests that as more octene is produced at lower GHSVs, this is converted to aromatics, in this case ST. The confirmation of using octene in the aromatisation process to produce aromatics will be investigated later on in the chapter.

It was shown that CO₂ can dehydrogenate EB to ST. This is why the CO_x decreases at 1000 h⁻¹ at 550 °C (1% octane C:O ; 8:1). Therefore the redox mechanism using FeMoO₄ is used to activate the CO₂ molecule.



The mechanism using coke to dehydrogenate the terminal bond which was evident from the investigation of coke on the catalyst can also operate to produce ST from EB.

The mechanism that was proposed including the RWGS reaction produces hydrogen in the following reaction.



The hydrogen then reacts with CO to produce methane and water. However an increase in cracked product selectivity when the temperature was increased to 550 °C was not detected. At C:O ; 8:1 a decrease in the amount of CO_x was detected confirming that a RWGS mechanism cannot operate as shown in in Figure. 4.16. Therefore the only plausible mechanisms that can operate are the 'coking' mechanisms and the redox mechanism to give direct dehydrogenation of EB to ST, CO and H₂O.

The experiment using the reduced JM ironmolybdate catalyst with 5 % EB in octane using CO₂ as the oxidant (Fig. 4.18a) produced octene in this reaction. The reaction with octane and 10 % CO₂ was completed to provide potential alternative oxidising agents to produce octene selectivity (Figs. 4.19a and b).

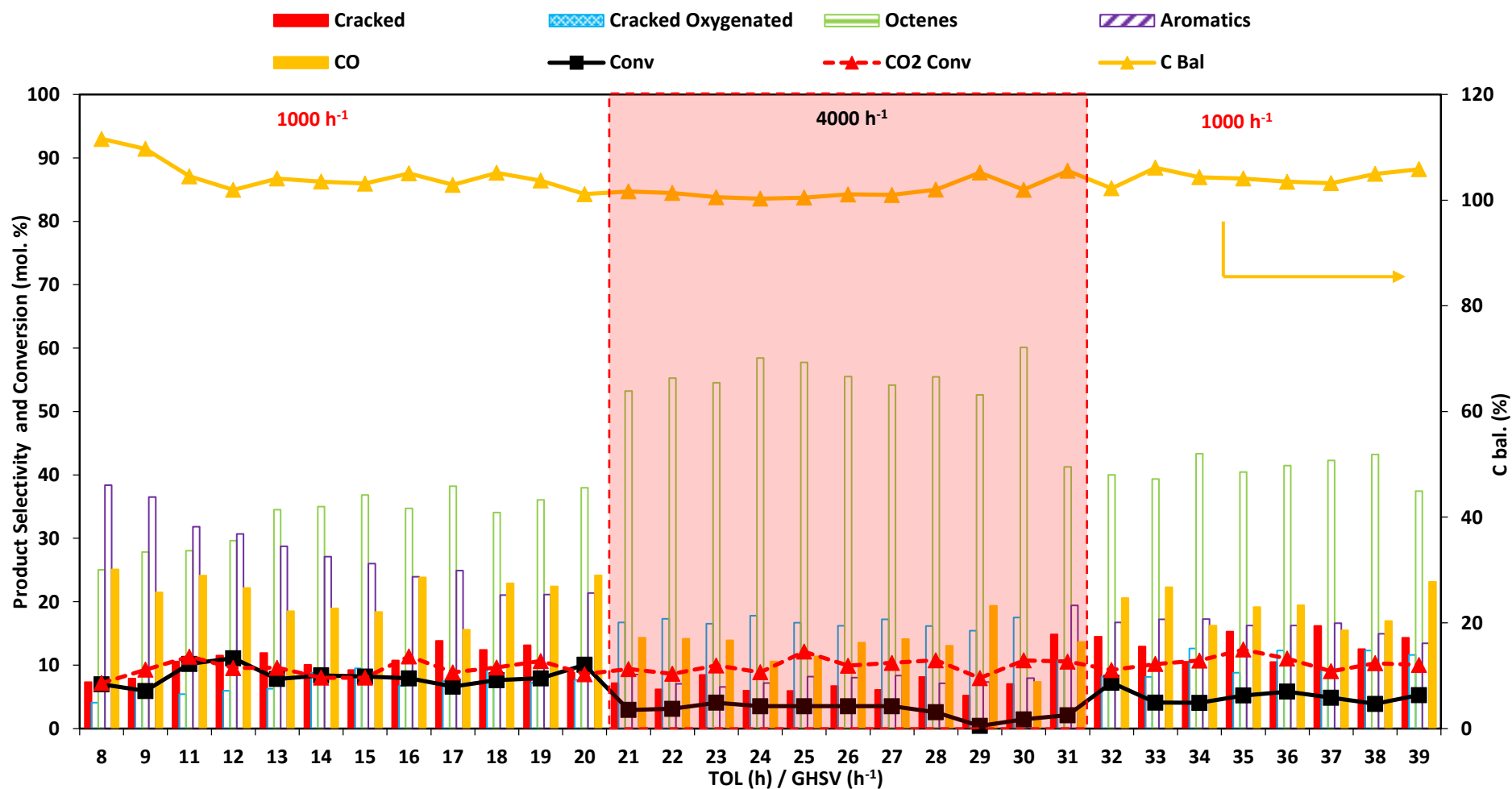
4.5.2. Testing of *n*-octane and the reduced JM iron molybdate catalyst at 550 °C using CO₂ as the oxidant

Figure. 4.19a: Reaction of *n*-octane with 10 % CO₂ with the reduced JM iron molybdate catalyst. Temperature at 550°C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹ at 550 °C.

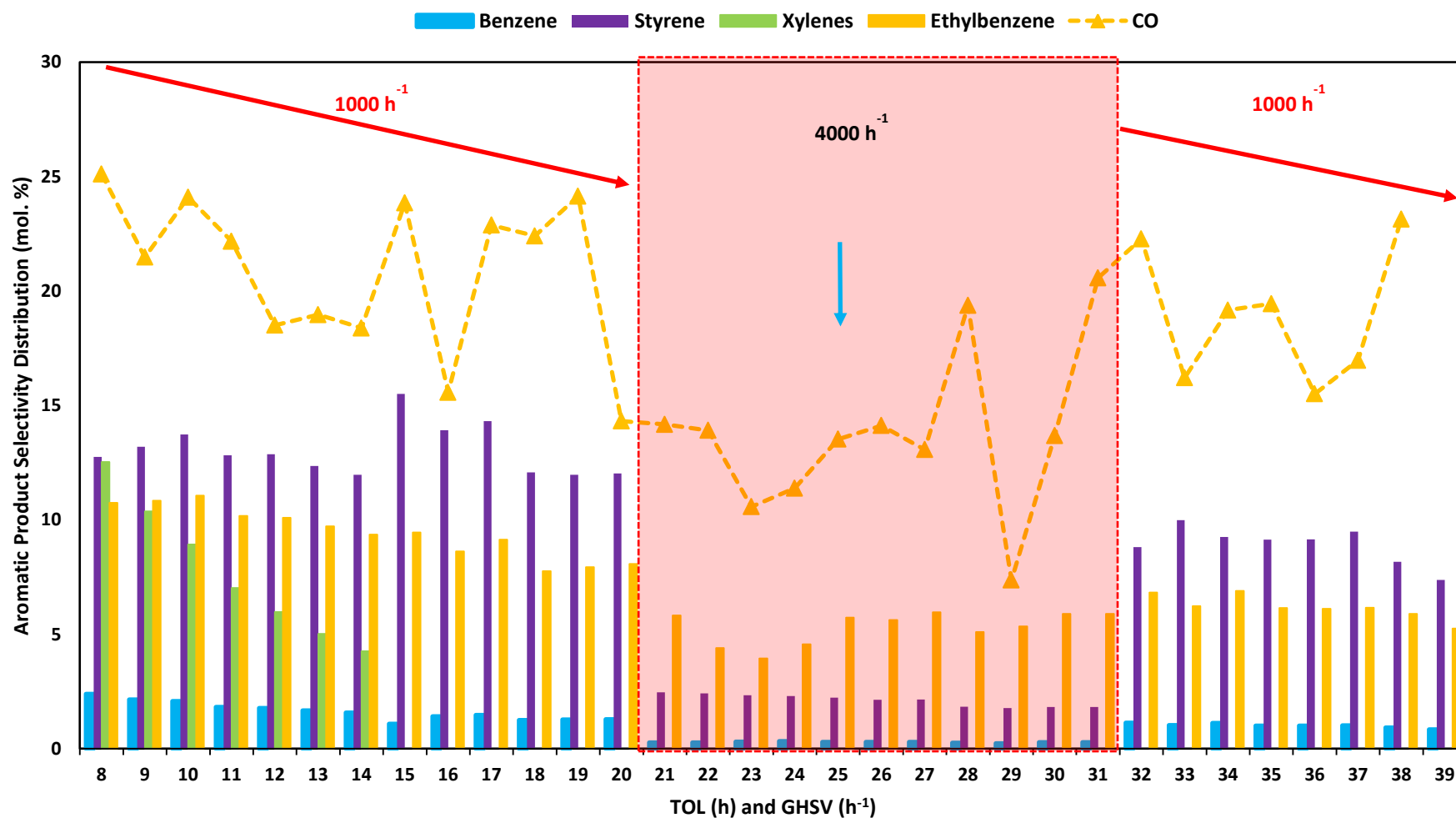


Figure. 4.19b: Aromatic product distribution for the reaction of *n*-octane with 10 % CO₂ with the reduced JM iron molybdate catalyst. Temperature at 550°C. GHSV range from 4000 h⁻¹ and 1000 h⁻¹ at 550 °C.

The results showed that CO₂ can be used as an oxidant to dehydrogenate *n*-octane to octene. From 8 h - 20 h at 1000 h⁻¹ aromatics are the most dominant product produced, but these decreased with increasing time whilst the selectivity to octene increased, probably due to the coke building on the surface blocking surface sites for further dehydrogenation of octane to produce aromatics. The conversion of octane is stable during this period *ca.* 7.5 %, as well as the CO₂ conversion *ca.* 8%. Initially the dominant aromatic produced is exclusively *o*-xylene, but this rapidly decreased over time whilst ST production increased. The *o*-xylene is likely to be produced from lattice oxygen from the catalyst. Remembering that oxygen is excluded from the feed, the lattice oxygen are unable to be replenished and therefore xylene selectivity decreased. The selectivity to ST increased whilst EB decreased with time suggesting that the coke is activating EB to ST as well as the CO₂²¹. As the coke increases on the surface less active sites are available for dehydrogenation to facilitate aromatisation. Octene selectivity therefore increased due to less consecutive dehydrogenation steps along the octene chain, i.e. octadienes are responsible for the aromatics produced.

When the GHSV was then changed to 4000 h⁻¹ (21-31 h) the octane conversion decreased which is expected with increasing GHSVs due to shorter contact time. The CO₂ conversion remains the same suggesting that the CO₂ could be responsible for the dehydrogenation of octane to octene which is favoured using these conditions. EB is now the dominant product with little ST being produced. Aromatic selectivity decreased during this period which compares with previous data, whilst octene production increased.

When the GHSV was decreased to 1000 h⁻¹ (32 h -39 h) aromatic selectivity increased with the dominant product now being ST as before. Octene is still the dominate product as before when the change in GHSV was initially made. The conversion of octane does not return to prior levels in this period and but is stable *ca.* 5 %, suggesting deactivation of the catalyst with time.

4.6. Determining the Source of Aromatic Products

4.6.1. Using Oct-1-ene and the Reduced JM Iron Molybdate catalyst

This section explores the reaction of oct-1-ene with the reduced JM iron molybdate catalyst. The replacement of *n*-octane with oct-1-ene was used to model the possible aromatisation mechanism of octene as one of the possible intermediates in the production of benzene, toluene, xylenes (BTX) and ST. Testing using a variety of C:O ratios and GHSVs using the reduced JM iron molybdate catalyst was conducted.

4.6.1.1. Controls: Reactivity of oct-1-ene with no catalyst

Oct-1-ene was reacted in the blank stainless steel reactor tube at 3.5 mlmin^{-1} and 13.5 mlmin^{-1} to emulate the 1000 h^{-1} and 4000 h^{-1} reactions respectively (Figs. 4.19 and 4.20).

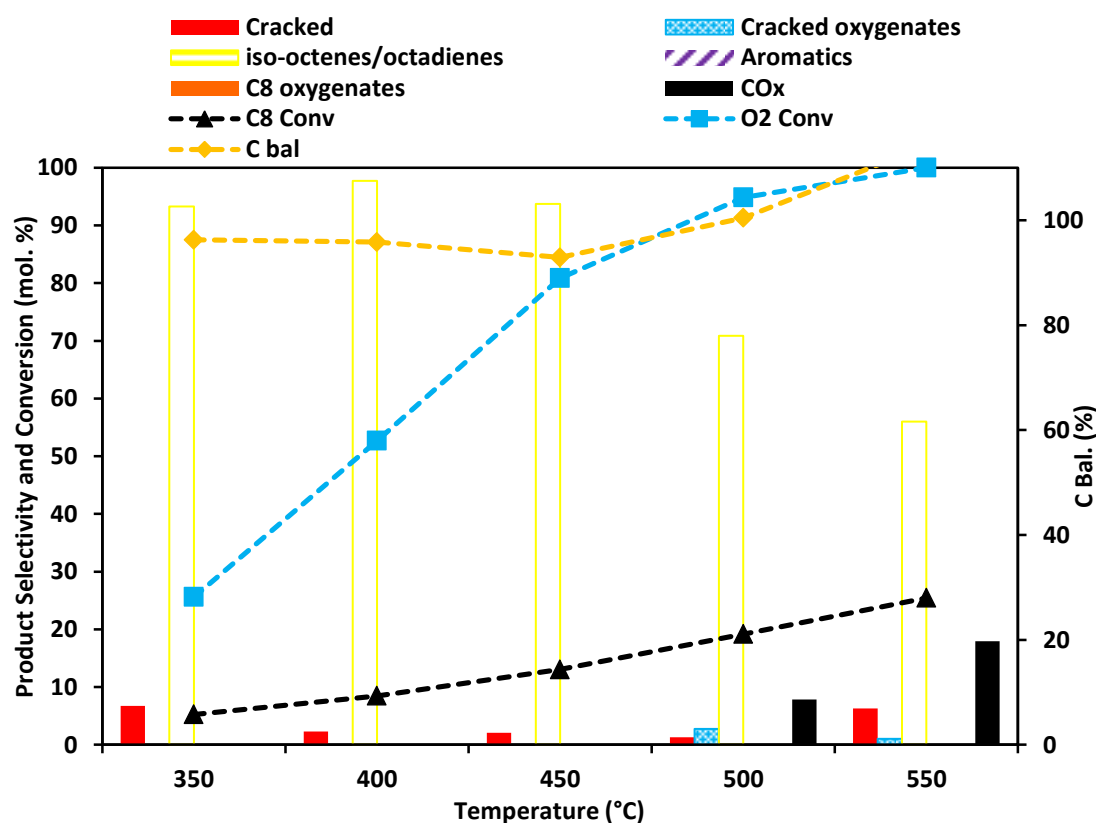


Figure 4.20a: Oct-1-ene (1.32 %, C:O ; 8:1) was tested in a blank stainless steel tube at 3.5 mlmin^{-1} to mimic the conditions used at 4000 h^{-1} . Temperature was ramped from 350-550 °C in 50 °C increments and held at each temperature for 1 h.

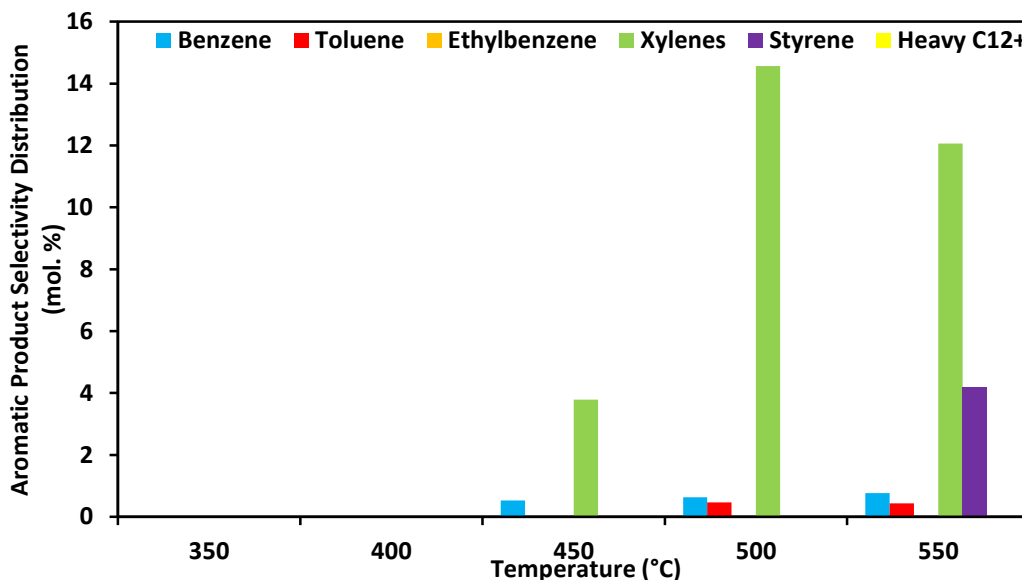


Figure 4.20b: The selectivity breakdown for the aromatics produced by the reaction of oct-1-ene (1.32 %, C:O ; 8:1) in a blank stainless steel tube at 3.5 mlmin^{-1} to mimic the conditions used at 4000 h^{-1} . Temperature was ramped from 350-550 °C in 50 °C increments and held at each temperature for 1 h.

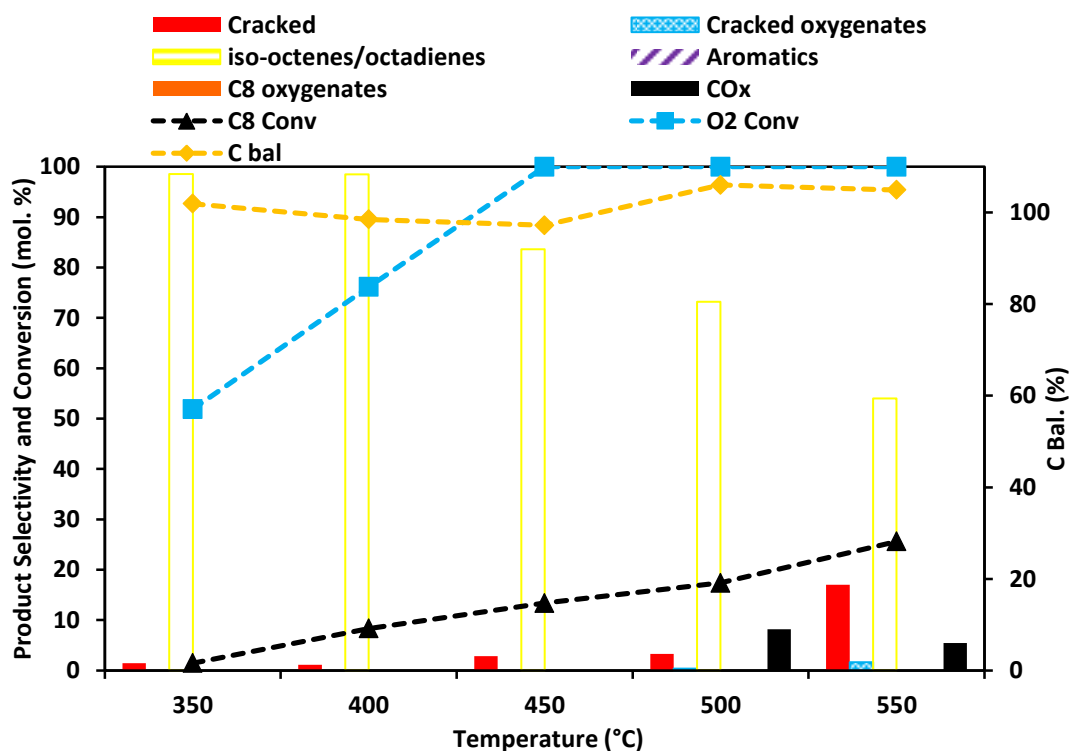


Figure 4.21a: Oct-1-ene (1.32 %, C:O ; 8:1) was tested in a blank stainless steel tube at 13.5 mlmin^{-1} to mimic the conditions used at 1000 h^{-1} . Temperature was ramped from 350-550 °C in 50 °C increments and held at each temperature for 1 h.

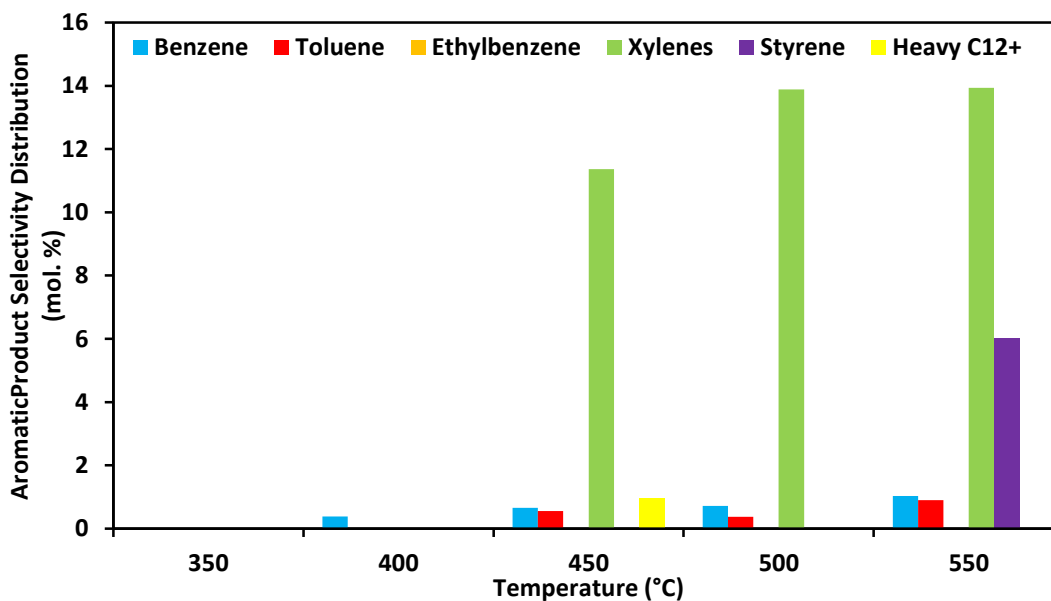


Figure 4.21b: The selectivity breakdown for the aromatics produced by the reaction of oct-1-ene (1.32 %, C:O ; 8:1) in a blank stainless steel tube at 13.5 mlmin⁻¹ to mimic the conditions used at 1000 h⁻¹. Temperature was ramped from 350-550 °C in 50 °C increments and held at each temperature for 1 h.

Blank reaction tubes showed that the oct-1-ene can be isomerised to iso-octene and further dehydrogenation to octadienes. However the conversion is appreciably lower when the catalyst is not present across all temperature ranges, especially at lower temperatures.

4.6.1.2. Reactivity of Oct-1-ene with the JM Iron Molybdate Reduced Catalyst

Oct-1-ene (1%, C:O; 12:1, 4000h⁻¹) was reacted with the reduced JM iron molybdate catalyst from 350-550 °C to establish whether aromatisation of oct-1-ene was the direct route in the production of ST.

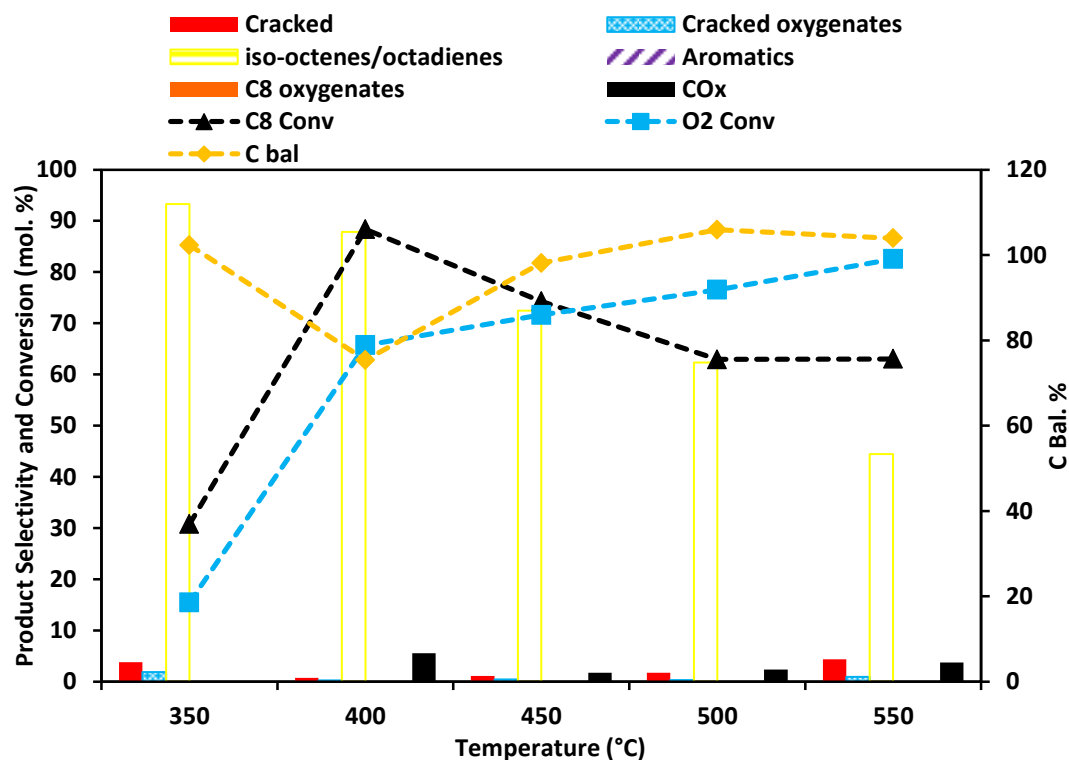


Figure 4.22a. The reduced JM iron molybdate catalyst with oct-1-ene (1%, C:O; 12:1, 4000 h⁻¹). Temperature range from 350-550°C

Figure 4.22a shows that changing the substrate from octane to oct-1-ene resulted in a much higher conversions at all temperatures. At 350 °C the plot shows that iso-octene and octadienes are produced, *ca.* 93 %. It is shown that once one bond is dehydrogenated it is far easier to dehydrogenate other bonds along the chain. As the temperature increased from 350 °C to 550 °C the selectivity to the iso-octene/octadienes decreased while the aromatic product selectivity increased. Figure 4.22b shows the aromatic breakdown across the temperature range.

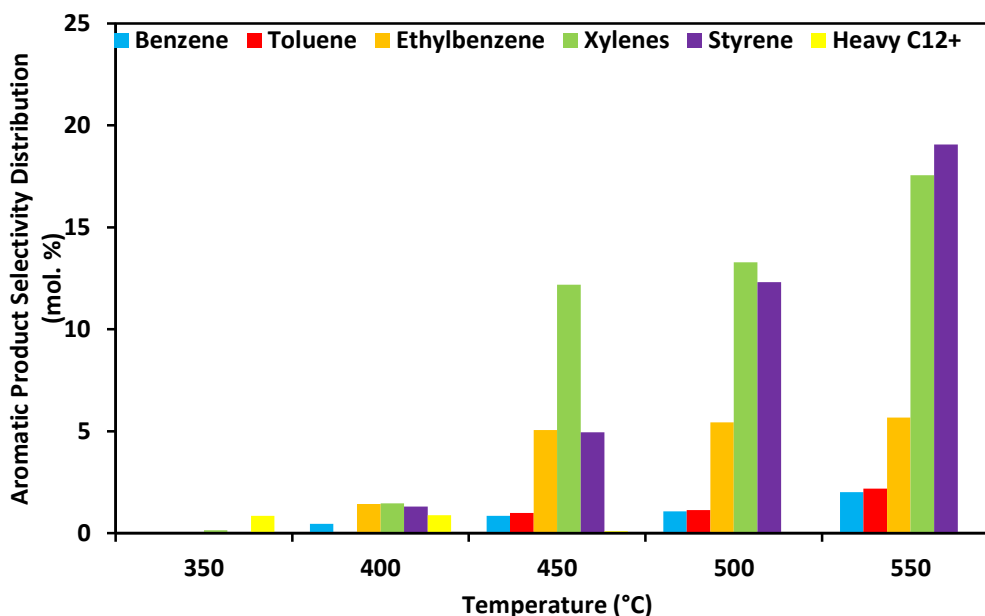


Figure 4.22b. The reduced JM iron molybdate catalyst with oct-1-ene (1%, C:O; 12:1, 4000 h⁻¹).
Aromatic product selectivity distribution

Figure. 4.22b shows as the temperature exceeds 450 °C the dominant aromatic species produced were xylenes and ST. EB was also produced at temperatures ≥ 450 °C but does not increase as the temperature increased, unlike the xylenes and ST. This suggests that EB may be an intermediate in the selective production of ST from octene.

What is noteworthy is that Fig. 4.22a showed little CO_x was produced from 400 °C to 550 °C (*ca.* 5%) with none produced at 350 °C. This indicates that a reaction pathway leading to CO_x production is suppressed whilst the other iso-octene/octadienes and aromatics are produced. What is also evident is that there is little benzene, toluene and cracked products produced throughout the temperature range, this indicates that the most favourable pathway for oct-1-ene is to aromatise to xylenes and ST and not crack down to butene and propane and cyclise *via* a peri-cyclic Diels Alder mechanism. However the mechanism cannot rule be ruled out and will be tested in the future using propene and butene as the substrates.

4.6.2. Optimisation of Experimental Parameters to Produce Octadienes and Aromatics from Oct-1-ene

4.6.2.1.A Temperature, GHSV and C:O Ratio Study

Figures 4.23 - 4.25 show that changing the C:O ratios and GHSV can optimise the selectivity towards octene and aromatics. Each graph from 4.23 to 4.25 displays these changes at 350 °C, 450 °C and 550 °C respectively.

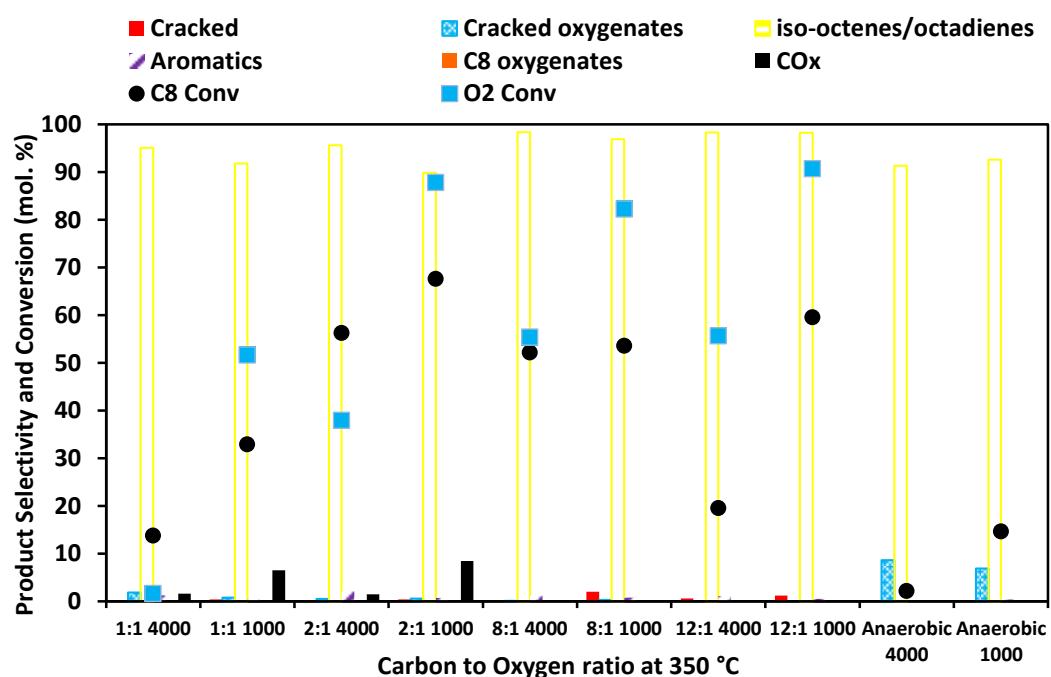


Figure 4.23: Reaction of oct-1-ene with the reduced JM iron molybdate catalyst using various carbon to oxygen ratios between 1:1- 12:1 and GHSVs of 4000 h⁻¹ and 1000 h⁻¹ at **350 °C**

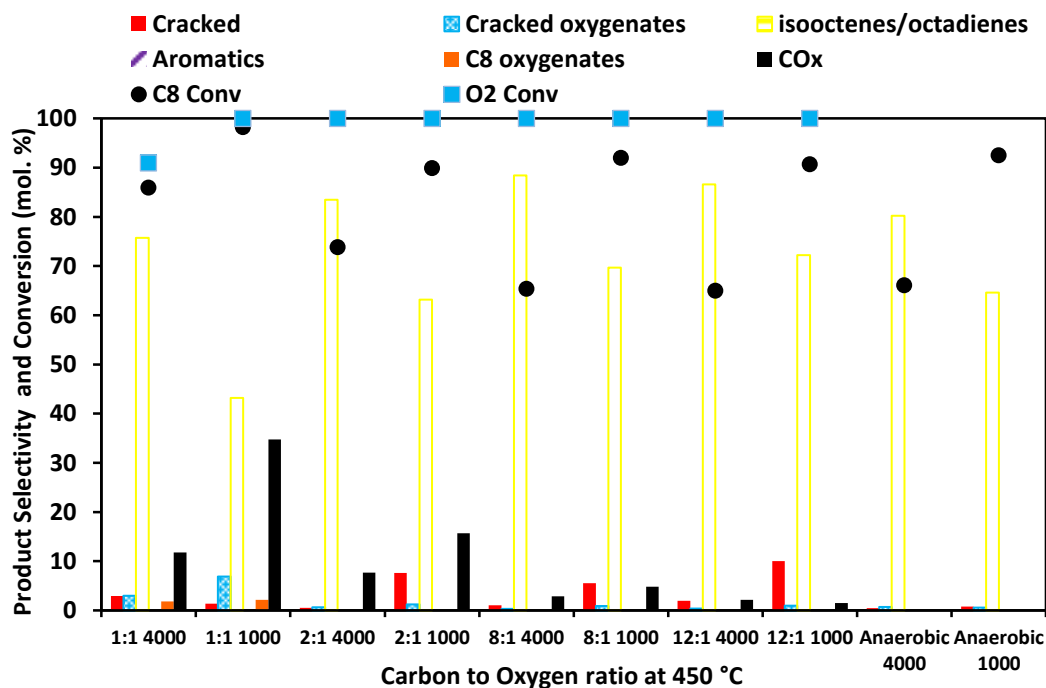


Figure 4.24: Reaction of oct-1-ene with the reduced JM iron molybdate catalyst using various carbon to oxygen ratios between 1:1- 12:1 and GHSVs of 4000 h⁻¹ and 1000 h⁻¹ at 450 °C.

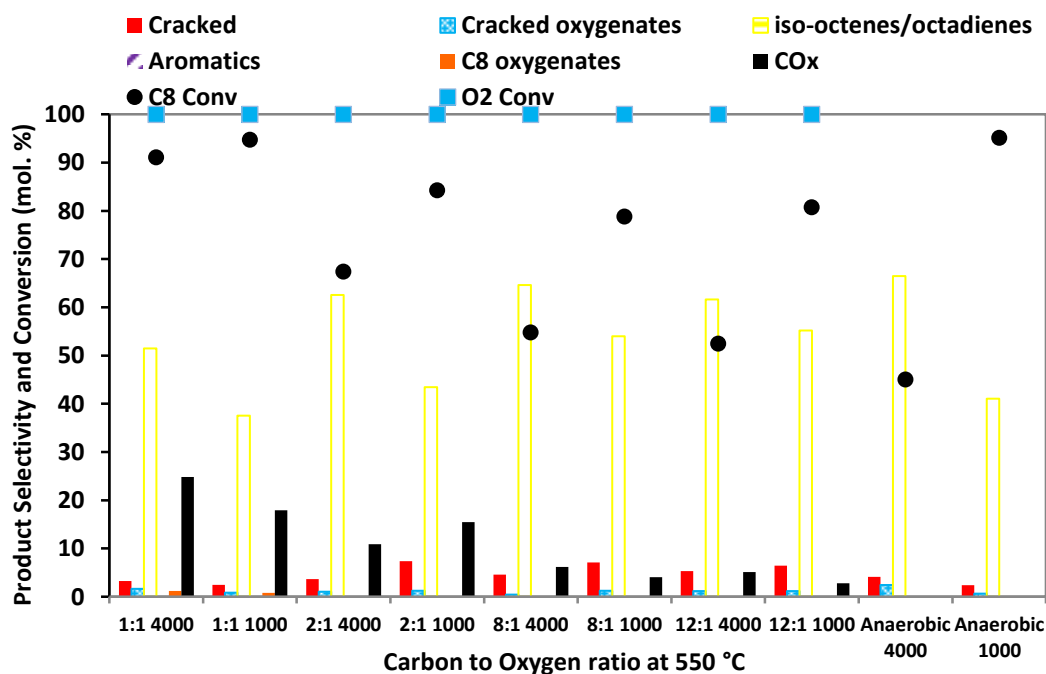


Figure 4.25: Reaction of oct-1-ene with the reduced JM iron molybdate catalyst using various carbon to oxygen ratios between 1:1- 12:1 and GHSVs of 4000 h⁻¹ and 1000 h⁻¹ at 550 °C.

The reaction at 350 °C (Fig. 4.23) produced isomers of octene and octadienes with very high selectivity and with high conversion in the presence of the reduced catalyst. Little CO_x was produced when the C:O ratio was very low. This emphasises the stability of the octene molecule once dehydrogenated from octane. As the C:O ratio increased cracked products were detected but the selectivity was low, *ca.* < 5 %. At 1000 h⁻¹ the conversion increased which was due to a longer contact time between the substrate and the catalyst. This in turn increases the CO_x selectivity especially with lower C:O ratios as CO_x is the thermodynamically favoured product. Under anaerobic (DH) conditions conversion was low but the selectivity towards the octene remained high *ca.* 90 %. This suggests that the reaction is oxygen dependent from the Mars van Krevelen (MvK) mechanism.

At 450 °C (Fig. 4.24) the aromatisation of the oct-1-ene molecule to aromatics is facilitated as predicated from previous results using *n*-octane as the substrate. It is evident that lower C:O ratios produced more CO_x and this is also demonstrated when the GHSV was lowered. As the C:O ratio increased the aromatic selectivity increased whilst the selectivities to iso-octene/octadienes decreased. It is shown under anaerobic conditions and higher C:O ratios and higher GHSVs (4000 h⁻¹) that little cracked products are formed and those produced are exclusively octene and aromatics. When the GHSV was lowered to 1000 h⁻¹ the cracked and aromatic products increased. Conversion decreased with increasing C:O ratios with the same GHSVs in the reaction. The aromatisation process depends on the oxygen content for the ODH-MvK mechanism to operate and to further dehydrogenate the octane chain. When the GHSV was lowered for each C:O ratio the conversion increased as a result of longer contact times.

At 550 °C (Fig. 4.25) the conversion decreased when the C:O ratios increased from 2:1 to anaerobic conditions. The conversion also decreased compared to 450 °C at both 4000h⁻¹ and 1000 h⁻¹. The decrease in conversion was attributed to aromatisation of the octene/octadienes produced and the absence of oxygen in the feed, because more oxygen is required to dehydrogenate the octene to octadienes. CO_x was also produced in the range of 2:1 to 12:1 but decreased with increasing C:O ratios; less oxygen was available in the gas feed therefore CO_x decreased. At 1000 h⁻¹ more CO_x was produced relative to 4000 h⁻¹ because the contact time between the catalyst and substrate was increased which facilitates the thermodynamically favoured product, CO₂. The anaerobic conditions confirmed that CO₂ cannot be produced *via* the MvK

mechanism because no CO_2 was produced under these conditions at both 1000 h^{-1} and 4000 h^{-1} . If this mechanism were to operate as literature has previously indicated¹ then the CO_2 must be produced from active oxygen surface species and not the lattice oxygen.

4.6.2.1.1. Summary

The results show once octane has become dehydrogenated the chain can further dehydrogenate and aromatise. At 350°C the products produced are octene isomers and octadienes with little CO_x produced. When the temperature increased aromatic selectivity increased. When oxygen rich conditions were used (C:O ; 1:1) the octene underwent minimal complete combustion, showing that once the octane molecule is dehydrogenated it is stable and can either undergo further dehydrogenation or aromatisation. This suggests CO_x is produced from a different mechanism/pathway and not from the combustion of octene/octadiene.

4.7. Conclusions

Reducing the JM iron molybdate catalyst significantly increased the selectivity to octene at temperatures $< 450^\circ\text{C}$, whereas the oxidised form of the catalyst, studied in Chapter 3, mainly produced CO_2 and cracked products. The best conditions for the production of octene with high selectivity was shown to be at a C:O of 8:1 at 4000 h^{-1} at 400°C (Fig. 4.5). This showed high selectivity to octene *ca.* 82 % with a conversion of 8 %. Testing was completed from 400°C to 405°C (Fig. 4.8) and showed that the catalyst was stable under these operating conditions. Only when the GHSV was lowered to 1000 h^{-1} was CO_2 produced, due to a re-oxidisation of the catalyst and the removal of coke. Temperatures above $\geq 450^\circ\text{C}$ produced aromatics, including EB, benzene and ST using specific conditions. The production of CO_x decreased at 550°C at 1000 h^{-1} . These conditions increased the amount of coke on the surface which was shown by CHN analysis and identified using Raman spectroscopy as a sp^2 hybridised material i.e. polyaromatic hydrocarbon (PAHs). At high temperatures it is thought that a molybdenum oxide monolayer forms at the surface¹¹, and this along with the carbon species can cause aromatisation of octane/octene⁶. However XPS revealed

that multiple oxidation states of molybdenum (4+/5+/ 6+) exist at the surface as well as iron (2+/3+). It has been well documented that iron oxide can activate CO₂ and EB to produce ST^{15, 22}. Therefore the mechanism that I propose at 550 °C uses molybdenum coated carbon under these reaction conditions to produce EB and xylenes¹⁶. Exposed iron oxide at the surface activates the CO₂ and EB to produce ST²², and therefore the CO₂ decreased because it is being consumed during the reaction and consequently the production of ST and EB selectivity increased and decreased respectively.

The reaction data showed that a blank stainless steel tube can activate octene into isomers of octene and octadienes albeit at much lower conversions compared to when the catalyst was present. As the temperature increased, the aromatics become more selectively desired as well as CO_x and cracked products, those including ethane and propane. Anaerobic conditions confirmed that CO₂ cannot be produced *via* the MvK mechanism because no CO₂ was produced under these conditions at both 1000 h⁻¹ and 4000 h⁻¹. If this mechanism were to operate the CO₂ must be produced from active oxygen surface species and not the lattice oxygen. The oxygen rich conditions showed that once octene is produced it is stable and it not responsible for the CO₂ produced seen by the previous octane reactions. Therefore CO₂ is likely to be produced by a separate pathway and not from octane combustion.

4.8. References

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Chapter 5: Pure Oxide Phase Components of the Reduced JM Iron Molybdate Catalyst

5.1. Introduction

The chapter investigates the separate phases of the reduced JM iron molybdate, $\text{FeMoO}_4\text{-MoO}_2$, catalyst. Chapter 4 revealed that the catalyst, was superior in producing octene at temperatures $< 450\text{ }^\circ\text{C}$, whereas the oxidised catalyst, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ discussed in Chapter 3 produced mainly CO_2 . This chapter investigates the reaction of *n*-octane with the reduced pure phase components, i.e. FeMoO_4 and MoO_2 to identify what phases are responsible for the production of aromatics and octene.

5.2. Results and Discussion

5.2.1. Pure Phase FeMoO_4

5.2.1.1. Optimisation for the Production of Octene

The FeMoO_4 catalyst was prepared by heat treatment under flowing hydrogen at $500\text{ }^\circ\text{C}$, see Chapter 2 Section 1 for more details. The catalyst was tested using 1 % (v/v %) octane at C:O ; 8:0, 8:1, 12:1, by increasing the temperature from $350\text{ }^\circ\text{C}$ to $550\text{ }^\circ\text{C}$, in $50\text{ }^\circ\text{C}$ increments, at 1000 h^{-1} , 4000 h^{-1} , 6000 h^{-1} shown by Figures 5.1- 5.5 respectively. The reaction parameters were chosen to find the optimal conditions for the production of octene.

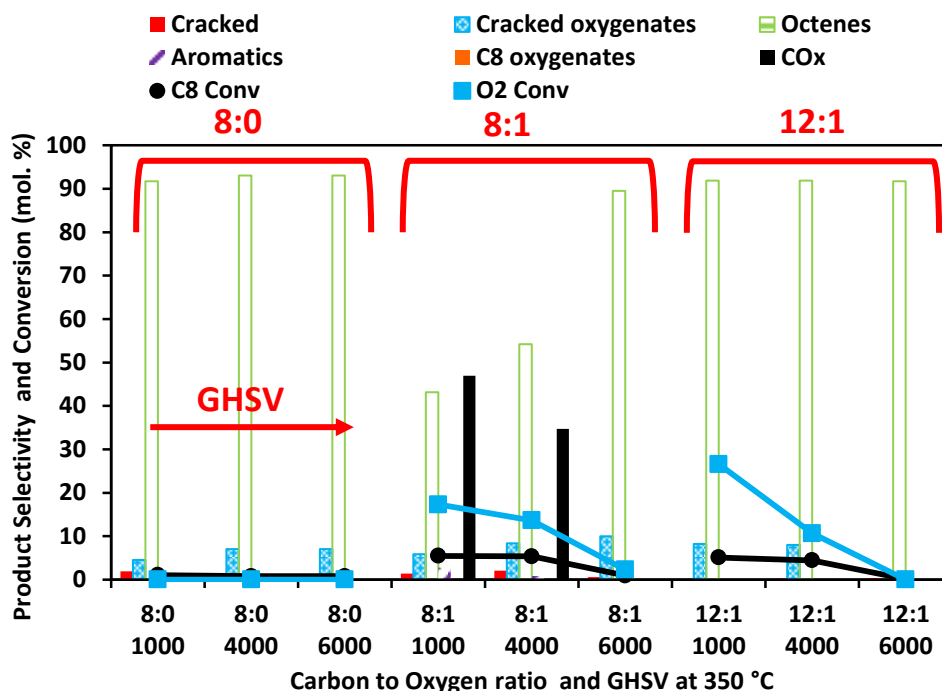


Figure 5.1: Reaction of *n*-octane (1 %) with the FeMoO_4 catalyst using various carbon to oxygen ratios between 8:0 - 12:1 and GHSVs of 1000 h^{-1} to 6000 h^{-1} at **350 °C**

At 350 °C (Fig. 5.1) under anaerobic/dehydrogenating (8:0) conditions the conversion of octane was negligible. Under oxidative dehydrogenating (ODH) conditions the conversion of octane became observable. The dominant product produced at a C:O of 8:1 at 1000 h^{-1} was CO_2 (47 %) followed by octene (43 %). When the GHSV was increased to 4000 h^{-1} the conversion slightly decreased from 6 % to 5 % but the selectivity to octene increased to 54 % whilst CO_2 decreased to 35 % as a result of a shorter contact time. When the GHSV further increased to 6000 h^{-1} the selectivity increased to 90 %, however the conversion of octane dropped to less than 1 %.

Increasing the C:O ratio (12:1) increased the selectivity to octene to $\geq 91 \%$. The conversion of octane at 1000 h^{-1} and 4000 h^{-1} did not change and was similar to the conversions achieved at 8:1. However at 12:1 the selectivity increased whilst the CO_2 decreased to zero. This suggest that the system had enough oxygen to replenish the lattice oxygen, particularly at 12:1 compared to 8:1 where the oxygen consumption was greater, and less oxygen was available for combustion. An increase in the GHSV to 6000 h^{-1} resulted in a decrease in conversion due to a shorter contact time.

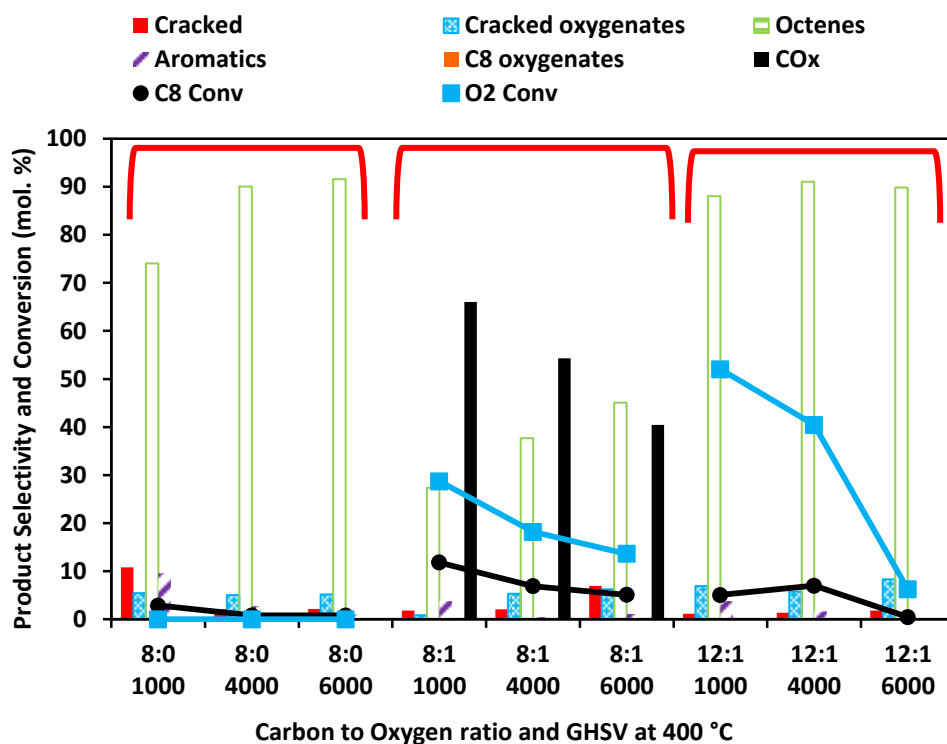


Figure 5.2: Reaction of *n*-octane (1 %) with the FeMoO_4 catalyst using various carbon to oxygen ratios between 8:0 - 12:1 and GHSVs of 1000 h^{-1} to 6000 h^{-1} at **400 °C**

When the temperature was increased to 400 °C (Fig. 5.2) the results obtained were similar to the data collected at 350 °C (Fig 5.1). However the production of aromatics increased with increasing temperature. Under anaerobic/dehydrogenating (8:0) conditions the conversion of octane at 1000 h^{-1} increased to 3 % from < 1 %. The selectivity to aromatics and cracked products slightly increased and octene decreased (74 %). The dominant product using a C:O of 8:1 at 1000 h^{-1} was again CO_2 but increased significantly from 47 % at 350 °C to 66 % at 400 °C. When the GHSVs increased conversion of octane and oxygen decreased and the selectivity to CO_2 also decreased. At a C:O of 12:1 again a significant increase to the selectivity to octene (≥ 91 %) was observed. The conversion of octane at 1000 h^{-1} was slightly lower than at 4000 h^{-1} , 5 % and 7 % respectively, because more oxygen is needed to produce aromatics. Upon Increasing the GHSV from 4000 h^{-1} to 6000 h^{-1} the octane conversion decreased from *ca.* 5 % to < 1 %.

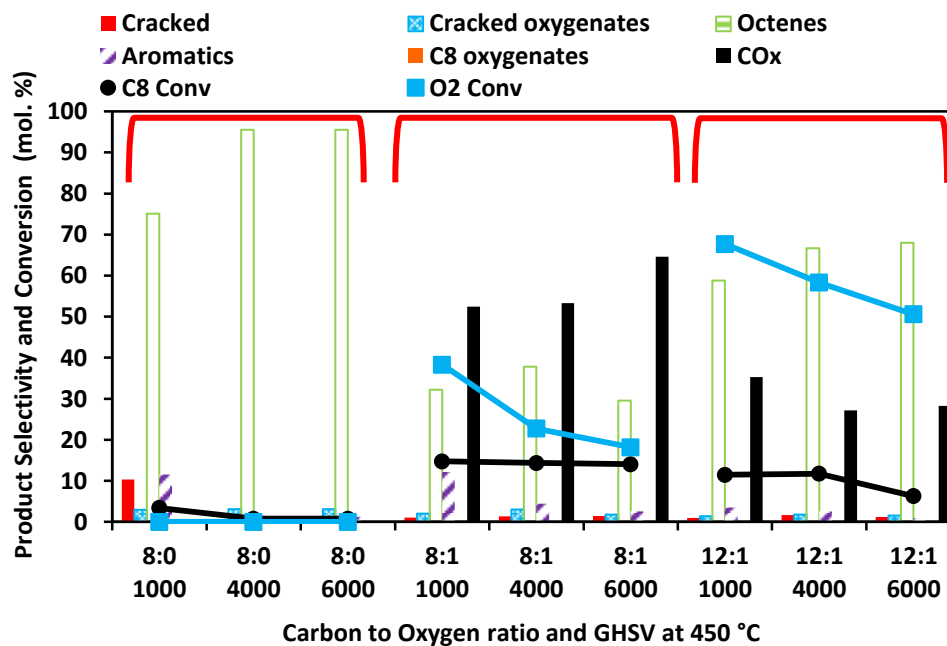


Figure 5.3: Reaction of *n*-octane (1 %) with the FeMoO_4 catalyst using various carbon to oxygen ratios between 8:0 - 12:1 and GSVs of 1000 h^{-1} to 6000 h^{-1} at **450 °C**

Increasing the temperature to 450 °C (Fig. 5.3) resulted in an increase in conversion. The selectivity to aromatics increased especially at 8:1 at 1000 h^{-1} which resulted in a decrease in CO_x to 52 % from 66 %. This suggests that CO_2 is dehydrogenating ethylbenzene (EB) to styrene (ST)^{1,2}, as seen in Chapter 4. Increasing the C:O ratio to 12:1 produced CO_x . With increasing GHSV the oxygen consumption and CO_x selectivity decreased. This suggests that oxygen is responsible for combustion due to a decrease in CO_x selectivity.

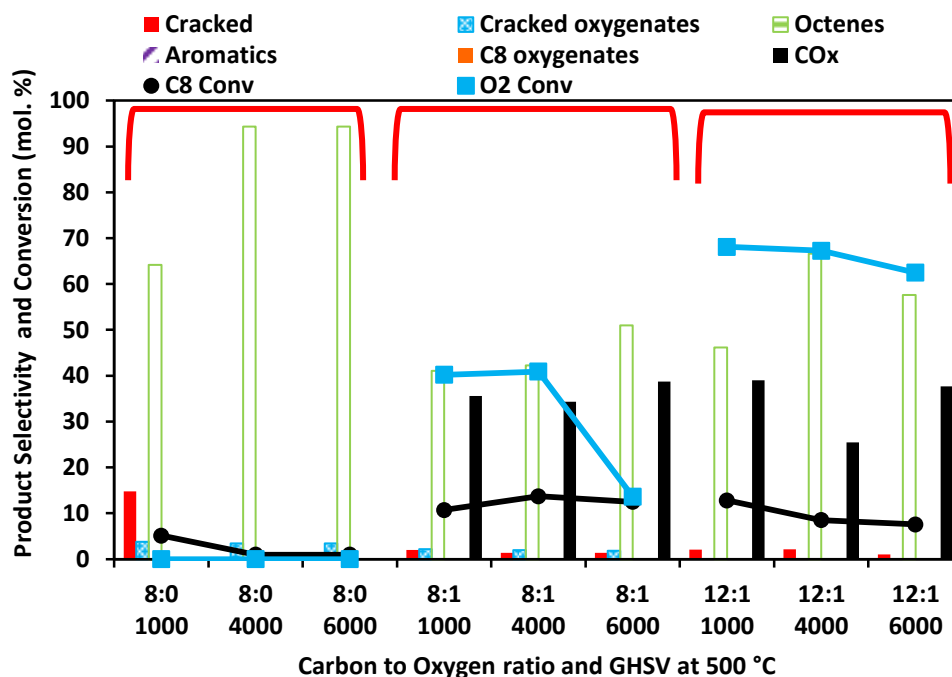


Figure 5.4: Reaction of *n*-octane (1 %) with the FeMoO₄ catalyst using various carbon to oxygen ratios between 8:0 - 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at 500 °C

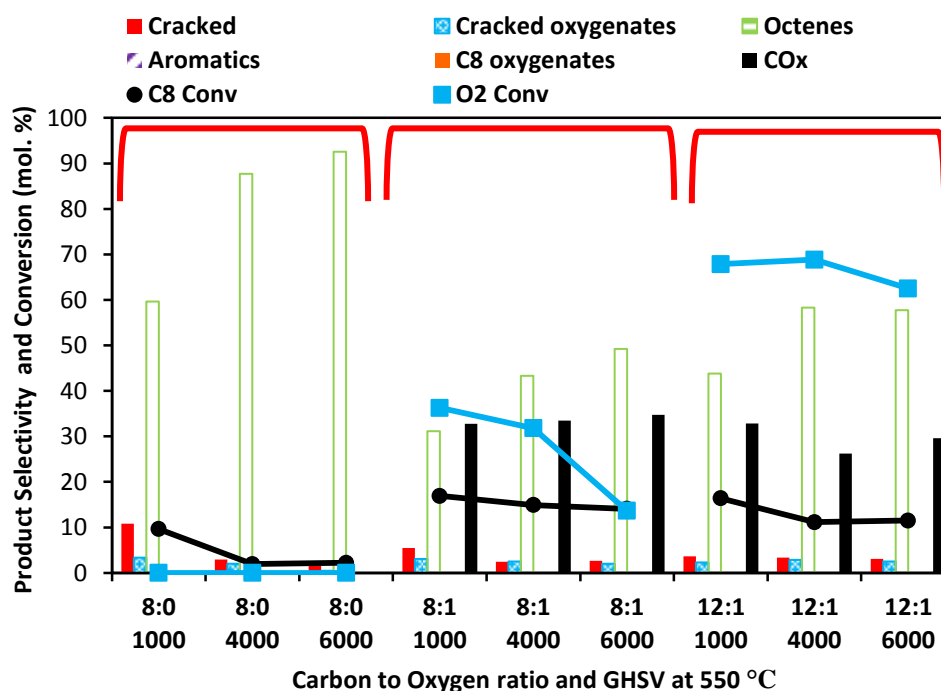


Figure 5.5: Reaction of *n*-octane (1 %) with the FeMoO₄ catalyst using various carbon to oxygen ratios between 8:0 - 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at 550 °C

When the temperature was increased to 500 °C and 550 °C (Figs. 5.4 - 5.5) the selectivity to aromatics increased and CO_x decreased. Lower GHSVs produced more aromatics whereas higher GHSVs produced octene. Using more fuel rich conditions (12:1) requires more oxygen from the gas feed to produce the aromatics and octene

compared to leaner systems. It is shown that high contact times are required to produce aromatics and octene under DH conditions.

The optimum conditions for the production of octene was at a C:O of 12:1 at 4000 h^{-1} at 400°C . The catalyst produced 7 % conversion at 91 % selectivity. As a comparison, the reduced JM iron molybdate catalyst described in Chapter 4 produced similar amounts of octene with similar conversion, 8 % conversion and 87 % selectivity. However stoichiometric ratio catalysts are often avoided due to catalyst stability issues, even when greater conversions and selectivities are achieved^{3, 4}. Future work would be to monitor the reaction over time and examine conversion and selectivity. According to literature, upon reduction the catalyst produces the Fe_2O_3 phase which is found to be inactive for methanol synthesis⁵, and so the catalyst is often over engineered. As a result a greater proportion of molybdenum to iron is introduced to maintain the iron molybdate phase. The MoO_3 component sublimates and the excess molybdenum replaces this and therefore extends the life time of the catalyst⁶.

5.2.1.2.Detailed Analysis: Eliminating or Consuming CO_2

This section looks into the above analysis in more detail. Figures 5.6-5.8 show the reaction conditions at C:O 12:1. Figure 5.6 represents the reaction at 1000 h^{-1} and Figures 5.7 and 5.8 represent the reactions at 4000 h^{-1} and 6000 h^{-1} respectively. These conditions were chosen because the optimisation to octene was found when using these particular conditions, see Figure 5.2.

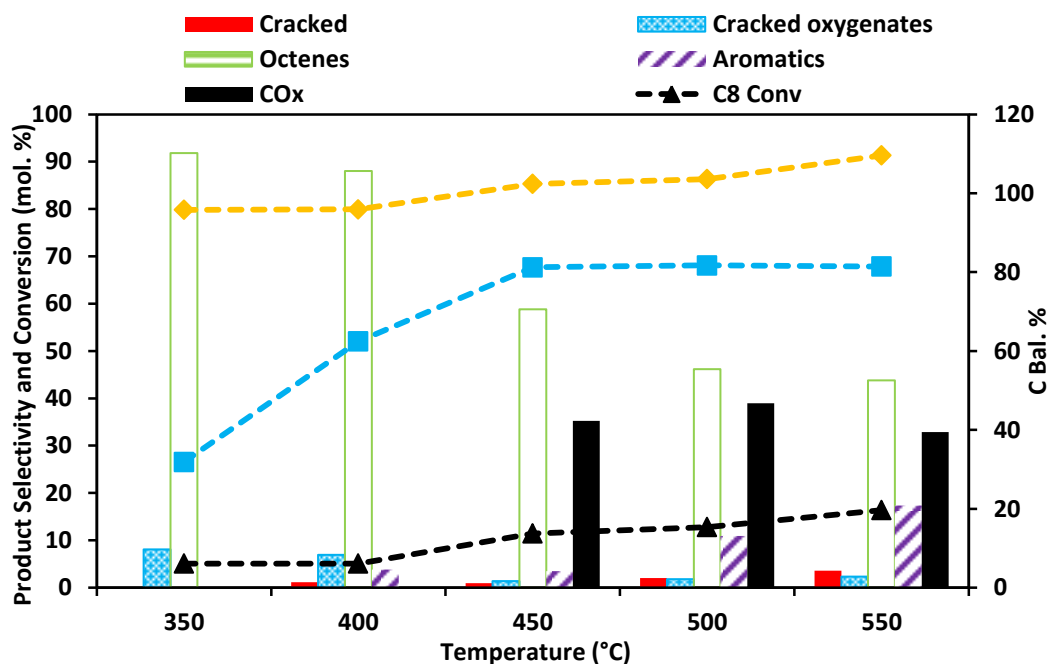


Figure 5.6a: Reaction of *n*-octane (1 %) with the FeMoO_4 catalyst. C:O ; 12:1 at 1000 h⁻¹. Temperature range from 350 °C to 550 °C.

Figure 5.6a shows when the temperature increased the conversion of octane increased. A sharp increase in octane (11. 5%) at 450 °C was detected and this coincides with an increase in CO_x. Temperatures below 450 °C produced octene as the dominate product reaching selectivities of *ca.* 90 % and conversions of *ca.* 5 %. With increasing temperature the oxygen conversion increased, from 27 % at 350 °C to 68 % at 450 °C and plateaued there on. Increasing the temperature promotes aromatic production whilst octene selectivity decreased, suggesting that octenes cyclise and then aromatise. Figure 5.6b shows the aromatic product distribution.

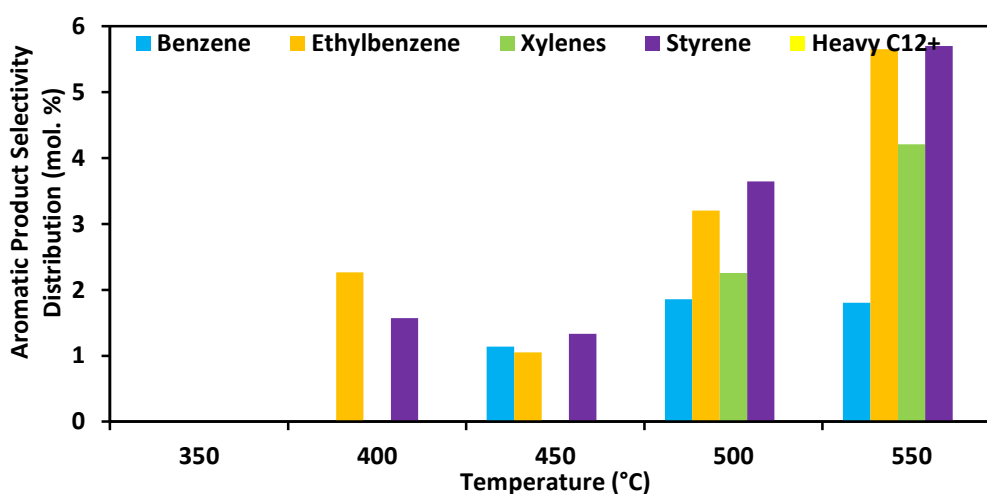


Figure 5.6b: Aromatic product distribution for the reaction of *n*-octane (1 %) with the FeMoO_4 catalyst. C:O ; 12:1 at 1000 h⁻¹. Temperature range from 350 °C to 550 °C.

Octene selectivity was dominant at $< 450\text{ }^\circ\text{C}$, and little aromatics were produced. At $350\text{ }^\circ\text{C}$ aromatics were not detected but when the temperature increased an increase in aromatics was observed. At $400\text{ }^\circ\text{C}$ both EB and ST were produced. When the temperature further increased, the selectivities to benzene, xylene, EB and ST along with CO_x increased. The production of xylene was detected at higher temperatures, $\geq 500\text{ }^\circ\text{C}$, suggesting it probably formed from the 2,7-ring closure of octane and further ODH^{7,8}.

When the GHSV was increased to 4000 h^{-1} (Figures 5.7a and b) the conversion of *n*-octane decreased. The octene selectivity increased and CO_x decreased as a result of a lower contact time. It shown that xylene is only produced at $550\text{ }^\circ\text{C}$, suggesting that that xylene is both temperature and contact time dependent.

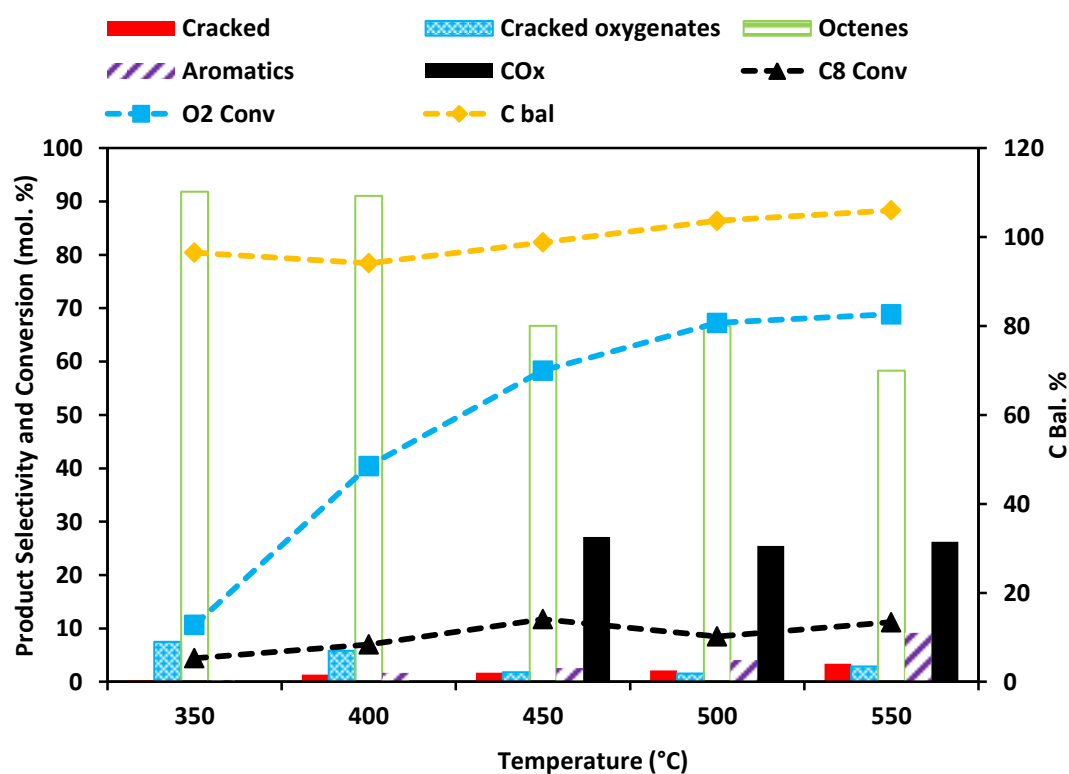


Figure 5.7a: Reaction of *n*-octane (1 %) with the FeMoO_4 catalyst. C:O ; 12:1 at 4000 h^{-1} . Temperature range from $350\text{ }^\circ\text{C}$ to $550\text{ }^\circ\text{C}$.

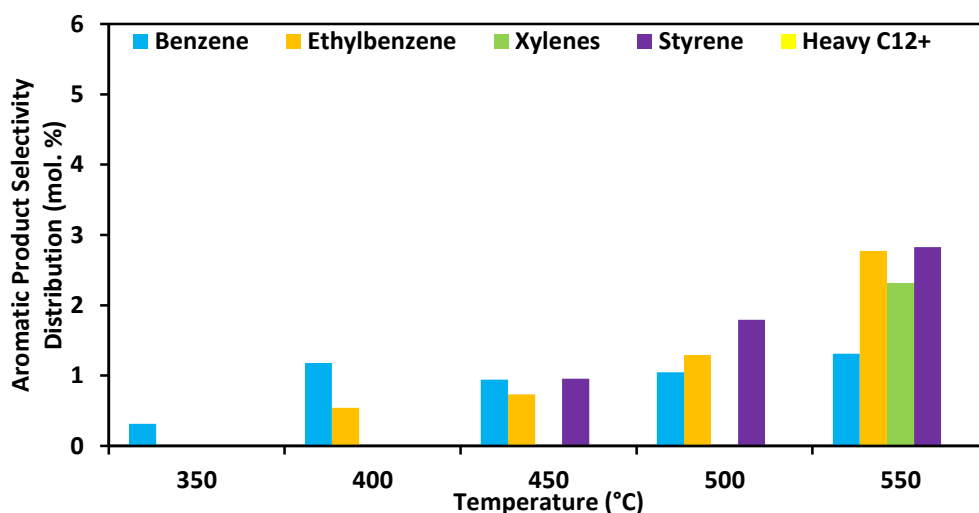


Figure 5.7b: Aromatic product distribution for the reaction of *n*-octane (1 %) with the FeMoO_4 catalyst. C:O ; 12:1 at 4000 h^{-1} . Temperature range from 350 °C to 550 °C.

When the GHSV was increased to 6000 h^{-1} (Figures 5.8a and b) the conversion of *n*-octane decreased. Conversions of octane were negligible at temperatures below 450 °C. At temperatures $\geq 450 \text{ °C}$ *n*-octane conversion increased but was lower than at 4000 h^{-1} as expected with a shorter contact time. Aromatic selectivity also decreased with increasing GHSV. Xylene production decreased at 550 °C suggesting that the 2,7-ring closure of *n*-octane is less favourable than the 1,6 ring closure. This was also shown in Chapter 4 when the reaction of oct-1-ene was reacted with the reduced JM iron molybdate catalyst.

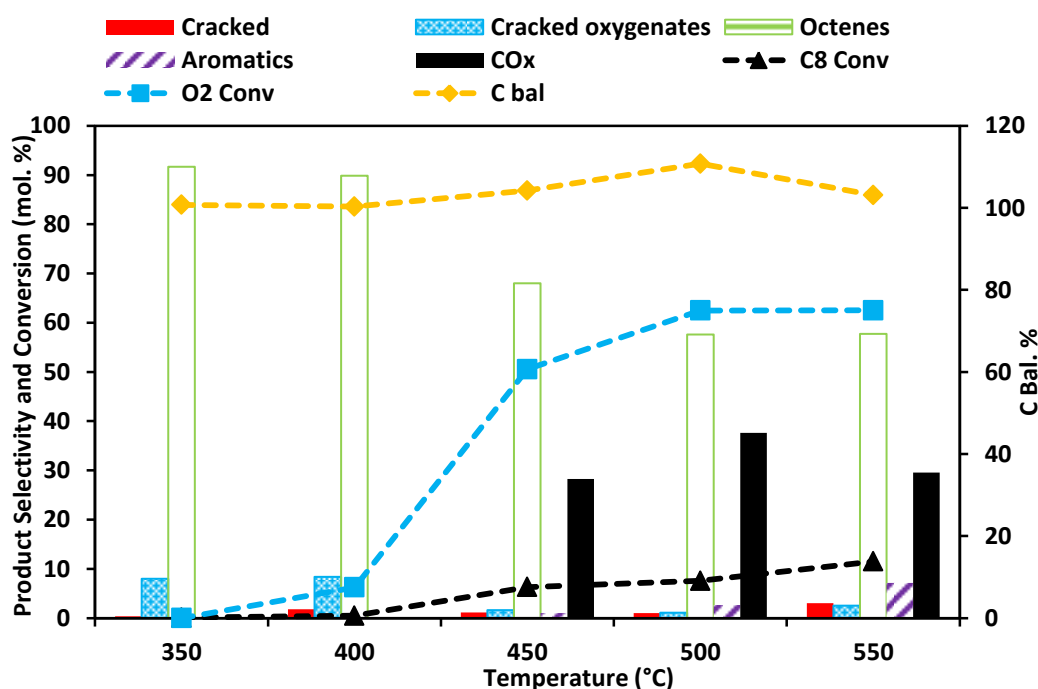


Figure 5.8a: Reaction of *n*-octane (1 %) with the FeMoO_4 catalyst. C:O ; 12:1 at 6000 h^{-1} .
Temperature range from 350 °C to 550 °C.

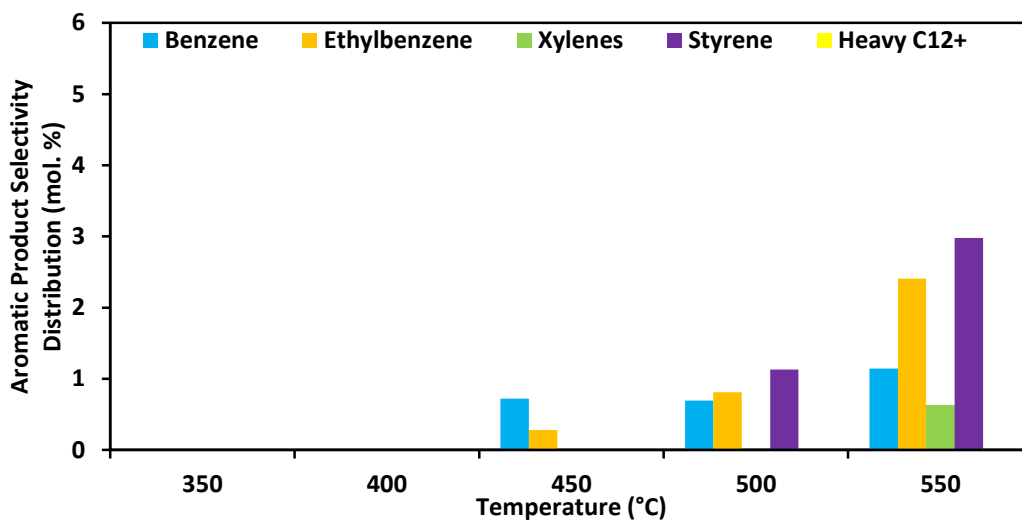


Figure 5.8b: Aromatic product distribution for the reaction of *n*-octane (1 %) with the FeMoO_4 catalyst. C:O ; 12:1 at 6000 h^{-1} . Temperature range from 350 °C to 550 °C.

5.2.1.3. Summary

It is shown that the FeMoO_4 catalyst can activate *n*-octane. At temperatures $< 450 \text{ °C}$ the dominant product produced was octene and no CO_2 was produced. At higher temperatures, $\geq 450 \text{ °C}$, octene was still the dominant product, however aromatics and CO_x increased. However, comparing the catalyst with the reduced JM iron molybdate, described in Chapter 4, at temperatures $\geq 450 \text{ °C}$ less aromatics were produced and the conversions were lower. This suggests the excess molybdenum(IV)oxide found in both the reduced and non-reduced JM iron molybdate catalyst (because the catalysts are the same after the reductive phase transition at 450 °C) may be responsible for the aromatics and CO_x produced.

5.2.2. Pure Phase MoO₂

5.2.2.1. Optimisation for the Production of Aromatics

The JM iron molybdate catalyst was produced with a large proportion of molybdenum compared to iron, Mo:Fe = 2.75: 1. It was found that majority of the molybdenum oxide formed upon reduction was MoO₂. This section assesses the MoO₂ catalyst with octane under various conditions, 1 % (v/v %) *n*-octane at a C:O ; 2:1, 8:1, 12:1, by increasing the temperature from 350 °C to 550 °C, in 50 °C increments, at 1000 h⁻¹, 4000 h⁻¹ and 6000 h⁻¹ shown by Figures 5.9- 5.13 respectively.

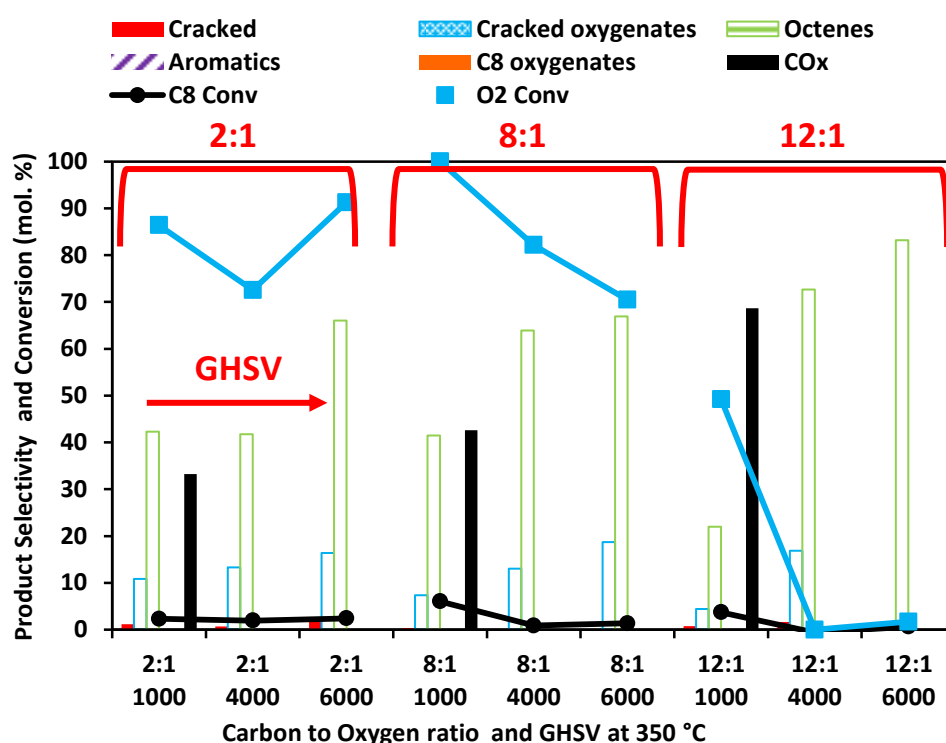


Figure 5.9: Reaction of *n*-octane (1 %) with the MoO₂ catalyst using various carbon to oxygen ratios between 2:1 - 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at **350 °C**

The reaction of *n*-octane with the MoO₂ catalyst at 350 °C (Fig. 5.9) at 1000 h⁻¹ shows CO_x to be the dominant product associated with long contact times. At this temperature the conversion of *n*-octane was negligible. With increasing C:O ratios the CO_x increased, however the aromatics decreased suggesting a competing reaction between CO_x and aromatics. Increasing the GHSV increased the selectivity to octene. Longer contact times produce mainly aromatics and CO_x, where the aromatics are formed from cyclisation and aromatisation octene *via* ODH. At lower C:O ratios, in

particular 2:1, more oxygen was consumed in the reaction. The oxygen in the gas phase is required to replenish the lattice oxygen used in the production of octene and aromatics *via* the Mars-van Krevelen (MvK) mechanism, and the CO₂ produced at 1000 h⁻¹ is likely to be produced from gas phase oxygen *via* the Eley-Rideal or Langmuir-Hinshelwood type mechanism.

When the temperature was increased to 400 °C (Fig. 5.10) the conversion of *n*-octane increased particularly at a C:O ratio of 2:1.

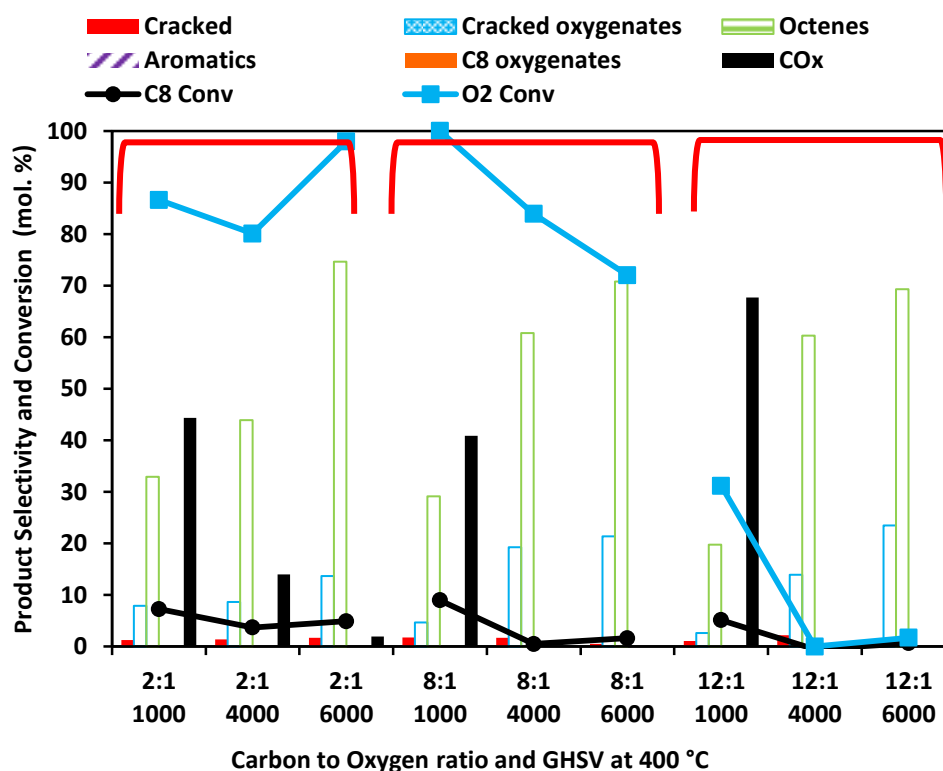


Figure 5.10: Reaction of *n*-octane (1 %) with the MoO₂ catalyst using various carbon to oxygen ratios between 2:1 - 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at **400 °C**

The increase in conversion coincides with an increase in CO_x selectivity. Whilst CO_x selectivity increased the aromatics decreased suggesting that the aromatics are being oxidised to CO_x because the production of octene remained the same from 350 °C to 400 °C. This corresponds with the octene experiments in Chapter 4, where it was shown that once the octane molecule is dehydrogenated it is stable and does not undergo combustion, suggesting that combustion of aromatics or octane and cracked chained alkanes.

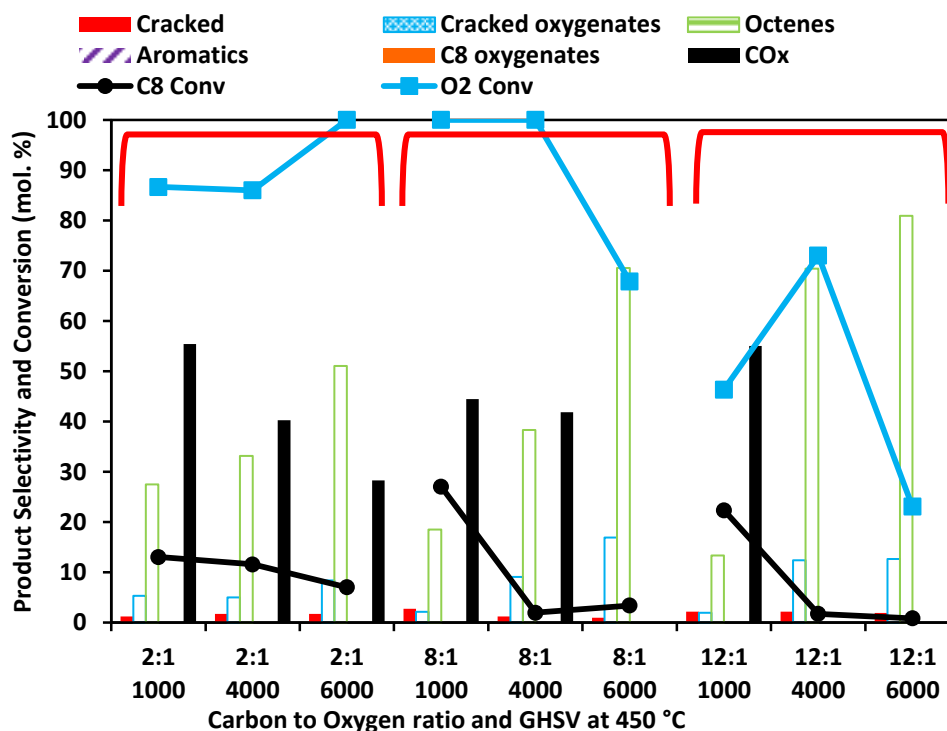


Figure 5.11: Reaction of *n*-octane (1 %) with the MoO₂ catalyst using various carbon to oxygen ratios between 2:1 - 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at **450 °C**

The temperature was then increased to 450 °C (Fig. 5.11). At a C:O of 12:1 at 1000 h⁻¹ the selectivity to CO_x decreased from *ca.* 68 % at 400 °C to 55 % while the aromatics increased from 9 % to 27 %. Octene selectivity decreased from *ca.* 20 % at 400 °C to 13 %. This suggests that octene is cyclising and further dehydrogenating to produce aromatics. More oxygen is consumed at 8:1 at 1000 h⁻¹ compared to 12:1 which resulted in an increase in aromatic production. More oxygen is required to dehydrogenate octane and the further dehydrogenate to produce aromatics accounting for the increase in selectivity. However at 2:1 this is not observed because the system is not oxygen limited and so more oxygen is available for combustion.

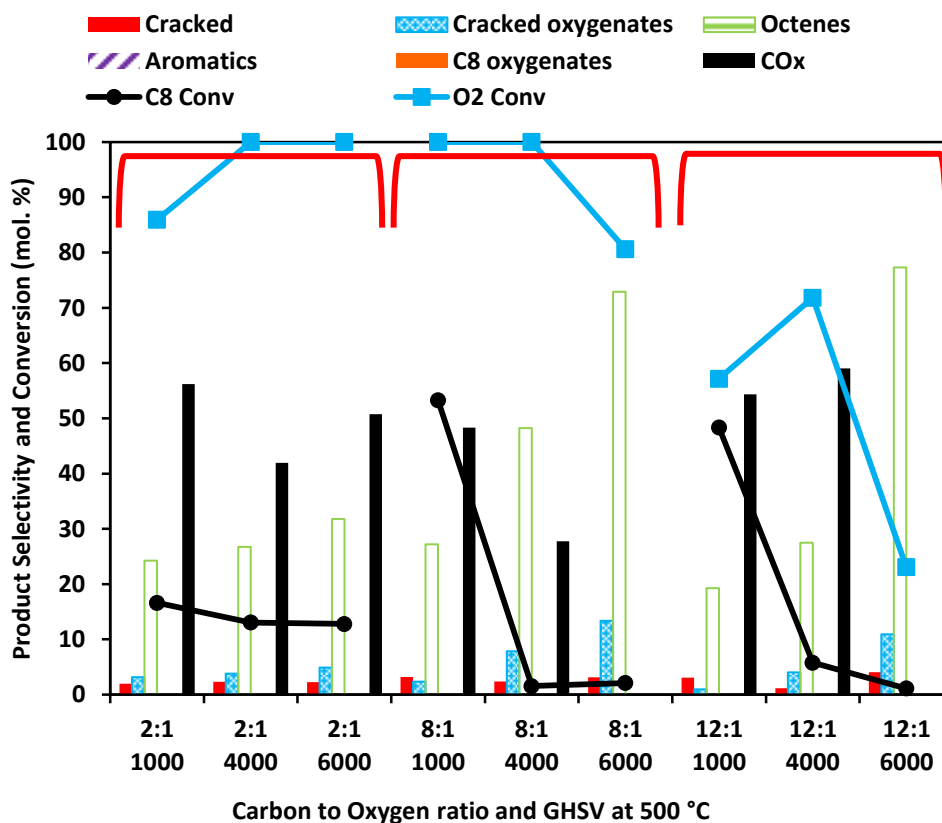


Figure 5.12: Reaction of *n*-octane (1 %) with the MoO₂ catalyst using various carbon to oxygen ratios between 2:1 - 12:1 and GHSVs of 1000 h⁻¹ to 6000 h⁻¹ at **500 °C**

With a further increase in temperature, to 500 °C (Fig. 5.12), octane conversion increased. Octene selectivity increased with increasing GHSV as a result of shorter contact times which prevents the cyclisation/aromatisation process. Conversion is still low at both 4000 h⁻¹ and 6000 h⁻¹ at 8:1 and 12:1, however at 1000 h⁻¹ the conversion is high achieving *ca.* 50 %, where CO_x is dominant.

Increasing the temperature from 500 °C to 550 °C (Fig.5.13) increased conversion and the selectivity to aromatics and CO_x. Octane conversion decreased when the GHSV increased due to shorter contact times which resulted in an increase in octene selectivity. Higher conversions were achieved at 4000h⁻¹ and 6000h⁻¹ when using a C:O of 2:1 as more oxygen was available for combustion. This suggests that the excess molybdenum oxide present in the JM iron molybdate catalyst is responsible for the majority of CO_x produced.

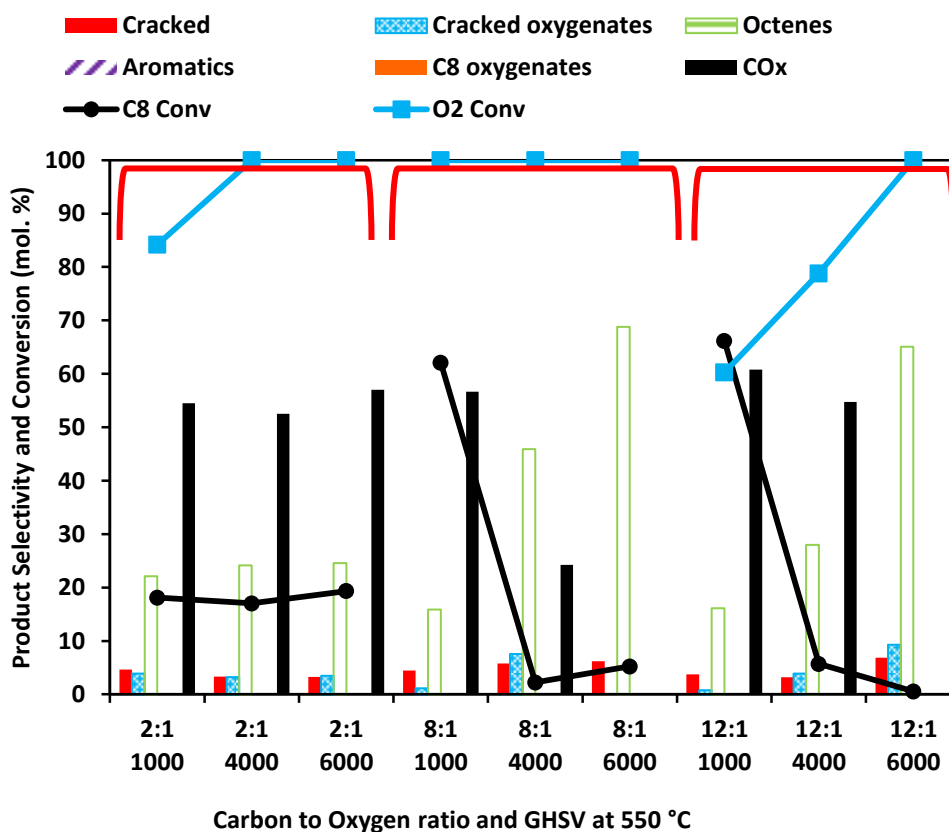


Figure 5.13: Reaction of *n*-octane (1 %) with the MoO₂ catalyst using various carbon to oxygen ratios between 2:1 - 12:1 and GSHVs of 1000 h⁻¹ to 6000 h⁻¹ at **550 °C**

5.2.2.2. Detailed Analysis: The production of aromatics

This section looks into the above analysis in more detail. Figures 5.14 to 5.16 reveals a detailed review using the reaction conditions at C:O 8:1. Figure 5.14 represents the reaction at 1000 h⁻¹ and Figures 5.15 and 5.16 represent the reactions at 4000 h⁻¹ and 6000 h⁻¹ respectively. The conditions were chosen because the selectivity to aromatics and CO_x was the highest and lowest respectively. The conditions will be used to compare to the conditions used to achieve the highest aromatic selectivity shown by the reduced JM iron molybdate catalyst, FeMoO₄-MoO₂, at 8:1 at 1000 h⁻¹ at 550 °C.

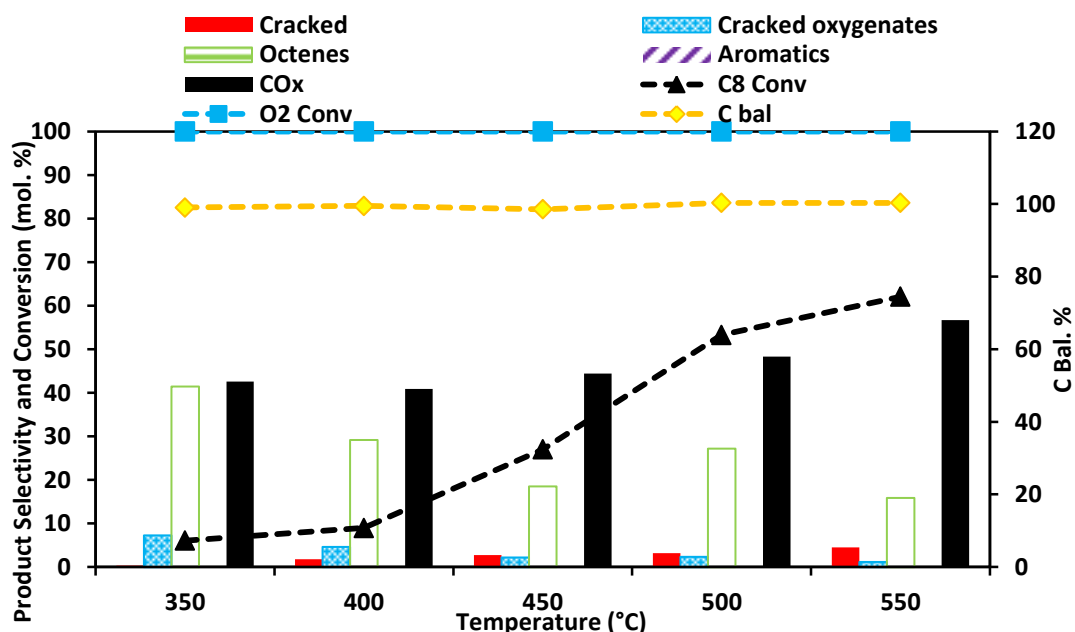


Figure 5.14a: Reaction of *n*-octane (1 %) with the MoO₂ catalyst. C:O ; 8:1 at **1000 h⁻¹**.

Temperature range from 350 °C to 550 °C.

Figure 5.14a shows with increasing temperature the conversion of octane increased. The selectivity to octene decreased with increasing temperature whereas the CO_x increased. From 350 °C to 450 °C octene selectivity decreased whilst the production of aromatics increased which suggests aromatisation. However with increasing temperatures beyond 450 °C the aromatic selectivity decreased and stabilised at *ca.* 20 % at both 500 °C and 550 °C. CO_x increased during the temperature increase suggesting combustion of the aromatics particularly at 550 °C. Figure 5.6b shows the aromatic product distribution from 350 °C to 550 °C using these conditions.

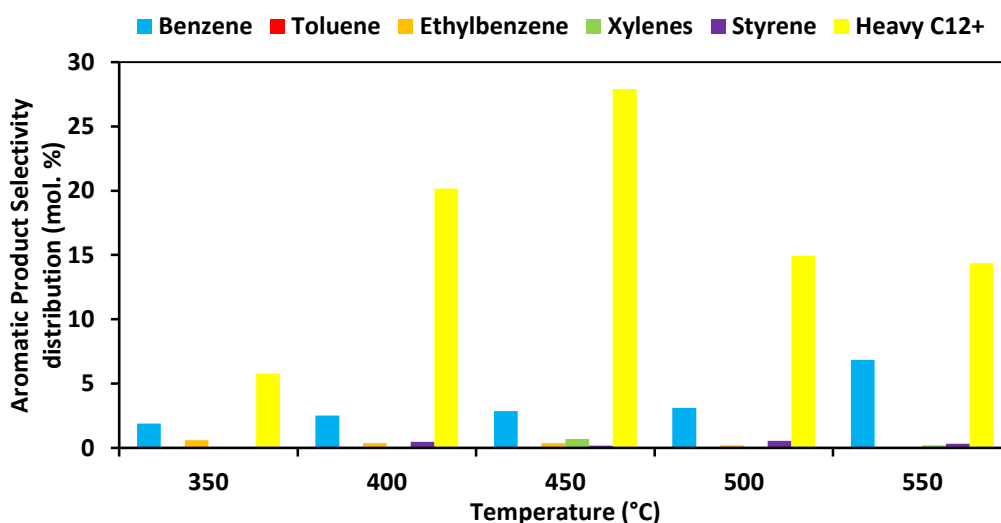


Figure 5.14b: Aromatic product distribution for the reaction of *n*-octane (1 %) with the MoO₂ catalyst. C:O ; 8:1 at **1000 h⁻¹**. Temperature range from 350 °C to 550 °C.

Figure 5.14b shows that the selectivity to heavy aromatics, which include naphthalene and ethyl-naphthalene, are the dominant aromatics produced which have a carbon chain length ≥ 12 . With increasing temperature the selectivity to benzene increased, particularly at 550 °C, which coincides with the increase in cracked products (i.e. ethane) observed in Figure 5.14a.

The GHSVs were then increased to 4000 h⁻¹ and 6000 h⁻¹ represented by Figures 5.15 and 5.16 respectively.

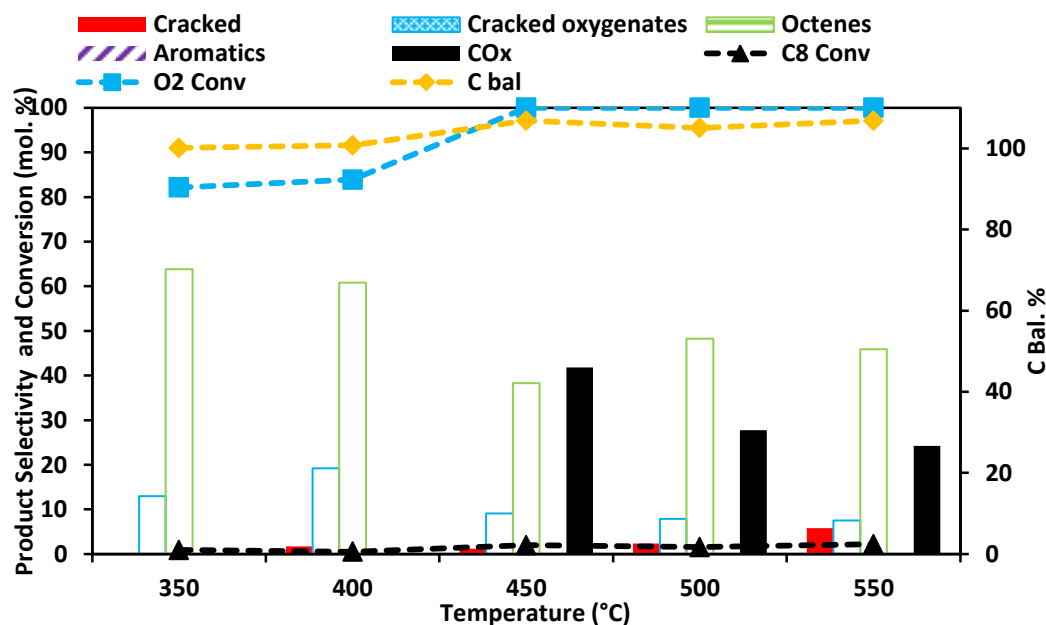


Figure 5.15a: Reaction of *n*-octane (1 %) with the MoO₂ catalyst. C:O ; 8:1 at 4000 h⁻¹.

Temperature range from 350 °C to 550 °C.

Increasing the GHSV to 4000 h⁻¹ (Fig. 5.15a) resulted in a decrease in the conversion as a consequence of a shorter contact time. The selectivity to octene, below 450 °C, was high *ca.* 60 % but at negligible conversion. Aromatics were also produced, *ca.* 23 % and 18 % at 350 °C and 400 °C respectively. CO_x was not produced at temperatures below 450 °C but when the temperature was increased the selectivity to CO_x increased. However at 500 °C and 550 °C the selectivity to CO_x decreased. The decrease in selectivity is associated with the consumption of oxygen, where the system has become oxygen limited.

The aromatic product distribution at 4000 h⁻¹ (Figure 5.15b) resulted in the production of EB, particularly at temperatures ≤ 450 °C which indicates 1,6- ring closure of octene.

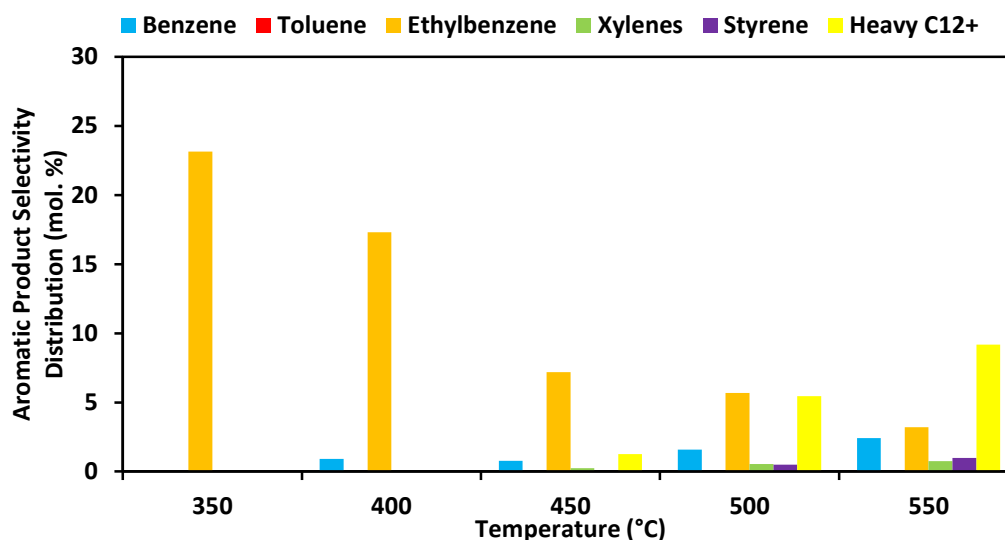


Figure 5.16b: Aromatic product distribution for the reaction of *n*-octane (1 %) with the MoO₂ catalyst. C:O ; 8:1 at 4000 h⁻¹. Temperature range from 350 °C to 550 °C.

No ST or xylene was produced suggesting that the MoO₂ component of the reduced JM FeMoO₄-MoO₂ catalyst produces EB, and that the iron molybdate component produces the xylene and more importantly ST from EB by activating CO₂, which was hypothesised in Chapter 4. The selectivity to EB decreased with increasing temperature while octene selectivity remained stable (Fig.5.15a) and CO_x increased. This suggests that EB is less stable than styrene and will undergo combustion if not converted.

Increasing the GHSV to 6000h h⁻¹ (Fig.5.16a) resulted in similar conversion to 4000 h⁻¹ (Fig.5.15a), however the selectivity to CO_x reduced to zero from temperatures ≥ 450 °C unlike the reaction at 4000 h⁻¹. The selectivity to octene remained high throughout the temperature change from 350-550 °C. An increase in aromatic selectivity was observed at 550 °C associated with an increase in heavy aromatic production (Fig 5.16b). The cracked oxygenates also disappear at 550 °C when the system became oxygen limited (represented by the consumption of oxygen in the system). The decrease in octene selectivity suggests that octene is undergoing a cycloaddition reaction but this is far from conclusive and further studies would be needed to confirm this.

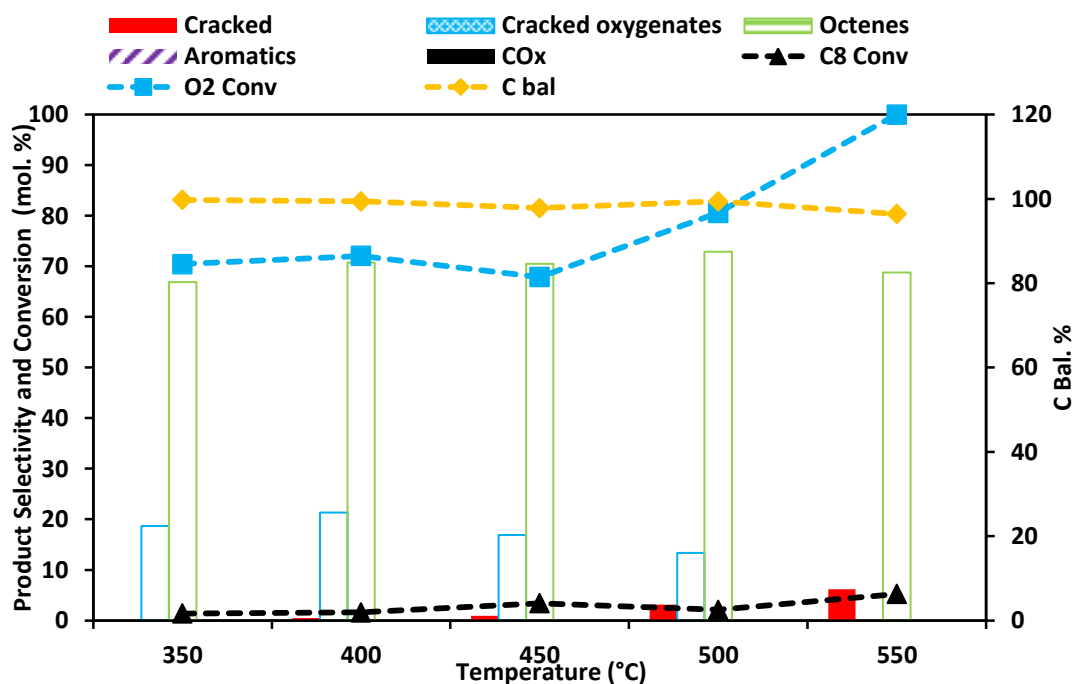


Figure 5.16a: Reaction of *n*-octane (1 %) with the MoO₂ catalyst. C:O ; 8:1 at 6000 h⁻¹. Temperature range from 350 °C to 550 °C.

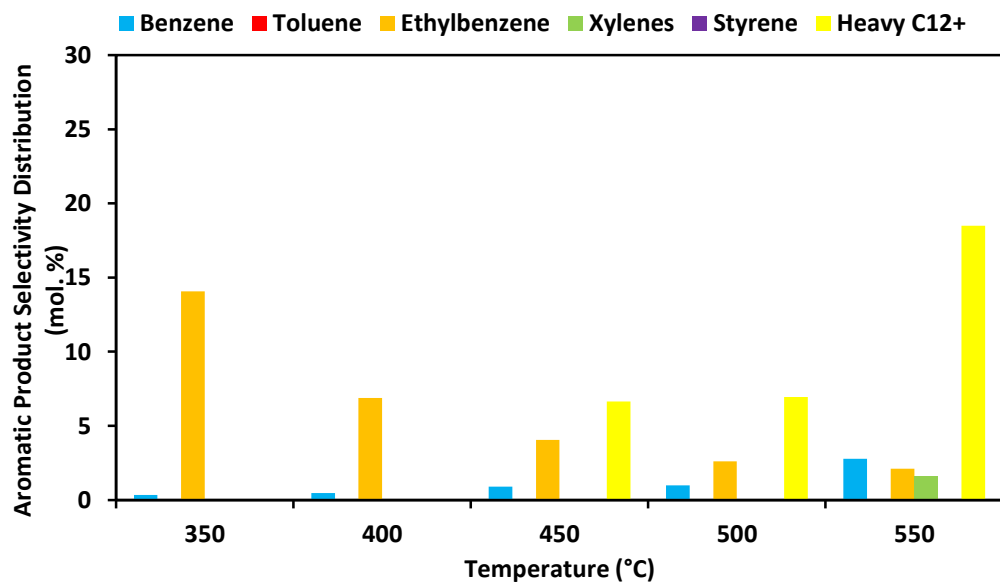


Figure 5.16b: Aromatic product distribution for the reaction of *n*-octane (1 %) with the MoO₂ catalyst. C:O ; 8:1 at 6000 h⁻¹. Temperature range from 350 °C to 550 °C.

5.3. Conclusions

The FeMoO₄ catalyst produced octene with high selectivity. The optimal conditions for the production of octene were a C:O ratio of 12:1, 4000 h⁻¹ at 400 °C achieving 91 % selectivity at 7 % conversion. Increasing C:O ratios produced less CO_x and the selectivity to the octene increased. This is the same as was observed for the reduced JM iron molybdate, FeMoO₄-MoO₂, catalyst. When the GHSV was increased the conversions generally decreased and the aromatics produced decreased, but the selectivity to octene increased. This is attributed to shorter contact times. As the temperature increased, conversion and selectivity to both aromatics and CO_x increased while octene selectivity decreased due to aromatisation.

The MoO₂ catalyst assists in the aromatisation process and the dominant products produced with reasonable conversion were CO_x. MoO₂ produces heavy aromatics at 1000 h⁻¹ which may be from the cycloaddition of alkene molecules. Increasing the GHSVs to 4000 h⁻¹ and 6000 h⁻¹ resulted in the production of EB, particularly at temperatures ≤ 450 °C which indicates 1,6- ring closure of octene. No ST or xylene was produced suggesting that the MoO₂ component of the reduced JM FeMoO₄-MoO₂ catalyst produces EB, and that the iron molybdate component produces the xylene and more importantly ST from EB by activating CO₂, which was hypothesised in Chapter 4. EB selectivity decreased with increasing temperature. Octene selectivity remained high and the selectivity to CO_x increased suggesting that EB is less stable than styrene and will undergo combustion if not converted to ST.

The results show that once octene is produced it is stable and can either undergo aromatisation or remain unchanged which is in agreement with the results obtained in Chapter 4. The proportion of molybdenum to iron is greater in the JM iron molybdate catalyst and therefore the MoO₂ upon reduction at high temperatures, will enrich the surface⁹. The exposed iron species will activate EB to ST using CO₂ as the oxidant. A synergistic effect between the FeMoO₄ and MoO₂ catalysts (i.e. the reduced JM iron molybdate catalyst) at high temperatures for the production of ST is evident.

5.4. References

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6

Chapter 6: Conclusions and Future Work

6.1. Conclusions

The gas phase activation of *n*-octane was investigated using an industrially supplied iron molybdate catalyst, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, from Johnson Matthey (JM). The characterisation of the catalysts was vital in the understanding of possible reaction mechanisms, as well as physical and chemical properties, which subsequently assisted the experimental progression. This section reveals the key features and discoveries found throughout the project and provides insight to crucial work to be carried out in the future.

6.1.1. The JM Iron Molybdate Catalyst

The oxidative dehydrogenation (ODH) of *n*-octane with the JM iron molybdate catalyst at temperatures between 350 °C and 550 °C produced octene, aromatics and CO_x . The changes in activity and selectivity of the catalyst were attributed to the phases present at specific temperatures, which were shown using *in situ* XRPD. The catalyst undergoes a reductive phase transition when reacted with *n*-octane at 450 °C where the phase changes from $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ to $\text{FeMoO}_4\text{-MoO}_2\text{-Mo}_4\text{O}_{11}$. If the temperature is taken back below this point the catalyst does not revert back to the original phase and therefore the same activity and selectivity cannot be achieved and therefore the system can be considered as two different catalysts: i) the oxidised phases at temperatures < 450 °C, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, which is associated with the production of octene and CO_x , and ii) the reduced phases at temperatures ≥ 450 °C, FeMoO_4 , MoO_2 and Mo_4O_{11} , which led to the formation of CO_x and aromatics.

It was shown at 550 °C when the catalyst was exposed to dehydrogenating (DH) conditions, where the carbon to oxygen (C:O) ratio is 8:O (i.e. no oxygen present in the gas feed), CO_x was suppressed suggesting the formation of CO_x was produced from the oxygen species in the gas phase through a Eley-Rideal or Langmuir-Hinshelwood style mechanism and not through the Mars-van Krevelen (MvK) ODH mechanism.

Reintroduction of oxygen (i.e. using ODH conditions) resulted in an increase in CO_x selectivity. Styrene was the dominant aromatic produced under specific conditions (C:O 8:1, 1000 h^{-1} , 550 °C) accounting for 36 % selectivity at 34 % conversion. Adjusting the gas hourly space velocity (GHSV) from 1000 h^{-1} to 4000 h^{-1} decreased the selectivity to styrene and increased CO_x production. This is counterintuitive because at lower GHSVs a longer contact time should result in the production of the more thermodynamically favourable product, CO_2 . This suggested that the reaction was consuming CO_2 in order to activate ethylbenzene to styrene, which is discussed in detail in Chapter 4.

It was found adjusting other parameters such as the C:O ratio and GHSV could manipulate the product distribution and conversion. Low C:O ratios resulted in higher conversions but the major products were CO_x . Increasing the ratio led to an increase in the aromatics and octene produced. The restriction of oxygen in the gas feed hinders combustion which would otherwise proceed through an Eley-Rideal or Langmuir-Hinshelwood style mechanism. With less CO_x produced the selectivity to octene and aromatics increased *via* the dehydrogenation of *n*-octane which proceeds through the MvK-ODH mechanism, but at a cost of lower conversion. Lower GHSVs often produced CO_x and high conversions whilst higher GHSVs produced octene at the cost of lower conversion due to the associated contact times of the substrate and the catalyst.

Increasing the partial pressure of *n*-octane increased the selectivity to octene with the highest selectivity reaching 44 % at 350 °C at 6 % conversion. The highest conversion was 16 % at 33 % selectivity to octene at 550 °C. According to Le Chatelier's when more substrate is introduced into the feed the position of equilibrium will shift to produce more octene. The kinetic control was further explored by colleagues in the University of Kwazulu-Natal (UKZN) situated in Durban when 11 % (v/v %) *n*-octane

was introduced into the feed and an increase in both conversion and selectivity was detected.

6.1.2. The Reduced JM Iron Molybdate Catalyst

The pre-reduction of the JM iron molybdate catalyst, $\text{FeMoO}_4\text{-MoO}_3$, improved the selectivity to octene at temperatures $< 450\text{ }^\circ\text{C}$, whereas the oxidised form of the catalyst mainly produced CO_x and cracked products at these temperatures. The optimum conditions for the production of octene was using a C:O ratio of 8:1 at 4000 h^{-1} at $400\text{ }^\circ\text{C}$, achieving ca. 82 % selectivity and 8 % conversion. TOL studies showed that the catalyst was stable under these operating conditions. Lowering the GHSV to 1000 h^{-1} at this temperature produced CO_2 , due to a re-oxidisation of the catalyst and the removal of coke. Temperatures above $\geq 450\text{ }^\circ\text{C}$ produced aromatics, including ethyl benzene, benzene and styrene. The production of CO_x decreased at $550\text{ }^\circ\text{C}$ and 1000 h^{-1} relative to 4000 h^{-1} . An increase in the amount of coke on the surface was detected by CHN analysis and was complemented by Raman spectroscopy. The carbonaceous material was assigned as a sp^2 hybridised carbon material, specifically polyaromatic hydrocarbons (PAHs). At high temperatures it is thought that molybdenum oxide enriches the surface¹, and this, along with the carbon species, can induce the aromatisation of octane/octene² to ethylbenzene. It has been well documented that iron oxide can activate CO_2 and ethylbenzene to produce styrene^{3,4}. Therefore a possible mechanism uses molybdenum coated carbon under these reaction conditions to produce ethylbenzene and xylenes⁵, and the exposed iron species at the surface activate the CO_2 and ethylbenzene to produce styrene⁴, and therefore the amount of CO_2 decreased as it is consumed during the process. This accounts for the production of styrene and the decrease in ethylbenzene seen at $550\text{ }^\circ\text{C}$ because ethylbenzene was previously observed at lower temperatures.

Two possible mechanisms appear to be in operation for the production of styrene from *n*-octane. Firstly the dehydrogenation of octane to octene to produce ethylcyclohexane *via* cyclisation. This can then undergo further ODH to produce styrene proposed in similar mechanisms⁶, as well as possible ring closure followed by ring expansion^{7,8} to ethylbenzene and ODH to styrene. Secondly octene can also further dehydrogenate along the chain length to produce octadienes/trienes intermediates that then go on to cyclise/aromatise to produce styrene and xylenes. The reduced JM iron molybdate catalyst was tested with oct-1-ene under ODH and DH conditions. It

was found that the process produces isomers of octene and octadienes with high selectivities and conversions. Under ODH conditions with increasing temperature, from 350 °C to 550 °C, the aromatics, CO_x and cracked hydrocarbons selectivity increased.

DH conditions (i.e. with no oxygen in the gas feed) confirmed that CO₂ cannot be produced *via* the MvK mechanism because no CO₂ was produced under these conditions at both 1000 h⁻¹ and 4000 h⁻¹. If this mechanism were to operate the CO₂ must be produced from active oxygen surface species and not the lattice oxygen. The oxygen rich conditions showed that once the octene/octadienes are produced they are stable and do not combust. Therefore CO₂ is likely to be produced by a separate pathway and not from octene combustion.

6.1.3. The Pure Reduced Oxide Phase Catalysts: FeMoO₄ and MoO₂ Catalysts

It was observed that the FeMoO₄ catalyst produces octene with high selectivity. The optimal conditions for the production of octene were a C:O ratio of 12:1, 4000 h⁻¹ at 400 °C achieving 91 % selectivity at 7 % conversion. The improved selectivity of the reduced stoichiometric catalyst compared with the reduced JM iron molybdate catalyst is likely to be attributed to molybdenum content. Molybdenum oxide is acidic and therefore cracking would increase with increasing molybdenum content. However the life time of the stoichiometric catalyst would be expected to decrease, which was observed with previous methanol oxidation studies, compared to the over engineered JM reduced iron molybdate catalyst, because the molybdenum would be lost to sublimation at high temperatures resulting in deactivation^{9, 10}. Therefore a compromise would be needed between catalyst stability, selectivity and activity for industrial applications.

Increasing the C:O ratios produced less CO_x and the selectivity to octene increased. This is the same as was observed for the reduced JM iron molybdate catalyst. When the GHSV was increased the conversions generally decreased and the aromatics produced decreased, but the selectivity to octene increased. This is attributed to shorter contact times. As the temperature increased, conversion and selectivity to

both aromatics and CO_x increased while octene selectivity decreased due to aromatisation.

The JM iron molybdate, $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$, catalyst consists of an excess of MoO_3 and this is likely to form a monolayer at high temperatures^{1, 11-13}, as well as undergoing reduction. The MoO_2 monolayer therefore aids the aromatisation process at 550 °C, and the exposed iron species on the surface help to activate CO_2 to CO to dehydrogenate ethylbenzene to styrene⁴. However it is worth noting that carbonaceous species aid the ethylbenzene to styrene reaction⁵, as previously shown using the reduced JM iron molybdate, $\text{FeMoO}_4\text{-MoO}_2$, catalyst.

6.2. Future Work

Main objectives would be to improve the low temperature conversion, at 350 – 400 °C, for the production of octene in order to compete with the Honeywell UOP PACOL process. This would involve subtle manipulation of GHSV, C:O ratios and catalyst bed temperatures to name a few. Alternative preparation methods that increase the surface area and the introduction of promoters may be beneficial but may also lead to combustion resulting in a decrease in selectivity.

Other necessary work would be to assess a range of alkanes from $\text{C}_9\text{-C}_{20}$ produced from the Fischer-Tropsch process with the reduced iron molybdate catalyst to determine whether the same chemistry can be achieved with increasing chain length. Difficulties were initially seen when increasing the chain length from *n*-octane to *n*-decane with the $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalyst, however *n*-decane was not tested under optimum conditions found for *n*-octane with the $\text{FeMoO}_4\text{-MoO}_2$ catalyst.

It was observed that increasing the partial pressure of *n*-octane and oxygen increased the selectivity and conversion to octene with the $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalyst. It was found that the $\text{FeMoO}_4\text{-MoO}_2$ catalyst under operating conditions at low temperature improved conversion and selectivity to octene. Therefore increasing the partial pressure could improve conversion and retain high selectivity to the alkene.

The production of styrene using the JM iron molybdate catalyst at 550 °C using specific operating conditions is not clear. Therefore probing the reaction mechanism

using both *in situ* XRPD-GCMS and temporal analysis of products (TAP) to provide information on the active catalyst phases to evaluate the production of styrene could then provide information to synthesise improved catalysts.

The manufacture of molybdenum carbide and more importantly the iron molybdenum carbide¹⁴ and other carbon systems including graphene and graphitic oxide may improve the selectivity to octene and aromatics. Szechenyi *et al.*⁵ reported that molybdenum carbide can aromatise *n*-octane into ethylbenzene and *o*-xylene. Therefore adding an iron redox component could initiate the activation of CO₂ to produce styrene from ethylbenzene which was previously shown from the experimental results. The catalysts would also be tested for the production of alkenes, especially at the optimum conditions found for the reduced iron molybdate catalysts (400 °C, 4000 h⁻¹, C:O ; 8:1). It was shown that the carbon mass balance decreased with increasing time and that conversion also increased. Although it was not conclusive, from the previous reaction with octane and the reduced iron molybdate catalyst under these conditions, that carbon was present on the surface due to conflicting CHN analysis and Raman spectroscopy. However it would be worth testing because carbides have been reported to activate alkanes¹⁵ TGA coupled with IR-MS with oxygen would confirm whether carbon is on the surface of the reduced JM iron molybdate catalyst by detecting the production of CO₂.

6.3. References

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Appendix

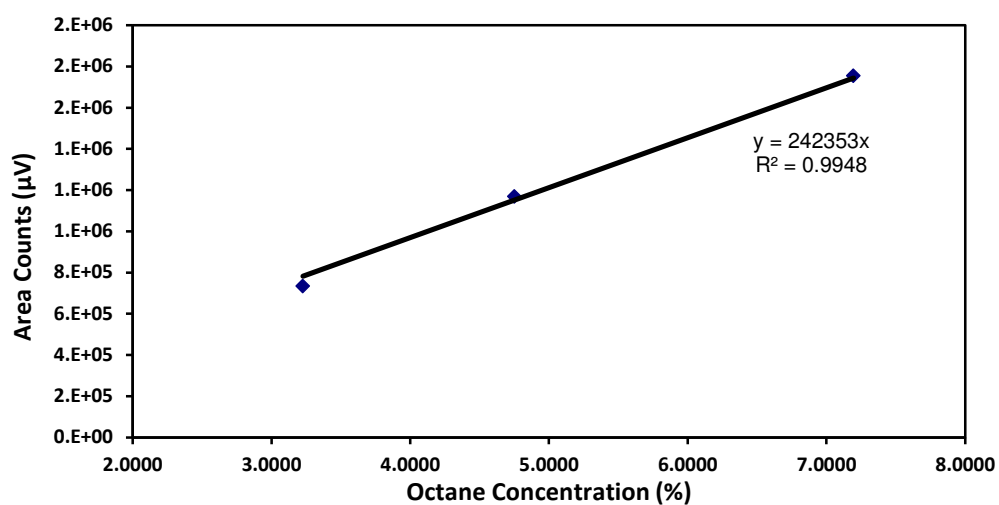


Figure 1: *n*-Octane calibration.

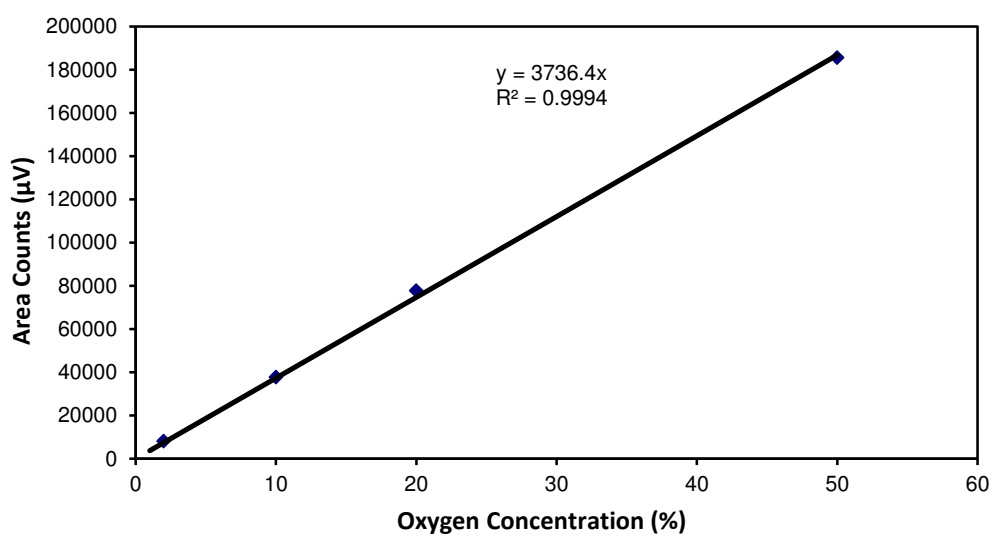


Figure 2: Oxygen calibration.

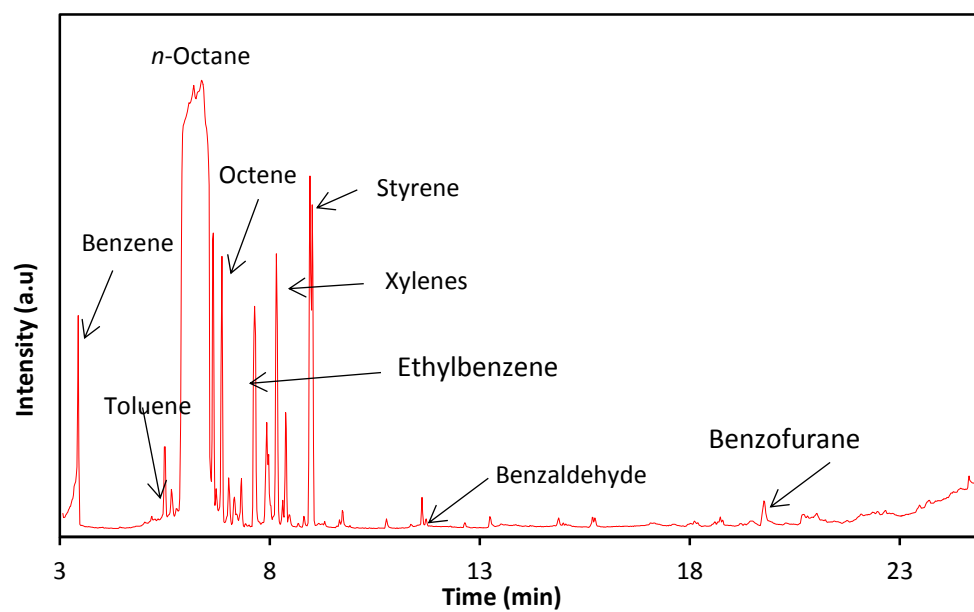


Figure 3: GC-EIMS chromatogram of octane reaction with JM iron molybdate catalyst at 460 °C with C:O ratio 8:1.