



GAS-PHASE EPOXIDATION OF HEXAFLUOROPROPENE OVER SUPPORTED COPPER OXIDE CATALYSTS: MECHANISM AND KINETICS

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Declaration

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Professor David Lokhat

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ULindelani ka-maSokhela no Bhekumuzi ka-Shefa ka-Ndolo ka-Duka,

NGIYABONGA

Abstract

The mechanism and kinetics were investigated for the catalytic production of hexafluoropropene oxide via the gas-phase epoxidation of hexafluoropropene with molecular oxygen. The cesium-doped copper oxide catalysts with 10 wt% loadings were synthesized using the impregnation technique. Characterization of catalysts was performed for the assessment of their structural morphology as well as their chemical and physical properties. The techniques used in the characterization studies included microscopic, diffraction, and surface analysis: X-Ray Diffraction, surface area Brunauer-Emmet-Teller analyzer, Transmission Electron Microscopy, and Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy. The results from these studies confirmed the correct material prepared and expounded the structure reactivity correlation. The catalysts displayed well-dispersed spherical-shaped particles, mesoporous material with high surface area. With the shape and size of the particles used in this research, good flow distribution with low-pressure drop was possible. Also, the resulting surface area allowed reasonable accessibility of active sites, hence the good catalytic activity.

The copper oxide catalyzed reaction was investigated in an isothermal, continuous flow fixed bed reactor system at 4.5bar pressure over the temperature of 453K. A stream of $20\text{ cm}^3\text{min}^{-1}$ hexafluoropropene and $10\text{ cm}^3\text{min}^{-1}$ oxygen was used, introduced into a coiled copper reactor tube of 10 mm internal diameter and a length of 2 m. The exit stream from the reactor was analyzed using gas chromatography. Analysis of the reaction exit stream composition gave hexafluoropropene oxide and carbonyl fluoride as major products. A minor product was trifluoroacetyl fluoride produced at a certain stage during the reaction progress. Cesium dopant (alkali) improved hexafluoropropene oxide selectivity and also provided greater stability, which explained the increased catalyst's lifetime inside the reactor under the reaction conditions. Maximum HFPO selectivity of 52.5% was obtained at the HFP conversion of 13.4% under reaction conditions. This was obtained with a residence time of 113 seconds, which was less than 120 seconds obtained from a non-catalytic process, hence implying that the catalyst significantly increased the reaction rate. It was proposed that epoxidation occurs via the Mars-van-Krevelen mechanism. The mechanism was used as a basis of the kinetic model developed. The least-squares minimization procedure was used to determine the rate parameters for the oxidation reactions. Amongst the reactions occurring on the catalyst surface, CF_3COF decomposition to form COF_2 in the presence of oxygen had the larger rate constant,

and therefore a higher rate. The results of the model show that quite a satisfactory agreement has been reached between the experimental and the theoretical results. The change in catalytic activation towards the formation of the products was observed. This was probably the reflection of the reaction being simultaneously affected by activation and deactivation processes occurring onto the catalyst during the reaction.

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NOMENCLATURE

Symbol	Description	Units
$\text{\AA}$	metric unit of length	10^{-10}m
C_i	concentration of species I	mol.m^{-3}
C_{Tot}^0	total inlet concentration	mol.m^{-3}
C_{WP}	Weisz–Prater parameter	
D_{AB}	Molecular diffusivity	$\text{cm}^2.\text{s}^{-1}$
D_{eA}	effective diffusion coefficient	$\text{cm}^2.\text{s}^{-1}$
D_{KA}	Knudsen diffusivity	$\text{cm}^2.\text{s}^{-1}$
D_{mA}	diffusivity of component A through a gaseous mixture in pores	$\text{cm}^2.\text{s}^{-1}$
D_p	crystallite size	nm
F	molar flow-rate	mol.s^{-1}

k_a	activation rate constant	
k_d	deactivation rate constant	
k_{ox}	rate constant of oxidation	$\text{mol.kg}^{-1}.\text{s}^{-1}$
k_{red}	rate constant of reduction	$\text{mol.kg}^{-1}.\text{s}^{-1}$
P_A	actual pressure on the lines	Pa
R	universal gas constant	$\text{m}^3.\text{Pa}.\text{mol}^{-1}.\text{s}^{-1}$
R_i	net rate of production of component i per unit mass of catalyst	mol/kg/s
S_g	specific surface area of the catalyst	m^2/kg
T_A	actual temperature on the lines	K
W_{cat}	catalyst mass	kg
μ	mu (micrometer or micron)	10^{-6}m
η	effectiveness factor	
ϕ_s	thiele modulus	

Greek Symbols

Symbol	Description
α	alpha
γ	gamma
σ	sigma
λ	lambda

Subscripts/ superscripts

Symbol	Description
$exit$	reactor exit
i	species i
tot	total
ad	adsorbed species

<i>g</i>	gaseous species
<i>latt</i>	lattice oxygen species
<i>o</i>	inlet, reference

List of Abbreviations

BET	Brunauer, Emmet and Teller
COD	Crystallography Open Database
COV	Coefficient of Variation
EDX	Energy Dispersion X-ray spectroscopy
E-L	Eley-Rideal
FBCR	Fixed Bed Catalytic Reactor
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared
GHSV	Gas Hourly Space Velocity
GC	Gas Chromatography
HFP	Hexafluoropropene
HFPO	Hexafluoropropene Oxide
H-W	Hougen-Watson
HGSBCs	Higher Grade Silica Based Catalysts
IEP	Isoelectric point
IWI	Incipient Wet Impregnation
LGSBCs	Lower Grade Silica Based Catalysts
L-H	Langmuir-Hinshelwood
MVK	Mars Van Krevelen
PFCP	Perfluorocyclopropane
PFR	Plug Flow Reactor
PZC	Point of Zero Charge
RDS	Rate Determining Step

SEM	Scanning Electron Microscopy
SSR	Sum of Squares of Residuals
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TFE	Tetrafluoroethylene
WI	Wet Impregnation
Wt%	Weight percent
XRD	X-Ray Diffraction

Chapter One

Introduction

South Africa's rich mineral resources have been highlighted as key in exploiting huge commercialization opportunities, and hence there is a need for the country to up the standard in maximizing the value of these natural deposits. World reserves of 100 percent equivalent fluorspar are estimated at 310 million tonnes, as disclosed in the Mineral Commodity Summaries (Survey, 2020), and South Africa is the world's third-largest country having fluorspar reserves of 41 million tonnes (13.2% of total world reserves). Fluorspar is a naturally occurring mineral that is a principal source of the element fluorine and the precursor to almost all industrial fluorochemicals. Though the survey reveals that the country has high reserves, it has got a low percentage of the global fluorochemicals market. This clearly shows that South Africa is not sufficiently benefiting from fluorspar, its resource. For this reason, Fluorochemical Expansion Initiative (FEI) was established as part of the manufacturing technology strategy. The South African Research Chair Initiative (SARCHI), managed by the National Research Foundation (NRF), supports key areas of competency in South Africa. The research chair in fluorine process engineering and separation technology supports the FEI drive. The main objectives of the government's FEI are the beneficiation of the local fluorspar and the development of domestic fluorochemical technology base. FEI is an initiative endorsed by the Department of Trade and Industry. It is sponsored by the South African Nuclear Energy Corporation (NECSA) who entrusted the South African research chair in Fluorine Process Engineering and Separation Technology at the University of KwaZulu-Natal with the development of a process for the production of 2,2,3-trifluoro-3-(trifluoromethyl)-oxirane (commonly known as hexafluoropropylene oxide, HFPO), a valuable fluorochemical intermediate that can be converted to inert oils, high-performance fluids, elastomers, and membranes.

The traditional methods of HFPO preparation include nucleophilic, electrophilic, and radical synthesis from hexafluoropropene (HFP) using different oxidizers such as hypohalites, hydrogen peroxide, organic peroxides, and molecular oxygen in the liquid phase. Although these methods give a good selectivity and yield towards the HFPO, these reactions require potentially explosive peroxide, high pressure and also generate a large amount of organic waste, which makes the whole process unsafe, uneconomical, and environmentally unfriendly (Huang et al., 2006). To these drawbacks, the gas phase epoxidation of HFP to HFPO will be a viable option, since it bypasses most of the problems associated with the liquid-phase approach.

In line with this aim, a non-catalytic, direct gas-phase epoxidation of HFP with molecular oxygen has been recently developed as an alternative means of producing HFPO with the 56% selectivity and 40% yield (Lokhat, 2012). Since this process is non-catalytic, the yield of HFPO can be further improved using a suitable catalytic system. The development and use of catalysts is the most important part of the ongoing search for new ways of improving product yield and selectivity from a chemical reaction. The solid-catalysed, selective oxidation of HFP remains a predominantly undeveloped route concerning higher valued epoxide product, HFPO. Ample information concerning solid-catalysed oxidation of HFP is encompassed in the patent literature. Moreover, none of the proposed methods in the patents have achieved commercialization. SiO_2 ; CuO – silica-supported; Barium compounds; CuO – SiO_2 – Al_2O_3 supported are catalysts noted from the patents. Crystalline porous silicon dioxide, often carrying a well-dispersed metal oxide, is found to be utilized in most of the proposed patented methods, as the catalyst. The catalysts required some form of pre-treatment, in the basic situation, heating under nitrogen gas. The pure silica catalyst would be at the disadvantage of fast deactivation, a problem that was somewhat moderated by the addition of the transition metal oxide (Castellan et al., 1992). Metals preferred were copper, cerium, cobalt, and chromium.

Up to date, no method has been successful in terms of selectivity towards HFPO and terms of the lifetime of a catalyst. In catalyst development, selectivity is the most important target parameter and it facilitates, among other factors, the maximum yield of a product. The lifetime of a catalyst is of vital importance for process economics. Most catalysts do not sustain their activities at the same levels for unlimited periods. Hence, the investigation of the catalyst is very important. A lifetime of a catalyst inside a reactor is determined by the stability of a catalyst which is one of the factors that determines the suitability of the catalyst alongside

selectivity. Also, from the work done in the available literature, there is no mechanism available that has been proposed for HFP epoxidation. Hence, investigation of the reaction mechanism will form part of this work which will involve the chemistry of a reaction taking place at the surface of a solid catalyst.

The current work aims to develop a catalyst that can improve the selectivity obtained from the available previous work done on gas-phase epoxidation of HFP with molecular oxygen. Huang et al. (2006) achieved 47.8% selectivity towards HFPO in a catalysed reaction while (Lokhat, 2012) managed to achieve 56% selectivity in a non-catalytic process. The development of a practicable and competitive process for HFPO production, satisfactory catalytic reaction model along with an improved selectivity towards HFPO is believed to be going to contribute to the knowledge in the field and account for novel work.

The overall purpose of this study is to understand the mechanism and kinetics of HFP oxidation over copper-based catalysts. To accomplish this aim, the following tasks are performed:

- Preparation of a catalyst
- Optimization of the catalyst characteristics
- Catalyst performance testing in the HFP epoxidation reaction
- Optimization of the reaction conditions for the catalytic reaction for better selectivity and yield towards HFPO
- Kinetic and reactor modelling

Selective oxidation catalysis is crucial in establishing green and sustainable chemical processes. The optimization of the characteristics of a catalyst is an important requirement to improve the selectivity of the targeted product. The development of heterogeneous catalytic systems using molecular oxygen or air as an oxidant, which is cheap and safe, and produces water as the sole by-product, would contribute to establishing green and sustainable chemical processes (Guo et al., 2014).

The use of molecular oxygen as an oxidant for selective catalytic oxidation to achieve a high yield of HFPO (targeted product) is the ultimate aim in the current work. On the special issue which looks at the reflections on catalytic selective oxidation (opportunities and challenges), (Taylor, 2017) highlighted that even though continuous signs of progress in catalyst discovery and development are there, it is still necessary to produce high yields of desired products for

many reactions employing selective catalytic oxidation. Based on this and because the world is moving towards processes that reduce waste, risk, negative environmental impact, as observed in liquid phase methods of HFPO preparation, it is recommendable to develop new catalytic oxidation processes to substitute the current energetically inefficient and/ environmentally unfriendly multi-step reactions.

This thesis consists of six chapters and five appendices.

Chapter one is a general, broad introduction of the current work, including the rationale and motivation for the project. The aims and objectives that served as targets during this investigation are also concisely described.

Chapter two, presents, within the framework of a comprehensive literature review, the current knowledge overview regarding HFP oxidation. The literature survey focuses on the detailed discussion of the previous work conducted on the non-catalytic and catalytic processes for HFPO production. The chapter further presents the review on heterogeneous catalysis by looking at heterogeneous catalytic oxidation in general, heterogeneous epoxidation of the alkenes, and then specifically epoxidation of HFP.

In chapter three, the theory of catalyst synthesis and characterization is discussed. Different methods for heterogeneous catalysts preparation are presented here. Regarding catalysts characterization theory in this chapter, attention is paid only to the characterization techniques utilized in this study.

In chapter four, the experimental apparatus, materials, catalyst synthesis, performance testing procedures, and analytical techniques that were used are described in detail.

Chapter five presents all the results of the research including preliminary experiments results and optimization of operating conditions. Also, the chapter presents the discussion and interpretation of the findings, challenges encountered, reaction mechanism, the identification of kinetic parameters, and reactor modeling.

Finally, chapter six presents conclusions for the present research work and recommendations for possible improvement of the current research. The five appendices contain information on extra graphical results, instrument calibrations, raw experimental data, calculation procedures as well as software programming files.

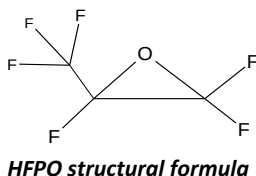
Chapter Two

Literature review

2.1 Hexafluoropropene Oxide

2.1.1 Properties and structure

2,2,3-trifluoro-3-(trifluoromethyl)-oxirane (commonly known as hexafluoropropylene oxide, HFPO) is a colourless non-flammable gas with a molecular formula C_3F_6O .



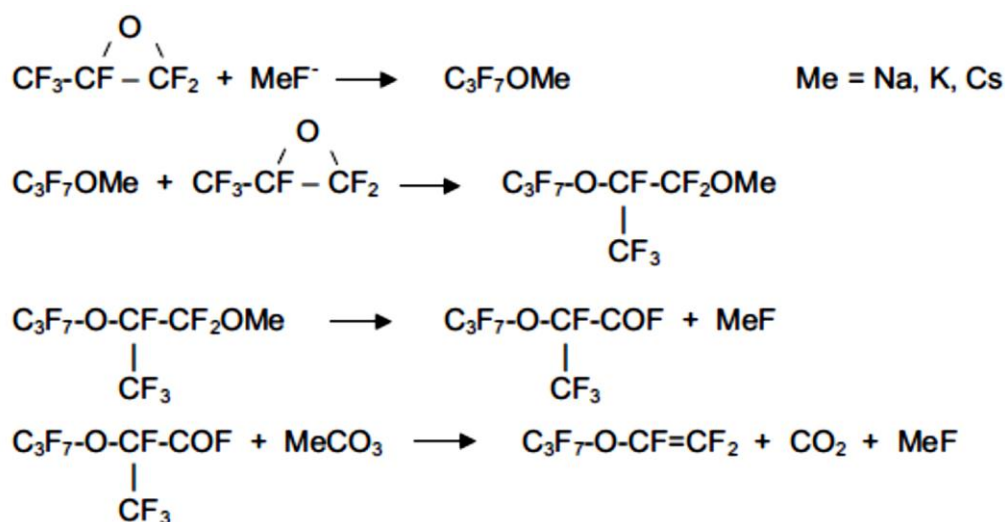
The epoxide has a boiling point of -27°C (at 1 atm) and vapour pressure of 96 psia (at 25°C) (FluoroIntermediates, 2008). At high temperatures, HFPO forms carbonyl fluoride (COF_2) as a dominant pyrolysis product, a gas that is susceptible to hydrolysis, readily yielding hydrofluoric acid and carbon dioxide (HSDB, 1971). HFPO is known to decompose thermally at low temperatures (above $\approx 420\text{K}$) to give the reactive carbene CF_2 and the unreactive trifluoroacetyl fluoride (Ng et al., 2014). Such characteristics as these have been proven valuable in the HFPO utilization as a feed-gas to deposit low dielectric constant fluorocarbon thin films. Regarding interatomic distances and bond angles, unlike the analogous hydrocarbon compound, propylene oxide, the HFPO is reported to have a shorter C-O distance and a lengthened C- CF_3 bond (Beagley et al., 1981, Millauer et al., 1985). HFPO is a relatively non-toxic compound.

2.1.2 Industrial Applications of HFPO

HFPO is a crucial intermediate in the synthesis of the organofluorine compounds. It is used in various commercial fluoropolymers either as a monomer or a monomer precursor and is an important component in the production of high-performance lubricating oils and heat resistant fluids (Ohsaka and Tohzuka, 1981). A valuable monomer that is subjected to oligomerization

in order to prepare the intermediates for the syntheses of highly effective non-ionic, ionic, and amphoteric surface-active agents (Wróblewska et al., 2009). HFPO is employed for preparing polymers which are especially important as inert liquids, lubricant liquids, and hydraulic liquids (Millauer, 1977). HFPO is used as the key intermediate in producing perfluorinated vinyl ethers utilized in the production of commercial fluoropolymers. The ethers are useful in the preparation of elastomers (Atkins, 1973). Additionally, according to Lee et al. (2015), the HFPO polymers are widely used in vacuum pumps, automobiles, memory-hard disks for storing information, high-performance diluents for use in aerospace engineering, due to their lubricative durability. Such applications are a reflection of the properties such as good thermal, and mechanical stability. The application of the HFPO polymers has been also broadened into various areas such as greases, release agents, liquids with a relatively low refractive index and oils. They can be used at extremely high or low pressures.

As an intermediate, by definition, HFPO reacts readily with nucleophiles. In the presence of fluoride salts, it forms the intermediate perfluoropropyl oxide salt, which reacts with the next HFPO to form an acid fluoride after the elimination of a fluoride ion. This compound is the precursor for perfluoro(propyl vinyl ether) (PPVE) (scheme 2.1).

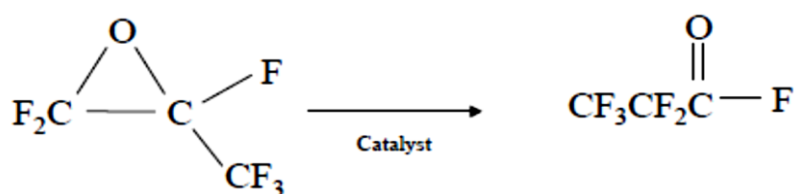


Scheme 2.1 Synthesis of PPVE (Dams and Hintzer, 2016)

During the synthesis of PPVE shown above, the fluorinated epoxide (HFPO) obtained from the epoxidation of HFP undergoes an alkali metal fluoride catalyzed rearrangement and dimerization to afford the acid fluoride. PPVE is then formed by pyrolysis of the acid fluoride over an alkali metal carbonate or phosphate at 75-300°C (Banks et al., 1994, Eleuterio, 1967, Martini, 1978). PPVE can be added as a co-monomer during the preparation of perfluorinated

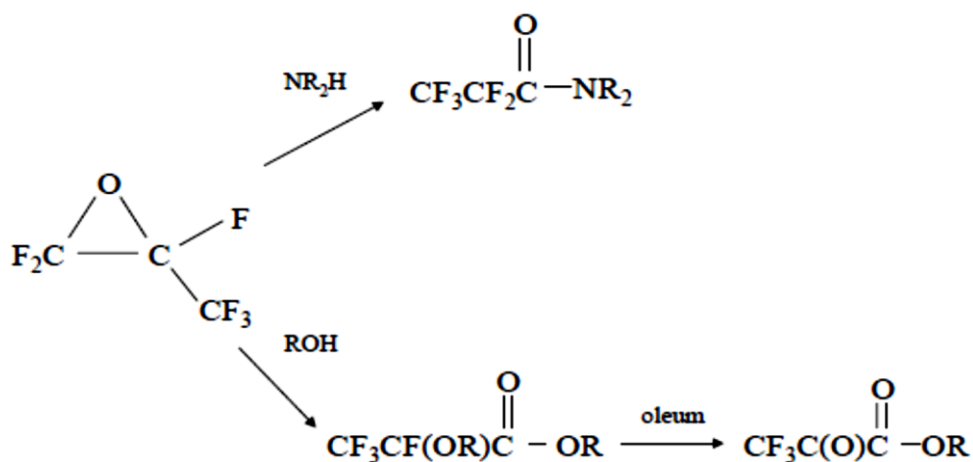
plastics such as Poly(tetrafluoroethylene) (PTFE) and perfluoroalkoxy (PFA). Teflon PTFE and Teflon PFA (Du Pont) are the proprietary names under which the copolymers are manufactured. These perfluorinated plastics generally possess outstanding electrical, chemical resistance, and flame resistance properties, hence they find large applications in wiring insulation, including electrical, coaxial, and computer cables. In addition, since multilevel interconnections in ultra-large-scale integration circuits have recently gained importance, low dielectric interlayer materials are therefore needed. Fluoropolymers such as PTFE are well suited for this application as they have low dielectric constants (≈ 2.0) (Ng et al., 2014).

HFPO is easily isomerized to pentafluoropropionyl fluoride (PPF) by nucleophilic catalysts such as halides or amines (FluoroIntermediates, 2008).



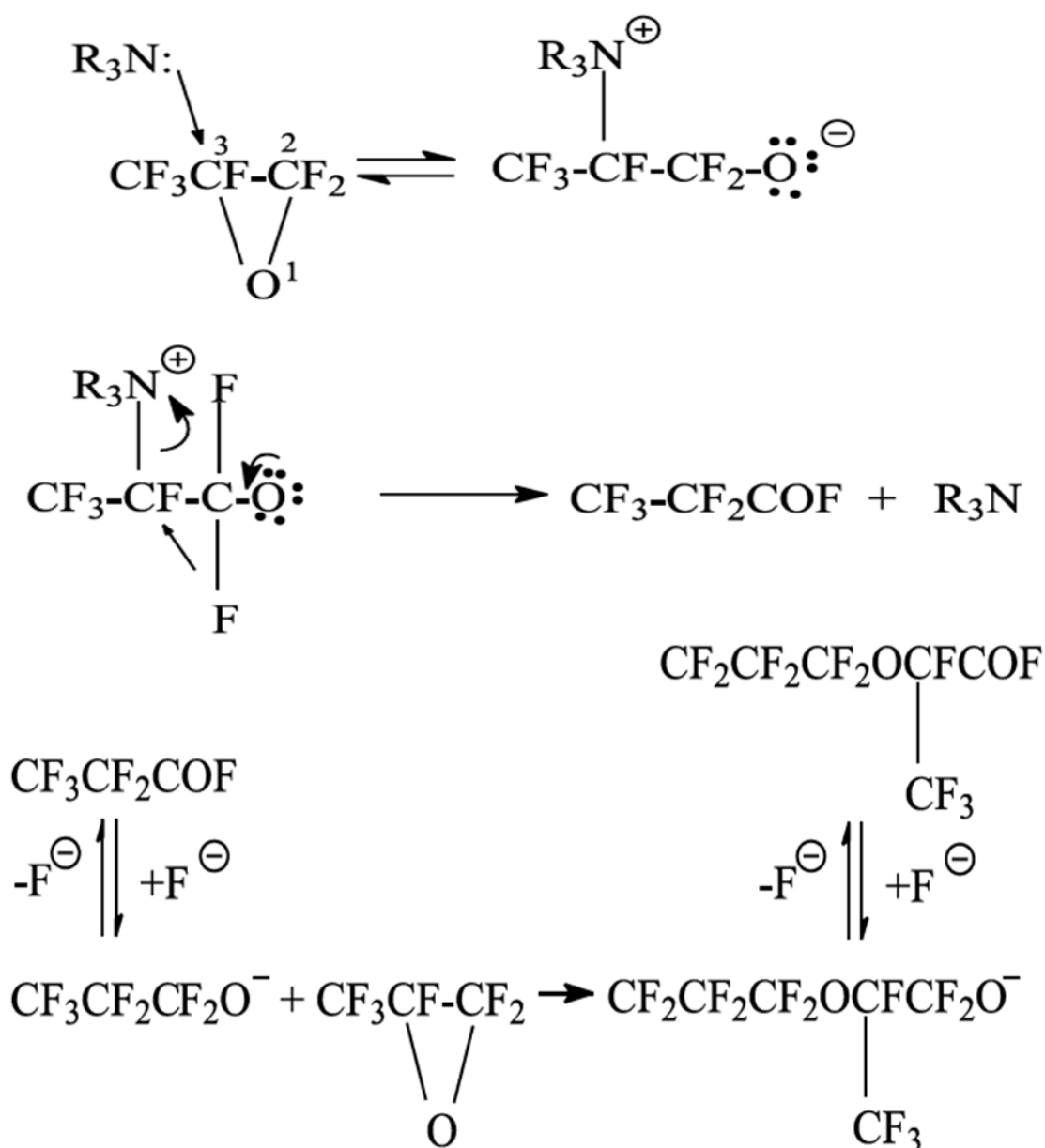
Scheme 2.2 Isomerization of HFPO to PPF (FluoroIntermediates, 2008)

PPF derivatives are formed in the presence of alcohols or secondary amines. Methyl 2,3,3,3-tetrafluoro-2-methoxy propionate, prepared from methanol and HFPO, may be converted to methyl 3,3,3-trifluoropyruvate, a useful building block in organofluorine chemistry (FluoroIntermediates, 2008).



Scheme 2.3 Preparation of PPF derivatives (FluoroIntermediates, 2008)

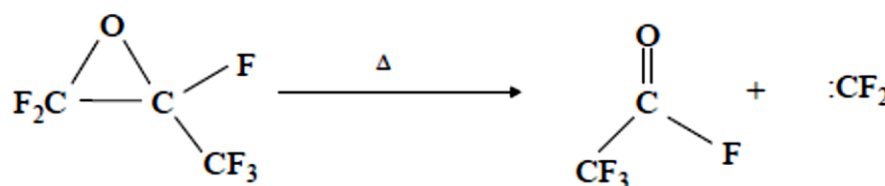
Moreover, the oligomers of HFPO are known for being raw materials for the synthesis of compounds having such unique properties as high chemical and thermal resistance. The products of HFPO oligomerization are oligomers with the structure of a linear polyether terminated with a fluorocarbonyl group (Meissner and Wróblewska, 2007). The first stage of the oligomerization is the isomerization of the HFPO to perfluoropropionic acid fluoride, attacked by nucleophilic reactants such as amine, enamine, and halide ions. The perfluoropropionic acid fluoride, in equilibrium with the ion of the perfluoropropionic oxide, reacts with the HFPO molecule to give the alkoxy compound.



Scheme 2.4 Oligomerization of HFPO (Meissner and Wróblewska, 2007)

The extent of oligomerization depends on the catalyst type and reaction conditions. Higher oligomers of the HFPO demonstrating high thermostability and chemical resistance be as useful as oil.

Thermolysis of HFPO gives difluorocarbene and trifluoroacetyl fluoride. The difluorocarbene may be generated *in situ* to prepare useful intermediates such as CF_2I_2 or cyclopropanes (FluoroIntermediates, 2008).



Scheme 2.5 Thermolysis of HFPO (FluoroIntermediates, 2008)

2.2 Methods of preparing HFPO

2.2.1 Non-catalytic oxidation of HFP

There exist different processes of this type of system:

- a) Liquid-phase non-catalytic oxidation
- b) Gas-phase non-catalytic oxidation

Further classification of the liquid-phase non-catalytic oxidation of HFP may be according to the type of oxidant that is used and also the nature of the reaction conditions. The traditional methods of HFPO preparation include nucleophilic, electrophilic, and radical synthesis from hexafluoropropene (HFP) using different oxidizers such as hypohalites, hydrogen peroxide, organic peroxides, and molecular oxygen in the liquid phase. Moreover, there are traditional "wet" oxidation processes that are commonly used in industry: carried out at or below room temperature, are nucleophilic processes, employing inorganic peroxides or hypohalites as the oxidizing agents (Lokhat, 2012, Furin, 2006, Millauer et al., 1985). Alternatively, the condensed phase radical-based synthesis, at very low temperatures using molecular oxygen may be used to carry out the oxidation, or high pressure and temperature carried out in an inert solvent, also in the presence of molecular oxygen (Lokhat, 2012, Furin, 2006).

The initial reported nucleophilic synthesis of HFPO involved the batch reaction of HFP with 30% hydrogen peroxide in an aqueous potassium hydroxide/methanol solution at 233 K

(Eleuterio, 1967). A 35% HFPO yield was produced from the reaction. HFPO higher yield was obtained using an aqueous hydrogen peroxide solution in the presence of acetonitrile (Millauer et al., 1985). In only a few instances of the epoxidation of hexafluoropropene under electrophilic conditions that have been observed so far, a 30% yield of HFPO was obtained on the reaction of hexafluoropropene with potassium permanganate in anhydrous hydrogen fluoride (Millauer et al., 1985). In a similar reaction, when chromium trioxide is used in fluorosulfuric acid, the yield obtained was about 55%. Furthermore, methods for the production of HFPO with molecular oxygen have been thoroughly investigated. Based on the reaction conditions, the different methods are carried out in the liquid phase or the gas phase. According to Millauer et al. (1985), the HFP oxidation using O_2 requires some form of activation, either via the use of high energy radiation, thermal initiation, or the addition of species (chemical initiators) that generate radicals. The syntheses in the liquid phase are usually carried out under pressure in an autoclave with oxygen being added to the HFP. The photo-initiated reaction of HFP with oxygen in the gas phase was investigated by (Heicklen and Johnston, 1967). Substantial quantities of COF_2 and CF_3COF were detected in addition to HFPO as reaction products at room temperature and with the use of UV light.

In the investigation conducted by Arce et al. (2005) for gas-phase HFP epoxidation, the thermal gas-phase reaction between NO_2 and HFP was carried out using a 270 cm³ quartz bulb reactor at temperatures of 413.1, 421.0, and 432.8 K. Four compounds were reported to have been observed from this work: NO, HFPO, $CF_3CFNO_2CF_2NO$, and $CF_3COCF_2NO_2$. From a set of 15 experiments that were conducted, an HFPO yield of 63-89% was obtained (Lokhat, 2012, Arce et al., 2005).

A direct gas-phase non-catalytic epoxidation of HFP using O_2 has been recently developed. The maximum combined HFPO selectivity and yield obtained in this work using multi-response optimization techniques were 56% and 40%, respectively (Lokhat, 2012). The non-catalytic high-temperature oxidation of HFP by gaseous oxygen was carried out isothermally in a long tubular reactor (114.3m length, 1=8-inch nominal diameter). In this process, 4.5 bar moderate operating pressures were used and were found as the minimum pressures at which the satisfactory level of HFP conversion was achieved. For this non-catalytic process, a maximum HFPO selectivity of 55.81% was determined at 478.2 K, HFP/ O_2 molar feed ratio of 1.34 mol mol⁻¹, and space-time of 113 seconds. In addition, an HFPO yield of 40.10% was identified at 483.2 K, HFP/ O_2 molar feed ratio of 1.16 mol mol⁻¹ and space-time of 121 seconds as an optimum yield. By comparing, the HFP epoxidation using hydrogen peroxide, the most

popular commercial method of producing HFPO, the method gives about 55% yield of the epoxide product ((Millauer et al., 1985).

2.2.2 Catalytic oxidation of HFP

2.2.2.1 Heterogeneous catalysis

2.2.2.1.1 Heterogeneous catalytic oxidation

Catalytic oxidation reactions are recognized as of principal importance at an industrial level. Currently, more than 60% of chemical synthesis and 90% of chemical transformations in chemical industries are using catalysts (Ali et al., 2014, Fechete et al., 2012, Shiju and Guliants, 2009). Catalytic oxidation is regarded today as the keystone for the synthesis of a high proportion of the monomers or modifiers used for the production of fibers and plastics. Under the oxidation concept, homolytic and heterolytic are usually defined as two groups of reactions. Homolytic entails radicals formed by homolytic cleavage of interatomic bonds. Heterolytic, on the other hand, involves an active oxygen compound or a metal ion that oxidizes the starting material in a two electrons transfer reaction (Sheldon and Van Santen, 1995 :p 53). This further explains that for most situations, catalytic properties in oxidation reactions entail a redox mechanism between surface-active sites and the reactant molecules (This will be further discussed in the present work when looking at the mechanisms likely to be followed by heterogeneous catalytic oxidation reactions).

According to Centi et al. (2001), regarding the major industrial applications of catalytic oxidation for the synthesis of monomers, there exist some important limitations associated with this. This includes the following:

- 1) Because of the formation of undesired by-products, none of the reactions runs at maximum selectivity, and few reactions attain a total or close-to-total conversion.
- 2) Some processes require expensive oxidizing agents.

Moreover, the polymer industry continues to demand monomers that are not only less expensive but also increasingly pure (Centi et al., 2001). For catalytic oxidation processes, technological innovations are thus expected from:

1. Substantial modifications introduction in technology: New raw materials and catalysts are being used; new process technologies, new equipment, and new machinery are being developed.
2. Fine-tuning existing processes: Work continues optimizing all the process components.

3. Complying with new requirements and regulations: Processes that have a less severe environmental impact are being developed: this translates into lower pollutant emissions, less waste, and appreciable safety. Also, there is an increasing demand for purer products for high-quality polymers production.

Catalytic oxidation processes have several features in common:

- They are highly exothermic
- An important element of reactor design is to prevent catalyst deactivation by excessive temperature or runaway reaction (Satterfield, 1991).

With the catalytic oxidation reactions, it is sometimes possible to obtain relatively good selectivity to the desired product at low percent conversions.

In synthesizing high-value-added products in the chemical industry, the selective catalytic oxidation of organic molecules continues as a prominent reaction route in the synthesis of primary chemicals. Heterogeneous catalysts alongside homogeneous catalysts are utilized in these reactions. Oxidations involving oxygen eventually generate non-salt by-products, and for this reason, the selective oxidation of organic compounds using O_2 will continue to be an area of considerable potential for the chemical process industry.

The ease of separation of product from a catalyst, recovery of the high-valued heat from the reaction for energy export, and ease of conducting the reaction continuously, are important characteristics of the heterogeneous type of catalytic oxidation reactions. Having pointed out these important characteristics, it is also necessary to point out the fact that, any viable commercial catalytic system must be highly selective, highly active, and stable in the reaction media irrespective of the phase in which the catalyst is functioning (Foote et al., 1995). The electron-rich surface lattice o^{2-} has been reported to play a prominent role in heterogeneous catalytic oxygenations. Transition metals function as catalysts because of their ability to change oxidation states. The oxidation state of a metal refers to its ability to form chemical bonds. The transition metals easily lend and take electrons from other molecules, and they also tend to be more reactive as a result of their unfilled d-bands. Transition metal oxides are reported to generate surfaces with o^{2-} sites that can span a range of energy states. Above all, the extent of electron transfer to the oxygen in these compounds, and thus its reactivity, is dependent on the

nature of the metal, its oxidation state, ligand environment, and π -bonding abilities as determined by the occupancy of d orbitals (Foote et al., 1995).

Gas-surface interaction involves several steps. According to Deutschmann et al. (2009), for heterogeneous catalytic reactions, to generally describe the mechanism, the sequence of elementary reaction steps of the catalytic cycle which involves diffusion, adsorption, chemical transformations of adsorbed species, and desorption, can be used. The mechanism then becomes the basis for deriving the kinetics of the reaction. Also, the chemisorption of the reactants and products on the catalyst surface is of central importance (Thomas and Thomas, 1996). Therefore, among the steps that are involved in the catalytic cycle, the adsorption of the reactants, chemical reaction on the surface of a catalyst, and desorption of the products from the catalyst surface must be included in the micro kinetics of a reaction. Furthermore, since new bonds are generated during chemisorption, this is the implication that it has the chemical reaction characteristics in a sense that the starting material molecules react with the surface atom at the catalyst. Generally, chemisorption requires high activation energy. Also, the adsorption rate is temperature and pressure-dependent. Rapid adsorption rate is acquired at high temperatures, and it increases with an increase in pressure at constant temperatures. Moreover, heterogeneously catalyzed gas-phase reactions can follow several mechanisms which include:

- 1) Langmuir-Hinshelwood (L-H) mechanism. The assumption for this mechanism is that both gaseous reactants are adsorbed at free sites on the catalyst. The actual surface reaction between neighbouring chemisorbed molecules to give the product which is adsorbed on the surface then follows. In the final step, the product is desorbed. Adsorption can either be dissociative or associative (non-dissociative). On the dissociative adsorption, the adsorbate molecule splits when bonded to the surface.
- 2) Eley-Rideal (E-R) mechanism. Here the assumption is that only one of the gaseous reactants is chemisorbed and then it reacts in its activated state with the other reactant from the gas phase to give the chemisorbed product.

One other mechanism is the Mars-Van-Krevelen (MVK) redox mechanism. In this mechanism, the surface itself takes an active part in the reaction. The oxygen introduced into a reactant molecule come from the lattice structure of a catalyst. The characteristic feature of this mechanism is that some products of the reaction leave the solid catalyst with some constituents of the catalyst lattice.

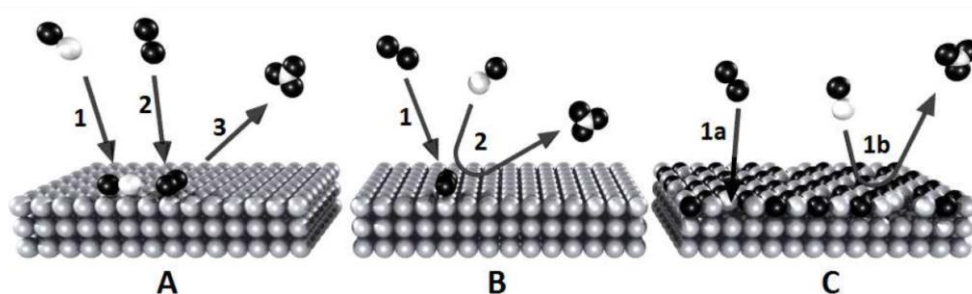


Figure 2.1: (A) Langmuir-Hinshelwood mechanism. (B) Eley-Rideal mechanism. (C) Mars-Van-Krevelen mechanism.

(Herbschleb and Reactor, 2011)

M-V-K redox mechanism reaction rate equation is reported to have the same mathematical form as Eley-Rideal kinetics (Herbschleb and Reactor, 2011). From Figure 2.1, when the reaction product desorbs, a vacancy is left behind on the surface. This vacancy will be filled again by the first reactant (reactant 1a). As for the oxidation reaction with molecular oxygen, which the current work focuses on, the reactant molecule is oxidized by reacting with the oxide. Hence, the oxide is reduced. To restore its initial state, the reduced oxide then reacts with molecular oxygen. For this particular mechanism, the ability of a metal oxide to be reduced appear to play a crucial role. Easily reducible oxides must be quite active. The activity increases but probably with the formation of undesired compounds, and if re-oxidation is not appropriate, the catalyst is quickly deactivated. The catalytic behaviour generally depends on the mobility of ions and electrons.

Metal oxides and noble metals are both used as catalysts for oxidation reactions, both in the supported and unsupported form. Metal oxides are said to be more resistant to poisoning (i.e. catalyst deactivation) even though they are less reactive than noble metals.

According to Oyama et al. (1993), the knowledge about the mechanisms operative in selective oxidation reactions is lacking. The epoxidation reactions of ethylene to ethylene oxide on supported silver catalysts and of propylene to acrolein on bismuth molybdate-type catalysts are the only exceptions. This is one of the research challenges in selective oxidation. The analogy

from these reactions can be drawn to be effectively used in understanding the behaviour of similar compounds, however, concerning perfluoroalkenes, it is more of a challenge since the presence of carbon-fluorine bonds in place of carbon-hydrogen bonds completely change the chemistry of the compound. The investigation of a perfluoropropene oxidation mechanism hence forms part of the current study.

Moreover, over the years of research in heterogeneous catalytic oxidation, the MVK redox mechanism has been seen as a predominant pathway in selective oxidation reactions employing metal oxides (Foote et al., 1995: p 232). The observation that selective oxidation of propene occurs in the presence or absence of molecular oxygen implicated the oxide of the catalyst structure as the reactive oxygen. Mechanistic studies, mostly done with hydrocarbons, have shown that most processes follow the MVK redox mechanism. On the other hand, catalytic CO oxidation on Pt(III) investigation led to the conclusion that the Langmuir–Hinshelwood mechanism is preferred for the vast majority of surface catalytic reactions (Baxter and Hu, 2002). One of the reasons why CO reaction oxidation was used in this investigation is because it is widely used as an exemplary system in understanding heterogeneous catalysis. Besides, the reaction is theoretically regarded as one of the simplest catalytic reactions. The conclusions reported in these investigations were somehow surprising, considering the common view that reactions follow mechanisms with lower reaction barriers. According to Baxter and Hu (2002), despite the higher reaction barrier L-H mechanism has over the E-R mechanism, the latter path involves a specific channel where factors such as the tilting of CO and the activation of O_a (the average bond length of Pt–O_a is 2.20 Å at the transition state compared to 2.02 Å in the initial state) come into play. Such views are important in the present investigation considering the adsorption of an alkene which can be achieved in different ways. Kolasinski (2012: p 128) explains using ethylene that alkenes can bind onto the metal surface either by π -bonding between C=C double bond and the surface or by di σ -bonding from the two carbon atoms to different metal atoms in the surface. These are important to consider since they result in different energy barriers due to the nature of bonds, thereby contributing factors in determining mechanism followed by the reaction.

Furthermore, activity and selectivity remain the reaction parameters that will depend on the overall efficiency of the redox cycle. When the hydrocarbon oxidation rate becomes faster than the reduction of dioxygen, the catalyst surface becomes more reduced, and it has often been observed that such a surface state leads to lower reaction selectivity. One role of promoter elements (which will be further explained in this section) incorporated in metal oxide systems

is to maintain the surface in its optimum oxidation state (Foote et al., 1995: p 233). When looking at the influence of the medium on the catalyst, Boreskov and Matros (1983: p 553) mentioned that a solid catalyst itself undergoes some transformations as a result of its interaction with reagents. There can be a change in structure, properties, and chemical composition depending on the reaction mixture composition and temperature.

The catalysts' performance is often improved by additives. A modifier is called a promoter when it increases the catalyst activity in terms of reaction rate per site (Deutschmann et al., 2009). Alkali metals are mostly used as promoters. The effects of doping the catalyst with alkali metals usually increase the selectivity, increase activity, and prolong the effective lifetime of the catalyst (stability). Mross (1983a: p 604) cautioned in the work done on alkali doping in heterogeneous catalysis that it is necessary to note that alkali excessive quantities can also be counterproductive and have a negative effect. For nickel supported on alumina, higher concentrations of alkali were found to promote the recrystallization of the support, and by that, reduce the effective lifetime of the catalyst as a result of the decrease in the active surface area. Neutralization of acidic centers is amongst the roles that the alkali dopants are playing. In ethylene oxide, the function of the alkali metal is, to neutralize acidic centers which would otherwise catalyse the isomerization of ethylene oxide to acetaldehyde (Mross, 1983a: p 608). Besides, alkali metal adsorption onto the metal surface facilitates an electron donor effect by the neighbouring metal atoms.

2.2.2.1.2 *Heterogeneous epoxidation of alkenes*

The epoxidation of olefins plays an important role in the industrial production of several commodity compounds, as well as in the synthesis of many intermediates, fine chemicals, and pharmaceuticals (Oyama, 2008). An important aspect of epoxidation is the oxygen source, and molecular oxygen has been reported to be the most desirable terminal source due to some advantages amongst other possible oxidants which include availability and economic reasons. The review on the point that, epoxide intermediates were produced by direct oxygen transfer to olefins by a variety of stoichiometric methods until recently where considerable efforts have been made to conduct the transformations selectively under catalytic conditions by Oyama (2008: p 10), provides an insight about the developments regarding the methods used in catalytically converting alkenes into epoxides.

The literature, mainly patent literature that is available for the gaseous phase catalytic epoxidation of HFP, reveals copper (Cu) and silver (Ag) as the most successful catalysts for

this reaction. In explaining the uniqueness of metal for a particular selective reaction, van Santen (2017: p 334-337) reveals challenges the selective oxidation of a hydrocarbon by transition metals must overcome:

In the case of the epoxidation reaction, no C-H or C-C bonds should be cleaved. This requires the use of a transition metal catalyst that has low reactivity to these activation processes. Since the group VIII transition metals (groups 8-10) readily activate C-H and C-C bonds, it is no surprise that Cu, Ag, or Au are relevant candidates. Au is excluded because the O₂ required for the epoxidation reaction has to dissociate, which is not thermodynamically feasible for metallic Au. The only other alternative metal catalyst is Cu.

Similarly, concerning the oxidation of perfluoroalkene which is a task performed on the current work, the C-F, and C-C bonds should not be cleaved too. Based on the exclusion of the other transition metals due to their reactivity with the bonds that need not take part in the reaction and from the literature information regarding HFP epoxidation, Cu and Ag remain the metals that can carry out the HFP epoxidation. This isolates these elements from the rest of the transition metals.

On the study of the reactivity of transition metal surfaces for hydrocarbons oxidation reactions by Sheldon and Van Santen (1995: p 86), Cu was found to have higher reactivity than Ag. Furthermore, the study reported that oxygen adsorbed on Cu is nucleophilic while Ag adsorbed oxygen could be electrophilic. Generally, O₂ in its ground state contains two unpaired electrons, which are localized on the degenerate antibonding pi-2p orbitals, making a triplet ground state. Due to the rule of spin conservation, as mentioned by Sheldon and Van Santen (1995: p 17), reactions of such triplet oxygen and singlet organic molecules experience high activation energies. To overcome this symmetry barrier, either activating oxygen to the singlet state or activating the organic molecule making it susceptible to the reaction with molecular or atomic ions may help the situation. In addition to this, the nucleophilic attack by the oxide ion O²⁻ is reported to be of particular importance. Regarding perfluoroalkenes, the combined effect of fluorine to both increase the electrophilicity of double bond and stabilize carbanions ensures that perfluoroalkenes will be much more susceptible to nucleophilic attack than hydrocarbons. Unlike in hydrocarbons, the double bond in perfluoroalkenes is electron deficient due to high electronegative fluorine atoms attached to the double-bonded carbons. In the investigation of the origins of selectivity in ethylene epoxidation on promoted and unpromoted Ag/ α -Al₂O₃

catalysts, (Waugh and Hague, 2008) concluded that silver's uniqueness dwells in its bond strength to adsorbed O atoms, its aptitude for lowering the energy barrier for breaking the O=O bond. It was shown that the weaker the Ag-O bond is, the more selective it becomes. In an industrial Ag/ α -Al₂O₃ catalyst containing Cesium (Cs), the Cs is held in submonolayer quantities on steps on the Ag surface where it prevents the formation of a strong, unselective Ag-O bond.

2.2.2.2 Epoxidation of HFP

2.2.2.2.1 Liquid and gaseous phase approaches on HFP catalytic epoxidation

Ikeda et al. (1990) proposed that the hypohalite method may be refined using a two-liquid-phase process. The two-phase batch system is comprised of an aqueous hypohalite solution and a reaction phase containing HFP and an organic liquid. The presence of a phase transfer catalyst ensured the reaction proceeded. Quaternary ammonium salts, phosphonium, and arsonium salts, as well as lipophilic complexing agents in the presence of an inorganic base, were all found to be suitable catalysts (Millauer et al., 1985). Lawson (1991) further modified the two-liquid-phase method of (Ikeda et al., 1990) aiming to maximize the selectivity towards HFPO. The batch process used the aqueous phase containing hypohalite ions of pH 7.5-9.6 and a reaction phase consisting of an organic liquid in which a phase transfer catalyst was soluble and in which there was a higher affinity for the HFP rather than HFPO, its epoxide. The most appropriate solvent selected for the reaction was toluene. The best selectivity towards HFPO achieved was 86% at a conversion of 43% for the reaction carried out at 273.95 K. Lawson (1991) again presented a three-liquid-phase batch process which involved agitation to maintain an aqueous phase containing hypohalite ions, an epoxide phase comprising the bulk of the epoxide with almost no phase transfer catalysts and a reaction phase comprising an organic liquid in which a phase transfer catalyst was dissolved and which has a higher affinity for the HFP than for the HFPO. The maximum selectivity towards HFPO obtained was 80.5% at a conversion of 55%. Lee et al. (2001) showed that the inclusion of ferric chloride to two-liquid-phase mixtures of sodium hypochlorite or hydrogen peroxide, HFP, tetrabutyl ammonium chloride, and F113 enhanced the HFPO yield. An epoxide yield of 66.3% was obtained at a 273.15 K reaction temperature.

Most recently, Huang et al. (2006) published work on the gas-phase epoxidation of HFP with molecular oxygen where silver (Ag) catalyst was used in a fixed bed reactor. A catalyst was supported on γ -Al₂O₃. This catalytic process managed 41.1% selectivity of HFPO. With the

addition of a modifier (Cesium, an alkali metal), a significant improvement in the selectivity was observed. 47.8% was obtained. The addition of Cs improved both activity and selectivity.

2.2.2.2.2 Patented processes for catalytic gas-phase epoxidation of HFP

The selective oxidation of HFP using solid catalysts remains a predominantly undeveloped route concerning higher valued epoxide product, HFPO. Ample information concerning solid-catalyzed oxidation of HFP is encompassed in the patent literature. From the proposed methods patented, none have achieved commercialization.

Cavanaugh (1973) found a process for the epoxidation of HFP which comprises activating silica by contacting it with a mixture of oxygen and HFP, HFPO at higher temperatures (175 to 400°C) and contacting the activated composition with HFP/O₂ mixture at reaction temperatures (140 to 280°C). Good yields and conversions of HFPO were obtained between 10-80 hours, thereafter hexafluoroacetone was produced.

Table 2.1. Experiments results of HFP epoxidation using silica-based catalysts (Cavanaugh, 1973).

Patent	Catalyst	Temperature (K)	HFP Flowrate (mL/min)	O ₂ Flowrate (mL/min)	GHSV (h ⁻¹)	HFPO Yield (%)	Selectivity towards other product	Reactor type
<i>Cavanaugh, 1973</i>	Silica gel (Davison grade 02)	475	20	10	35	79	COF ₂ 21%	<i>Stainless steel tube in the form of a coil</i>
	Silica gel (Davison grade 45)	518	20	10	35	45	COF ₂ 55%	
	Pyrex glass	448	20	10	19	37	CO ₂ 25%	
	Silica sand	473	20	10	19	42	CF ₃ COF 42%	

Atkins (1973) aimed to improve work done by Cavanaugh (1973) by contacting the silica gel with hydrochloric acid (HCl), and thereafter water washing the silica gel before contacting it with a mixture of oxygen and HFP, HFPO at high temperatures. HCl treatment was aimed to improve conversions.

Table 2.2. Experiments results of HFP epoxidation using pre-treated silica-based catalysts (Atkins, 1973).

Patent	Catalyst	Temperature (K)	HFP Flowrate (mL/min)	O ₂ Flowrate (mL/min)	GHSV (h ⁻¹)	HFPO Yield (%)	Selectivity towards other product	Reactor type
<i>Atkins, 1973</i>	Silica gel (Davison grade 45)	473	20	10	35	80	CO ₂ 20%	<i>Stainless steel tube in a form of a coil</i>
	Silica gel (Davison grade 05)	483	20	10	35	84	CO ₂ 16%	

In the patent of Oda (1977) cited by (Lokhat, 2012), HFPO was produced from HFP and O₂ reaction over a silica-supported copper oxide (CuO) catalyst. Later in this work, used was CuO supported on SiO₂-Al₂O₃ to produce HFPO which showed the improvements in both the conversion of HFP and the selectivity towards HFPO.

Table 2.3. Experiment results of HFP epoxidation using a silica-supported CuO catalyst (Oda, 1977).

Patent	Catalyst	Temperature K	HFP Flowrate mL/min	O ₂ Flowrate mL/min	HFPO selectivity %	Selectivity towards other product	Reactor type
<i>Oda et al., 1977a</i>	silica-supported CuO	573	30	10	30	COF ₂ 60%	<i>Fixed-bed reactor</i>
<i>Oda et al., 1977b</i>	CuO supported on SiO ₂ - Al ₂ O ₃	573	30	10	45,7	COF ₂ 47,3%	<i>Fixed-bed reactor</i>

Ohsaka and Tohzuka (1981) used barium compounds as a catalyst for the reaction of HFP with O₂ for the preparation of HFPO. Before the catalyst is used, it is heated under the stream of inert gas at a temperature greater than a reaction temperature.

Table 2.4. Experiment results of HFP epoxidation using barium-based catalysts (Ohsaka and Tohzuka, 1981).

Patent	Catalyst	Temperature K	HFP Flowrate mL/min	O ₂ Flowrate mL/min	HFPO selectivity %	Selectivity towards other product	Reactor type
Ohsaka & Tohzuka, 1981	N ₂ pre-treated (773K) BaO	523			67,4	-	<i>No specific information for a reactor</i>
	N ₂ pre-treated (673K) BaSO ₄	523			60,3	-	
	N ₂ pre-treated (673K) BaCO ₃	473			64,3	-	
	N ₂ pre-treated (673K) BaO + BaF ₂	473			70,7	-	

Castellan et al. (1992) described the oxidation reaction which is conducted continuously conveying HFP (a fluorinated alkene) and oxygen over a fixed catalytic bed. A catalyst used was a copper oxide (transition metal oxide) supported on porous silicon dioxide (SiO₂). Prior to the oxidation reaction, the catalyst was subjected to an activation step with hydrofluoric acid.

Table 2.5. Experiment results of HFP epoxidation using silica-supported metal oxide catalysts (Castellan, 1992).

Patent	Catalyst	Temperature (K)	HFP Flowrate (mL/min)	O ₂ Flowrate (mL/min)	GHSV (h ⁻¹)	HFPO selectivity (%)	Reactor type
<i>Castellan et al., 1992</i>	CuO/SiO ₂ (activated in N ₂ stream/ 0,1% hydrofluoric acid)	433	1,5	1,2	8	75,6	<i>cylindrical 50cc reactor made of Incoloy</i>
	CuO/SiO ₂ (activated in N ₂ stream/ 0,5% hydrofluoric acid)	418	3	2,3		82,6	
	CuO/SiO ₂ (activated in N ₂ stream/ 0,1% hydrofluoric acid)	473	1,5	1,2	41	75,9	<i>10cc micro reactor made of Incoloy</i>
	CuO/SiO ₂ (activated in N ₂ stream/ 0,5% hydrofluoric acid)	473	1,5	1,2	41	69	<i>10cc micro reactor made of Incoloy</i>
	CoO/SiO ₂ (activated in N ₂ stream/ 0,1% hydrofluoric acid)	503	1,5	1,2	21	74,7	<i>20cc micro reactor made of Incoloy</i>
	CeO/SiO ₂ (activated in N ₂ stream/ 0,1% hydrofluoric acid)	503	1,5	1,2	41	61,2	<i>10cc micro reactor</i>

*Gas composition (outflowing gases) includes: O₂; CO₂+COF₂; C₃F₆O;
C₃F₆; C₃F₄;*

Overall, the compound-oxygen mixture, in this case, HFP/O₂, can usually react through several different pathways in the network of consecutive and competing parallel reactions, and therefore the catalyst must strictly control the relative rates promoting the steps leading to the desired product and hindering steps leading to the unwanted by-products. Once a catalytic system is established, there is a need to optimize influential factors that determine the catalytic performance. Usually, the critical reaction parameters involve the content of active metal, the ratio of active metal to the promoter, substrates concentration, flow rate of oxygen, temperature, and pressure. By selecting an appropriate catalyst and reaction conditions, it is possible to direct the reaction along one selected pathway and obtain the desired product.

Chapter Three

Catalyst Synthesis and Characterization

3.1 Introduction to catalyst synthesis

Although some catalytic materials comprise single substances, most catalysts have different types of components which are easily identifiable. The components of a typical heterogeneous catalyst are:

- *Active component* – this is the component that is primarily responsible for the catalytic activity. It is usually a metal that provides active sites where the chemical reaction takes place.
- *Support or Carrier* – a high surface area oxide that disperses and stabilizes the active component. Amongst the functions it exercises, the main one is to maximize the surface area of the active component by providing a large area over which it is spread.
- *Promoter(s)* – additive which improves catalyst properties. Promoters are not by themselves catalytically active but they allow the active component to function to its maximum capacity.

The aim of the preparation of catalytic materials that can be used on an industrial scale is to prepare a product with high activity, selectivity, and stability (Pinna, 1998). To this purpose, the active phase (in this case the metal/metal oxide) must be in a sufficiently high dispersed form to give a large specific surface area and consequently a maximum specific activity. Pinna (1998) went further to explain that in order to achieve this objective, the active metal component is normally deposited on the surface of a support, a highly porous and thermostable material (with a high surface area and suitable mechanical strength) which is able to disperse the metal and also increase its thermal stability, hence the catalyst life.

According to Perego and Villa (1997), the selection of support is based on it having certain desirable characteristics. Principally they are:

- **Inertness.** Ideally, support materials should be catalytically inactive.

- Desirable mechanical properties, including compressive strength, hardness, and attrition resistance.
- Reaction and regeneration conditions stability.
- A high surface area is most desirable.
- Porosity, including average pore size and pore size distribution. High area implies fine pores, however, relatively small pores could become plugged during impregnation, especially if high loading is sought.
- Low cost.

Alumina, Silica, and activated carbon, among a variety of possible materials, are three supports believed to possess a good combination of the required characteristics. The active component in catalysts can either be in the metallic (e.g. iron, copper, platinum, etc.) or metal oxide form or other forms (e.g. sulfides, carbides, etc.).

The production of heterogeneous catalysts consists of numerous physical and chemical steps. The conditions in each step are influential in the catalytic properties of a catalyst. Industrial catalysts can be broadly grouped into three categories:

- 1) ***Bulk catalysts and supports*** – for the entire catalyst consisting of the catalytically active substance, the solid catalyst is called a bulk catalyst. These are also known as precipitated catalysts due to the preferred method for their production, precipitation. Similar procedures are used in preparing the supports (e.g. aluminas, silicas, silica-aluminas).
- 2) ***Impregnated catalysts (supported catalysts)*** - in supported catalysts, the catalytically active materials are dispersed over the high surface area support material.
- 3) ***Mixed-agglomerated catalysts*** - these catalysts are agglomerated mixture of active substance and support. These types of catalysts are used less frequently.

Preparation methods are dependent on the choice of the base materials and the choice of a laboratory method for preparing a given catalyst depends on the final composition desired in physical and chemical characteristics. Despite the range of options for preparing catalysts, it must be considered that most of those can be reduced to a series of elementary steps or unit operations. Bulk catalysts and supports preparation is mainly done by precipitation and Sol-gel processes and for supported catalysts, active materials can be deposited on the supports via

numerous methods. Most of the methods involve aqueous solutions and the liquid-solid interface.

3.1.1 Preparation methods for heterogeneous catalysts

3.1.1.1 Precipitation method

In this process, the desired component is precipitated from the liquid solution. Co-precipitation is used for simultaneous precipitation of more than one component. Source materials are mainly metal salts, such as sulfates, chlorides, and nitrates (Deutschmann et al., 2009: p 44)., Carbonates, hydroxides, and hydroxocarbonates of potassium, sodium, or ammonium are basic precipitation agents on an industrial scale. Thermally decomposable anions, such as carboxylates and carbonates and cations like NH_4^+ are especially favored in catalyst production. Precipitation and co-precipitation can be carried out in continuous or batch operations.

Precipitation occurs in three steps: supersaturation, nucleation, and growth (Perego and Villa, 1997). The supersaturation region can be possibly reached either by increasing the concentration through solvent evaporation, increasing the pH, or lowering the temperature. The development of particles within the supersaturation region occurs in a two-stage process: nucleation and growth. Nucleation may proceed spontaneously (homogeneous nucleation) or be initiated with seed materials (heterogeneous nucleation). The nucleation rate can be accelerated by the purposeful inclusion of seed nuclei. The growth process depends on temperature, concentration, pH, and ripening. Most precipitates are crystalline precipitates.

The industrial production of precipitated catalysts usually involves the following steps (Deutschmann et al., 2009: p 45):

- Preparation of metal salt solution and the precipitating agent (dissolution, filtration)
- Precipitation
- Aging of the precipitate
- Washing of the precipitate by decantation
- Filtration
- Washing of the filter cake (spray drying)
- Drying
- Calcining
- Shaping

- Activation

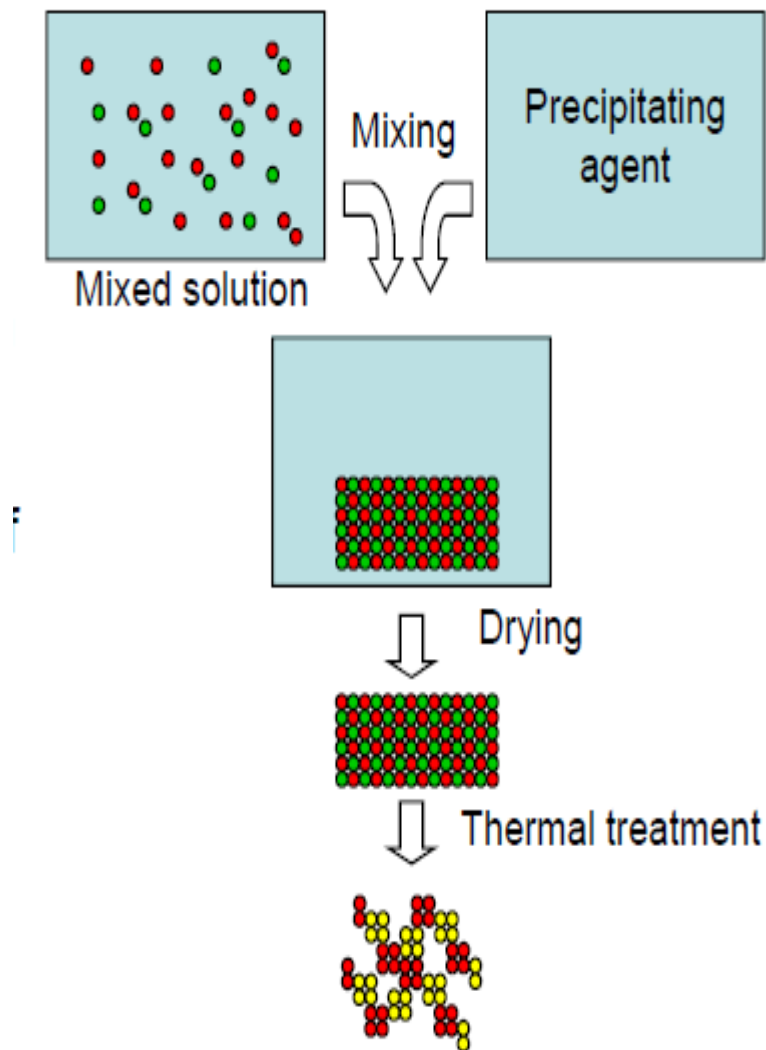


Figure 3.1 General scheme of preparation by precipitation method

3.1.1.2 Sol-gel method

The sol-gel method involves the formation of a sol, followed by the creation of a gel. A sol (liquid suspension of solid particles smaller than 1 μm) is obtained by the hydrolysis and partial condensation of an inorganic salt or a metal alkoxide (Deutschmann et al., 2009: p 45). The formation of gel results from sol particles being further condensed into a three-dimensional network. The encapsulated liquid can be eliminated from a gel by drying (the removal of the solvent, usually water, from the solid pores). The solid products resulting from this are known as xerogel and aerogel, depending on the type of drying process used.

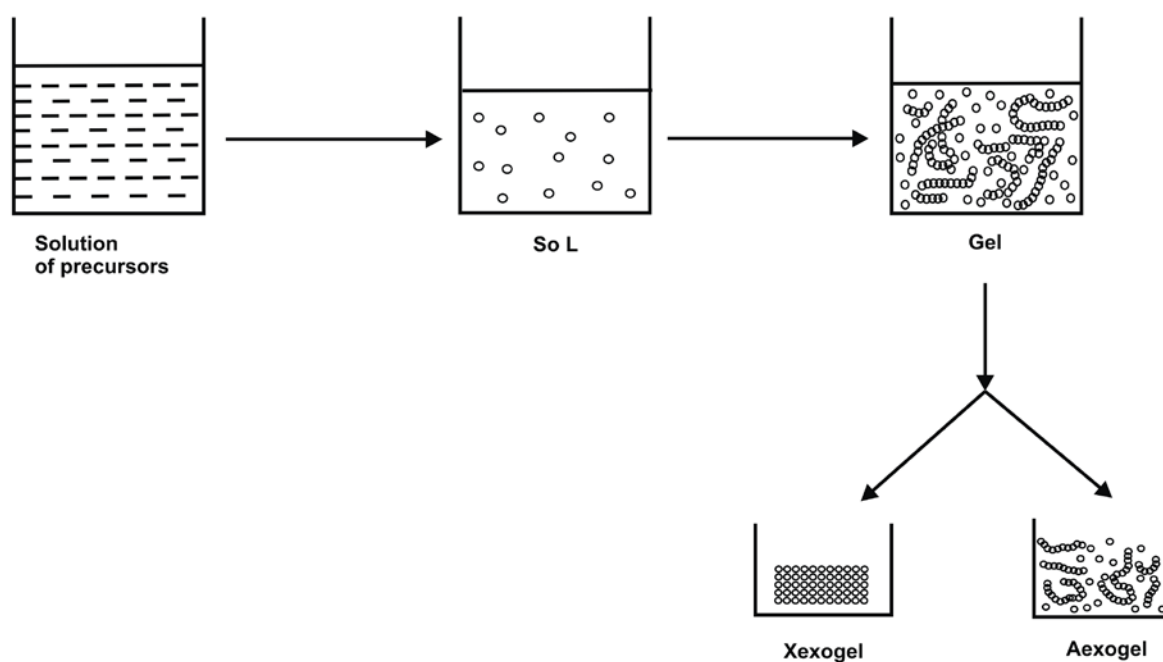


Figure 3.2 General scheme of preparation by sol gel method

In general, sol-gel synthesis offers better control over the surface area, pore volume, and pore size distribution (Perego and Villa, 1997). This is a promising advantage over the precipitation method.

3.1.1.3 Impregnation method

In this method, the support is contacted with a certain volume of the impregnating solution for a certain period, which is then followed by drying the support to remove the imbibed liquid and finally activating the catalyst by calcination, reduction, or other appropriate treatment.

The support is immersed in the active component solution under precisely defined conditions (concentration, mixing, temperature, time). Depending on the production conditions, selective

adsorption of the active component occurs on the surface or in the interior of the support. The result is a composite material consisting of the active component distributed on the support surface.

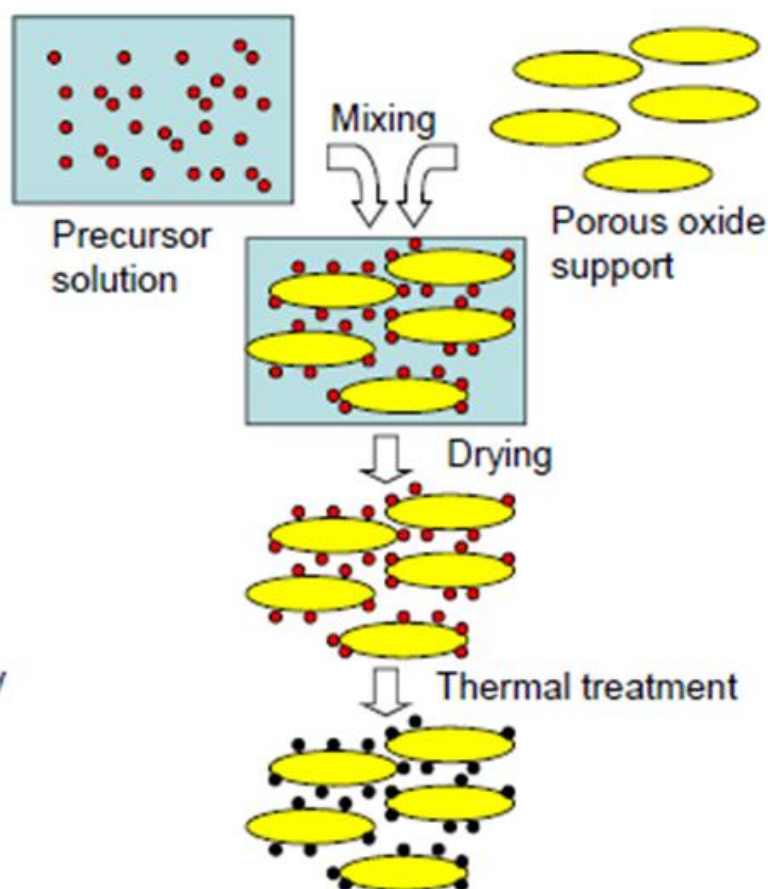


Figure 3.3 General scheme of preparation by impregnation method

Impregnation can be classified into two categories according to the volume of solution used (Pinna, 1998):

- 1) Incipient wetness or dry impregnation (IWI)
- 2) Wet impregnation (WI)

In the IWI, the solution contains the necessary amount of the active component. The volume of the solution containing the precursor does not exceed the pore volume of the support (it is equal or slightly less), just enough solution to fill the pore. In principle, this method appears to be simple, economic (especially when using solutions of expensive active components), and able to give a reproducible metal loading. In this method, the solubility of the catalyst precursors and the pore volume of the support determine the maximum loading available each time of impregnation (Mul and Moulijn, 2012). If higher loadings of the active component are

needed, it is mostly necessary to repeat the impregnation after drying or calcination of the intermediate (Deutschmann et al., 2009).

Wet impregnation, on the other hand, involves the use of an excess of the solution with respect to the pore volume of the support (Pinna, 1998). The system is left to age for a certain period under stirring, then filtered and dried. This procedure is applied when a precursor-support interaction can be envisaged. The concentration of the metal precursors on the support will therefore not only depend on the concentration of the solution and the pore volume of the support but also the type and/ concentration of adsorbing sites existing at the surface.

In the first step of impregnation, three processes occur (Mul and Moulijn, 2012):

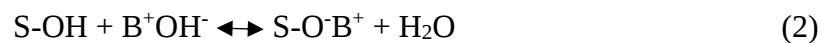
- a. transport of solute to the pore system of the support bodies;
- b. diffusion of solute within the pore system;
- c. uptake of solute by the pore wall.

In the case of WI, a fourth process is operative, transport of solute to the outer particle surface.

Soluble catalyst precursors are fixed to the support either by the reaction, exchange with surface OH groups, and/or by adsorption (Mul and Moulijn, 2012). To perform an impregnation with effective interaction, it is necessary to consider that true ion-exchange reactions between ions of the precursor in solution and the surface of the support occur during impregnation (Perego and Villa, 1997). Furthermore, it must be considered that the surface of the support changes its polarization according to the solution's pH value and the isoelectric point of the solid. Schematically, the equation involved in the surface polarization may be written, in an acidic medium (pH below the isoelectric point) (Perego and Villa, 1997):



While in a basic medium (pH above the isoelectric point) the equilibrium involved is:



At pH less than the isoelectric point, the surface is positively charged and will be surrounded by anions and will, therefore, attract and adsorb anions, while at pH above the isoelectric point the surface is negatively charged and will attract and adsorb cations from the solution. If it is intended to deposit anions onto the carrier surface, the preparation should proceed at pH values

below the Point of Zero Charge (PZC), whereas if cations are to be deposited, a pH value above that of the PZC is preferred (Mul and Moulijn, 2012).

3.1.1.4 Ionic exchange

Ion exchange consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species (Ertl et al., 2008: p 318). Inorganic oxides such as Al_2O_3 , SiO_2 , TiO_2 , MgO , which are commonly used as support materials, tend to polarize and to be surface charged once suspended in an aqueous solution (Pinna, 1998). The surface charge is controlled by the pH of the solution. For each inorganic oxide, there is a pH at which the oxide surface carries no charge. This pH is called Point of Zero Charge (PZC) or isoelectric point (IEP). Table 3.1 shows a summary of the isoelectric points of some oxides (Pinna, 1998):

Table 3.1: summary of isoelectric points of some inorganic oxides

<i>Oxide</i>	<i>IEP</i>	<i>Adsorption</i>
Sb_2O_5	<0.4	<i>Cations</i>
WO_3	<0.5	<i>Cations</i>
SiO_2	1.0-2.0	<i>Cations</i>
U_3O_8	≈ 4	<i>Cations or anions</i>
MnO_2	3.9-4.5	<i>Cations or anions</i>
SnO_2	≈ 5.5	<i>Cations or anions</i>
TiO_2	≈ 6	<i>Cations or anions</i>
UO_2	5.7-6.7	<i>Cations or anions</i>
$\gamma\text{-Fe}_2\text{O}_3$	6.5-6.9	<i>Cations or anions</i>
ZrO_2 hydrous	≈ 6.7	<i>Cations or anions</i>
CeO_2 hydrous	≈ 6.75	<i>Cations or anions</i>
Cr_2O_3 hydrous	6.5-7.9	<i>Cations or anions</i>
$\alpha\text{-}, \gamma\text{-Al}_2\text{O}_3$	7.0-9.0	<i>Cations or anions</i>
Y_2O_3 hydrous	≈ 8.9	<i>Anions</i>
Fe_2O_3	8.4-9.0	<i>Anions</i>
ZnO	8.7-9.7	<i>Anions</i>
La_2O_3	≈ 10.4	<i>Anions</i>
MgO	12.1-12.7	<i>Anions</i>

The knowledge of the isoelectric point is very useful in designing catalysts since it allows us to foresee the adsorption features of the different oxides as a function of the pH of the impregnating solution. If the oxide is immersed in a solution with a pH above its IEP, its surface will be negatively charged and will adsorb cations, and if the pH of the solution is below the IEP, the surface will be positively charged and will adsorb anionic species.

Oxide surfaces contacted with water are generally covered with hydroxy groups (Ertl et al., 2008: p 318). Some of these groups may behave as Brønsted acids, whereas other hydroxyl groups may behave as Brønsted bases. The resulting surface charge which arises from an excess of one type of charged site over the other is a function of the solution pH.

3.2 Introduction to catalyst characterization

The catalyst's performance is characterized by its activity for the reaction and its selectivity for a product. Catalytic activity and selectivity critically depend on the morphology and texture, surface chemical composition, phase composition, and structure of solid catalysts (Deutschmann et al., 2009: p 52). Numerous physical and chemical methods are therefore used in catalysis research to characterize solid catalysts. The primary objective in catalyst characterization is to understand the relationship between physical, chemical, and catalytic properties. The purpose of characterizing supported-metal catalysts is to establish a correlation between a structural feature and an aspect of catalyst performance (Wachs, 2010: p 18). It might then be possible to optimize the catalyst characteristics by manipulating its structure. Furthermore, the characterization of used catalysts can help to determine the causes of deactivation. For the mentioned purposes, physical and chemical properties are determined by various characterization techniques and related to the activity and selectivity.

Many characterization techniques are available. Some techniques such as Low Energy Electron Diffraction (LEED), Secondary-Ion Mass Spectroscopy (SIMS), and X-Ray Photoelectron Spectroscopy (XPS) are sophisticated and suitable only for specialized model systems (Thomas and Thomas, 1996: p 147). Some techniques are capable of characterizing a catalyst under its true operating conditions. Only characterization techniques utilized in this study are discussed below.

3.2.1 BET (Brunauer, Emmet and Teller)

As indicated in section 3.1, supported metal catalysts (as will be used in this study) are usually prepared using support materials with high surface area to give high metal dispersions. BET is a widely accepted method used for analyzing multilayer physisorption isotherms of inert gases

to determine the surface area. The method directly measures surface area & pore size distribution. Physical adsorption isotherms involve measuring the volume of an inert gas adsorbed on a material's surface as a function of pressure at a constant temperature (an isotherm). Using inert nitrogen gas, at a temperature close to its boiling point (near 77K), such isotherms are used to determine the amount of the inert gas needed to form a physisorbed monolayer on a chemically unreactive surface, through the use of the BET equation (Wachs, 2010: p 183). The relationship between volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage is described by the BET equation. This equation (equation 3.1) can be written in the form (Satterfield, 1991: p 135):

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0} \quad (3.1)$$

Where v is the volume of a gas adsorbed in a monolayer at pressure p ; p is the adsorbate partial pressure; p_0 is the saturation pressure of adsorbate gas at the experimental temperature; v_m is a monolayer volume of the adsorbate; c is a constant. By plotting the experimental data in the form of $p/v(p_0 - p)$ vs p/p_0 , a straight line graph should be obtained if equation 3.1 is obeyed, with the slope and intercept of which can be used to evaluate v_m and c . The surface area of the catalyst may then be calculated from v_m if the average area occupied by an adsorbed molecule is known.

The total surface area of a porous material is given by the sum of the internal and external surface areas. Pores are classified as micropores (pore width < 2 nm), mesopores (pore width 2 – 50 nm), and macropores (pore width > 50 nm) according to IUPAC definitions (Deutschmann et al., 2009: p 53). The pore width is defined as the diameter in the case of a cylindrical pore. There exist six types of adsorption isotherms as shown in figure 3.4 (Lowell et al., 2006: p 13). The reversible type I isotherm is concave to the relative pressure (P/P_0) axis and the adsorbed amount approaches a limiting value as P/P_0 approaches 1. Sorption isotherms obtained on microporous materials are often of type I. Type II sorption isotherms are typically obtained in the case of nonporous or macroporous adsorbents where unrestricted monolayer-multilayer adsorption can occur. Point B is described as the stage at which monolayer coverage is complete and multilayer adsorption begins. The reversible type III isotherm is convex to the P/P_0 axis over its entire range. Type IV isotherms are typical for mesoporous materials. At low values of P/P_0 , the isotherm is similar to type II, but then adsorption increases at higher values of P/P_0 where pore (capillary) condensation takes place (Satterfield, 1991: p 134). Type V is

similar to type III, but with pore condensation taking place at higher values of P/P_0 . Type VI represents stepwise multilayer adsorption on a uniform non-porous surface.

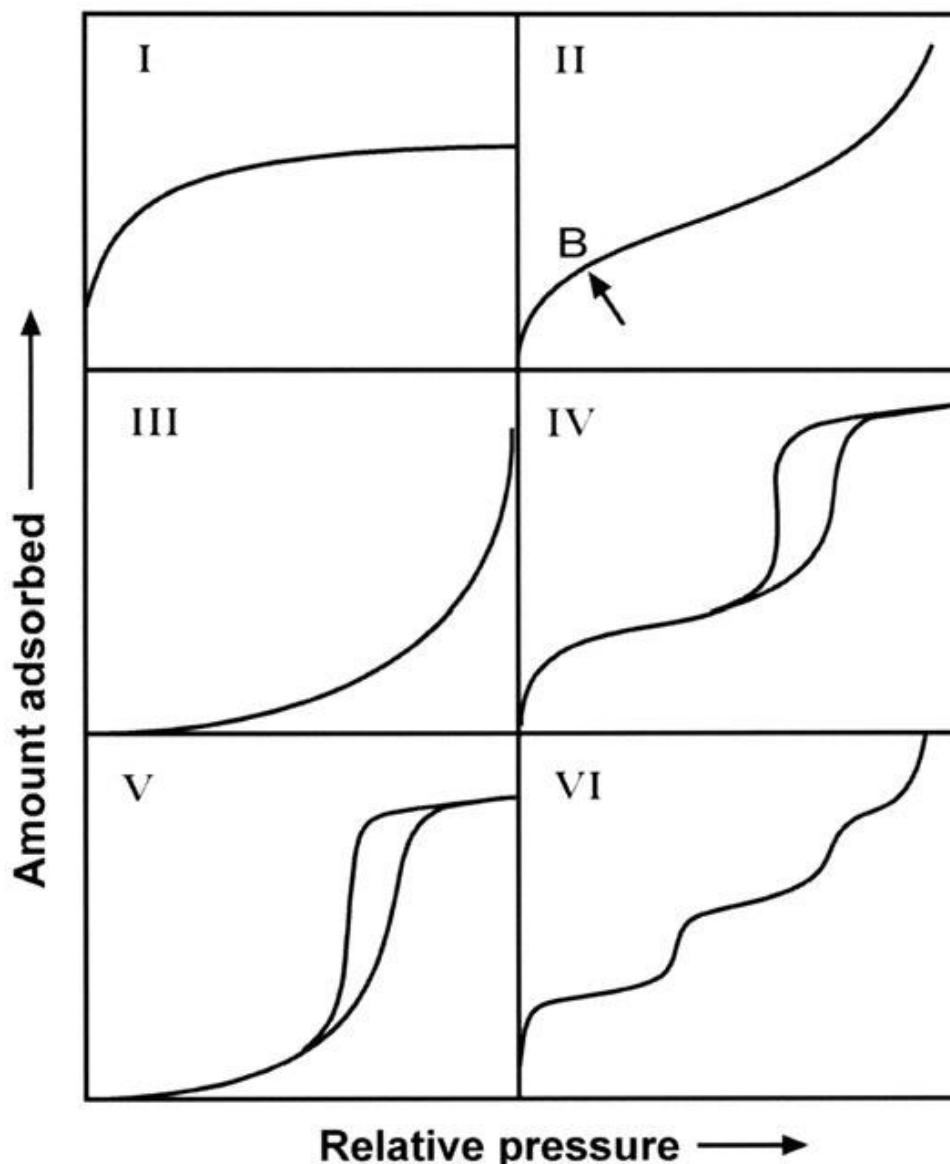


Figure 3.4 IUPAC classification of sorption isotherms

Any isotherm having only a gradual curvature at low values of P/P_0 represents a case in which adsorbent-adsorbate interaction is weak. These isotherms such as type III and V are reported to be difficult to use for the determination of surface area since the second and succeeding layers build up before the first one is complete. Moreover, to determine the pore size distribution within the catalyst, pore analysis is necessary. The information about the pore size distribution provides an insight into the accessibility of the reactants to the catalyst active sites. Pore analysis consists of determining the average pore volume, average pore size, and pore volume or pore size distribution. The two methods that can be used are physical adsorption of

the gas and mercury porosimetry (Satterfield, 1991: p 143). The true pore structure is of almost infinite complexity, and considerable literature exists for interpretation in terms of pore shapes. The pore size distribution reported depends on the model assumed for interpretation.

3.2.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is an effective method of obtaining information about the structure and composition of crystalline materials. Materials can be classified as crystalline or amorphous. Crystalline materials are comprised of atoms arranged in a regular ordered pattern in three dimensions. Amorphous materials are when the atoms are not arranged in a regular periodic manner. XRD can be used to determine the crystal structure, crystallite size, and phase composition, quantitative phase analysis to determine the relative amounts of phases in a mixture by referencing the relative peak intensities. When an incident beam of X-rays interacts with the target atom in a material, X-ray photons are scattered in different directions. The scattering of X-rays from atoms produces a diffraction pattern, which contains unique information about the atomic arrangement within the crystal. Amorphous materials do not produce a diffraction pattern. Bragg's law (Wachs, 2010: p 193):

$$\lambda = 2d \sin \theta \quad (3.2)$$

relates the spacing between planes, d , to the diffraction angle, 2θ , which is scanned to pick up diffraction from different crystal planes present. If the material is poly-crystalline, then instead of a spot pattern, diffraction rings are formed (powder diffraction). Distortions or broadenings of the diffraction beams carry information on crystal strain and grain size. Identification of phases present in a catalyst is based on the comparison of the observed set of reflections of the catalyst sample to those of pure reference phases or with a database (Powder Diffraction File (PDF) distributed by ICDD, the International Centre for Diffraction Data) (Deutschmann et al., 2009: p 54). From the lists for thousands of crystalline phases contained in such databases, the phases present in a sample can be determined via modern computer programs by quickly comparing the diffraction data to all of the database available patterns. The diffraction pattern of any crystalline phase is as unique as a fingerprint.

The technique of X-ray line broadening can be used to give information on particle sizes present in the catalyst sample. This method uses the Scherrer equation (Ross, 2012: p 95-96):

$$B(2\theta) = \frac{K\lambda}{L \cos \theta} \quad (3.3)$$

where the peak width, $B(2\theta)$, at a particular value of 2θ (θ being the diffraction angle, λ the X-ray wavelength) is inversely proportional to the crystallite size L ; the constant K is a function of the crystallite shape but it is generally taken as being about 1.0 for spherical particles. X-ray line broadening gives average values of crystallite size which in most cases agree quite closely with those obtained by TEM. The diffraction corresponding to the most intense peak is selected to calculate the average crystallite size using the Scherrer relation.

3.2.3 Electron Microscopy

In an electron microscope, to obtain the image of the specimen on a very fine scale, a focused electron beam is used instead of light to examine objects. High magnification and resolution make electron microscopes extremely useful for divulging ultrafine details of material microstructure. Electron micrographs of catalyst materials can help to identify phases, images of surfaces and their morphologies, and elemental compositions and distributions (Deutschmann et al., 2009: p 54). Discussed below are two main types of electron microscopy:

3.2.3.1 Transmission Electron Microscopy (TEM)

A typical TEM application in catalysis research is the examination of metal particle sizes and their distributions in supported catalysts (Deutschmann et al., 2009: p 55). The much higher resolution obtainable using transmission electron microscopy (TEM) allows one to observe even individual atoms of a surface, this being particularly useful when studying, for example, small metal crystallites on a particular support (Ross, 2012: p 95). Careful and systematic measurements using TEM also allow estimates to be made of the particle size distributions occurring in a particular sample. As the electron beam (consisting of electron energies) enters the sample, electrons may be elastically scattered back out of the specimen without energy loss, or backscattered inelastically in the form of low-energy secondary electrons (Satterfield, 1991: p 162). If the specimen is sufficiently thin, the unscattered penetrating beam provides the image for TEM.

3.2.3.2 Scanning Electron Microscopy (SEM)

SEM is the most widely used type of electron microscope for the study of microscopic structure. In SEM, the image is formed by a focused electron beam that scans over the surface area of the specimen. The image is produced from electrons backscattered from the specimen surface, usually the secondary-low energy electrons (< 50 eV) (Satterfield, 1991: p 162). The current generation SEM instruments can achieve approximately 1 nm as their best resolutions (Deutschmann et al., 2009: p 55). SEM is the most useful technique for studying sample

topographies (surface features, texture). The interaction of the beam with the sample material generates a variety of responses, including fluorescence emission, which can be used for elemental analysis (Wachs, 2010: p 185). SEM is often used in conjunction with an extra analytical technique, such as EDX, for the elemental analysis to go with the imaging.

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. EDX studies the interaction between a source of X-ray excitation and a sample. It is based on the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another. The particular strength of EDX is the simultaneous (or parallel) detection of elements rapidly and cheaply, by placing the physically small detector inside the SEM, or other electron beam system (Wachs, 2010: p 172). As such it adds an elemental analytical capability to imaging electron beam columns.

From different methods of preparing the catalyst described in this section, this research study will employ the impregnation method for the synthesis of the chosen catalysts. The advantages of this method are its simplicity, ease of scale-up as well as applicability to an industrial context. Also, having to possess all the properties and characteristics required, the catalyst cost should not place a burden on the economics of the process for which it will be used. Impregnation seems to be more economic since the content of the active component is often low. According to Bond (1987: p 79), the active phase in the supported catalyst (as also used in this study) usually constitutes between 0.1 and 20 percent by weight of the total catalyst.

Chapter Four

Experimental

4.1 Equipment

The gas-phase catalytic oxidation of HFP using O₂ was carried out in a pilot-scale reactor tube fabricated from a 2 m length of 10 mm internal diameter copper tubing, shown in Photograph 4.1. The tube was used in the form of a coil, having a coil radius of approximately 115 mm, and was



Photograph 4.1. Coiled-type fixed bed reactor used in the catalytic epoxidation of HFP

directly placed inside the coil bath-circulator reservoir (cf. Photograph 4.2). A $\frac{1}{16}$ inch Type K thermocouple was inserted about 150 mm within the reactor tube at the exit of the reactor coil to monitor the reaction temperature. The design of the reactor setup used in catalytic testing is outlined in Figure 4.1.



Photograph 4.2. Coiled-type reactor tube in a constant temperature oil bath

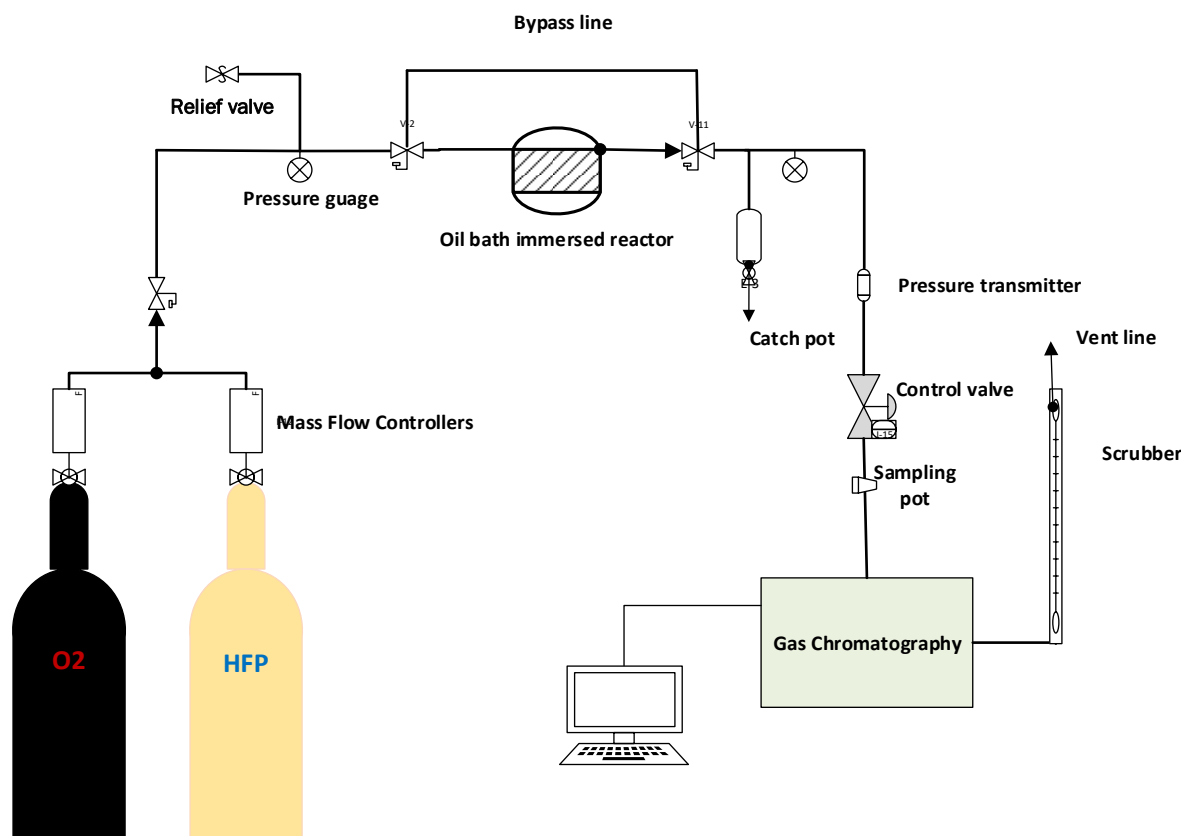


Figure 4.1: Schematic of a catalytic HFP epoxidation apparatus

The pipe fittings and tubing used for the setup were Swagelok stainless steel materials. The process piping was either $\frac{1}{4}$ or $\frac{1}{8}$ inch stainless steel instrumentation grade tubing. Oxygen and HFP gases were delivered to the system via gas cylinders which were controlled by high-pressure regulators. The gases were passed through $\frac{1}{4}$ inch stainless steel tubing which was then reduced to $\frac{1}{8}$ inch stainless steel tubing before entering the reactor system. The gas leaving through the regulators entered a two-way valve before entering the Bronkhorst mass flow controllers which were used to control the amount of each gas entering the reactor. The flow rate of HFP was controlled using a Bronkhorst El-flow mass-flow controller (accuracy: $\pm (0.5\%Rd + 0.1\%FS)$). The oxygen flow rate was controlled using a Bronkhorst El-flow mass-flow controller (accuracy: $\pm 0.5\%$ of $Rd + 0.1\%FS$). Initially, quartz glass rotameters were used, but there was an unsatisfactory control of inlet flow rates.

The reactants were continuously fed into one end of the reactor tube with the reaction products continuously withdrawn from the exit end. The oxidation in the reaction zone was performed

under isothermal conditions at an average total pressure between 1 and 4.5 bar. A stainless steel catch-pot was placed at the reactor exit for the collection of possible oligomeric liquid products. The pressure control system (Photograph 4.3) consisting of a valve positioner, pressure transmitter, and a Shinko controller was used to maintain the pressure in the system to the desired value. This complete setup was tested for leaks before the start-up.



Photograph 4.3. Pressure control valve positioner

4.2 Materials

Reagents for catalyst preparation

- Silica gel (SiO_2), Sigma-Aldrich
- Copper Nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Sigma-Aldrich
- Cesium Nitrate ($\text{Cs}(\text{NO}_3)$), Sigma-Aldrich

Chemicals used for testing and analysis

Hexafluoropropylene, with a purity of 99.8%, was obtained from the South African Nuclear Energy Corporation (NECSA) and was used without further purification. Technical grade oxygen (99.5%) was obtained from Afrox (Linde Group). Carbonyl fluoride (97%), trifluoroacetyl fluoride (99.5%), hexafluorocyclopropane (97%) and tetrafluoroethylene (99.9%) calibration standards were purchased from ABCR GmbH and Co. KG research chemicals. HFPO (99.5%) and carbon tetrafluoride (99.9%) were obtained from NECSA.

4.3 Catalyst synthesis

A catalyst (**10 wt% CuO/SiO_2**) was prepared using the impregnation method.

WI: 90g of support material, silica gel (Davisil grade 12, 28-200 mesh, Sigma-Aldrich), was dried in an oven at 100°C for 2 hrs. The impregnation solution was prepared by dissolving 30,371g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.1467g of $\text{Cs}(\text{NO}_3)$ in 100 ml of distilled water. The impregnation solution was then added onto the support and the slurry was obtained. The mixture was allowed to age at room temperature overnight (18 hrs), whilst stirring under the action of a decommissioned rotary evaporator (Photograph 4.4).



Photograph 4.4 Silica gel and copper trihydrate agitated during catalyst synthesis

It is discussed in section 3.1.1.3 that the support surface changes its polarization according to the solution pH value and the isoelectric point of a solid. The isoelectric point of SiO_2 lies between a pH of 1-2 (Pinna, 1998). On suspension in an aqueous solution with a pH close to 7, the surface of the silica support was expected to be negatively charged and is therefore expected to attract and adsorb cations from the solution. Since the intention was to deposit copper cations onto the support surface, no solution pH adjustment was necessary as the prepared solution may have just had sufficient pH-dependent capability of the copper cations adsorption.

The mixture was then dried on a rotary evaporator at 57°C, 65 mbar to remove the liquid. The remaining solid was dried in an oven at 100°C for 18 hrs after which it was packed into a calcination tube fabricated from glass and eventually placed in a calcination tube furnace (Photograph 4.5). The catalyst was then calcined at 500°C for 5 hrs under air flowing at 1.6 l/min, following a ramp of 2 °C min⁻¹ from room temperature to 500°C.



Photograph 4.5 Wire wound tube furnace used for calcination of the catalyst

IWI: 90g of support material, silica gel (Davisil grade 12, 28-200 mesh, Sigma-Aldrich) was dried in an oven at 100°C for 2 hrs. The impregnation solution was prepared by dissolving 29.2g of Cu(NO₃)₂·3H₂O and 0.7332g of Cs(NO₃) in 38.7 ml of distilled water. The impregnated catalyst was allowed to digest for 4 hrs at room temperature after which it was dried at 120°C for 16 hrs. The catalyst was then activated through calcination at 500°C for 5hrs under air.

It should be noted that the cesium (the dopant) amount was being varied for the 10%wt CuO/SiO₂ catalyst to investigate the effect of the alkali metal loading on the product formation. This was done in both impregnation methods (WI & IWI)

4.4 Catalyst characterization

All characterizations were carried out within UKZN. The TEM/SEM analyses were carried out at the UKZN Microscopy and microanalysis Unit (MMU), the XRD analyses carried out at Geological Sciences, and the surface area analyses (BET) were carried out at the Catalysis

Research Group. The necessity of catalyst characterization has been mentioned in Chapter 3. The information obtained from the characterization techniques explained in Section 3.2, provides insight into the various properties of the catalyst. Also, it may indicate the interactions that exist between the catalyst and reactants/products in the reaction system.

In evaluating the physical, chemical, and textural properties of the prepared catalysts, the characterization techniques outlined in the sub-sections below have been utilized:

4.4.1 X-Ray Diffraction (XRD)

XRD was carried out using a PANalytical Empyrean Diffractometer with an X'Celerator detector and operated at 40 kV and 40 mA and a divergence slit size of 1°. The source of radiation was Co K α ($\lambda = 1.78901 \text{ \AA}$). The 2θ covers the range between 5° and 90° with a scan step time of 8.2550s and a step size of 0.0080° 2θ . The powder samples were analyzed at room temperature. Scherrer equation was used to calculate the crystallite size of the catalysts (equation 3.3). This technique was used in analyzing both fresh and spent catalysts.

4.4.2 BET

The pore volumes and specific surface area of the catalyst were obtained by using the BET nitrogen physisorption analyzer. This was done using a Micromeritics instrument II 3020 3.02. Before the analysis, samples were degassed in a stream of nitrogen at 200°C for 24 hours. Based on the nitrogen physisorption isotherms and using the BET equation, the surface area, pore volume, and pore diameter values were then calculated. The surface area measurements provide the total surface area of the catalyst (including internal and external surfaces) and the pore volume determined is the total pore volume which is an indication of the total pore volume per unit mass of a catalyst.

4.4.3 SEM

SEM images were obtained using a Zeiss Ultra Plus FEG SEM instrument (Germany). For sample preparation, a piece of two-way carbon tape was placed onto a metal stub. The catalyst powder was added to the tape and the excess powder was removed by gentle tapping. The powder was then coated with carbon to provide an electron-active surface. The samples were analyzed on the instrument. The energy dispersion X-ray spectroscopy (EDX) mapping was done using the Bruker EDX detector and was analyzed with the Espirit 1.8.5 software.

4.4.4 TEM

TEM images of the various catalysts were obtained using a Jeol JEM-1010 electron microscope. Samples were prepared as follows: a small quantity of sample was dissolved in

ethanol and sonicated for about 10 minutes. The holey copper grids were dipped into the solution containing the catalyst and the ethanol and were then left aside to dry. In this manner, the deposition of a small amount of the catalyst onto the grid was achieved for viewing under the microscope. TEM analysis evaluated the physical state and morphology of the support and the catalysts.

4.5 Catalytic performance testing

Before testing, a copper-coiled reactor tube was charged with a freshly synthesized catalyst (90 grams). To fill the tube, the vacuum was applied at the reactor exit end and the catalyst was introduced in small batches at the opposite end. To avoid catalyst being sucked into the vacuum, a circular stainless steel mesh was placed at the exit end. The reactor was sealed and installed into a reaction system set up. The coil (immersed in the oil bath) was then heated for 2 hours at 200°C temperature and atmospheric pressure under a stream of 20 ml/min HFP and 10 ml/min O₂ (2:1 volume to volume ratio), following recommendations given by Ohsaka and Tohzuka (1981). The flow rates of the feed gases were controlled by the mass flow controllers. After 2 hrs, the temperature was decreased to 180°C and the pressure was increased to 4,5 bar using a controller connected to a pressure control valve positioner.

4.6 Product analysis

The quantitative composition of both feed and the reactor effluent was analyzed by gas chromatography (GC). Due to the high cost as well as expensive maintenance of the electron-capture detector, which according to Lokhat (2012), (O'Mahony et al., 1993) is the most selective and sensitive for halogenated compounds, a flame ionization detector (FID) was chosen. Also, the FID is suitable for the analysis of perfluorocarbons (Lokhat, 2012, Andrawes et al., 1980). The FID was used for the analysis of C₂F₄, *c*-C₃F₆, C₃F₆, and C₃F₆O, whereas a thermal conductivity detector (TCD) was used to quantify the amounts of COF₂, un-reacted O₂, and CF₃COF. A capillary column containing a proprietary silica-based porous-layer stationary phase provided adequate separation of perfluorocarbons and particularly satisfactory resolution between HFP and HFPO (Lokhat et al., 2014). Two Shimadzu GC instruments were used in this work: A GS-GasPro PLOT capillary column (30 m × 0.32 mm) from Agilent technologies was installed in a GC-FID system. A stainless steel column (3 m × 2 mm) packed with Hayesep D (80–100 mesh) was installed to a GC-TCD system. Samples of the reactor effluent were taken at fixed time intervals. A septum-sealed sample point that was installed was used to

withdraw 20-50 μ l samples for manual injection into the G.C. using a gas-tight syringe. The specific conditions for each instrument are presented in Tables 4.1 and 4.2. The calibration work of the gas chromatography instruments was carried out by other members of the team in the research group.

Table 4.1 Shimadzu GC 2010 gas chromatograph specifications

Item	Specification
Column	GS-GasPro PLOT(30m x 0.32mm ID)
Injection Temperature (°C)	200
Column Temperature (°C)	30
Injection mode	Split
Flow control mode	Linear velocity
Pressure (kPa)	80.2
Total flow (ml/min)	500.7
Column Flow (ml/min)	2.83
Linear Velocity (cm/sec)	41.7
Purge Flow (ml/min)	3.0
Split ratio	175.0
Make up gas flow (He) (ml/min)	7.5
H ₂ flow (ml/min)	40
Air flow (ml/min)	400

Table 4.2 Shimadzu GC 2014 gas chromatograph specifications

Item	Specification
Column	Haysep D Parked column (3m x 80-100 mesh)
Injection Temperature (°C)	120
Oven Temperature (°C)	95
Carrier gas	He
Carrier flow (ml/min)	17.0
Detector temperature (°C)	200
TCD current (mA)	80

Chapter Five

Results and Discussion

5.1 Preliminary catalytic testing and determination of optimum reaction conditions

The main aim of the preliminary investigations done in the initial study of this catalytic process was to validate the reaction operating conditions defined for the non-catalytic process (HFP epoxidation). Validating their applicability in the current study. Investigations were also carried out to test the activity of different catalysts for the epoxidation of HFP. The factors that were investigated included temperature, pressure, and feed flow rates. A series of investigative experiments were conducted at a temperature range of 120°C - 200°C and a pressure range of 1bar – 4.5 bar. All experiments were conducted using a 2:1 HFP/O₂ molar feed ratio. Conversion of HFP and selectivity towards HFPO were defined as follows:

$$X_{HFP} = \frac{N_{HFP(in)} - N_{HFP(out)}}{N_{HFP(in)}} \times 100\%$$

$$S_{HFPO} = \frac{N_{HFPO}}{N_{p(tot)}} \times 100\%$$

Where X = conversion, N_{HFP} = moles of HFP, (in) = HFP feed in, (out) = HFP in the product stream; S = selectivity, N_{HFPO} = moles of HFPO, $N_{p(tot)}$ = total number of moles of the products formed in the reaction.

Rotameters used in the early stages of the research to control the gas flows might not have been able to keep up with the reaction pressure, hence it was not easy to accurately detect how much O₂/HFP (ratio) was going inside the reactor. It was also not easy (almost impossible) to obtain the stable flows of the feed. Due to the challenge of gas control, the alternative method of mixing gases inside a small vessel to obtain a fixed HFP/O₂ ratio was used. The mixture was then again passed onto the catalyst under defined reaction conditions. Though the ratio problem was solved through gas mixing in a vessel, the reaction was allowed to run for a limited amount of time, restricted by the size of a vessel which could put in a maximum of 6 bar gas mixture that could allow approximately a maximum of 4-5 hours reaction time. In addition to that, the

flow of gases throughout the system (product stream) was not manageable with the backpressure regulator, hence resulting in the instability of the product flow. Overall, no steady state of the reaction was achieved, mainly as a result of the incontrollable flows which probably affected, mostly, the reaction pressure. From the reaction results, the carbonyl difluoride was a major product. The results obtained in the reactions using 5%CuO/Al₂O₃ catalyst are summarized in figure 5.1.

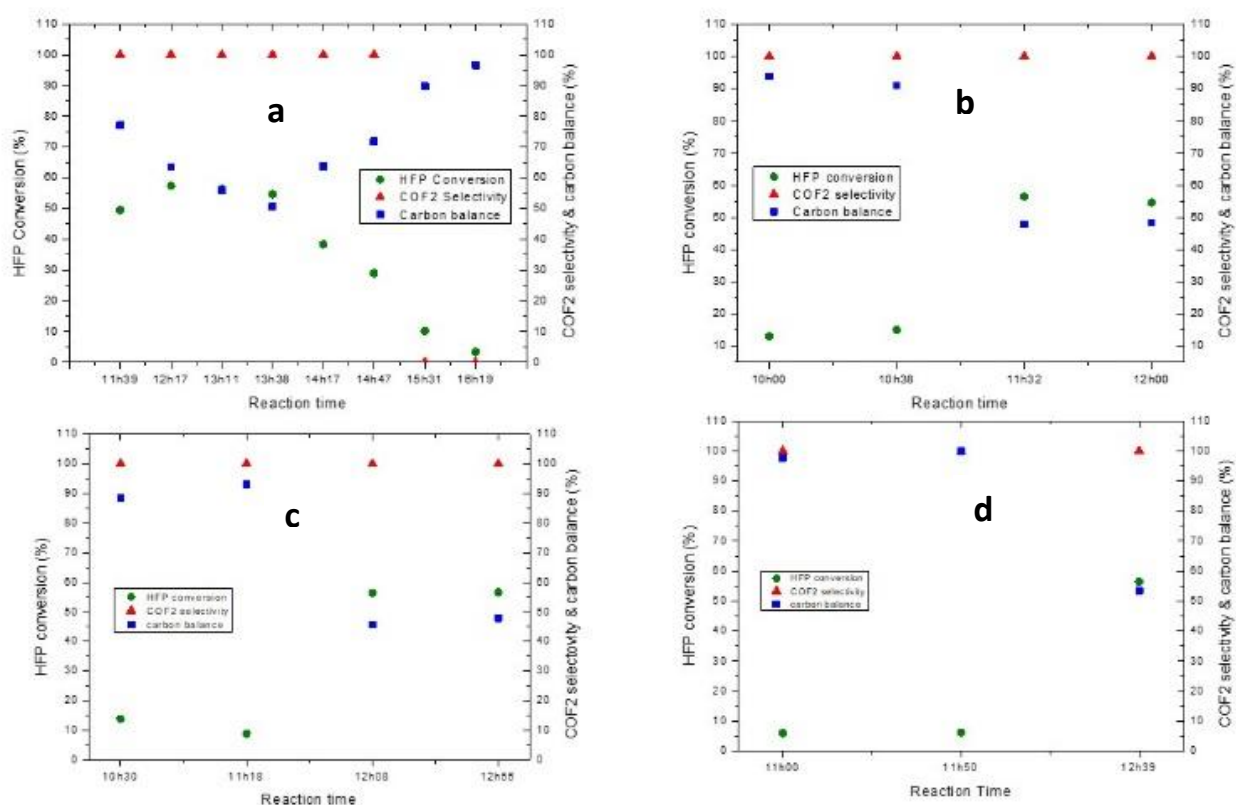


Figure 5.1: Conversion of HFP, Selectivity towards COF₂, and carbon balance of a reaction performed at 2.8 bar pressure and temperatures (a) 120, (b) 160, (c) 180, and (d) 200°C.

From figure 5.1, it is observed that selectivity towards COF₂ seems to be the only parameter that showed stability throughout the reaction. As much as there is no stability observed for conversion and carbon balance due to the flow control challenges experienced, the catalyst, however, proved to be selective towards COF₂ formation. The carbon balance was calculated based on the moles of carbon-containing molecules (in and out). The number of moles of the carbon atom was obtained by multiplying the number of moles of a molecule by the number of carbon atoms present in that particular molecule. The basis of one mole of feed and one mole of the product was used for this purpose. The low numbers observed for the carbon balance for some parts of the reaction, probably reveal the formation of some other products other than

COF₂, which may have not been possibly quantified in this experiment. Overall, it was not possible to draw solid conclusions in the behaviour of all parameters since the reaction was not allowed a sufficient running time due to the limitations discussed in this section above. The only observable trend which is common for all the results reported in figure 5.1 was the decrease in carbon balance with the increase in conversion at every reported point during the reaction. The inverse proportion relationship. The peak areas of the product, unreacted HFP, and O₂ are shown in appendix B. The product peak areas showed inconsistency which probably resulted from the instability of the reaction conditions and the complexity of the reaction.

The experiments that were run with clean silica (lower grade SiO₂), as recommended by Cavanaugh (1973) in the patent literature, showed activity for the reaction. COF₂ and c-C₃F₆ were formed in the experiments run in the temperature range of 140-180°C and pressure range of 2-4 bar. The ideal product for HFP epoxidation (HFPO, the epoxide) was not amongst the products formed.

CuO (active component) was then impregnated on silica (support). For the reactions with this catalyst, again the pressure was being decreased during the reaction progress restricted by the size of the vessel containing the HFP/O₂ mixture. The temperature and pressure ranges used in these reactions were 140-180°C and 1-4.5bar, respectively. The catalyst was active, but not selective towards HFPO. COF₂ was again the major product with 100% selectivity under defined conditions. Having mentioned this, the variation of the reaction conditions (temperature and pressure) were gradually improvising in terms of the catalyst performance and stabilization of the observed parameters. That was the positive observation in moving towards the optimum operating conditions anticipated. The results for these reactions are summarized in figure 5.2. There is a better trend observed for the conversion of the starting material, especially at 180°C temperature for both starting pressures of 3.5bar and 4.5bar. Also, the COF₂ peak area plots (appendix B) at tested reaction conditions showed some stabilization/consistency at certain stages which were much better than the previously tested ones. It should be noted that the reaction after pressure drop could only be allowed the running time of approximately 2 hours. At this stage, it was not easy to make full sense of the reaction nature.

The CuO/SiO₂ composite was then doped with a cesium alkali metal. Improved conversions were obtained when the catalyst was doped with Cs. The products were again COF₂ and c-C₃F₆ for reactions performed at 180°C temperature at a pressure range of 2-3bar. For the reactions

ran for both undoped and Cs doped CuO/SiO₂ at different conditions, the doped catalyst produced higher conversions of the starting material at corresponding pressures and temperatures. Cs doped catalyst was found to be active, but again non-selective. The summary of the results for these reactions is shown in figure 5.3.

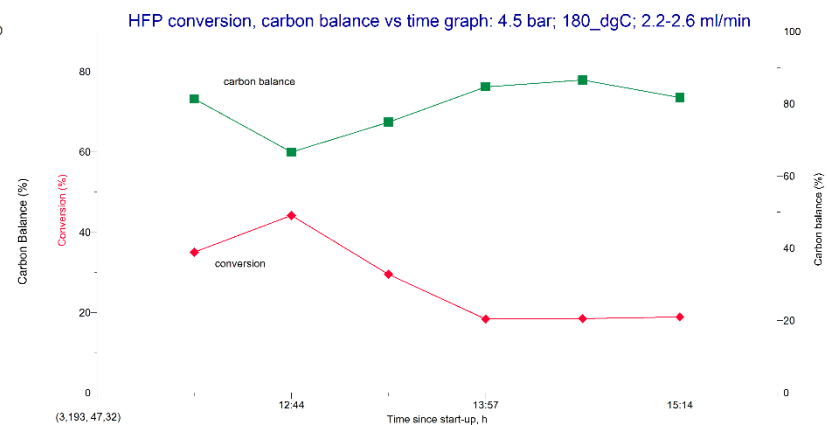
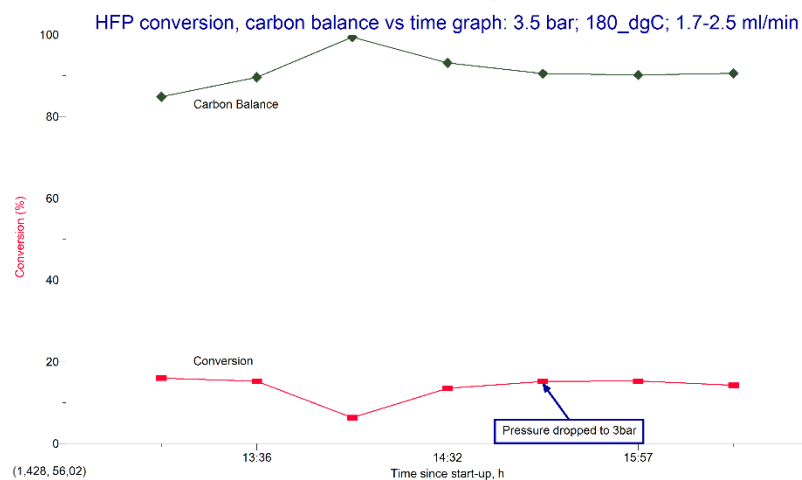
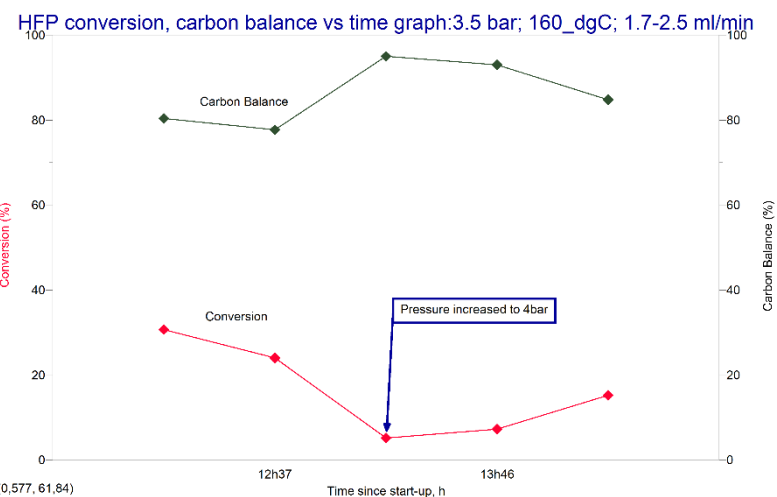
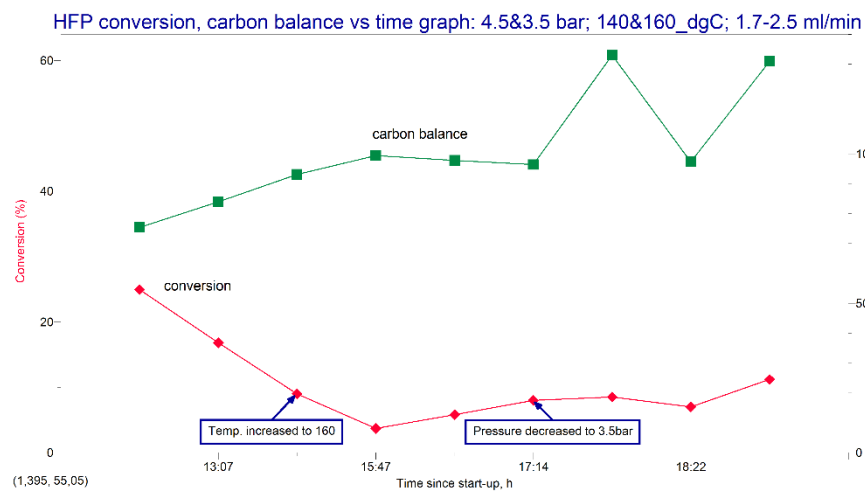


Figure 5.2: Conversion and carbon balance as a function of time for silica supported CuO catalyst performance test at different temperatures and pressures at GHSV of 32 h^{-1}

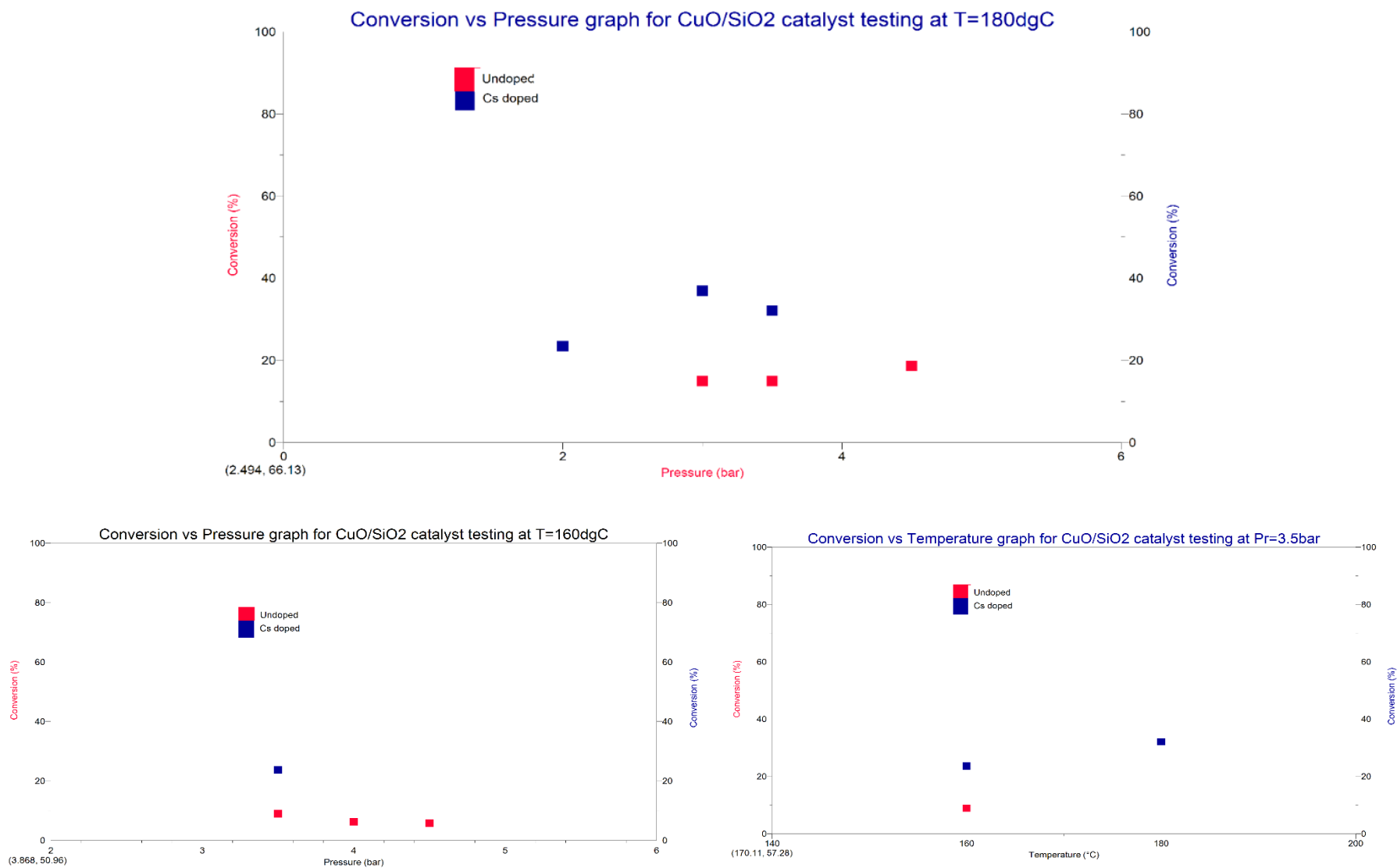


Figure 5.3: Conversion, temperature, and pressure comparisons for the undoped and Cs doped CuO-silica catalysts

In conclusion, the catalysts tested showed activity for the reaction, conditions were identified, but the reaction nature (catalyst-reactants interaction) was not identified, mainly due to the restrictions in reaction time allowance. Literature conditions were produced using both alumina and silica-supported catalysts with and without Cs as a promoter. Higher conversions were obtained with alumina-based catalysts.

5.2 Fresh catalyst characterization

The results obtained using the characterization techniques outlined in Chapter 3 (section 3.2) are reported and discussed hereunder. The information presented below is that for the ‘fresh’ catalyst, i.e. the catalyst that has not been used in the catalytic reaction. The chemical and textural structure of a catalyst can significantly influence the catalytic behavior concerning activity and selectivity to certain products. Every effort, therefore, has been made to establish the link between the structure of the material and its associated contribution to activity/selectivity.

5.2.1 SEM-EDX

The morphologies of freshly synthesized CuO/SiO₂ and Cs-CuO/SiO₂ are shown in the SEM images in figure 5.4.

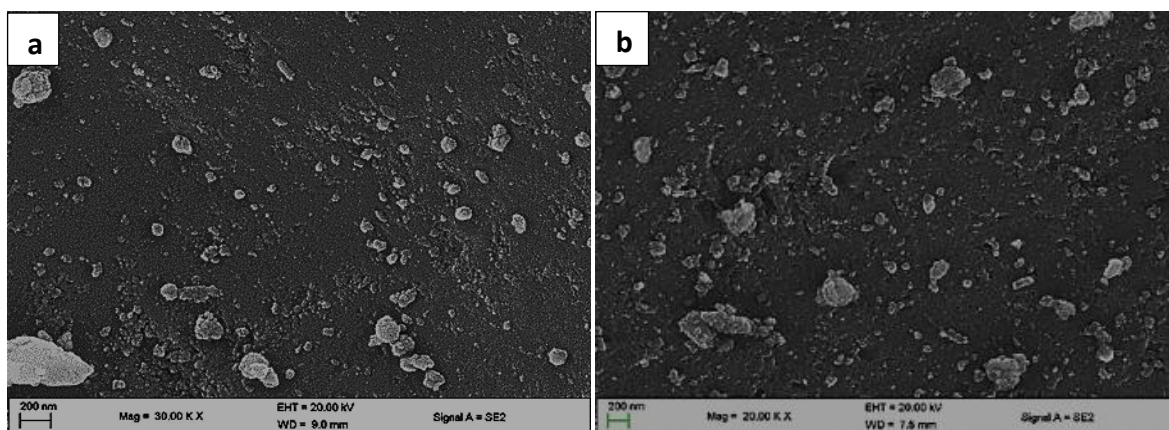


Figure 5.4: SEM images of 10wt%CuO/SiO₂ (a) undoped catalyst (b) Cs doped catalyst

The images obtained show the morphology of the copper supported on silica. The function of the support is to allow good dispersion of the catalytically active phase. SEM micrographs from figure 5.4 show that the support and catalyst material comprises predominantly of spherically shaped particles that appear to have aggregated and clustered at some regions to form small ‘florettes’. A closer look at the catalysts’ images to compare them, it appears that there is a better dispersion of particles in the cesium doped catalyst. There is a greater number of smaller-sized particles in comparison to the undoped catalyst.

EDX elemental identification/mapping was able to approximate the surface composition of the catalysts, the breakdown of which appears in Table 5.1 below, and corresponds to the images (a) and (b) in Figure 5.4 above.

Table 5.1: Quantitative EDX data for CuO/SiO₂ and Cs-CuO/SiO₂

Element	Wt% for figure 5.4a	Wt% for figure 5.4b
O	25.54	39.68
Si	51.15	47.72
Cu	23.31	12.49
Cs		0.11
Total	100	100

Though the EDX results may vary by a few percent, it is sufficient to express the elemental constituents of the catalyst surface. This provides also evidence for the non-existence of the impurities on the prepared material (possible from the chemical compounds used during catalyst synthesis, impregnation). In addition, the mapping was done to obtain information on the metal dispersion. The results are summarized in figure 5.5.

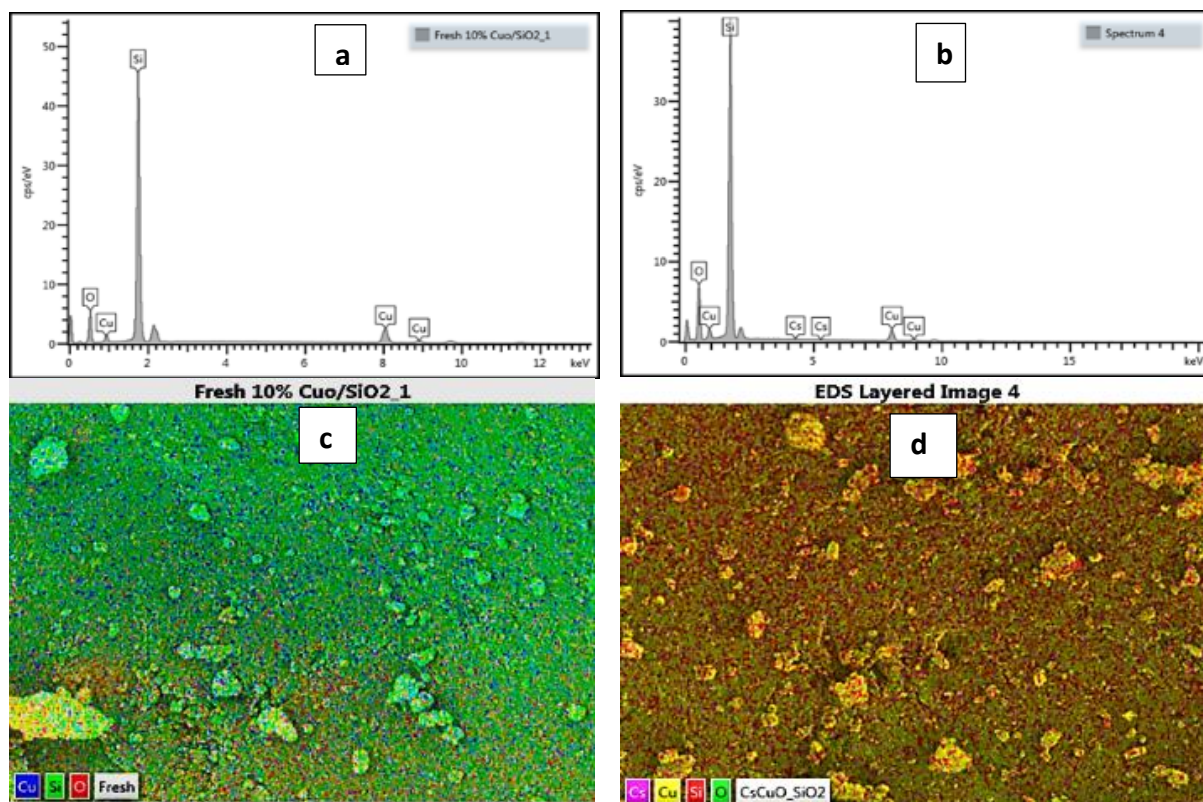


Figure 5.5: SEM-EDX (1 μ m) elemental identification/mapping indicating CuO dispersion on SiO₂ (a) and (c) undoped catalyst (b) and (d) Cs doped catalyst

From figure 5.5, it can be seen that copper (blue in (c) and yellow in (d)) is distributed over the catalyst surface with the traces of cesium alkali dopant (purple) spread in (d).

5.2.2 XRD

The crystalline structures of all catalyst samples were examined by X-ray diffraction (XRD). Mean crystallite sizes of the studied catalysts were calculated by the Scherrer equation from X-ray line broadening using the full-line width at half-maximum (FWHM) of the highest intensity X-ray peaks.

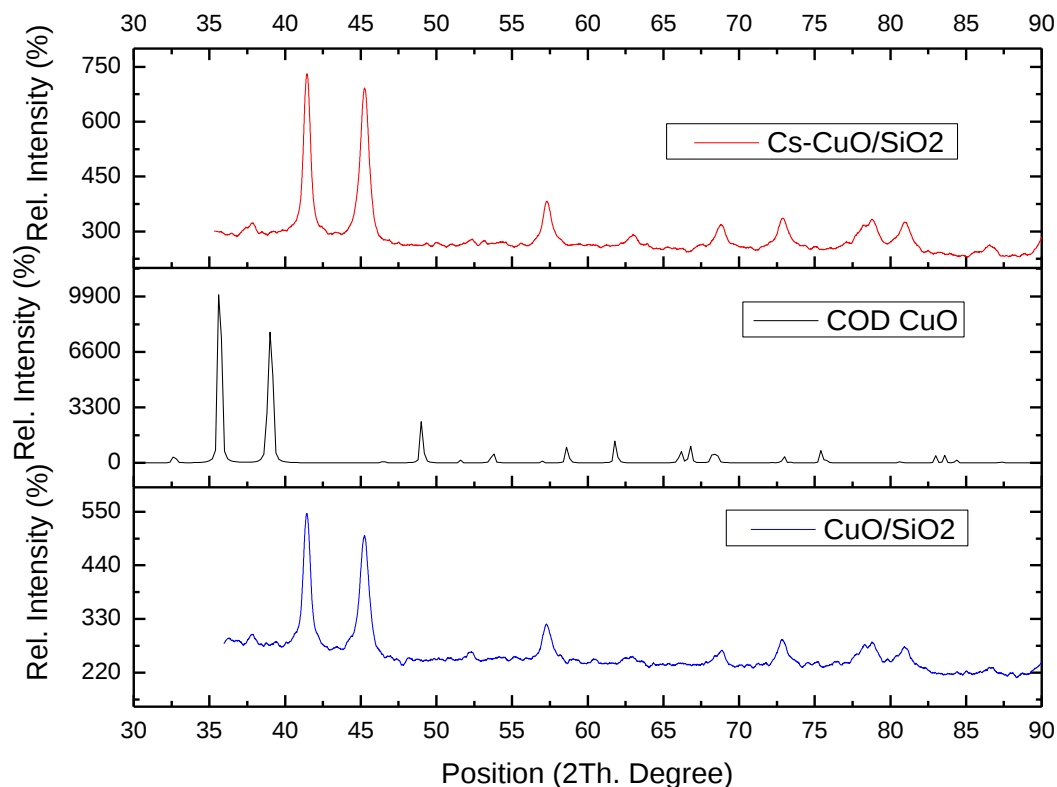


Figure 5.6: XRD pattern for CuO particles supported on the lower grade silica compared with CuO pattern from the crystallography open database.

From figure 5.6, diffractograms for CuO/SiO₂ (both undoped and cesium doped catalysts), 10wt% metal loading, display peaks corresponding to the tenorite CuO phase. The sharp intense peaks are the indication of the crystalline nature of the catalyst. The XRD pattern of a prepared catalyst sample is similar to that of CuO constructed from Crystallography Open Database (COD) (Day et al., 2012). The crystallite size of CuO was calculated by the Scherrer equation (equation 3.3) from the width of XRD peaks, and this is shown in table 5.2

Table 5.2: Showing the XRD crystallite size for CuO at the highest intensity peak

Catalyst	D _p average (nm)
10wt%CuO/SiO ₂ (lower grade silica)	6.52
10wt%Cs-CuO/SiO ₂ (lower grade silica 0.1%Cs)	15.23
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.2% Cs)	38.46
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.5% Cs)	40.12

D_p represents crystallite size (represented by the letter L in equation 3.3). A Cs doped catalyst showed a larger crystallite size at the same weight percent metal loading as the undoped catalyst. This is probably due to the presence of the cesium metal in the compound which must have brought an increase in the diameter.

The diffractogram of the catalyst supported on Davisil grade silica is shown in figure 5.7

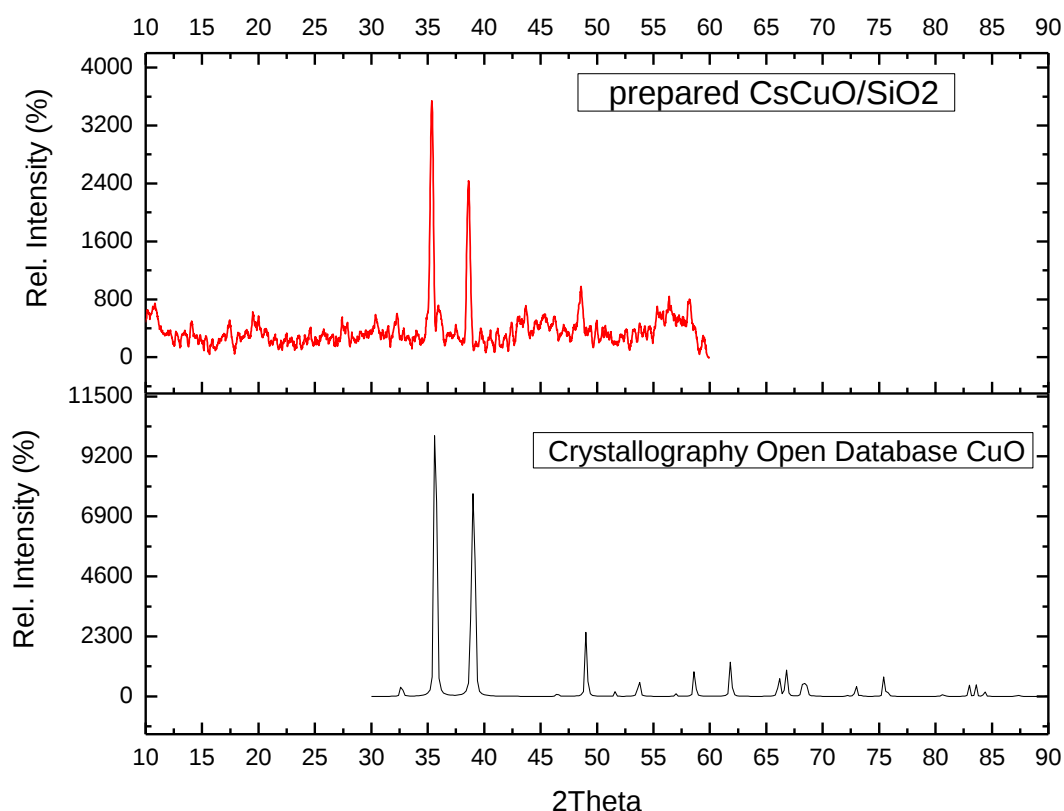


Figure 5.7: XRD pattern of 10wt%Cs-CuO/SiO₂ catalyst, 0.5% Cs content, synthesized from smaller particle size (higher grade) silica compared with a database constructed CuO pattern.

If the size of crystallites in a crystalline powder sample becomes small less than 0.005 μm (5 nm), the measured diffraction peak profile deviates from that of the same sample with the standard size of 0.5–10 μm in diameter (Waseda et al., 2011: p. 123). Nanomaterials have a small particle size. For XRD analysis, if the crystalline domain is too small, there are fewer diffracting materials available, and therefore, the intensity is less. Figure 5.7 shows the XRD pattern of higher grade silica-supported catalyst (red coloured) with high-intensity particles in comparison to the lower grade silica-supported particles (figure 5.6). Broadening (in lower grade silica) is believed to cause a loss of intensity in the signal of the nanomaterial diffraction. The less intense pattern is a result of a compound not being able to diffract X-Rays more efficiently. Peaks' intensity magnitudes are known to be related to the crystallinity of a solid

catalyst. This strongly affects the catalyst activity even though it is not easy to predict the degree of activity from the peak intensity magnitude. From figures 5.6 and 5.7, the peaks' intensity magnitude of the catalyst of higher grade silica is higher than the peaks shown in figure 5.6 (red and blue graphs). This difference in magnitude also showed an effect in terms of catalyst activity during performance testing in the reaction. Better results were obtained with higher grade silica. Moreover, the XRD pattern of the prepared catalyst in figure 5.7 corresponds to the pattern constructed from the COD. This serves as a confirmation that the correct material was prepared. As a concern of nanomaterials behaviour in XRD, it can also be emphasized that, with very small nanoparticles, extensive peak broadening can be observed as well as peak overlap. In addition, compared with TEM, the particle size results of the catalysts based on the silica grade used were not in agreement for the two instruments. XRD showed that the lower grade silica-based catalysts (LGSBCs) had smaller crystallite sizes while TEM showed the opposite. However, XRD results were, both graphical and numerical, were corresponding and consistent since LGSBCs produced a pattern with broader peaks, indicating smaller crystallite size.

5.2.3 TEM

TEM analysis evaluated the physical state: particle shape, particle size, surface morphology, and particle distribution of the prepared catalysts. The particle size values are shown in table 5.3.

Table 5.3: Average particle sizes of the catalysts

Catalyst	Average particle size (nm)
10%CuO/SiO ₂ (lower grade silica. Fresh catalyst)	10.76
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.2% Cs)	3.86
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.5% Cs)	2.25

The average particle size for an undoped catalyst was found to be bigger than the doped catalyst average particle size as can be seen in table 5.3. This is in agreement with the XRD results. The same trend was observed from both instruments. However, the particle size obtained for TEM was smaller compared to the XRD results. The observed difference (decreased size for a doped catalyst) had a significant impact on the catalytic properties. Better catalytic performance for smaller particles. Higher grade silica-based catalysts (HGSBCs) produced

smaller-sized particles in comparison to LGSBCs. Again, it was observed that the catalyst performance improved with the decrease in catalyst particle size. Better selectivity towards HFPO was obtained with HGSBCs.

The TEM images for CuO/SiO₂ catalysts are shown in Figures 5.8 and 5.9. The images are in accordance with the SEM-EDX analysis. The good dispersion of the oxide particles on silica is verified by the existence of nanosized particles in the catalysts measured by TEM. The extra high-resolution transmission electron microscopy (HR-TEM) micrographs for both doped and undoped catalysts are shown in appendix B (*Figure B.19*), and these clearly witness the observable difference in particle size as numerically summarized in table 5.3 above. Though the good dispersion of particles is observed in both types of catalysts, the undoped catalyst displayed a bigger particle size.

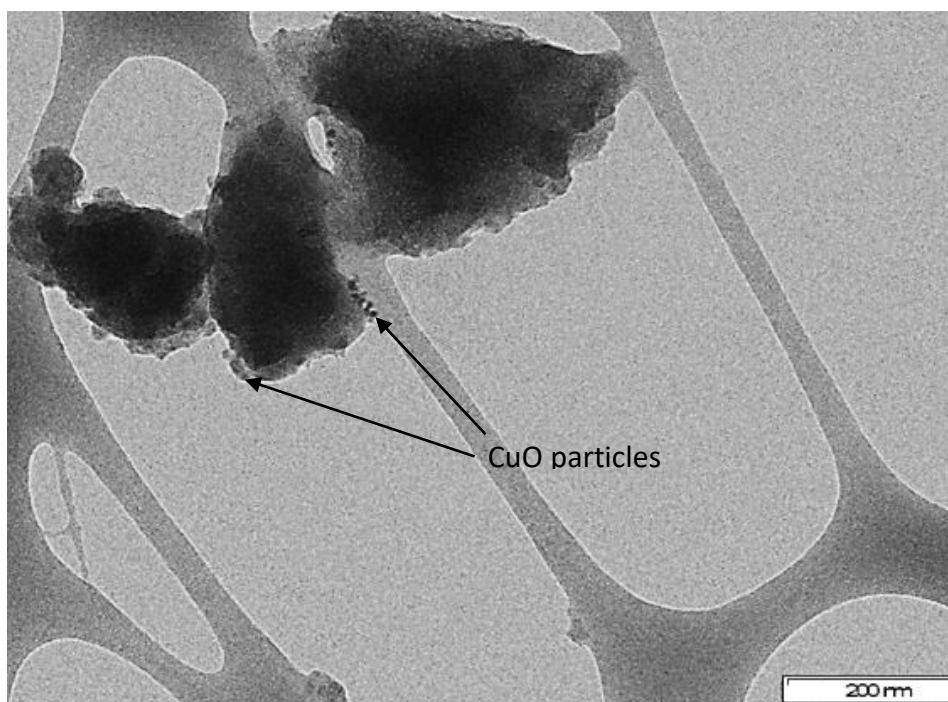


Figure 5.8: TEM image for CuO/SiO₂

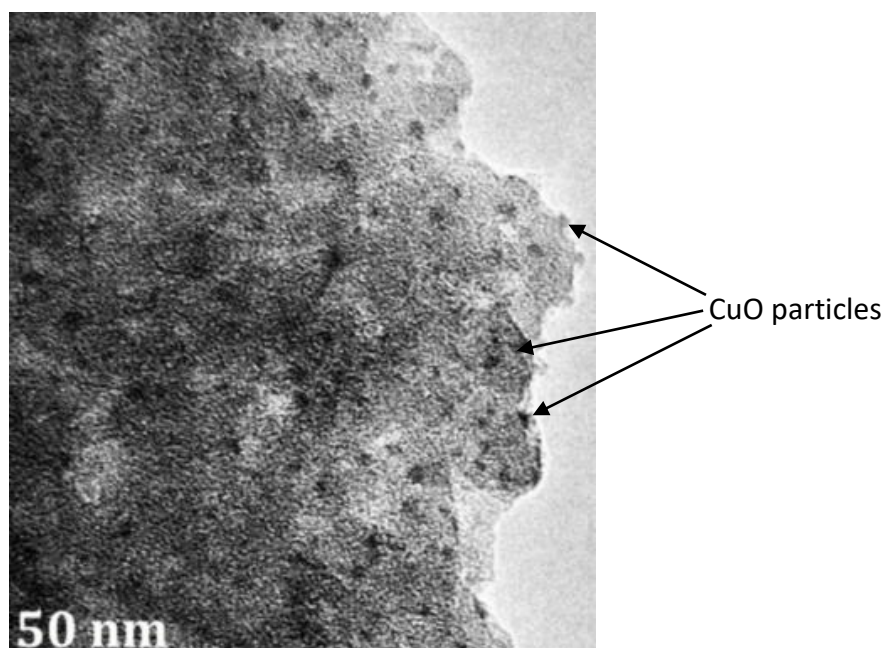


Figure 5.9: HR-TEM image for Cs-CuO/SiO₂

From the HR-TEM image in figure 5.9, the catalyst comprises irregularly spherical-shaped particles of varying sizes ranging between 1.19–2.72 nm. A good distribution of particles was observed on the catalyst with signs of agglomeration of particles in some regions. The micrographs for catalysts used for preliminary experiments are shown in Appendix B. The silica-based catalysts showed better particle distribution in comparison to the alumina-supported ones.

5.2.4 BET

The level of exposure to the gas phase is an important property of catalytic material and is evaluated through surface area measurements. The pore volumes and specific surface area of the catalyst were obtained by using the BET nitrogen physisorption analysis. The results are summarized in Table 5.4.

Table 5.4: BET surface areas, pore volume, and pore sizes of the catalysts

Catalyst	Surface Area m ² /g	Pore Volume cm ³ /g	Pore Size nm
Commercial SiO ₂	800	0.43	2.20
10wt% CuO/SiO ₂	400	0.21	2.83
10wt% Cs-CuO/SiO ₂ (IWI)	407	0.26	2.97
10wt% Cs-CuO/SiO ₂ (WI)	486	0.24	2.70

The commercial silica (Davisil grade) was reported to have a surface area of 800 m²/g and a pore volume of 0.43 cm³/g. Using the BET equation (equation 3.1), the surface area, pore volumes, and pore sizes of the catalysts were calculated. Upon impregnating with the metal precursor solution, a significant decrease in surface area and pore volume was obtained for fresh CuO/SiO₂ catalysts (both undoped and Cs doped). Generally, the decrease in surface area is due to pore blocking/clogging. The surface area of the catalysts doped with cesium was higher in comparison to the catalysts without cesium. This difference had an observable impact on catalyst performance. A clear explanation for this is that the doped catalysts had a greater amount of surface area accessible to the reactants, hence there was a larger amount of reactant converted to product. There also exists a direct proportion relationship between the surface area and the crystallite size obtained from the XRD for the doped and undoped catalysts. As the crystallite size increase with cesium addition, so is the surface area.

Moreover, for the doped catalysts, the surface area of the catalyst prepared by the IWI method was lower in comparison to the surface area of a catalyst prepared by the WI method. This is in agreement with the impregnation theory (in both methods) as described in section 3.1.1.3 of this thesis. For the two methods, amongst the processes taking place during catalyst preparation is the uptake of the solute (active component) by the pore walls. For WI, an extra process does occur, transport of solute to the outer particle surface. Hence, a larger surface area was obtained. This is also confirmed by the smaller pore size from a catalyst prepared by wet impregnation. Excess active component solution with respect to the pore volume of the support is used as opposed to the IWI method where the volume of the active component solution used is just enough to fill the support pores. Hence, the smaller diameter of the pore for the catalyst was prepared by the WI method. The pore volume obtained from both methods is slightly the same.

However, with the increase in the dopant content, there is an observed decrease in surface area and an increase in both pore size and a pore volume as shown in table B.1 in appendix B, compared with the respective catalyst of lower cesium content. Again, this had a significant impact on the catalyst performance in terms of selectivity towards HFPO, the targeted product. A possible explanation regarding an increase in the catalytic performance could be the fact that the active sites are located inside the pores, hence an increase in pore size and the volume results in the extra number of active sites available for the conversion of HFP. With the increase in both parameters, there is probably less chance for the product to be further converted into

by-products as a result of the product molecules taking long to be diffused out of the pores once the product has been formed.

5.3 Used catalyst characterization

The characterization of the spent catalysts revealed the changes to the catalyst induced by its use in the reaction.

5.3.1 SEM-EDX

SEM images in figure 5.10 reflect significant changes in the morphology of the catalysts, upon comparison to the fresh catalysts.

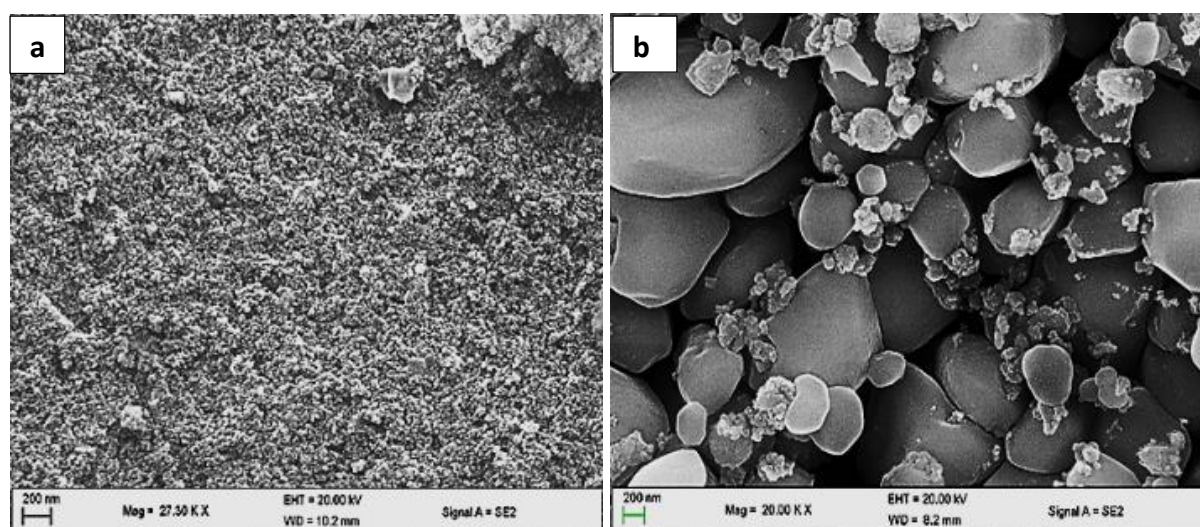


Figure 5.10: SEM images of 10wt%CuO/SiO₂ (a) undoped catalyst (b) Cs doped catalyst

As part of the reaction, the gas phase reacts with the catalyst surface. Reactions of gas with solid restructure the surface by chemical-assisted sintering (i.e. loss of catalytic activity due to a degrading active surface area resulting from an overlong exposure to higher gas-phase temperatures). From figure 5.10, it can be seen that there is a difference in the appearance of the catalysts' images in comparison to their respective fresh catalysts. For the undoped catalyst (figure 5.10a), not much evidence on the dispersion of particles, but quite a rough surface is observed on a used catalyst. No clear particles were observed on the catalyst surface. This should be due to the presence of some other compounds from the reaction as well as the deactivation of a catalyst. Also, there appear to be some changes on the surface of a support material itself after the reaction.

In discussing the thermally induced deactivation of catalysts resulting from the loss of catalytic surface area due to crystallite growth of the catalytic phase, Argyle and Bartholomew (2015) reveal the principal mechanisms of this growth, and these include crystallite and atomic

migration. For the doped catalyst (figure 5.10b), though the migration took place on the surface resulting in the agglomeration of particles to a higher extent, there seems to be no (or minimal) collapse in the support. Cesium dopant, therefore, proves to provide improved stability to the catalyst, hence an increased catalyst lifetime in the reactor.

Table 5.5: Quantitative EDX data for CuO/SiO₂ and Cs-CuO/SiO₂

Element	Wt% for figure 5.10a	Wt% for figure 5.10b
O	33.44	18.85
Si	45.89	21.90
Cu	12.30	34.00
Cs		0.01
F	8.37	25.25
Total	100	100

From table 5.5, EDX results for elemental identification showed extra elements in a used catalyst which is an indication of the occurrence of other chemical reactions on a catalyst surface, gas-solid/solid-solid reactions. These reactions contribute to catalyst deactivation.

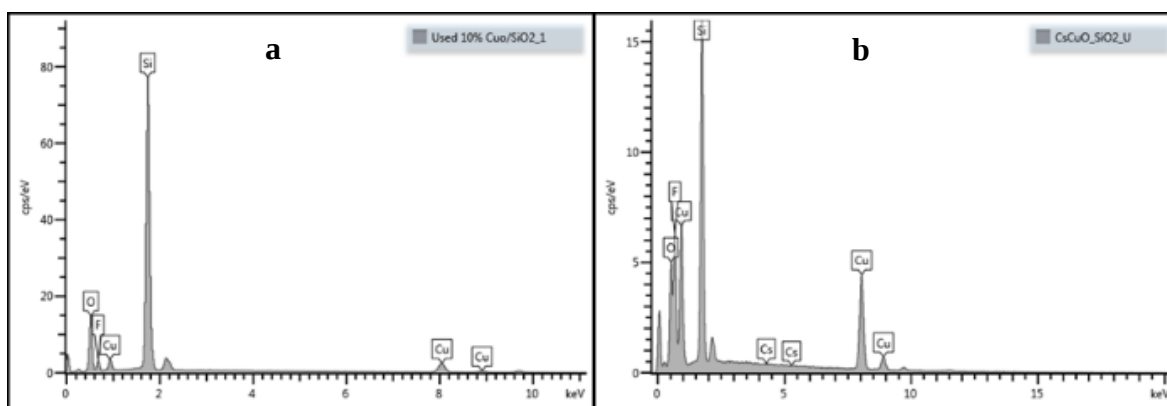


Figure 5.11: SEM-EDX elemental identification indicating CuO dispersion on SiO₂ for used catalysts (a) 10wt% CuO/SiO₂ (b) 10wt% Cs-CuO/SiO₂

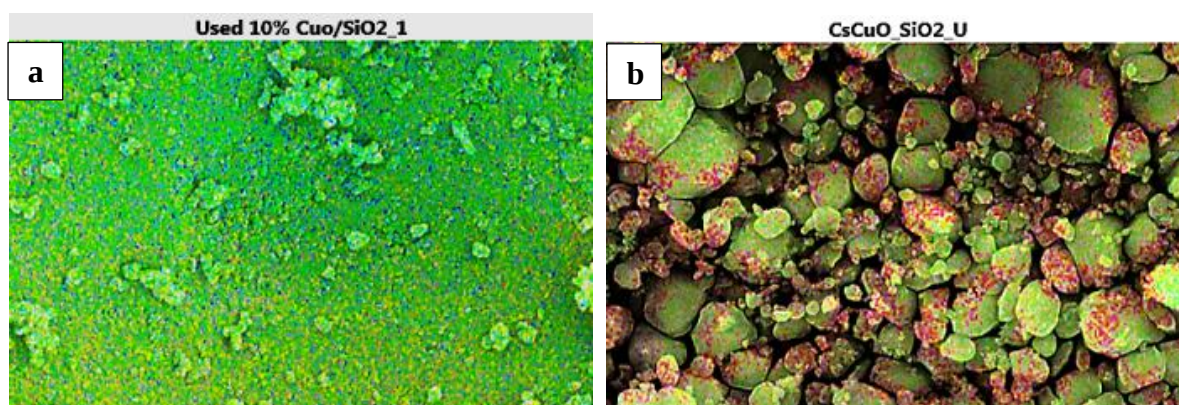


Figure 5.13: SEM-EDX (2 μ m) mapping indicating CuO dispersion on SiO₂ for used catalysts (a) 10wt% CuO/SiO₂ (b) 10wt% Cs-CuO/SiO₂

The mapping was done to obtain information on the metal dispersion. From both doped and undoped catalysts in figure 5.12, the fluorine element is dispersed on the surface of a catalyst. This is clearly from the gas-solid reaction which occurs and contributes as one of the deactivation processes. There is also more particle clustering as a result of crystallite and atomic migration.

5.3.2 XRD

The diffractograms of the spent (used) catalysts from the epoxidation reaction are shown in figures 5.13 and 5.14 below.

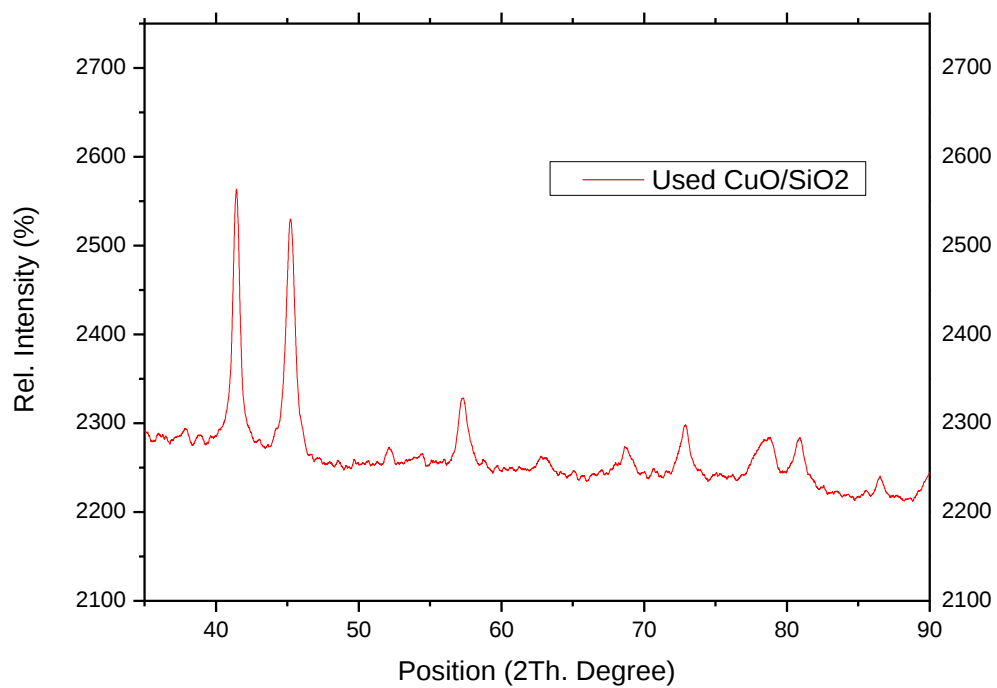


Figure 5.13: XRD pattern of a used CuO/SiO₂ catalyst

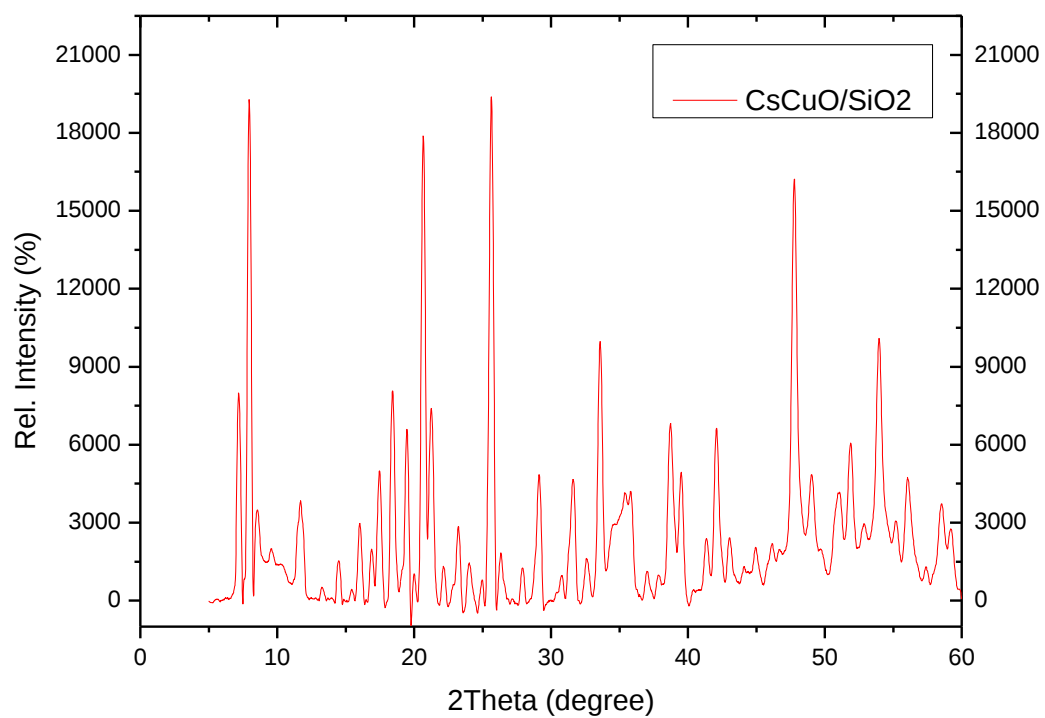


Figure 5.14: XRD pattern of a used 10wt%Cs-CuO/SiO₂ catalyst, 0.5% Cs content, synthesized from smaller particle size (higher grade) silica.

The diffractogram in figure 5.13 is for the catalyst sample synthesized from a lower grade silica support. As can be seen in the figure, there is not much of a difference in crystallinity compared to the same fresh catalyst. However, no solid conclusions can be drawn from this observation since the reactions performed using this silica type were not allowed sufficient time to run restricted by the equipment used at that stage (a maximum of approximately ± 4 hours).

According to Argyle and Bartholomew (2015), thermal degradation may occur in the form of active phase crystallite growth. The active phase for the present research work is CuO. For the experiments performed using catalyst synthesized from higher grade silica, the reaction was allowed to run for ± 43 hours and an extra 2 hours of catalyst pretreatment at a temperature higher than the reaction temperature before running. From figure 5.14, the used catalyst showed a pattern (structure) that is different from a fresh catalyst pattern. This shows that chemical deactivation is also taking place during the reaction. It is therefore evident that during the reaction, under specified conditions, there is a loss in the catalyst's structural integrity. The reactions of gas with solid restructure the surface by chemical-assisted sintering. The observed change in the structure of the Cs-CuO/SiO₂ catalyst indicates that sintering and other chemical processes do play a role in the deactivation of the catalyst towards the formation of HFPO.

Table 5.6: Showing the XRD crystallite size for CuO at the highest intensity peak for the used catalyst

Catalyst	D _p average (nm)
10wt%CuO/SiO ₂ (lower grade silica)	16.86
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.5% Cs)	38.72
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.2% Cs)	24.93

There was a decrease in crystallite size in the HGSBCs. This was calculated using the Scherrer equation based on the obtained diffractogram in figure 5.14. This is not in agreement with what is observed for used catalysts in TEM and SEM. More importantly, it is known that this equation has some limitations, one of which alludes to the fact that the value of the constant used changes with the shape of the particles. This makes the numbers obtained less precise compared to the aforementioned instruments.

5.3.3 TEM

From the HR-TEM images in figure 5.15, the catalysts comprise spherical-shaped particles of varying sizes ranging between 2,48-4,90 nm with an average particle size of 3,68 nm.

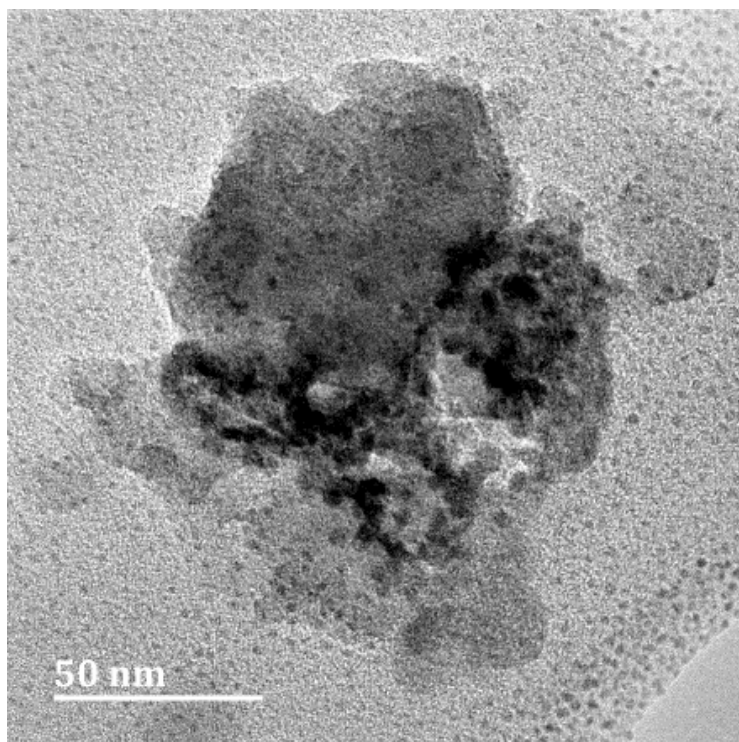


Figure 5.15: HR-TEM micrograph of 10%Cs-CuO/SiO₂ catalyst. 0.5wt% Cs content.

Table 5.7: Average particle sizes of the used catalysts

Catalyst	Average particle size (nm)
10%CuO/SiO ₂ (lower grade silica. Used catalyst)	12.67
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.2% Cs)	3.68
10wt%Cs-CuO/SiO ₂ (higher grade silica. 0.5% Cs)	3.87

There is still evidence of particle distribution observed on a used catalyst surface, however, there is more agglomeration of particles in comparison to the respective fresh catalyst. The increase in particle size in the used catalyst compared to the fresh one may be attributed to the sintering and agglomerating of individual particles. The particle size increase is witnessed in both the image in figure 5.15 and table 5.7. This simply means, the effect is probably due to thermal degradation since this type of deactivation is also reported to occur in a form of active phase crystallite growth for a reaction conducted at high temperatures. The results are in

correspondence with the XRD results of used catalysts except for HGSBCs where there was a decrease in size observed.

5.3.4 BET

The results of the surface area for the spent catalyst are shown in table 5.8 below.

Table 5.8: BET surface areas, pore volume, and pore sizes of the catalysts

Catalyst	Surface Area m ² /g	Pore Volume cm ³ /g	Pore Size nm
10wt% CuO/SiO ₂	77	0.17	4.58

For the used catalyst in comparison to the fresh ones, there is an observable decrease in the surface area and the pore volume (also refer to table B.1 in appendix B). The decrease in the pore volume is due to the clogging/blocking of the pores as there are several gas-solid reactions taking place resulting in unwanted products as well. This also has an impact on catalyst deactivation. Moreover, there is an opposite behavior for pore size in the used catalysts as there is an increase. Again, this is associated with the migration of the particles during the reaction under reaction conditions. The resulting agglomeration particles as witnessed by SEM and TEM results are the reason for increased pore size.

5.4 Catalytic performance

5.4.1 Catalyst testing and surface chemistry

The work carried out in this study involved an investigation of a reaction system used for the epoxidation of hexafluoropropene. The catalysts that were synthesized were 10 wt % CuO/SiO₂ and 10 wt % Cs-CuO/SiO₂. For a similar reaction, Huang et al. (2006) obtained the highest selectivity and yield at 10 wt% metal loading. The synthesis and characterization of these catalysts were discussed in Chapter 4 and section 5.2 of chapter 5 respectively. The primary product of the reaction is hexafluoropropene oxide (HFPO, an epoxide), which forms when HFP is oxidized. Other products formed during the reaction are mainly carbonyl difluoride (COF₂) as well as trifluoroacetyl fluoride (CF₃COF) and tetrafluoroethylene (C₂F₄) to a lesser extent depending on the reaction conditions and catalyst state as the reaction progresses. Catalytic testing was carried out as a function of time. A constant 2:1 HFP/O₂ feed ratio and 32h⁻¹ GHSV were maintained. The interactions amongst the variables were not investigated due to time constraints and the unavailability of the starting material (HFP gas). The results obtained are outlined in this chapter.

For most, if not all, experiments done for HFP epoxidation, during pre-treatment, the COF_2 peak was detected in a GC-TCD after 30 minutes implying the occurrence of a reaction inside the reactor. COF_2 peak height obtained after 1 hour has been shorter in height than the one obtained at 30 minutes. Again, the small amount of the liquid was collected in a catch pot (~1ml) after 30 min of pre-treatment time. No HFPO peak was detected during this period. From the practical endeavors in trying to understand the reaction mechanism, the Fourier Transform Infrared (FTIR) spectroscopy analysis of the liquid formed during the pre-treatment stage was done, and the spectrum obtained is shown in figure 5.16.

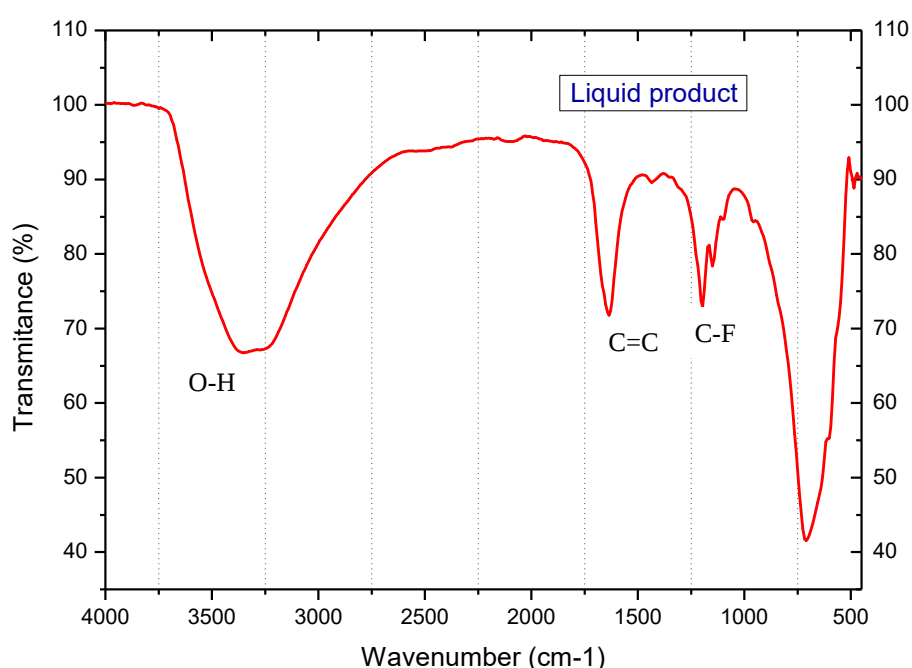


Figure 5.16: FTIR spectrum of liquid product formed during the pre-treatment period of HFP oxidation reaction.

The spectrum showed different absorption zones. A strong, broadband in the region between $3750 - 2750 \text{ cm}^{-1}$ (absorption centered near 3300 cm^{-1}) indicates the presence of the hydroxyl group. This is generally associated with water. This is anticipated due to the presence of terminal silanol groups in the silica support which might react with the reactants or one of the products to form water. The absorption band in the region $1750 - 1500 \text{ cm}^{-1}$ (absorption centered at nearly 1643 cm^{-1}) indicates the presence of a carbon-carbon double bond. C-F bond is said to be in the region between $1400 - 1000 \text{ cm}^{-1}$, there is also a strong peak in this region from the liquid product spectrum as can be seen in the spectrum above.

Generally, high-temperature treatment of the oxide catalyst results in the surface form possessing catalytic activity. Molecular rearrangement or bond-breaking on the surface has to be activated by temperature.

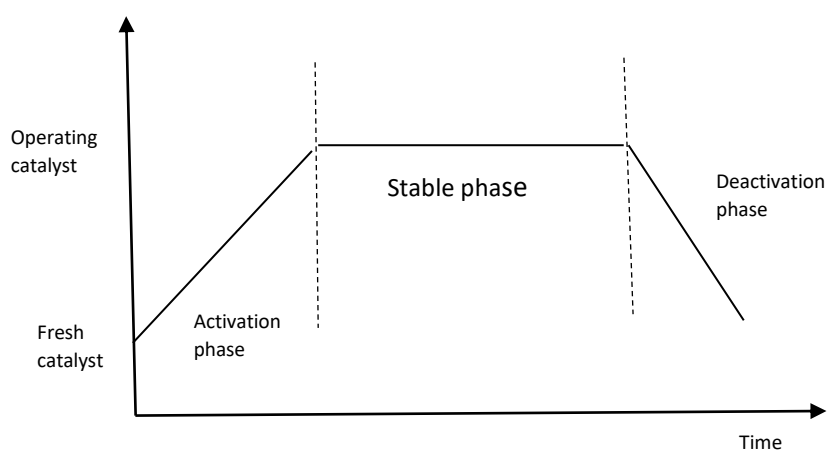
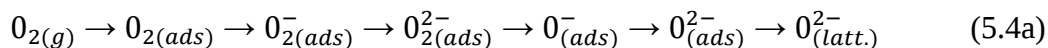


Figure 5.17: Changes of the freshly introduced catalyst activity with time.

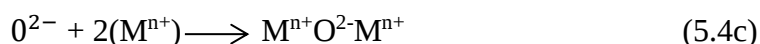
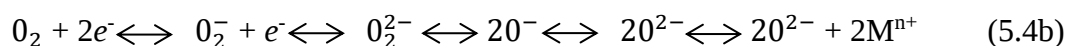
Though COF_2 is the only main detectable product during the pre-treatment of the catalyst, its formation is the evidence that the catalytic reaction is taking place during this activation phase shown in figure 5.17, but not directed to the desired product at this stage. Activation, by definition, is simply improving the catalyst's capability of catalyzing the conversion of the reactants into products. The interaction of molecular oxygen (the oxidizer) with transition metal atoms located at the surface of solid oxide as constituents of the crystal lattice results in the activation of the oxidizer. Once the pre-treatment period is done and the reaction is operating at the reaction pressure and temperature, the first HFPO peak for most reaction experiments conducted in this research appeared after more than 20hrs. The explanation of such a lengthy induction period is the fact that, during metal-oxygen interaction, there exists the transference of electrons from the metal to the oxygen. It is a general occurrence that the formation of the surface chemical bond is accompanied by the charge redistribution in the adsorbate and the substrate. Considering that fact, Haber et al. (1987) reported that studies done on oxide groups of transition metal cations in their highest oxidation state have shown that such systems are not able to chemisorb and activate gaseous oxygen. Their performance is said to be associated with the ability to insert the lattice oxygen atom into the organic molecule, desorption of the product

formed leaves behind oxygen vacancies, and reduced transition metal cations. Gaseous oxygen then fills the vacancies and reoxidizes the reduced cations to complete the redox cycle.

Furthermore, the assumption is that, during the adsorption on the reduced surface, oxygen can accept electrons one by one going in succession to the fully reduced form (Panov et al., 1998, Boreskov, 1982):



A series of different adsorbed oxygen species are formed, gradually enriched with electrons until the state O^{2-} of lattice oxygen is attained. Again, Centi et al. (2001) also argue that in the process of oxygen incorporation into the oxide structure, several types of electrophilic activated oxygen species form before being incorporated as structural (lattice) oxygen of the oxide (i.e. species with a nucleophilic character). To be more precise on the overall process of incorporation of oxygen into an oxide lattice:



From the literature, the existence of some radicals was confirmed through the conduction of experiments and was observed by the Electron Spin Resonance (ESR), the paramagnetic ones. The exact thermodynamic data necessary to calculate the conditions at which adsorbed oxygen species should appear and to estimate their stability are not available (Bielański et al., 1979). Overall, according to Centi et al. (2001), during the transformation (O_2 to O^{2-}) the nature of the metal-oxygen bond and its polarizability changes from an electrophilic character ($M^{\delta-} - O^{\delta+}$) for the negatively charged species to a nucleophilic character ($M^{\delta+} - O^{\delta-}$) for structural O^{2-} . Unlike in hydrocarbons, the double bond in HFP, the fluorinated alkene, is electron deficient due to the high electronegative fluorines attached to the carbons as opposed to hydrogens. Also, since HFP is non-symmetrical, the carbon that is directly attached to two fluorines is more electropositive, hence susceptible to nucleophiles. The conclusion drawn is that the lengthy induction period probably results from the fact that the correct oxygen nature (nucleophilic O^{2-} lattice oxygen) required for the organic molecule (HFP) oxidation takes time to be completely created, the last species to be formed in the chemical transformation of adsorbed O_2 as can be seen in equation 5.4a. From the transformations of O_2 adsorbed on the surface, the creation of O^{2-} is said to require the highest energy in comparison to the formation of all other species.

This is believed to be the result of the high dissociation energy of O_2 and the strongly negative electron affinity of the O^- ion.

Overall, as an overview of the oxygen transformation, it is worth mentioning that both electrophilic and nucleophilic types of oxygen species formed during this process can react with the alkene depending on the reaction conditions, and they result in different types of products. Hence, different products are expected in the current research, however, at different levels of formation since the species are themselves not of the same reactivity and stability under reaction conditions.

Figures 5.18 (a) and (b) present the catalytic results obtained using the cesium doped CuO catalyst. Figures 5.18 (c), (d), and (e) present graphs of this reaction for each parameter with the error bars for the authentication of the obtained values' accuracy. The HFP conversion, selectivity, and carbon balance at the reaction temperature as a function of time-on-stream are shown. The catalyst used in this particular reaction was prepared via the IWI method with an alkali dopant of 0.5 wt% content.

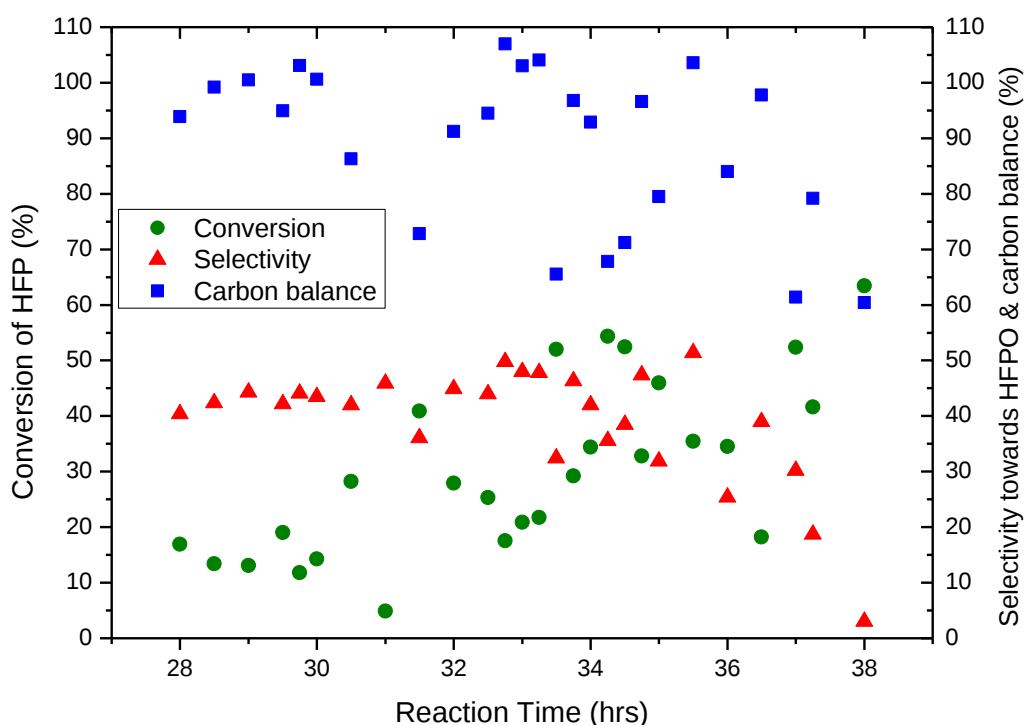


Figure 5.18(a): Conversion, carbon balance, and selectivity towards HFPO as a function of time over 10wt% Cs-CuO/SiO₂ catalyst, 0.5wt% Cs content.

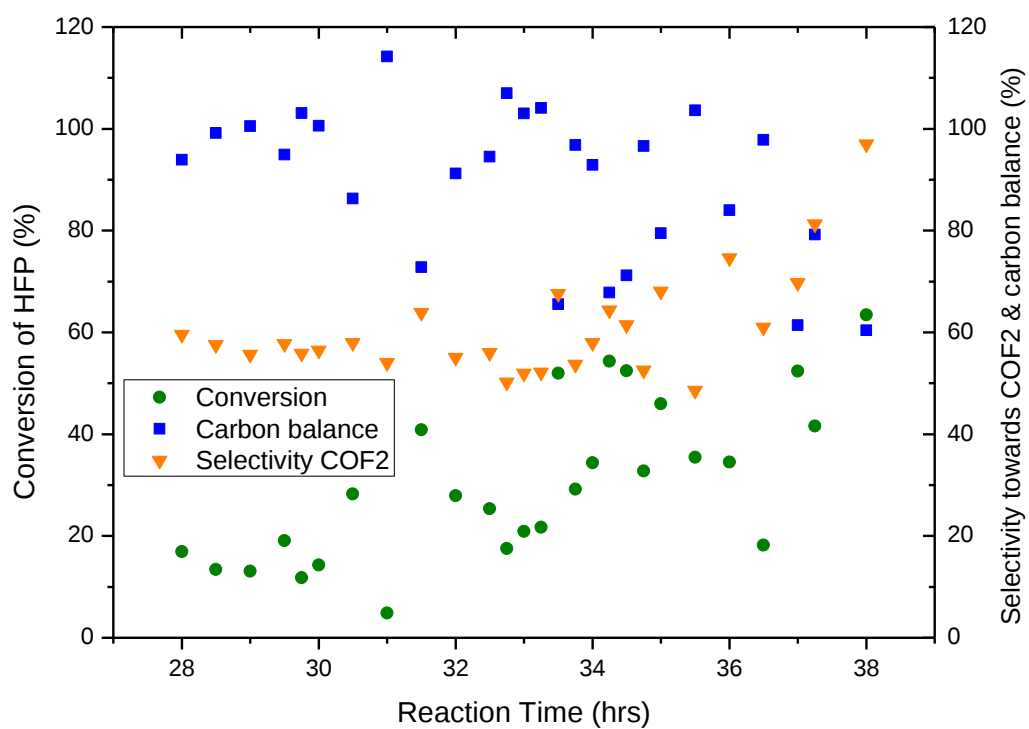


Figure 5.18(b): Conversion, carbon balance, and selectivity towards COF₂ as a function of time over 10wt% Cs-CuO/SiO₂ catalyst, 0.5wt% Cs content.

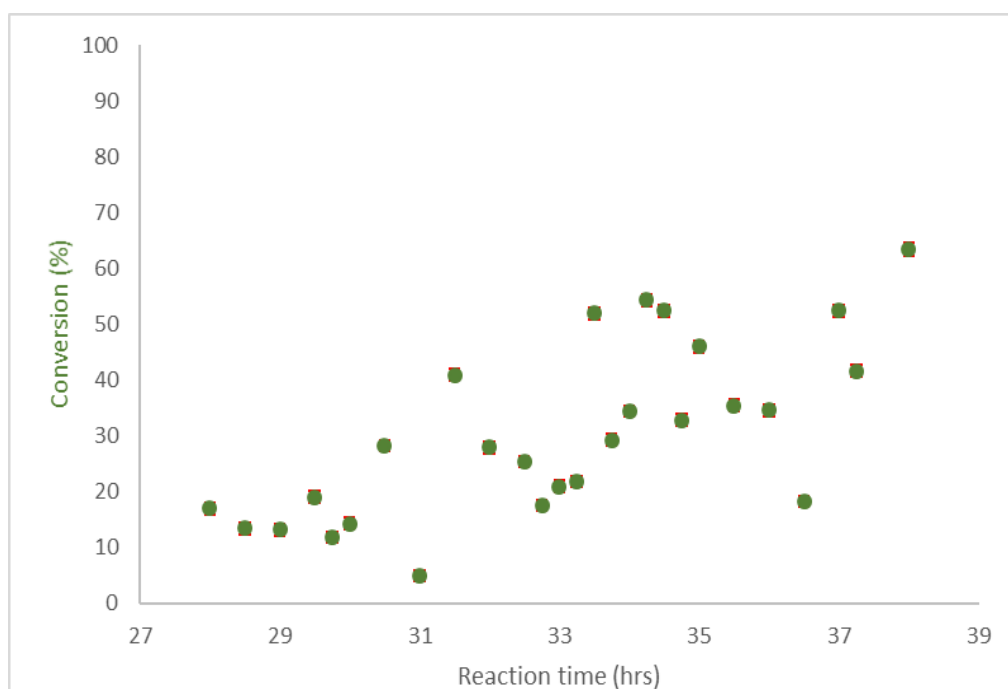


Figure 5.18 (c): Conversion of HFP over 10wt% Cs-CuO/SiO₂ catalyst, 0.5wt% Cs content showing error bars.

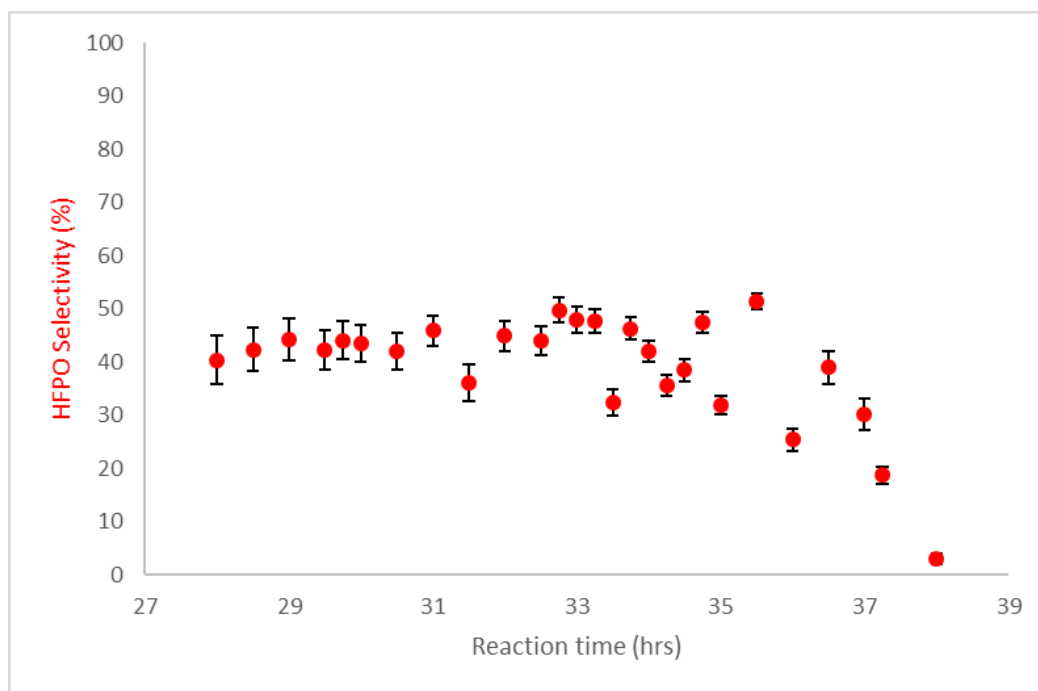


Figure 5.18 (d): HFPO selectivity using 10wt% Cs-CuO/SiO₂ catalyst, 0.5wt% Cs content showing error bars.

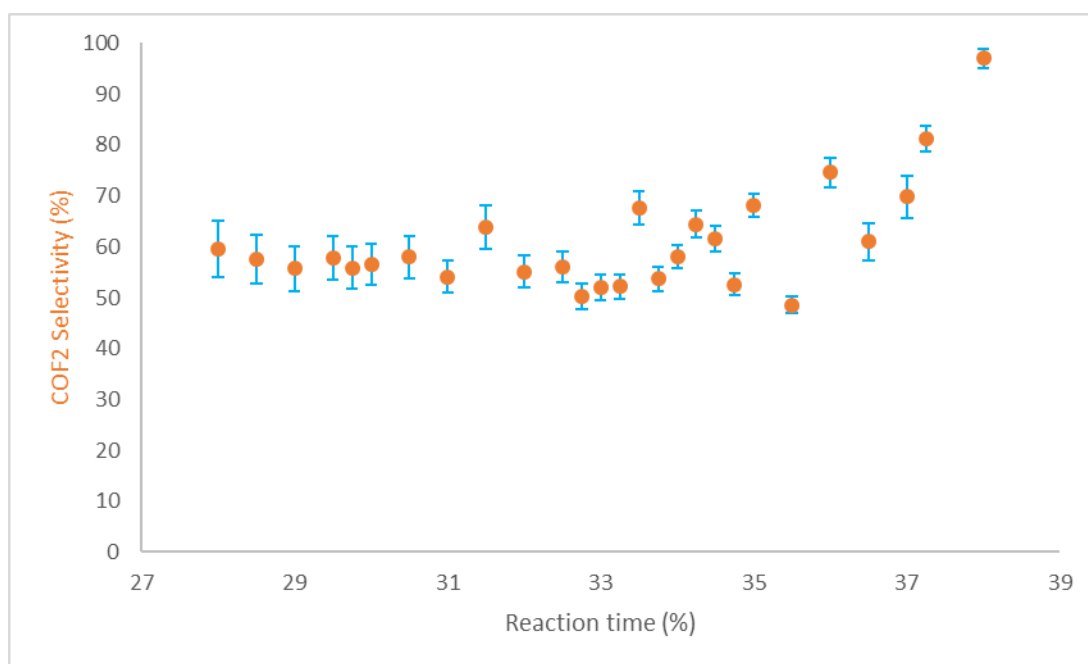


Figure 5.18 (e): COF₂ selectivity using 10wt% Cs-CuO/SiO₂ catalyst, 0.5wt% Cs content showing error bars.

The reaction was carried out under operating conditions for 38 hours. The first peak of HFPO (primary HFP epoxidation product) appeared after approximately 27 hours. The average conversion and selectivity towards HFPO for this reaction were 30.5% and 39.2%,

respectively, with the highest selectivity of 51.4% obtained at 35.5% conversion. HFPO production lasted for a duration of 10 hrs, i.e. catalyst activity for the primary product. On the other hand, COF_2 is the part of the products formed throughout the reaction duration. Towards the end of the reaction, shoulder peaks as shown in figure 5.19 were observed near oxygen, COF_2 , and HFP/HFPO from the GC-TCD which is likely to be the emergence of CF_3COF . The formation of this product analytically brought a decrease in HFPO formation. The rapid increase in COF_2 (a toxic gas) and CF_3COF was then observed. More COF_2 was then formed. HFPO formation decreased significantly after which the reaction was stopped since the catalyst stability in the current work was based on the catalyst's activity towards HFPO formation.

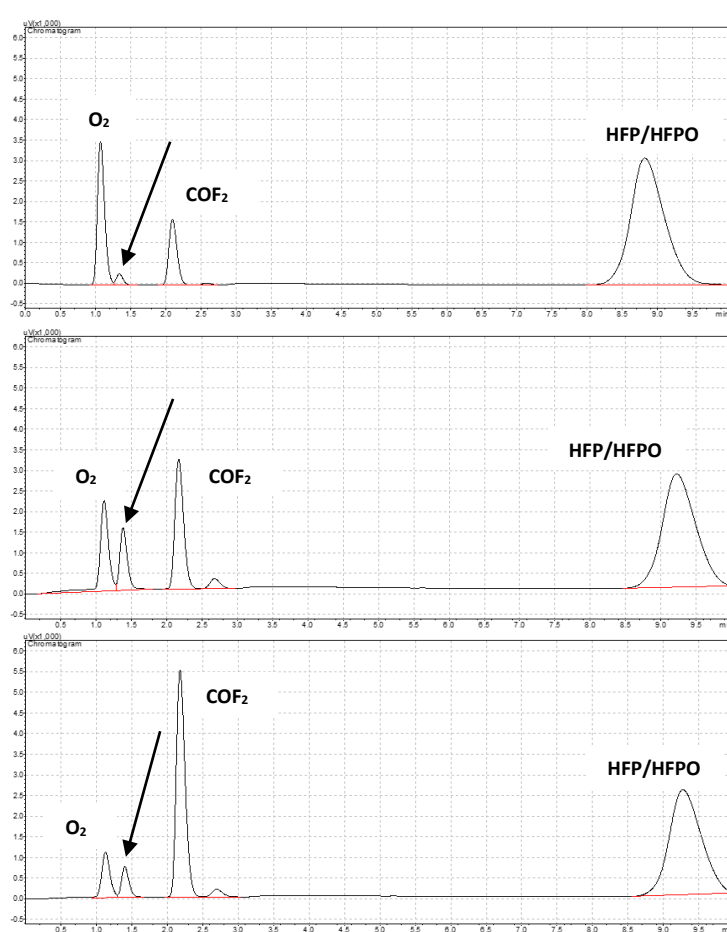


Figure 5.19: GC-TCD chromatograms towards the end of the Cs-CuO/SiO_2 catalyzed HFP epoxidation showing formation of byproducts.

From these observations, the takeaway point is that the catalyst at this stage is not getting deactivated, but inactive towards the formation of the primary product. The catalyst's lifetime inside the reactor is, therefore, more than 10 hours.

Figures 5.20 (a) and (b) present the catalytic results obtained using the cesium doped CuO catalyst. Again, graphs with error bars for the targeted parameters were plotted. The catalyst used in this reaction was prepared via the WI method with an alkali dopant of 0.2 wt% content.

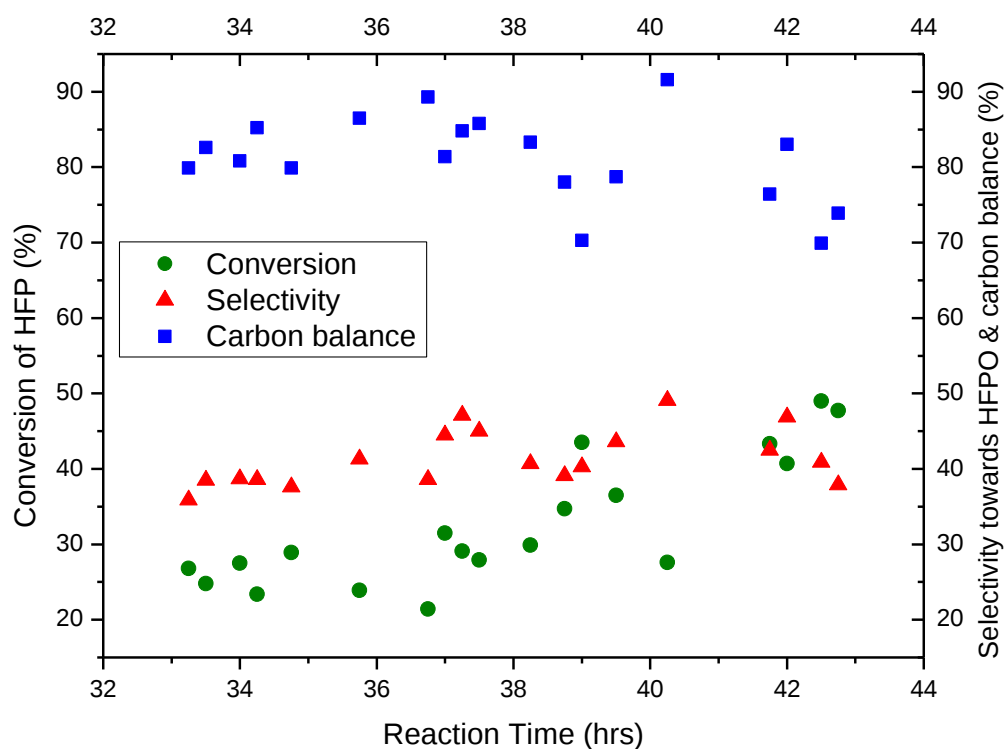


Figure 5.20(a): Conversion, carbon balance, and selectivity towards HFPO as a function of time over 10wt% Cs-CuO/SiO₂ catalyst, 0.2wt% Cs content.

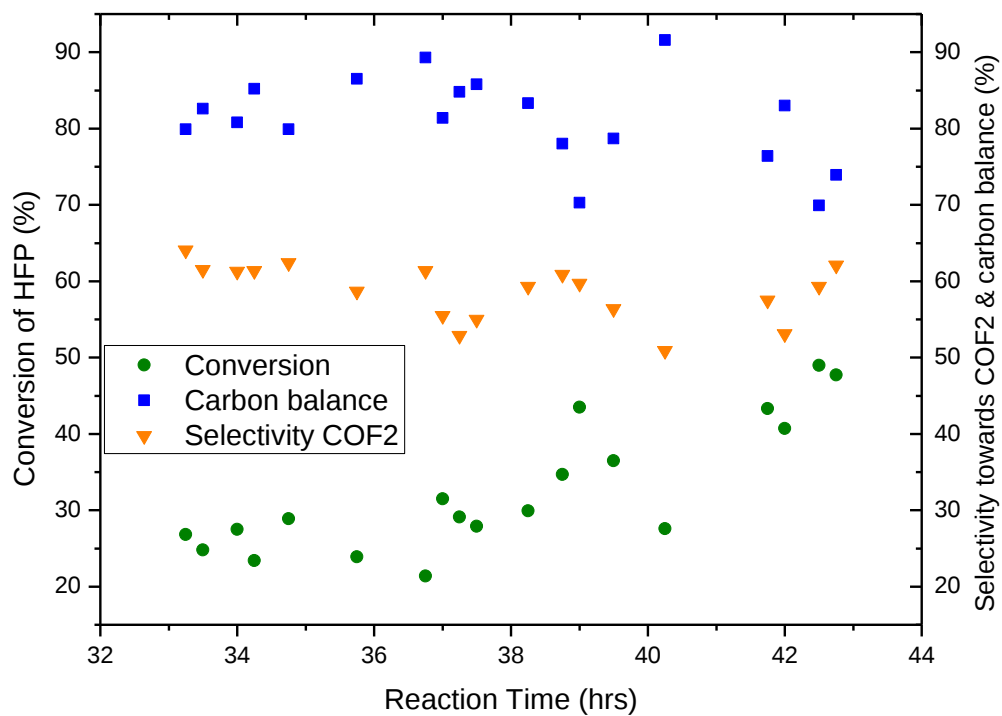


Figure 5.20(b): Conversion, carbon balance, and selectivity towards COF₂ as a function of time over 10wt% Cs-CuO/SiO₂ catalyst, 0.2wt% Cs content.

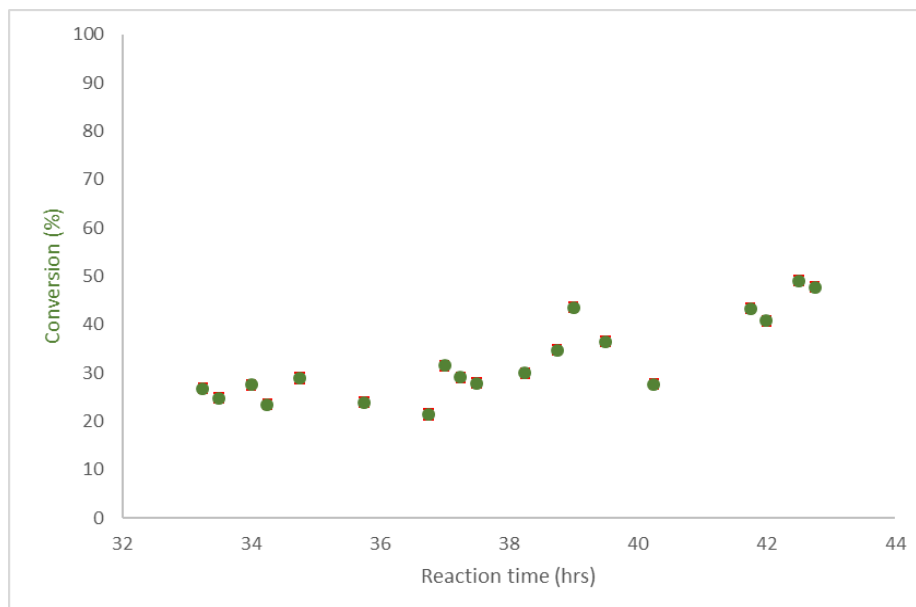


Figure 5.20 (c): Conversion of HFP over 10wt% Cs-CuO/SiO₂ catalyst, 0.2wt% Cs content showing error bars.

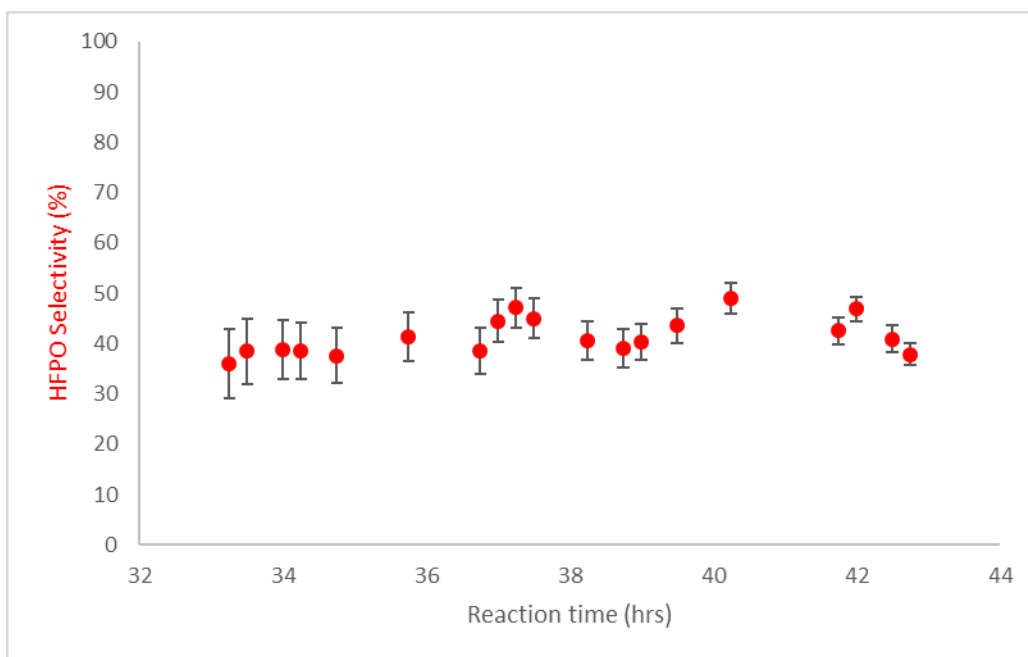


Figure 5.20 (d): HFPO selectivity using 10wt% Cs-CuO/SiO₂ catalyst, 0.2wt% Cs content showing error bars.

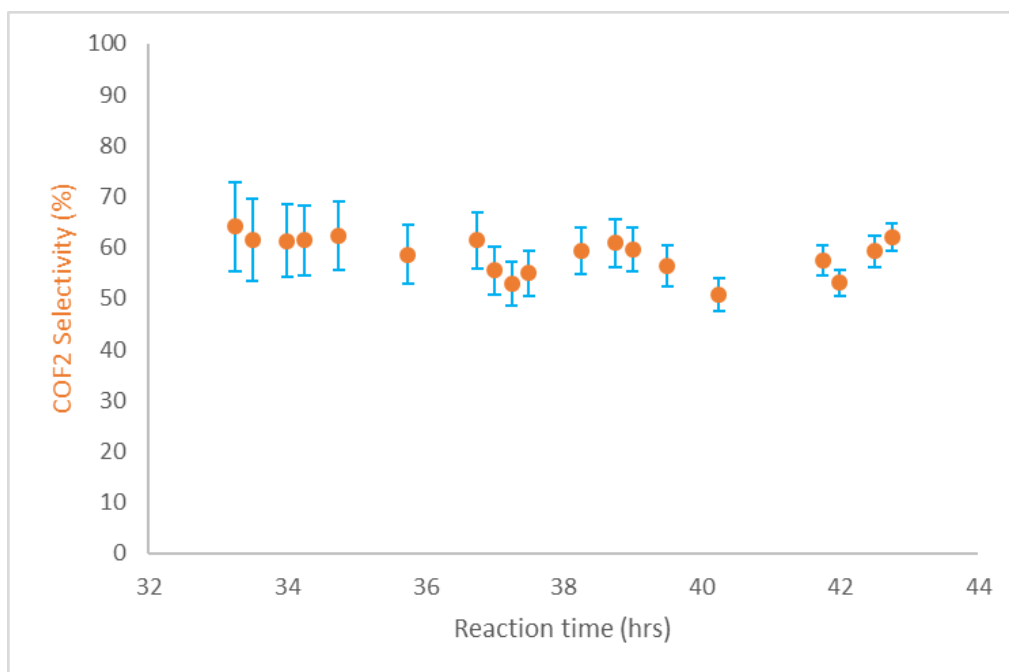


Figure 5.20 (e): COF₂ selectivity using 10wt% Cs-CuO/SiO₂ catalyst, 0.2wt% Cs content showing error bars.

The reaction was carried out under operating conditions for 43.5 hours. The average conversion and selectivity towards HFPO for this reaction were 32.5% and 41.4%, respectively, with the highest selectivity of 49.1% obtained at 27.6% conversion. Again the reaction was stopped

after HFPO production before more of the toxic COF_2 started forming. Similar behaviour was observed for the rest of the reaction runs performed and the results are shown in appendix B. For some reactions, the pressure increase during the reaction was experienced at certain times, hence the variation of results is observed. The similarity for all the reactions is the observation that the carbon balance drops with an increase in the conversion and vice versa. This implies that the starting material is also converted to some other by-products besides the ones that are known and quantified in this reaction. The summary of what results are showing regarding measured parameters of the reaction (descriptive statistics) is shown in tables 5.9 and 5.10 for the two reactions presented above.

Table 5.9: Descriptive statistics for 10 wt% Cs-CuO/SiO₂ (0.2%Cs) WI prepared catalyst

10% Cs-CuO/SiO₂ (0.2%Cs) - WI	Mean	Standard Deviation	Coefficient of Variation	Maximum
<i>Conversion (%)</i>	32.53158	8.50882	0.26156	49
<i>Selectivity HFPO (%)</i>	41.41053	3.69848	0.08931	49.1
<i>Carbon balance (%)</i>	81.12105	5.7945	0.07143	91.6
<i>Selectivity COF₂ (%)</i>	58.6	3.7003	0.06315	64.1

Table 5.10: Descriptive statistics for 10 wt% Cs-CuO/SiO₂ (0.5%Cs) IWI prepared catalyst

10% Cs-CuO/SiO₂ (0.5%Cs) - IWI	Mean	Standard Deviation	Coefficient of Variation	Maximum
<i>Conversion (%)</i>	30.46778	15.58045	0.51137	63.43
<i>Selectivity HFPO (%)</i>	39.15556	10.48854	0.26787	51.4
<i>Carbon balance (%)</i>	89.7037	14.98323	0.16703	114.2
<i>Selectivity COF₂ (%)</i>	60.84444	10.48854	0.17238	97

The variation measure of focus in the current work to discuss the statistics is the coefficient of variation (COV), i.e. measure of the precision of measurements. It is a ratio of the standard deviation to the mean. Conversion and selectivity towards HFPO comparison within and between the experiments are done. Though there is no clear range available that can be used to scale the accuracy, it is generally known that smaller COV is an indication of low variation (less dispersion). From both reactions presented, tables 5.9 and 5.10, the selectivity towards HFPO indicates low variation compared to the respective conversion during the reaction. From this observation, it appears that, between the two parameters, conversion seems to be the most affected one by the changes occurring on the surface of a catalyst as the reaction progresses. Furthermore, in comparing the respective parameters (conversions and selectivities) between

these reactions, low variation from the results obtained by 10 wt% Cs-CuO/SiO₂ (0.2%Cs) WI prepared catalyst. From the overview of all results conducted, the selectivity towards COF₂ constantly appears to be less dispersed for most experiments. Also, though the carbon balance seemed to be varying significantly with conversion during the reaction, it showed low variation (lower than other parameters) for most experiments conducted.

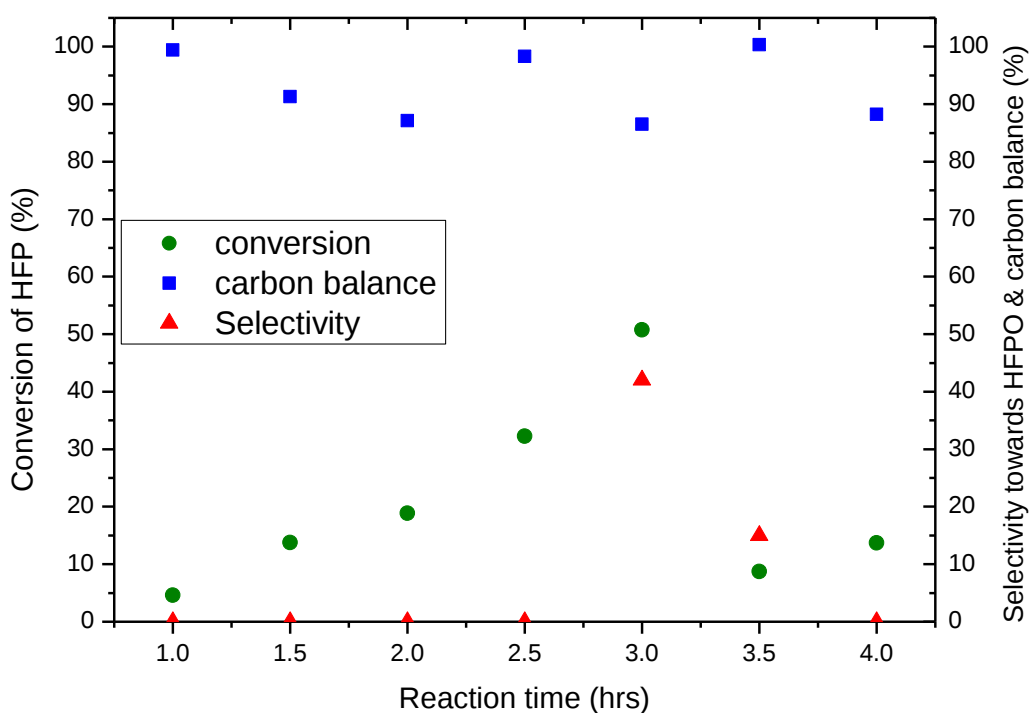


Figure 5.21(a): Conversion, carbon balance, and selectivity towards HFPO as a function of time over 10wt% CuO/SiO₂ catalyst

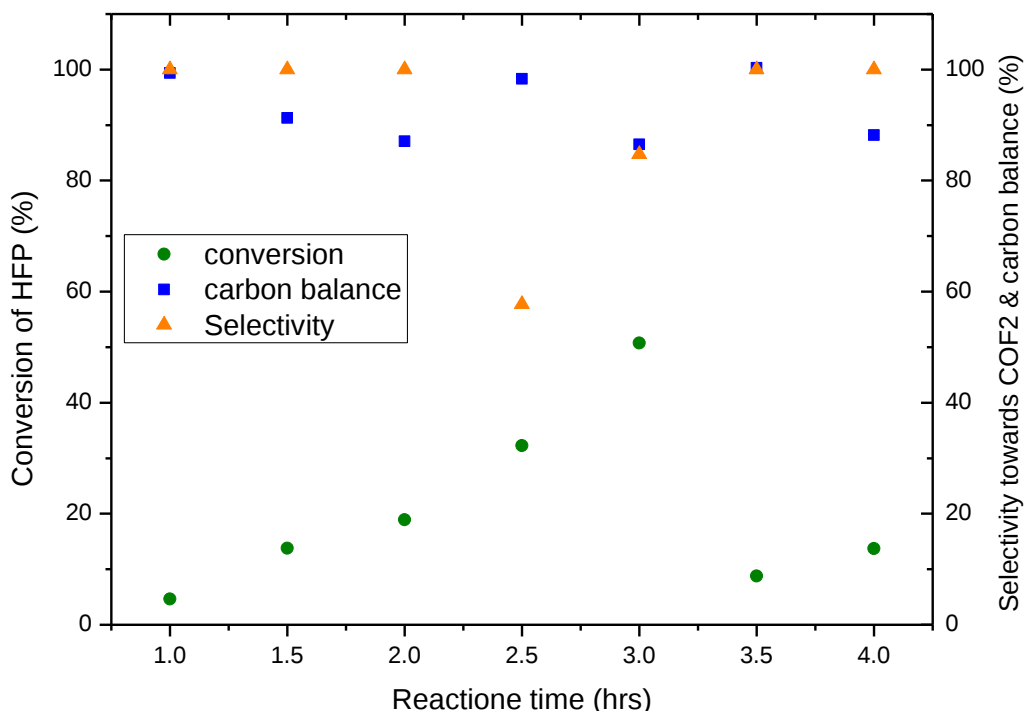


Figure 5.21(b): Conversion, carbon balance, and selectivity towards COF₂ as a function of time over 10wt% CuO/SiO₂ catalyst

The results obtained from the catalyst without the alkali metal dopant (Cs) showed mostly the formation of COF₂ in comparison to HFPO as shown in figures 5.21 (a) and (b). With these reactions, there were complications regarding pressure build-up in the system. This was detected to be from the formation of a sticky solid at the reactor exit and it was also sticking at the reactor walls. Consequently, some other reactions were stopped before completion as the pressure was increasing uncontrollably. Though the reactions with the undoped catalysts were producing mostly COF₂, practically there was evidence that HFPO was forming, but decompose or react further as soon as it is formed.

On the other hand, the experiments with alkali metal-doped catalysts were able to produce the reaction primary product (HFPO) for longer periods and at a good selectivity in comparison to the undoped catalysts. This implies that cesium plays a significant role in the reaction, improving HFPO selectivity. It also provided the stability, that is, the catalyst lifetime in the reactor under reaction conditions. Cs⁺ forms stronger interactions with CuO nanoparticles, and therefore successfully eliminates or decreases the Lewis acidity of the nanoparticles which is the property of the catalyst that has been reported to be responsible for the epoxide

isomerization after it has been formed. According to Jat and Kumar (2019), the epoxides are unstable due to a 3-membered ring, and they can easily isomerize to form carbonyl compounds (COF₂ and CF₃COF in this case) which are more stable than the epoxides. This occurs under acidic conditions by a process known as Meinwald rearrangement. The epoxide reactivity results from strain in a 3-membered ring which is usually relieved when the ring opens. In addition to that, the activity of CuO/SiO₂ as an effective acid catalyst in epoxide ring-opening has been reported by (Zaccheria et al., 2011). The catalyst's acidity property shows that it can promote epoxide conversion into carbonyl compounds. Cs is strongly basic compared to the weakly basic Cu, therefore Cs⁺ ion's presence decreases acidity, stabilizing HFPO, hence increasing selectivity. In addition, the HR-TEM results showed the smaller particle size of the Cs doped catalyst in comparison to the undoped one. According to Younas et al. (2017), the decrease in particle size brings an increase in bond length, band gap, as well as an increase in catalytic efficiency. The increase in bond length is because of the ionic radius of Cs in this case since it increases down the group in the periodic table.

The alkali metal as it is present in small amounts (dopant), practically seems to be achieving this (decreasing catalyst acidity and stabilizing it) at the initial stage of a reaction. There exist many factors associated with the catalyst's non-selectivity towards HFPO and an increase in the formation of the respective by-products, mainly COF₂ and CF₃COF, after some time in a reactor. Firstly, in selective oxidation, a compound-oxygen mixture can generally react along several different pathways in the network of consecutive and competing parallel reactions. Considering that fact and that the fluoride ion liberated from the reaction do react with Cs from the solid catalyst surface to form CsF, there are possible reaction routes to look at: in section 2.1.2 of this work it was mentioned that HFPO undergoes a rearrangement in the presence of an alkali metal catalyst; Warner (1958) provided a convincing proof that inorganic fluorides catalyze the oxidation of HFP, with CsF being the better catalyst in the alkali metal group.



The equations show the products forming in the HFP oxidation over both NaF and CsF catalysts under reaction conditions. Cesium is a large atom with few valence electrons, so, it is more likely to give electrons to small fluorine which has an almost closed shell of electrons, and is therefore likely to attract more to itself. The implication of this for the present research is that, once cesium fluoride is formed in the reaction, the COF₂ and CF₃COF products observed may

be from the HFPO further reactions or the direct oxidation of HFP. Since it is evident that the catalyst's copper is being converted to copper fluoride during the reaction, the activity for HFPO formation decreases, hence the formation of the above-mentioned products is unlikely to be generated from HFPO further reactions.

Overall, it can be confidently said that Cs in this system drives a catalyst into a chemically correct form for bringing about the desired conversion of the starting material as selectively as possible. Its presence enhances the electron transfer process. Cesium, basically modify the electronic structure of CuO since the additional electron is introduced, and the extent to which the structure changes, therefore depends on the amount of the cesium introduced. Based on its position in the periodic table, Cs^+ has a large size and is the alkali metal with d-orbital electrons, therefore improving efficiency in donating electrons to the adsorbed molecules, hence improving the catalyst's property of efficiently adsorbing O_2 in the form of electron-rich species. The d-electrons, just like in copper (a transition metal), do contribute to the surface chemical bond. Moreover, cesium is believed to contribute to the stabilization of the charged oxygen species at the crystal lattice surface to a required degree. Also, according to (Mross, 1983b), in oxidic catalysts, the electron-donating effect of the alkali metal ions increases the reactivity of the oxygen in the $\text{M}=\text{O}$ bond (M = transition metal ion in the catalyst). Thus, doping the catalyst results in an increase in reaction rate. The alkali dopant brought the anticipated effects: increase in selectivity, increase in the activity of a catalyst, prolonged effective catalyst lifetime. This is a good characteristic shown by the catalyst since, for an industrial process, the suitability of a catalyst depends mainly on activity, selectivity, and stability.

Nevertheless, during the reaction, the electron-donating cations ($\text{Cu}^{2+}/\text{Cs}^+$) tend to react with reaction intermediates to form other unwanted products resulting in the decrease in the concentration of these cations, hence the formation of the electrophilic O_2^- promoting the total oxidation, directing the reaction into the unwanted by-products. During EDX elemental identification in the used catalyst surface, the fluorine element was identified. This should probably be Copper(II)fluoride (CuF_2). HFP or COF_2 may have interacted with hydroxyl groups present on the support surface to give hydrogen fluoride (HF), which then reacted with the active component to give CuF_2 . It is therefore evident that a catalyst does undergo some chemical transformations as a result of its interaction with the reaction components (reagents/products). For real solids, Cs-CuO/ SiO_2 in this case, a heterogeneous distribution of surface sites potentially active in the reaction and/or in interface processes is generally

expected. This is mostly because of the defects making up the solid surface which may contribute to the imperfections on the surface.

Figures 5.22 and 5.23 show the exit concentrations of the HFP oxidation reaction products at a fixed reaction temperature, pressure, and HFP/O₂ molar feed ratio.

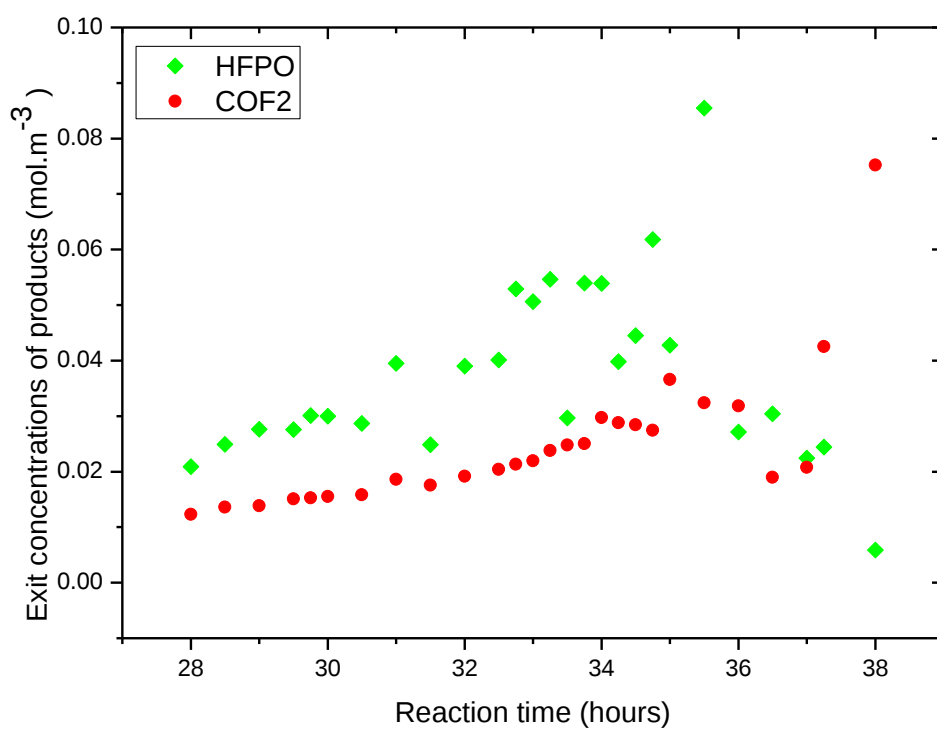


Figure 5.22: Exit concentrations of HFPO and COF₂ as a function of time over IWI prepared 10wt% Cs-CuO/SiO₂ catalyst, 0.5wt% Cs content.

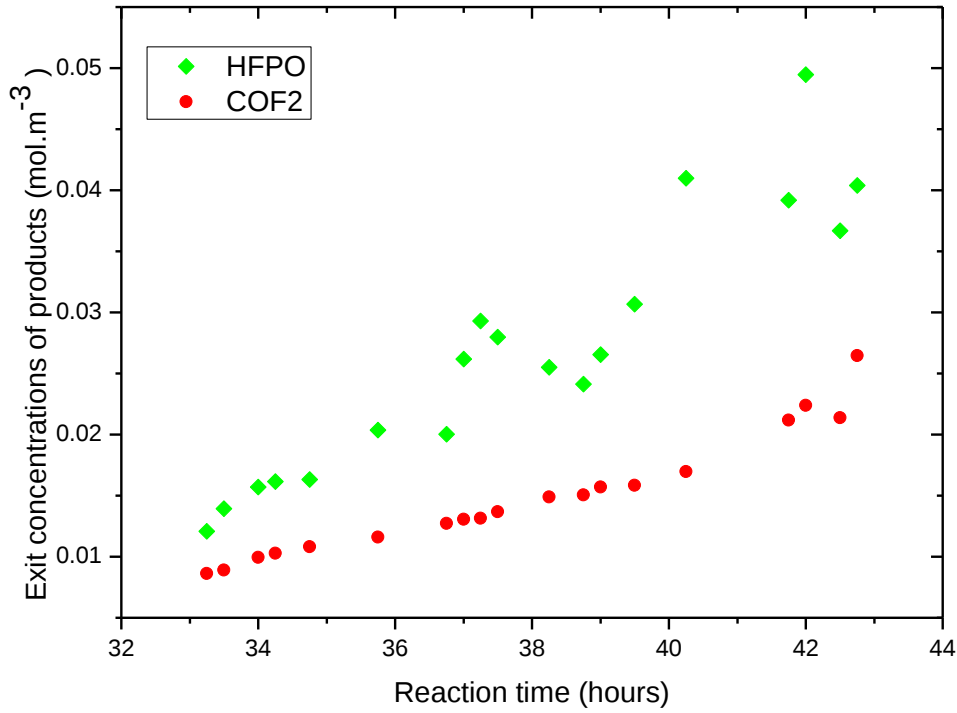


Figure 5.23: Exit concentrations of HFPO and COF₂ as a function of time over WI prepared 10wt% Cs-CuO/SiO₂ catalyst, 0.2wt% Cs content.

The gas-phase concentration of each species at the reactor exit was calculated according to the ideal gas law:

$$C_i^{exit} = X_i^{exit} \frac{P}{RT} \quad (5.4.2)$$

where X_i^{exit} is the exit mole fraction of species i , obtained by chromatographic analysis, and T and P are the reaction temperature and pressure, respectively.

From the figures above and the rest of the experiments conducted (refer to appendix B), the concentrations of the detected products were found to increase with time on stream. From equation 5.4.2, the concentration increase is actually due to the increase in the number of moles of the product. The implication is that the catalyst efficiency in the reactor improves with time. The possible explanation for this is that, at the beginning of the reaction, it is most likely to be the sites near the reactor entrance that will take part in the reaction. The number of sites participating increases further downstream as time continues, which then results in a greater number of moles of the product, hence more product concentration.

The summary of what exit concentration results are showing (descriptive statistics) is shown in tables 5.11 and 5.12 for the two reactions presented above.

Table 5.11: Descriptive statistics of products concentrations for 10 wt% Cs-CuO/SiO₂ (0.5%Cs) IWI prepared catalyst

10% Cs-CuO/SiO₂ (0.5%Cs) - IWI	Mean	Standard Deviation	Coefficient of Variation	Minimum	Maximum
<i>Exit concentration HFPO (mol.m⁻³)</i>	0.03754	0.0162	0.43162	0.0059	0.08551
<i>Exit concentration COF₂ (mol.m⁻³)</i>	0.02471	0.0126	0.50994	0.01234	0.07522

Table 5.12: Descriptive statistics of products concentrations for 10 wt% Cs-CuO/SiO₂ (0.2%Cs) WI prepared catalyst

10% Cs-CuO/SiO₂ (0.2%Cs) - WI	Mean	Standard Deviation	Coefficient of Variation	Minimum	Maximum
<i>Exit concentration HFPO (mol.m⁻³)</i>	0.02692	0.01053	0.39127	0.01209	0.04947
<i>Exit concentration COF₂ (mol.m⁻³)</i>	0.01488	0.00493	0.33167	0.00863	0.02645

The results in the tables show that a 0.2%Cs-WI prepared catalyst has a low variation of HFPO concentration, but it has a smaller HFPO maximum concentration managed in the reaction. For most results in this research using Cs-CuO/SiO₂ catalyst, a low variation of HFPO concentration and high COF₂ maximum concentration were observed.

Table 5.13 shows the results of experiments conducted using the 10 wt% CuO/SiO₂ catalyst (undoped and Cs doped) in the coil type fixed-bed reactor. These are results performed with Davisil grade silica support catalysts only. The results were achieved at 32h⁻¹ GHSV, reaction temperature, and pressure of 180°C and 4.5 bar, respectively. The predominant product was in the reactions was mostly COF₂.

Table 5.13 Results of experiments using 10 wt% CuO/SiO₂ catalyst in the coil-type fixed-bed reactor for the HFP epoxidation.

Catalyst	Temperature (°C)	Feed ratio (v/v)		HFP conversion (%)	HFPO selectivity (%)	COF ₂ selectivity (%)
		HFP	O ₂			
10%CuO/SiO ₂ (0.1%Cs) - WI	180	2	1	32.3	42.3	57.3
10% Cs-CuO/SiO ₂ (0.1%Cs) - IWI	180	2	1	34.6	46.2	53.8
10% Cs-CuO/SiO ₂ (0.1%Cs) - WI	180	2	1	13.4	52.5	47.5
10% Cs-CuO/SiO ₂ (0.1%Cs) - IWI	180	2	1	7.0	50.5	49.5
10% Cs-CuO/SiO ₂ (0.1%Cs) - WI	180	2	1	5.5	13.3	86.7
10% Cs-CuO/SiO ₂ (0.5%Cs) - IWI	180	2	1	35.5	51.4	48.6
10% Cs-CuO/SiO ₂ (0.2%Cs) - WI	180	2	1	27.6	49.1	50.9

5.4.2 Mathematical modelling of a catalytic gas-phase epoxidation of HFP

5.4.2.1 Mechanism

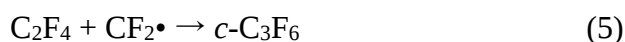
In the HFP epoxidation, as a selective oxidation reaction, the HFP-oxygen mixture can react along several different pathways in the network of competing parallel and consecutive reactions. Dos Santos Afonso et al. (2000), in their work on kinetics and mechanism of thermal gas-phase oxidation of HFP, provided some evidence on the complexity of this system's mechanism. In the present work, to provide a simple kinetic scheme that might be used in modeling the oxidation process, it was desired to combine the elementary steps. For this reaction, the primary step was the insertion of oxygen into the double bond of the alkene to yield the epoxide. The catalytic gas-phase HFP epoxidation mainly gave HFPO, COF₂, and CF₃COF as analytically detectable products with CF₃COF being only formed only when the catalyst shows signs of deactivation. The deactivation in this work refers to the catalyst's inactivity towards the formation of HFPO, the primary product. Consequently, the following two reactions were proposed:



According to Ng et al. (2014), at the reaction temperatures of this work, thermal decomposition of HFPO does occur, hence, the reactions involving the decomposition products also needed to be considered. The decomposition of HFPO above $\approx 150^\circ\text{C}$ gives, as initial products, difluorocarbene (CF_2) and CF_3COF (Ng et al., 2014, Lokhat et al., 2012, Craig Kennedy and B. Levy, 1976):



The difluorocarbene, $\text{CF}_2\bullet$ is in its singlet electronic state (Craig Kennedy and B. Levy, 1976), and the recombination of two difluorocarbenes produce tetrafluoroethylene (TFE), and perfluorocyclopropane (PFCP) arising by addition of a $\text{CF}_2\bullet$ carbene to TFE:



For the present catalytic system, the use of an alkali doped catalyst showed minimal to none detectable peaks of TFE and PFCP. This was observed at all the stages of the catalyst as shown in figure 5.17, unlike CF_3COF which would start showing mostly at the deactivation phase. COF_2 was produced in all phases of a catalyst. There is evidence that this carbonyl compound results from many different routes in the HFP epoxidation reaction to form HFPO. It is a product of direct HFP oxidation, a product of HFPO isomerization as well as the product of HFPO decomposition. However, the further reaction of HFPO (isomerization) as a result of the Lewis acidity property of a catalyst used in this reaction, was eliminated by doping the catalyst with cesium. For this reason, besides decomposition, the direct oxidation of HFP as discussed in section 5.4.1, catalyzed by the alkali fluoride, remains one other possible source of COF_2 :



Moreover, for all experiments conducted, there was always a greater amount of COF_2 than CF_3COF present in the product gas. It is, therefore, proposed that CF_3COF decomposes in the presence of oxygen according to (Lokhat et al., 2012)



Furthermore, based on the reaction surface chemistry discussed in detail in the previous section (section 5.4.1), it was then suggested that the current catalytic reaction investigated is likely to proceed via the Mars Van Krevelen (MVK) redox mechanism which is fully described in section 2.2.2 of this thesis. To recapitulate, the MVK mechanism, which besides the Langmuir-Hinshelwood (LH) and the Eley-Rideal (ER) mechanism is one of the three classical reaction mechanisms in heterogeneous catalysis, differs from the other two mechanisms in that the

catalyst is directly involved in the catalytic reaction. The complete catalytic cycle involving the Oad abstraction by HFP is summarized in Figure 5.24

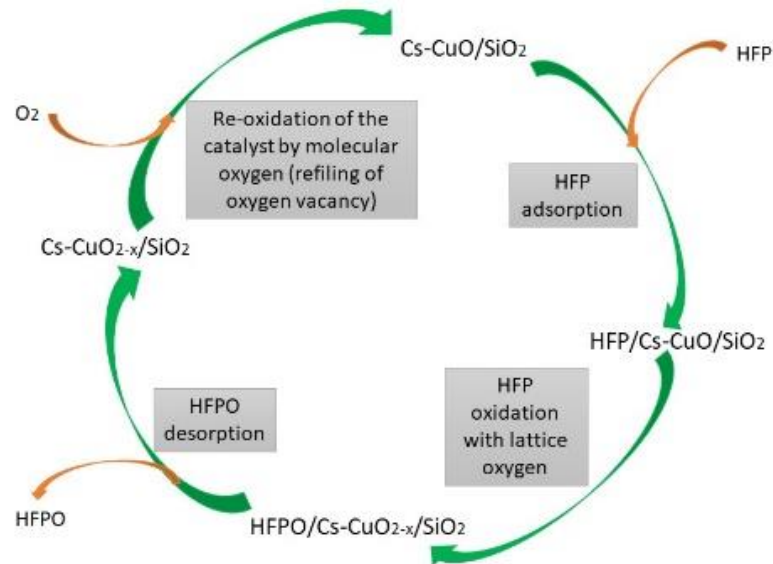
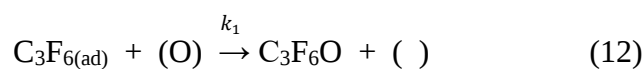
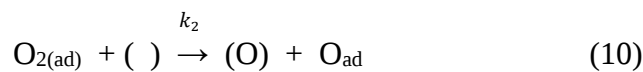
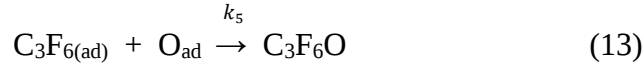


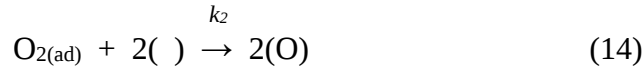
Figure 5.24: Possible catalytic cycle for HFP oxidation on Cs-CuO/SiO₂ based Mars-Van Krevelen redox reaction

The characteristic feature of the MVK mechanism is that at least one component of the catalyst participates in the product formation reaction, eventually leaving the catalyst surface as part of (some of) the reaction products (Widmann and Behm, 2018). The resulting (surface) vacancy is subsequently replenished in the reaction by another reactant. Also, drawing the analogy from Widmann and Behm (2018) of the oxidation of carbon monoxide to produce carbon dioxide, the following mechanism occurring at the catalyst surface for the current work is proposed:

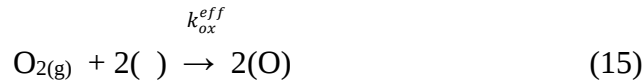




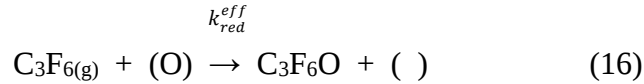
Where () denotes the lattice surface vacancy (an active site), (O) denotes lattice oxygen (the oxidized site), and O_{ad} is an adsorbed atomic oxygen intermediate. The transformation process of the adsorbed molecular oxygen on the surface of a catalyst until the state O^{2-} of lattice oxygen is attained, is discussed in section 5.4.1. The process has been declared slow. Furthermore, according to (Widmann and Behm, 2018), assuming that the reaction of an atomically adsorbed oxygen species with an oxygen vacancy is rather fast ($k_3 > k_2$), equations (10) and (11) can be combined as follows:



Also, since the amounts of adsorbed HFP ($\text{C}_3\text{F}_{6(\text{ad})}$ on Cs-CuO/SiO_2) and adsorbed O_2 ($\text{O}_{2(\text{ad})}$ on oxygen vacancies) are not known within this study, equations (8) and (14) to



And equations (9) and (12) to



Effective rate constants for the formation $k_{\text{ox}}^{\text{eff}}$ and removal $k_{\text{red}}^{\text{eff}}$ of (O) species by reaction with gaseous O_2 and C_3F_6 , respectively, are introduced. Overall, the experimental findings can be described by the following kinetic model based on the elementary reaction steps in the CuO assisted MVK redox mechanism:

$$r_R = \frac{k_{\text{ox}} k_{\text{red}} [\text{O}_2]^n [\text{R}]}{k_{\text{ox}} [\text{O}_2]^n + k_{\text{red}} [\text{R}]} \quad (5.4.18)$$

Where r = reaction rate, k_{ox} = rate constant of oxidation, k_{red} = rate constant of reduction, R refers to the reactant being oxidized, and n is the reaction order with respect to oxygen. Having said that, Vannice (2007), on the other hand, in the analysis of the MVK rate expression, suggested that Hougen-Watson (H-W) and Langmuir-Hinshelwood (L-H) models can provide similar rate equations of which he was convinced they can fit rate data better than MVK

expression. He pursued the analysis by first considering the H-W model assuming desorption of the product as the rate-determining step (RDS). Amongst the H-W expression forms derived, for this work we will consider the rate expression involving only atomic oxygen in the site balance

$$r_R = \frac{k_1 k_2 P_R P_{O_2}}{(k_2^2 P_R^2 + k_1^{1/2} P_{O_2}^{1/2})^2} \quad (5.4.19)$$

L-H rate expressions were believed to represent more realistic models as the RDS was the elementary step occurring on the surface (surface reaction step). Again, we consider the rate expression involving the addition of a single oxygen atom with the assumption of adsorption of R and oxygen on the same type of site (lattice vacancies), then

$$r_R = \frac{k' P_R P_{O_2}}{(1 + K_R P_R + K_{O_2}^{1/2} P_{O_2}^{1/2})^2} \quad (5.4.20)$$

Where $k' = k K_R K_{O_2}$, K_R and K_{O_2} represent adsorption equilibrium constants.

5.4.2.2 Reactor modeling

(a) Governing equations

The distributed nature of the tubular plug flow reactor (PFR) means that variables change with both axial position and time. Therefore the mathematical models consist of several simultaneous nonlinear partial differential equations in time and axial position. The mathematical dynamic model is developed from material and energy balances. For the present work, a small diameter reactor tube was used as well as the nano-sized particle catalyst which has a large external specific surface area. Having mentioned this, the following assumptions are followed for the reactor modeling:

- Plug flow in the bed, no radial profiles
- Neglect axial diffusion in the bed
- Steady-state

Since radial effects are neglected for a plug flow model, the balance differential equations for a fixed-bed catalytic reactor (FBCR) model based on pseudo-homogeneous considerations will be derived. According to Salmi et al. (2011), the characteristic feature of the pseudo homogeneous model is that the diffusion limitations inside the catalyst are neglected.

The rates related to the material balance considering steady-state plug-flow systems will be defined. Since multiple reactions are occurring in the investigated system, a material balance for each chemical species involved in the reaction is defined. According to Constales et al. (2016: p 43), the general equation for a PFR with a solid catalyst of mass W_{cat} and a molar flowrate F_i of component i at steady state is given by:

$$R_i = \frac{dF_i}{dW_{cat}} \quad (5.4.21)$$

Where R_i is the net rate of production of component i per unit mass of catalyst. For all the specific chemical species involved,

$$R_{HFP} = \frac{dF_{HFP}}{dW_{cat}} \quad (5.4.22)$$

$$R_{O_2} = \frac{dF_{O_2}}{dW_{cat}} \quad (5.4.23)$$

$$R_{HFPO} = \frac{dF_{HFPO}}{dW_{cat}} \quad (5.4.24)$$

$$R_{COF_2} = \frac{dF_{COF_2}}{dW_{cat}} \quad (5.4.25)$$

Initial Conditions:

$$\begin{aligned} \text{For } W = 0 : \quad & F_{HFP} = F_{HFP}^0; \\ & F_{O_2} = F_{O_2}^0; \\ & F_{HFPO} = F_{HFPO}^0; \\ & F_{COF_2} = F_{COF_2}^0 \end{aligned}$$

Concentrations along the length of the catalyst bed were given by (Pather and Lokhat, 2014):

$$C_i = C_{Tot}^0 \left(\frac{F_i}{F_{Tot}} \right) \quad (5.4.26)$$

Where C_i is the concentration of species i , C_{Tot}^0 is the total inlet concentration and is assumed to be constant since pressure and temperature are constant in a reactor, and F_{Tot} is the total molar flow rate. Concentrations for all the specific chemical species involved,

$$C_{HFP} = C_{Tot}^0 \left(\frac{F_{HFP}}{F_{Tot}} \right) \quad (5.4.27)$$

$$C_{O_2} = C_{Tot}^0 \left(\frac{F_{O_2}}{F_{Tot}} \right) \quad (5.4.28)$$

$$C_{HFPO} = C_{Tot}^0 \left(\frac{F_{HFPO}}{F_{Tot}} \right) \quad (5.4.29)$$

$$C_{COF_2} = C_{Tot}^0 \left(\frac{F_{COF_2}}{F_{Tot}} \right) \quad (5.4.30)$$

For a system with multiple chemical reactions, the following expression for the total concentration is naturally still valid (Salmi et al., 2011: p 55),

$$C_{Tot}^0 = \frac{P_A}{RT_A} \quad (5.4.31)$$

Where P_A and T_A are actual pressure and temperature on the lines, respectively, and R is the gas constant. The total molar flow rate is given by the sum of the flow rates of the individual species:

$$F_{Tot} = \sum_{i=1}^n F_i$$

Hence, $F_{Tot} = F_{HFP} + F_{O_2} + F_{HFPO} + F_{COF_2}$

Moreover, in the case where the intraparticle diffusional resistance is evaluated and found to be significant, the measurements are made on a catalyst and an observed reaction rate is reported. To account for variations of rates throughout the pellet, the effectiveness factor is introduced. Generally, nano-sized particles have a large external specific surface area which can significantly reduce internal mass transfer. The possible effects of the gradients can be evaluated using the particle effectiveness factor, η . Since the reactor is operating isothermally,

as suggested by (Missen, 1999), a single value of the effectiveness factor may be sufficient to describe thermal and concentration gradients. The overall rate per pellet (or per unit volume or mass of pellet) divided by the rate that would exist if there were no diffusion limitations is defined as the effectiveness factor, η (Harriott, 2003):

$$\eta = \frac{\text{overall reaction rate}}{\text{reaction rate based on external conditions}} \quad (5.4.32)$$

Mathematical form for the first-order case,

$$\eta = \frac{3}{\phi_s} \left(\frac{1}{\tanh(\phi_s)} - \frac{1}{\phi_s} \right) \quad (5.4.33)$$

For spherical particles,

$$\eta = \frac{1}{\phi_s} \frac{(3\phi_s)\coth(3\phi_s)-1}{3\phi_s} \quad (5.4.34)$$

Equation (5.4.33) gives the effectiveness factor for first order, irreversible, isothermal reaction in a sphere (Harriott, 2003). Where ϕ_s is a dimensionless parameter called Thiele modulus which determines how steep the concentration gradient is within the pellet:

$$\phi_s = \frac{R}{3} \sqrt{\frac{k\rho_p S_g}{D_e}} \quad (5.4.35)$$

Equation (5.4.35) gives the Thiele modulus for a first-order reaction occurring over a spherical catalyst pellet. R is the sphere radius, D_e is the effective diffusion coefficient, ρ_p is the density of the catalyst particle, S_g is a specific surface area of the catalyst (m^2/kg), k is an intrinsic reaction rate constant ($\text{m}^3/\text{m}^2/\text{s}$). For an n-th order irreversible reaction,

$$\phi_s = L \sqrt{\frac{n+1}{2} \frac{k\rho_p S_g}{D_e} C_A^{n-1}} \quad (5.4.36)$$

Where $L = R/3$, C_A is the concentration of component A.

The observed rate is related to the intrinsic rate in the following way:

$$r_{obs} = \eta r(C_s) \quad (5.4.37)$$

Where C_s is the concentration of the reactant at the exterior surface of the catalyst particle. If the external mass transfer resistance is ignored (if there is enough turbulence in the gas phase), then C_s is equal to the bulk concentration of the reactant. The observed rate in the current work is given on a weight catalyst basis (mol/kg/s). For the first-order reaction:

$$r_{obs} = \eta k_m C_s \quad (5.4.38)$$

Where $k_m = kS_g$ is the intrinsic reaction rate constant (m³/kg/s).

The relative significance of pore-diffusion resistance can be assessed by a criterion, known as the Weisz-Prater criterion, which requires only a single measurement of the rate, together with knowledge of D_e , L_e , C_{As} , and the order of the surface reaction (Missen, 1999: p 208)

$$C_{WP} = \frac{(n+1)(-r)_{obs} \rho_c L_e^2}{2 D_e C_{As}} \quad (5.4.39)$$

Where D_e is an effective diffusivity coefficient, L_e is an effective diffusion-path-length parameter, C_{As} is the concentration of component A at the surface of the pellet. Equation (5.4.39) represents the Weisz-Prater parameter (C_{WP}) for an nth-order surface reaction of species A.

5.4.2.3 Kinetic model identification

Apart from reaction 1 (which is reported to be following the MVK redox mechanism, thereby can be represented by the corresponding model), the individual rates of the reactions in section 5.4.2.1 were defined as follows:

$$r_2 = k_2 C_{C_3F_6} C_{O_2} \quad (5.4.40)$$

$$r_3 = k_3 C_{C_3F_6O} \quad (5.4.41)$$

$$r_4 = k_4 C_{CF_2}^2 \quad (5.4.42)$$

$$r_5 = k_5 C_{CF_2} C_{C_2F_4} \quad (5.4.43)$$

$$r_6 = k_6 C_{CF_3COF} C_{O_2} \quad (5.4.44)$$

It should be noted that all the reactions were considered to be irreversible. The net rates of change for each component were given by the following equations:

$$r_{HFP} = -\frac{k_{ox}k_{red}[O_2]^n[HFP]}{k_{ox}[O_2]^n + k_{red}[HFP]} - k_2 C_{HFP} C_{O_2} \quad (5.4.45)$$

$$r_{O_2} = -\frac{1}{2} \frac{k_{ox}k_{red}[O_2]^n[HFP]}{k_{ox}[O_2]^n + k_{red}[HFP]} - k_2 C_{HFP} C_{O_2} - k_6 C_{CF_3COF} C_{O_2} \quad (5.4.46)$$

$$r_{HFPO} = \frac{k_{ox}k_{red}[O_2]^n[HFP]}{k_{ox}[O_2]^n + k_{red}[HFP]} - k_3 C_{HFPO} \quad (5.4.47)$$

$$r_{COF_2} = k_2 C_{HFP} C_{O_2} + 2k_6 C_{CF_3COF} C_{O_2} \quad (5.4.48)$$

Table 5.14 Variables and parameters of the 1-D PFR model

Variable/Parameter	Symbol	Units/value
Molar flowrate of component i	F_i	mol.s ⁻¹
Catalyst mass	W_{cat}	0.09 kg
Concentration of species i	C_i	mol.m ⁻³
Total inlet concentration	C_{Tot}^0	181.538 mol.m ⁻³
Total molar flowrate	F_{Tot}	9.082x10 ⁻⁵ mol.s ⁻¹
Actual pressure on the lines	P_A	4.5x10 ⁵ Pa
Actual temperature on the lines	T_A	298.15 K
Gas constant	R	8.314 m ³ .Pa.mol ⁻¹ .s ⁻¹
Rate constant of oxidation	k_{ox}	mol.kg ⁻¹ .s ⁻¹
Rate constant of reduction	k_{red}	mol.kg ⁻¹ .s ⁻¹
Reaction order	n	
Reaction rate constants of individual reactions	k_2, k_3, k_4, k_5, k_6	m ³ .kg ⁻¹ .s ⁻¹
Bulk density	ρ_b	g/cm ³
Cross-sectional area	A_c	cm ²
Length of the reactor	W	cm

The kinetic parameters appearing in the rate equations for reactions 1, 2, and 7 were identified using the procedures described in this section. The kinetic parameters were obtained by least-squares regression of experimental and predicted mole fractions of reaction products from the

experiments. The parameters were estimated by minimizing the sum of squares of residuals (SSR). The objective function used was defined as:

$$SSR = \sum_{i=1}^n (N_i - y_i)^2$$

Where N_i is the experimental value (measured variable) and y_i is the estimated or calculated value of the individual species. The predicted mole fractions were calculated from models developed and implemented through the algorithm shown in figure 5.25. All computational procedures were programmed using MATLAB® (version R2016b, The Mathworks, Inc.). The MATLAB® script files are presented in Appendix E.

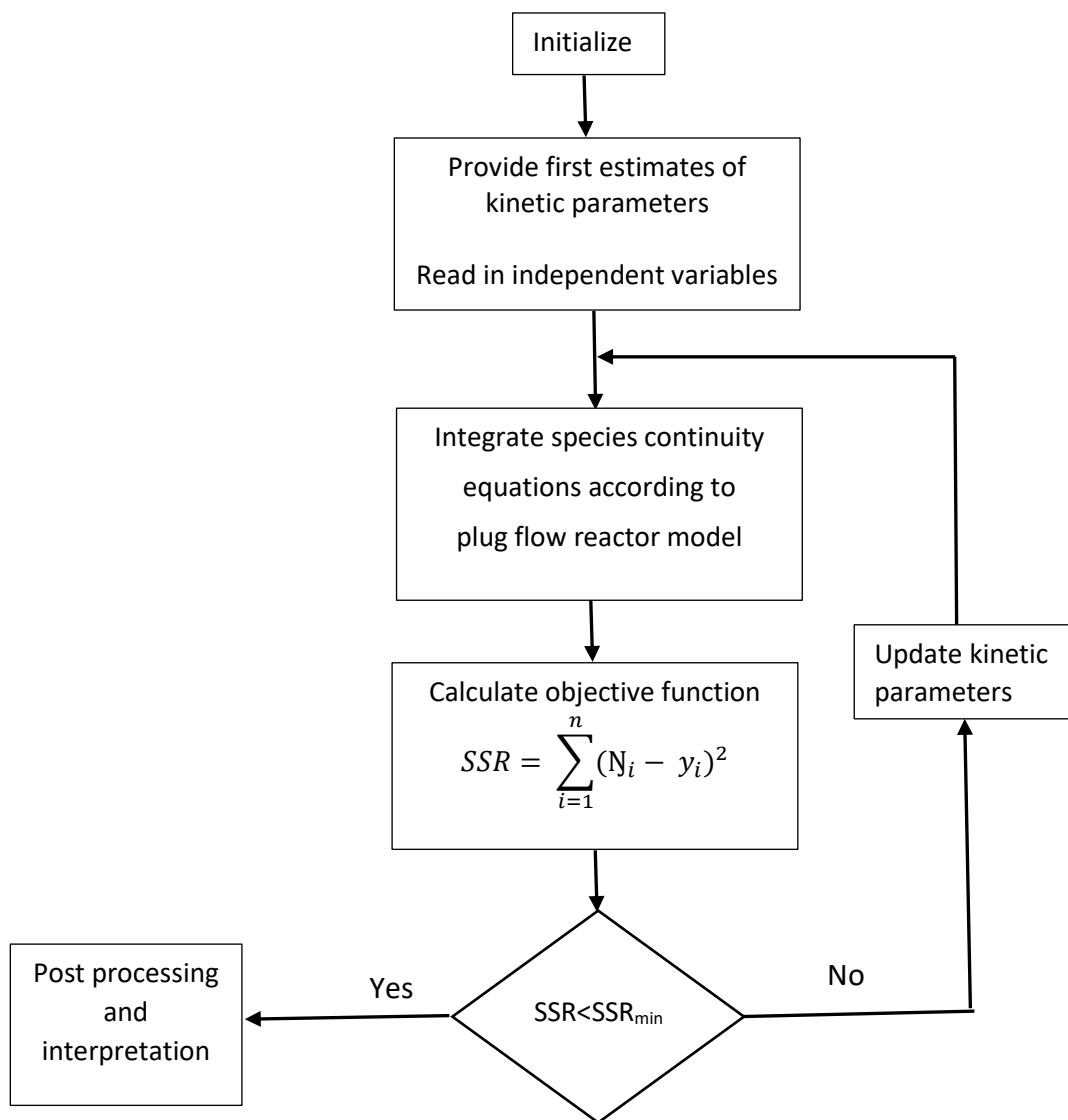


Figure 4.25: A flow diagram of the computational algorithm for kinetic parameter identification.

The calculation was initialized by firstly providing kinetic parameters estimates and reading in the measured dependent and independent variables. Integration of the system of ODE's, developed in section 5.4.2.2 describing the component material balances, was then performed using the MATLAB® function ode15s. This is a multistep solver that is particularly useful for stiff problems. Based on the measured and predicted exit mole fractions, the objective function was calculated. Depending on whether the predetermined tolerance on the objective function was met, the optimization was terminated, otherwise, the kinetic parameters were updated according to the chosen domain-searching algorithm for the next iteration. The built-in MATLAB® function lsqnonlin was selected as the optimization algorithm.

The results of each simulation were compared using a parity plot. A parity plot is an easy means of evaluating the fit of a model by comparing predicted values of response and actual values of the same response.

Furthermore, there is an increase in overall conversion with time. This is denoted by the increase in the activity of HFPO formation during the reaction progress. The selectivity to HFPO first increases and then rapidly decreases. The initial increase in HFPO selectivity (corresponding to an increase in the rate of the primary reaction), is due to the gradual build-up of O^{2-} species on the surface, which are required for the partial oxidation route. The decrease in HFPO selectivity (corresponding to a decrease in the rate of the primary reaction and an increase in the rate of the secondary or total oxidation route) is due to the gradual conversion of copper to copper fluoride, the latter which is responsible for the formation of electrophilic O_2^- promoting total oxidation. These two processes occur in parallel.

The conversion of copper to copper fluoride was observed from the used catalyst EDX analysis, section 5.3.1 of this thesis, which showed fluorine element dispersed on the catalyst surface as a result of the gas-solid reaction. This brings a decrease in the activity of the reaction producing HFPO (reaction 1) and increases the reactivity for the copper fluoride formation. In brief, two things are occurring:

- (i) an increase in the activity for the reaction (1)
- (ii) a decrease in the activity for the reaction (1) coupled with the increase in the activity for the reaction producing copper fluoride.

This is what the kinetics proposed for this work is presenting.

In further explaining the fundamental mechanism as represented by the model: there is activation which is described as the build-up of the oxygen species on the surface (equation 5.4a) and there is also deactivation which represents the change from copper to copper fluoride that accelerates the formation of electrophilic oxygen that induces total oxidation. The main reaction (1) is affected by both activation and deactivation simultaneously. The reaction producing copper fluoride is only affected by deactivation. To incorporate the processes described above into the model, the classical representations of activation and deactivation functions were used:

$$Activation = (1 + k_a t^n) \times rate$$

$$Deactivation = \frac{1}{(1 + k_d t^m)} \times rate$$

Where k_a and k_d are activation and deactivation rate constants, respectively. It must be noted that the increase in the secondary reaction rate is inversely proportional to the decrease in the primary reaction rate. In the present model, as per the experimental results, the fact that kinetics is different at each time point is considered, hence the reaction time is included in the present simulation. The reaction rates and rate constants for these reactions together with the activation (k_a) and deactivation (k_d) rate constants are shown in table 5.15.

Table 5.15 Estimated rate constants and reaction rates for the catalytic gas-phase oxidation of HFP (0.2%Cs catalyst) obtained at the temperature of 180 °C using the plug flow reactor model.

Parameter	Units	Rate constant value
k_{ox}	$\text{mol.kg}^{-1}.\text{s}^{-1}$	1.640×10^{-9}
k_{red}	$\text{mol.kg}^{-1}.\text{s}^{-1}$	3.017×10^{-9}
k_2	$\text{m}^3.\text{kg}^{-1}.\text{s}^{-1}$	6.22×10^{-12}
k_6	$\text{m}^3.\text{kg}^{-1}.\text{s}^{-1}$	2.3450
k_a	s^{-1}	1.560×10^{-1}
k_d	s^{-1}	5.600×10^{-3}
r_{HFP}	$\text{mol.kg}^{-1}.\text{s}^{-1}$	-1.2376×10^{-7}
r_{O2}	$\text{mol.kg}^{-1}.\text{s}^{-1}$	-9.8231×10^{-8}
r_{HFPO}	$\text{mol.kg}^{-1}.\text{s}^{-1}$	8.6811×10^{-8}
r_{COF2}	$\text{mol.kg}^{-1}.\text{s}^{-1}$	1.0846×10^{-7}
r_{CF3COF}	$\text{mol.kg}^{-1}.\text{s}^{-1}$	1.1904×10^{-9}

Figure 5.26 shows parity and residual plots of the single reaction for each of the reaction species based on the estimated rate constants and corresponding residual plots. The regression statistics related to the individual estimated model coefficients are presented in Table 5.16.

Table 5.16 Regression statistics for the catalytic epoxidation reaction species mole fraction response models

<i>Compound name</i>	<i>SSE</i>	<i>R-square</i>	<i>Adj R-square</i>	<i>RMSE</i>
<i>COF₂</i>	1.1696×10^{-4}	0.9657	0.9637	0.0026
<i>HFPO</i>	0.0011	0.6782	0.6593	0.0079
<i>HFP</i>	8.367×10^{-4}	0.7645	0.7507	0.0070
<i>O₂</i>	4.7102×10^{-4}	0.7955	0.7835	0.0053

The model coefficients were estimated with satisfactory R^2 values. A very high positive correlation was obtained for COF₂.

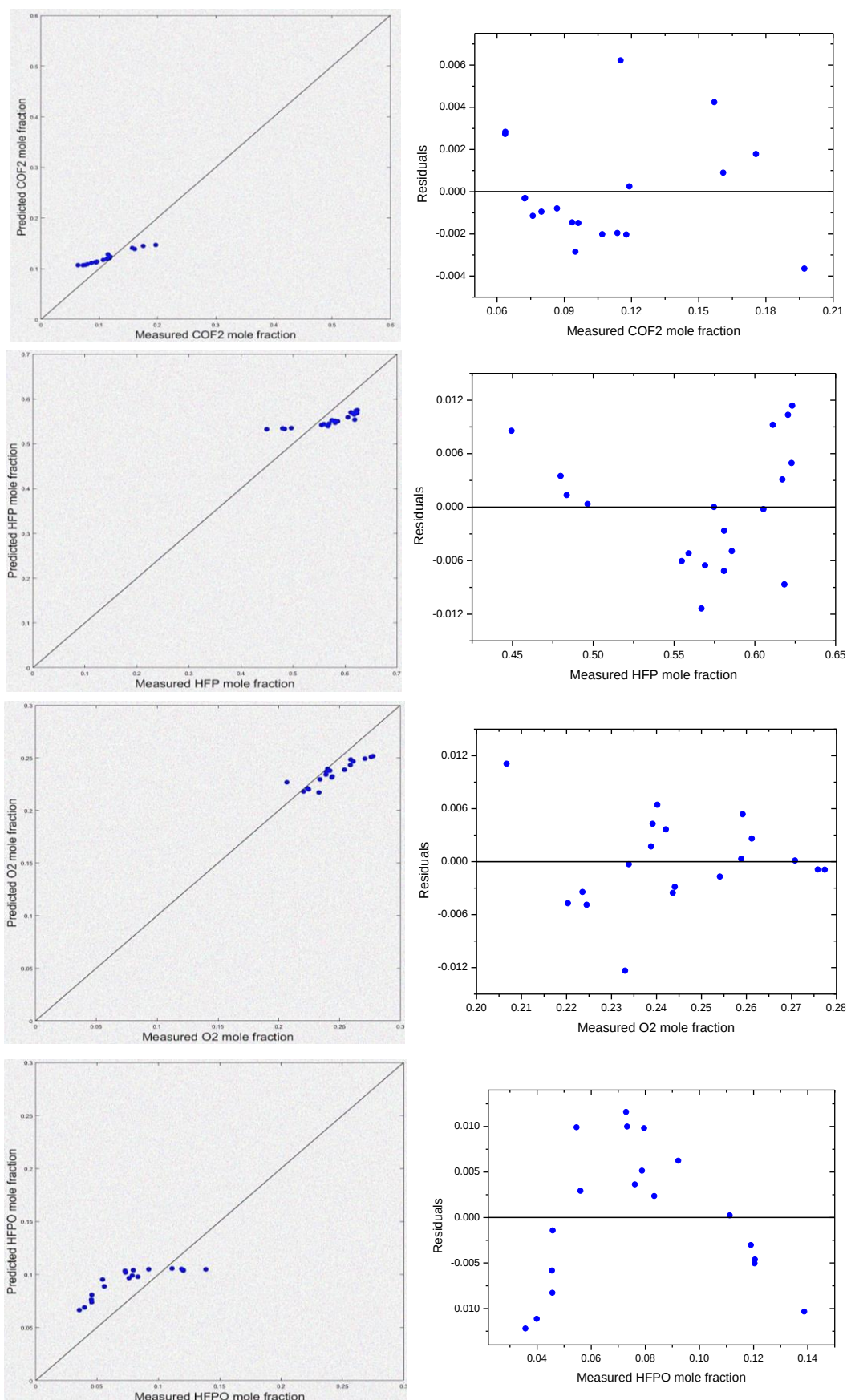


Figure 5.26: Parity and residual plots for individual species at 180°C (Plug flow reactor model). Residuals defined as the difference between measured and predicted values

Though HFP and O₂ were obtained at a lesser correlation strength but were satisfactory high. HFPO resulted in a moderate positive correlation. The difference between the observed values and predicted values as indicated by SSE is relatively small for the studied compounds. In addition, in assessing the model fit, low values of RMSE (root mean square error) indicate a better model fit. It is necessary that the kinetic model be able to reflect all essential aspects of the process mechanism. Though there was no consistency in the results for the catalyst activity period studied, the kinetic model results were satisfactory to draw clear conclusions. The good knowledge and control of the kinetic process may bring considerable improvement of the quality of the catalysts and optimization of the regimes of their use.

The catalyst used in this research contains pores, so, it is only wise to evaluate the pore diffusion effect within the particle to avoid errors in interpreting the experimental kinetic data. The catalytically active sites are located in the pore network, hence the diffusion of molecules in confined spaces is more likely to play a certain role in the observed reaction rate. Additionally, as has been highlighted in section 2.2.2.1 of this work, diffusion is amongst the sequence of elementary steps of the catalytic cycle used to describe the mechanism of the reactions of this kind. Mass is transported in a porous medium by a variety of mechanisms which include ordinary diffusion amongst many. According to Satterfield (1996), Knudsen diffusion occurs when the collisions of molecules with the pore walls are more important and dominant compared with molecular collisions in the free space of the pore. Knudsen diffusivity of component A can be calculated using the formula:

$$D_{KA} = 9700 \times R_{pore} \sqrt{\frac{T}{M_A}} \quad (5.4.49)$$

where R_{pore} is the pore radius in cm, T is the temperature in degrees Kelvin, and M_A is the molecular weight of A. The Knudsen diffusivity for the reaction components can then be calculated as follows:

HFP:

$$D_{KA} = 9700 \times 3.47 \times 10^{-6} \sqrt{\frac{453.15}{150.03}} = 0.058497 \text{ cm}^2 \cdot \text{s}^{-1}$$

O₂:

$$D_{KA} = 9700 \times 3.47 \times 10^{-6} \sqrt{\frac{453.15}{32}} = 0.12666 \text{ cm}^2 \cdot \text{s}^{-1}$$

The molecular diffusivity, D_{AB} , can be calculated using the Fuller, Schettler, and Giddings equation, which, according to Seader et al. (2010), is of greater accuracy and ease of use as it retains the form of the Chapman–Enskog theory but utilizes empirical constants derived from experimental data:

$$D_{AB} = \frac{0.00143T^{1.75}}{PM_{AB}^{\frac{1}{2}}[(\Sigma_V)_A^{\frac{1}{3}} + (\Sigma_V)_B^{\frac{1}{3}}]^2} \quad (5.4.50)$$

Where D_{AB} is in cm^2/s , P is in atm, T is in K,

$$M_{AB} = \frac{2}{\left(\frac{1}{M_A}\right) + \left(\frac{1}{M_B}\right)}$$

Σ_V = Summation of atomic and structural diffusion volumes.

To calculate the molecular diffusivity of the present system,

$$\begin{aligned} D_{AB} &= \frac{0.00143 \times 453.15^{1.75}}{4.4411535(52.74910729)^{\frac{1}{2}}_{AB}[(3 \times 15.9 + 6 \times 14.7)^{\frac{1}{3}} + (16.3)^{\frac{1}{3}}]^2} \\ &= 0.03348 \text{ cm}^2 \cdot \text{s}^{-1} \end{aligned}$$

To estimate the effective diffusivity, the following formula is used:

$$D_{eA} = \frac{\varepsilon_p}{\tau} D_{mA} \quad (5.4.51)$$

Where ε_p is the particle porosity, τ is the tortuosity, D_{mA} is the diffusivity of each component through a gaseous mixture in pores.

$$\frac{1}{D_{mA}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}} \quad (5.4.52)$$

From equation (5.4.52),

$$\begin{aligned} D_{HFP} &= 0.020797 \text{ cm}^2 \cdot \text{s}^{-1} \\ D_{O_2} &= 0.026480 \text{ cm}^2 \cdot \text{s}^{-1} \end{aligned}$$

Satterfield (1996: p 501) revealed that in the measurement of the variety of catalysts, the values of the tortuosity range from 2 to 7 and that of the porosity from 0.3 to 0.7. Furthermore, (Fogler,

2006) highlighted that the typical values of the tortuosity and porosity are 3.0 and 0.4, respectively. Therefore, from equation (5.4.51) we get

$$D_{eHFP} = \frac{0.4}{3.0} \times 0.020797 = 2.7729 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1} = \mathbf{2.7729 \times 10^{-7} m^2 \cdot s^{-1}}$$

$$D_{eO_2} = \frac{0.4}{3.0} \times 0.026480 = 3.5307 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1} = \mathbf{3.5307 \times 10^{-7} m^2 \cdot s^{-1}}$$

From equation (5.4.39), the Weisz-Prater parameter for the first-order surface reaction results in the following equation:

$$C_{WP} = \frac{-r_{(obs)} \rho_c R^2}{D_e C_{As}} \quad (5.4.53)$$

HFP:

$$C_{WP} = \frac{-(-1.2376 \times 10^{-7}) \times 1392 \times (3.47 \times 10^{-9})^2}{2.7729 \times 10^{-7} \times 96.62} = \mathbf{7.7424 \times 10^{-17} \ll 1}$$

O₂:

$$C_{WP} = \frac{-(-9.8321 \times 10^{-8}) \times 1392 \times (3.47 \times 10^{-9})^2}{3.5307 \times 10^{-7} \times 39.41} = \mathbf{1.1843 \times 10^{-16} \ll 1}$$

From the calculations above, it can be seen that the Weisz-Prater parameter is much less than 1 for both reactants. This is an implication that there are no significant internal diffusion limitations, hence no significant concentration gradient existing within the pellet. Moreover, the square of the pore radius is directly proportional to the assessing parameter. The results then witness the fact that smaller particles are a better option for such heterogeneous catalytic reactions as they also provide a short path for diffusion, hence minimizing the internal diffusion limitations.

Chapter Six

Summary, Conclusion, and Recommendations

6.1. Summary and Conclusion

This project involved the synthesis, characterization, and testing of copper oxide catalysts for HFP epoxidation. Using the impregnation method, copper oxide supported on alumina ($\text{CuO}/\text{Al}_2\text{O}_3$) and silica (CuO/SiO_2) were successfully prepared with the loading of 10 wt% of copper. The catalysts were characterized using XRD, BET, TEM, and SEM-EDX techniques. The characterization results of the fresh catalysts confirmed the correct prepared material. In addition, characterization results of the used catalysts allowed a good comparison of the structure and morphology of the catalysts. From the preliminary experiments using both alumina and silica-supported catalysts, the reaction operating conditions were identified to be 180 °C temperature, 4.5 bar pressure, 32 h⁻¹ GHSV, and 2:1 HFP:O₂ ratio. 10 wt% CuO/SiO_2 catalyst was used for the main experiments of the fluorinated alkene epoxidation. It was selected based on its proven ability to catalyze the partial oxidation of perfluorocarbons as shown in Chapter 2 of this thesis.

The results obtained using the catalyst without the alkali metal dopant (Cs) showed mostly the formation of COF_2 in comparison to HFPO. On the other hand, the experiments with alkali metal-doped catalysts produced the reaction primary product (HFPO) for longer periods and at superior selectivity in comparison to the undoped catalysts. Cesium improved HFPO selectivity and also provided the stability, that is, the catalyst's lifetime in the reactor under reaction conditions was increased. At a relatively low temperature of 453 K, HFPO selectivities between 46.2% and 52.5% were obtained from the Cs doped catalysts. The highest HFPO selectivity was obtained at the HFP conversion of 13.4% under reaction conditions.

Furthermore, it is proposed that epoxidation occurs via the Mars-van-Krevelen redox mechanism. A kinetic model was developed based on the mechanism. Nonlinear regression techniques, through minimizing the sum of squares of the residuals was used to estimate the parameters of the various rate expressions. The results of the model show that quite a good

agreement has been reached between the experimental and the theoretical results. The parity plots of the reaction species based on the estimated rate constants displayed a satisfactory correlation.

As presented by the proposed mechanism, the activity of HFPO formation decreases as the reaction progresses due to the chemical deactivation of the solid catalyst. The main reaction is affected by simultaneous activation and deactivation processes taking place. The observed difference in numerical values of rate constants probably expresses the influence of catalyst composition on the activity and the adsorption character towards the components of the reaction mixture. Also, this difference is likely to express the influence of the multi reactions taking place at the catalyst surface. Catalyst surface experienced chemical transformations as the buildup of O^{2-} species that is required for the partial oxidation and the conversion of copper to copper fluoride responsible for the formation of O_2^- which promotes total oxidation. Since the catalyst takes part in the reaction, it cannot be re-used and should be removed after about 43 hours and be replaced with a newly prepared catalyst. Overall, the aims and objectives of this study were met as the mechanism in which the reaction undergoes was successfully proposed, and the identified kinetic model representing experimental data was satisfactory.

6.2. Recommendations

The results obtained in this study provided sufficient information for a strong foundation into the use of copper oxide catalysts for selective oxidation of fluorinated compounds. Even though interesting results were obtained throughout this study, further investigation is still necessary to achieve a good understanding of the reaction nature, mechanism as well as reaction kinetics. This can be possibly achieved via the following recommendations:

- Method of catalyst preparation – the ultrasonic impregnation method is an alternative method that can be explored in this research. Ultrasound-assisted impregnation is reported to improve the surface area and pore volume. Compared to the standard method, the process can promote the penetration of impregnating liquid into the pores. The understanding is that the process promotes mass transfer and uptake of the impregnation liquid. Better dispersion of the active component particles could be achieved with higher adsorption capacities. Moreover, with ultrasonic impregnation, the aging time (impregnation time) is reduced.

- Mechanism – as was mentioned in chapter 5 of this thesis, the reaction is affected by catalyst deactivation occurring at the same time as the primary reaction. It is therefore recommended to investigate all the possible deactivation processes taking place as the deactivation causes are mostly threefold, that is, chemical, mechanical, and thermal. These have many different decay mechanisms under them. The experiments undertaken to investigate these processes will not only assist in more understanding of the reaction mechanism but also in minimizing and prevention of such decay mechanisms, hence increasing or extending catalyst stability (lifetime of a catalyst inside a reactor). There exist principles of prevention provided that the deactivation process is accurately identified and well understood. In addition, the knowledge of this will also show the direction of possible catalyst regeneration.

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Appendix A. Instrument calibrations

Gas Chromatography plots:

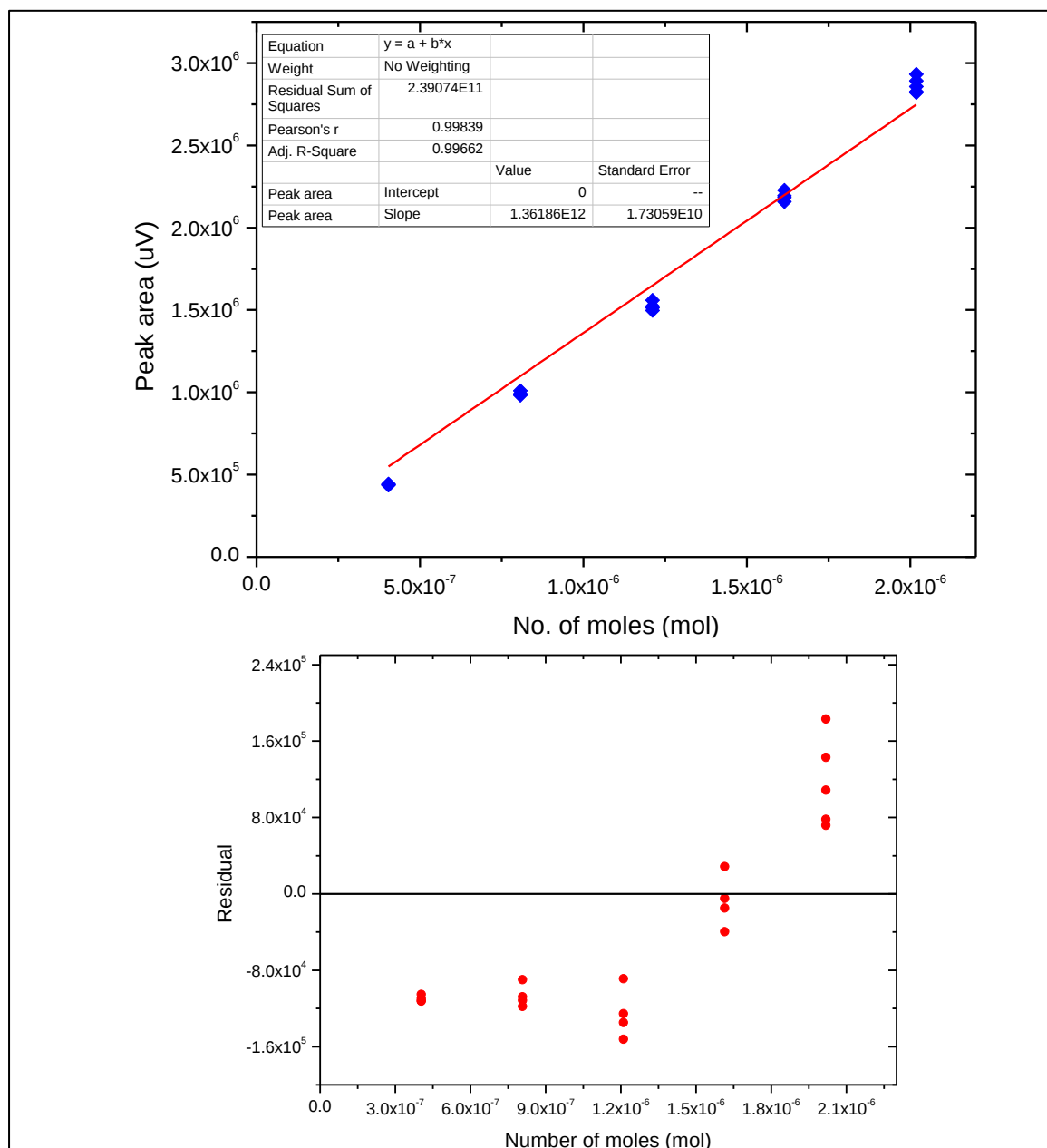


Figure A.1: Shimadzu G.C. 2010 FID calibration plot of HFP and residual deviation plot defined as the relative difference between measured and predicted value.

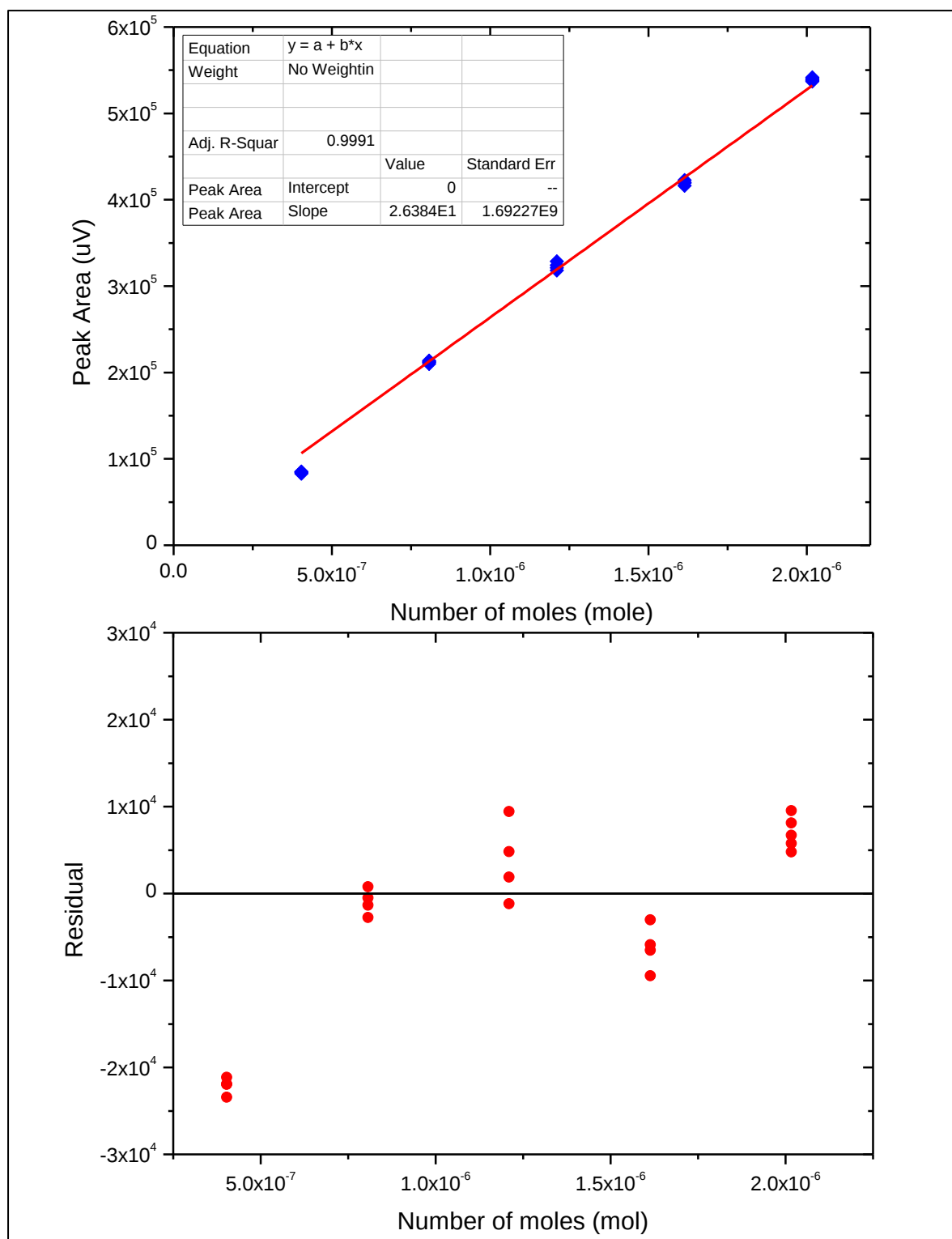


Figure A.2: Shimadzu G.C. 2010 FID calibration plot of HFPO and residual deviation plot defined as the relative difference between measured and predicted value.

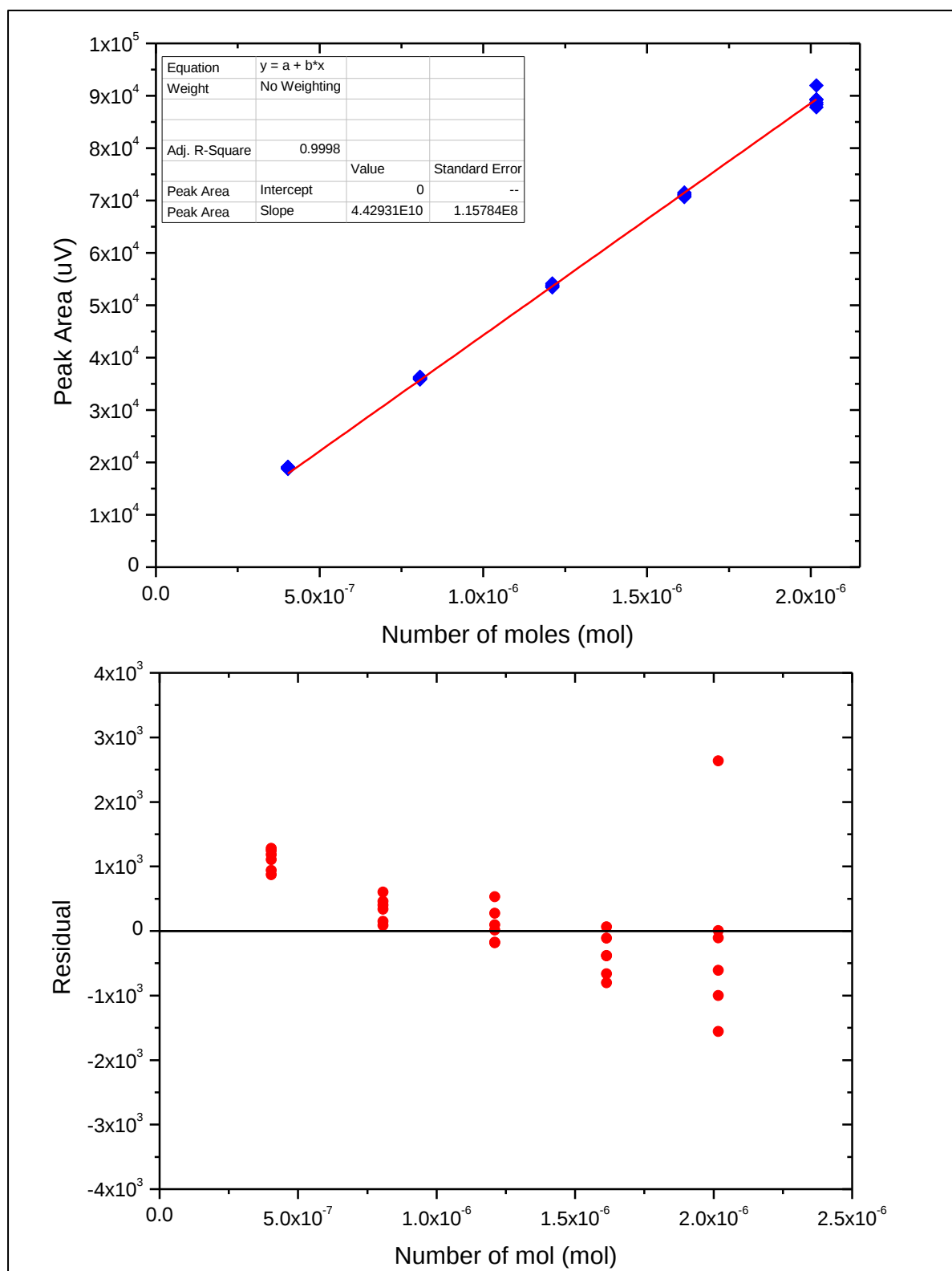


Figure A.3: Shimadzu G.C. 2014 TCD calibration plot of O₂ and residual deviation plot defined as the relative difference between measured and predicted value.

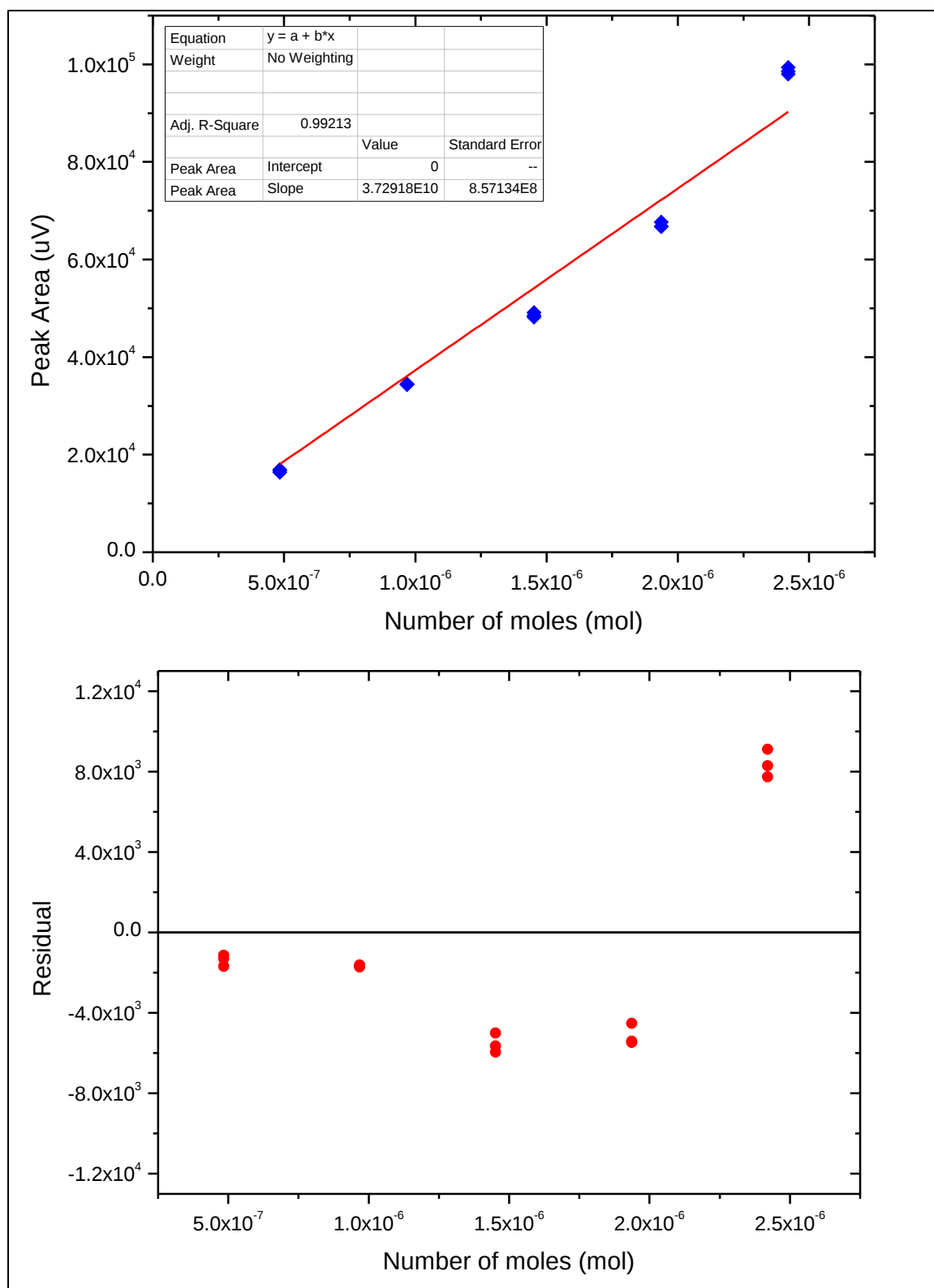


Figure A.4: Shimadzu G.C. 2014 TCD calibration plot of COF₂ and residual deviation plot defined as the relative difference between measured and predicted value.

Appendix B. Additional figures: reaction results and catalyst characterization

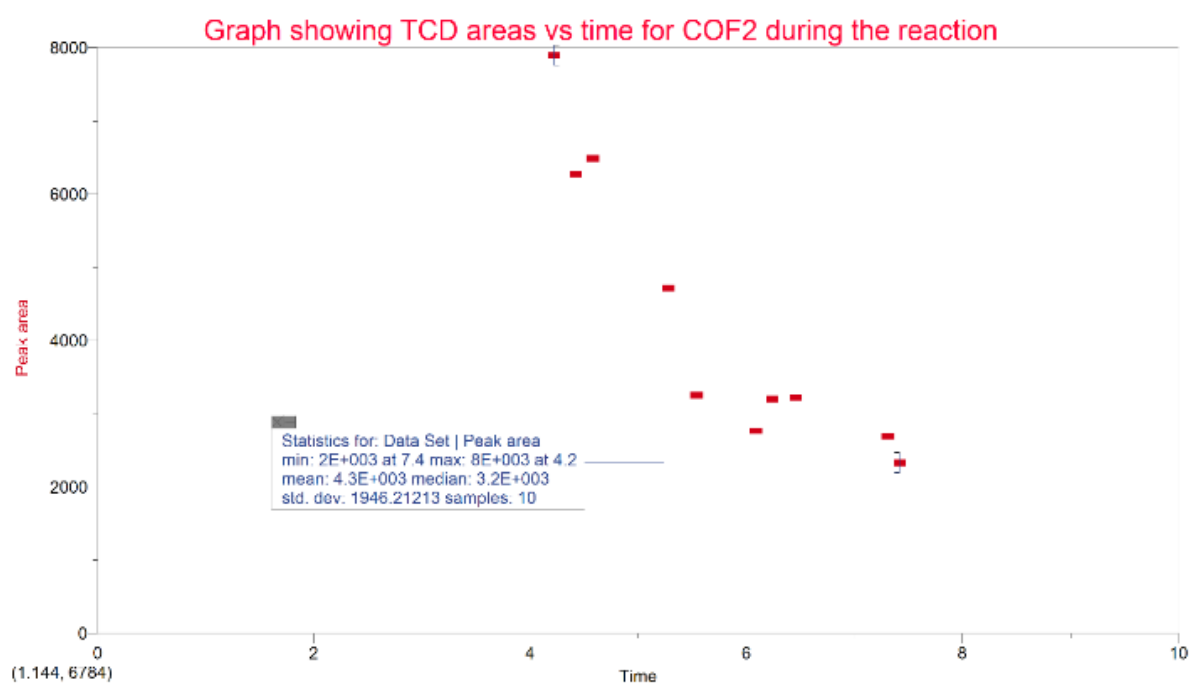


Figure B.1: GC peak areas of carbonyl difluoride during alumina supported catalyst performance testing for preliminary experiments

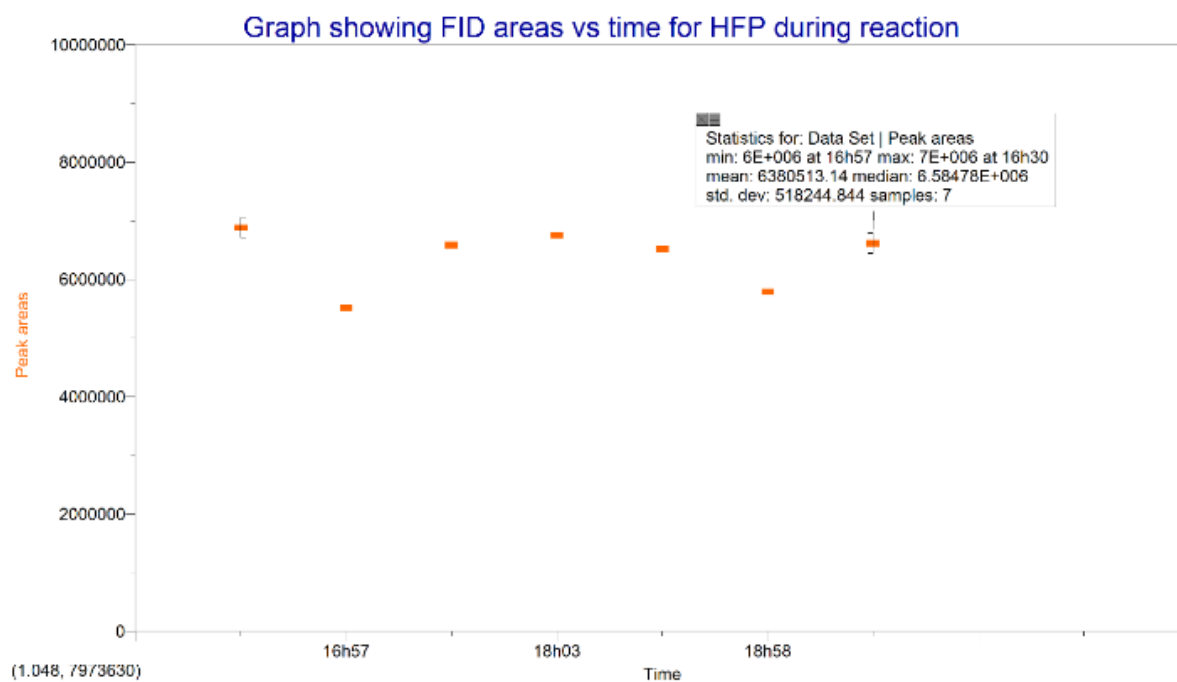


Figure B.2: GC peak areas of HFP during alumina supported catalyst performance testing for preliminary experiments

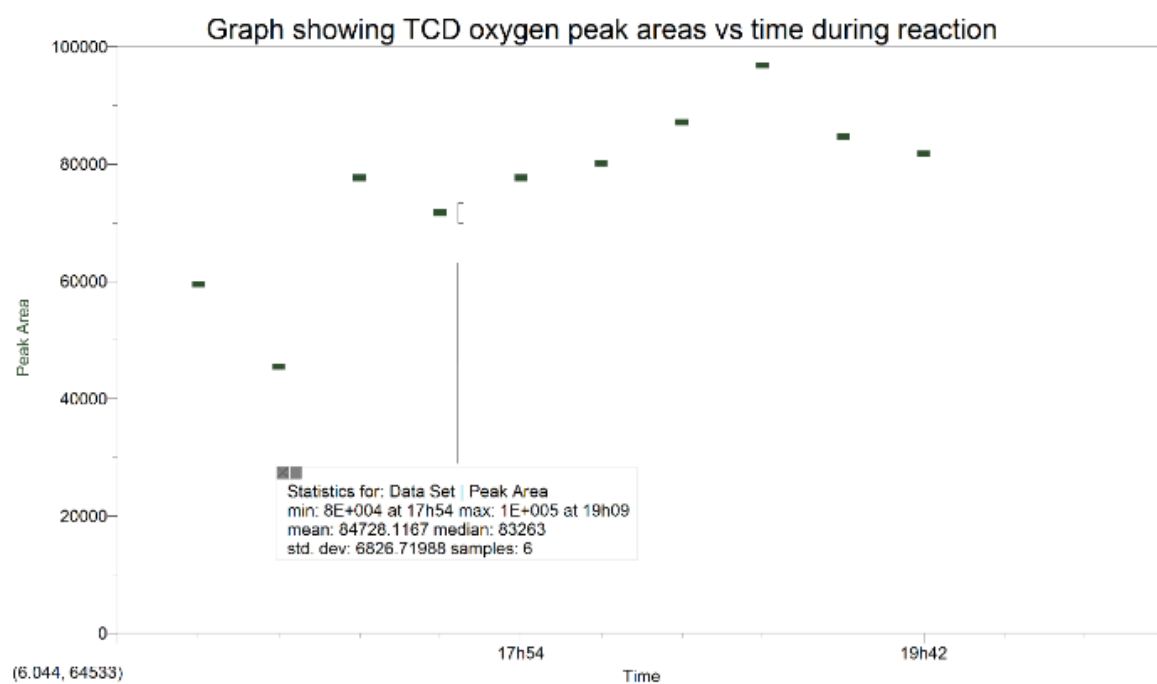


Figure B.3: GC peak areas of oxygen during alumina supported catalyst performance testing for preliminary experiments

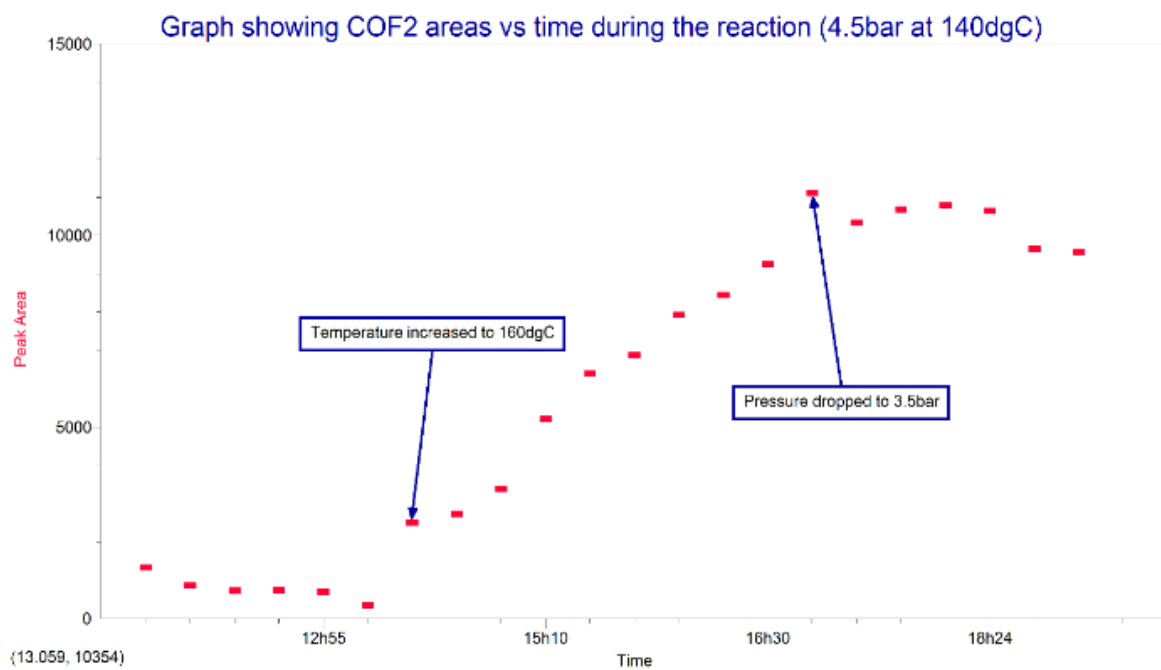


Figure B.4: GC peak areas of carbonyl difluoride during lower grade silica supported catalyst performance testing for preliminary experiments. (increasing temperature and dropping pressure)

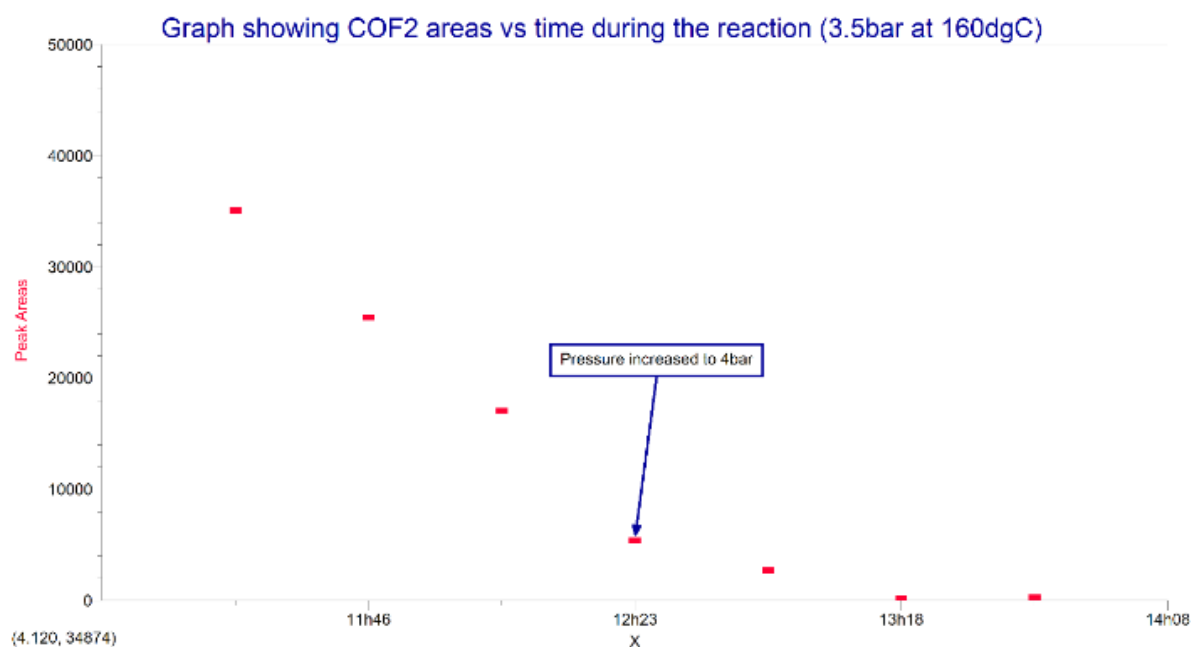


Figure B.5: GC peak areas of carbonyl difluoride during lower grade silica supported catalyst performance testing for preliminary experiments. (increasing pressure)

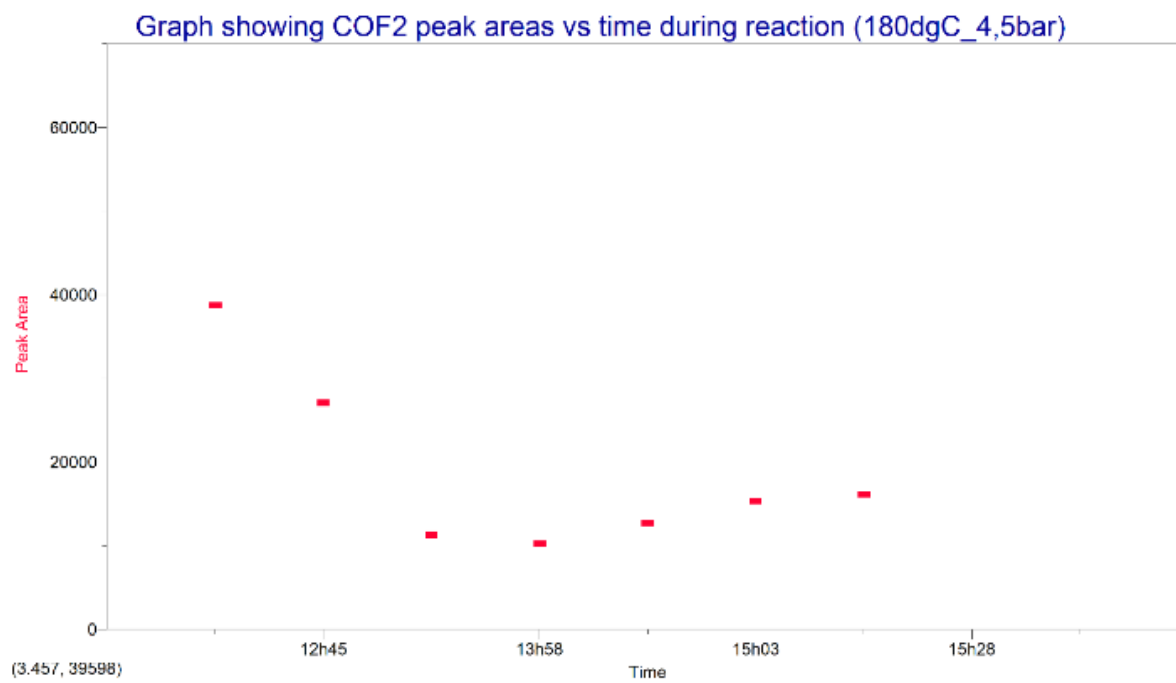


Figure B.5: GC peak areas of carbonyl difluoride during lower grade silica supported catalyst performance testing for preliminary experiments. (constant temperature and pressure)

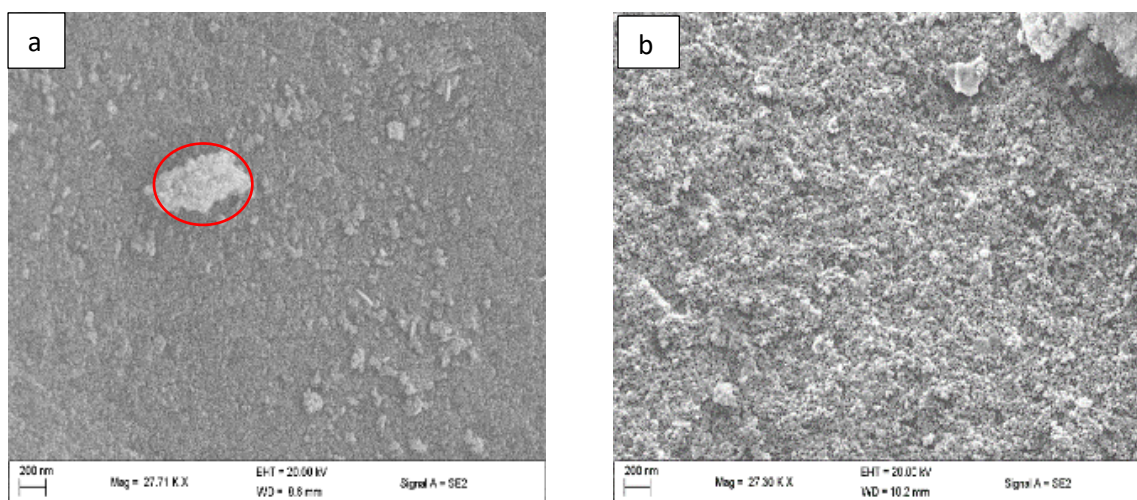


Figure B.6: SEM images of a 10wt% CuO/SiO₂ catalyst (a) fresh catalyst and (b) used catalyst.

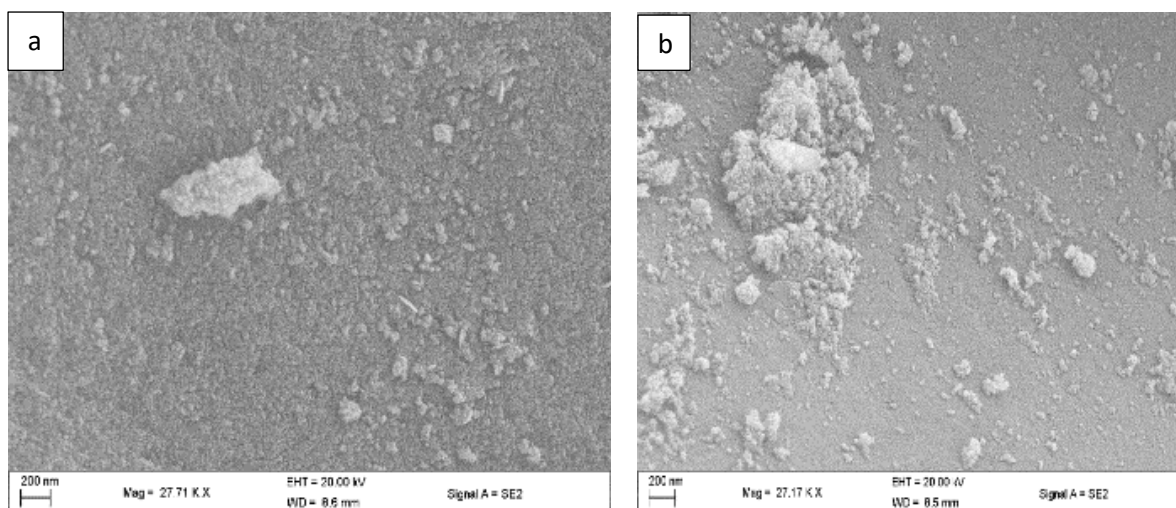


Figure B.7: SEM images of a fresh 10wt% CuO/SiO₂ catalysts (a) without a dopant and (b) with Cs dopant

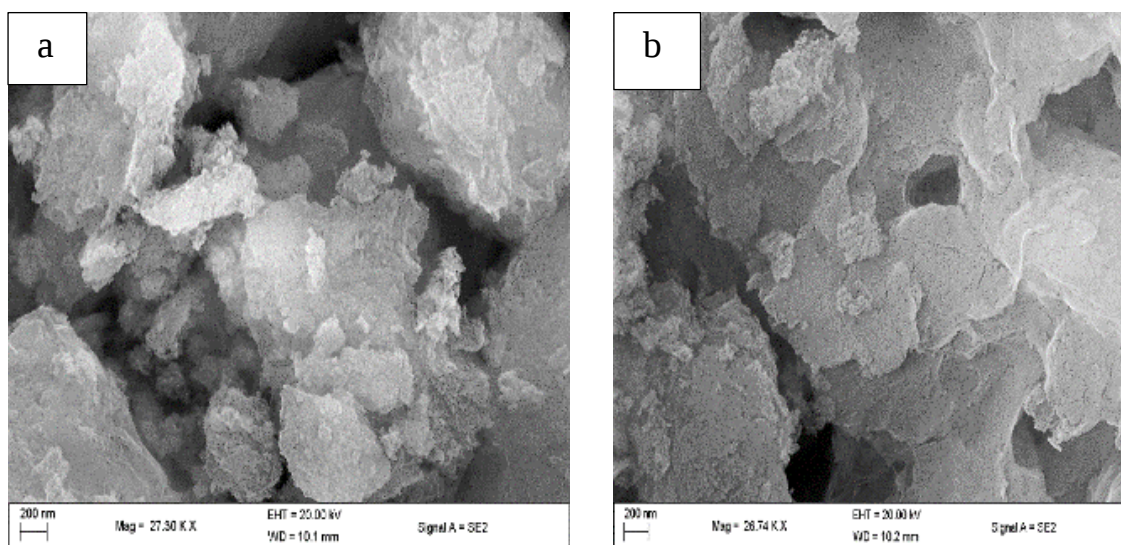


Figure B.8: SEM images of a 5wt% Cs-CuO/Al₂O₃ catalyst (a) fresh catalyst and (b) used catalyst.

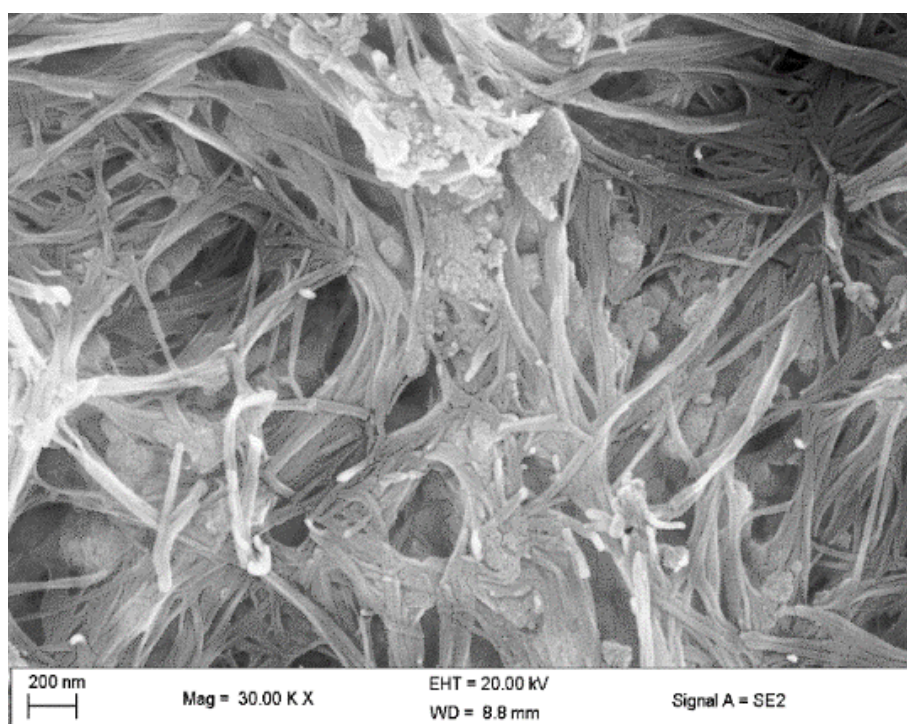


Figure B.9: SEM image of the exit line powder

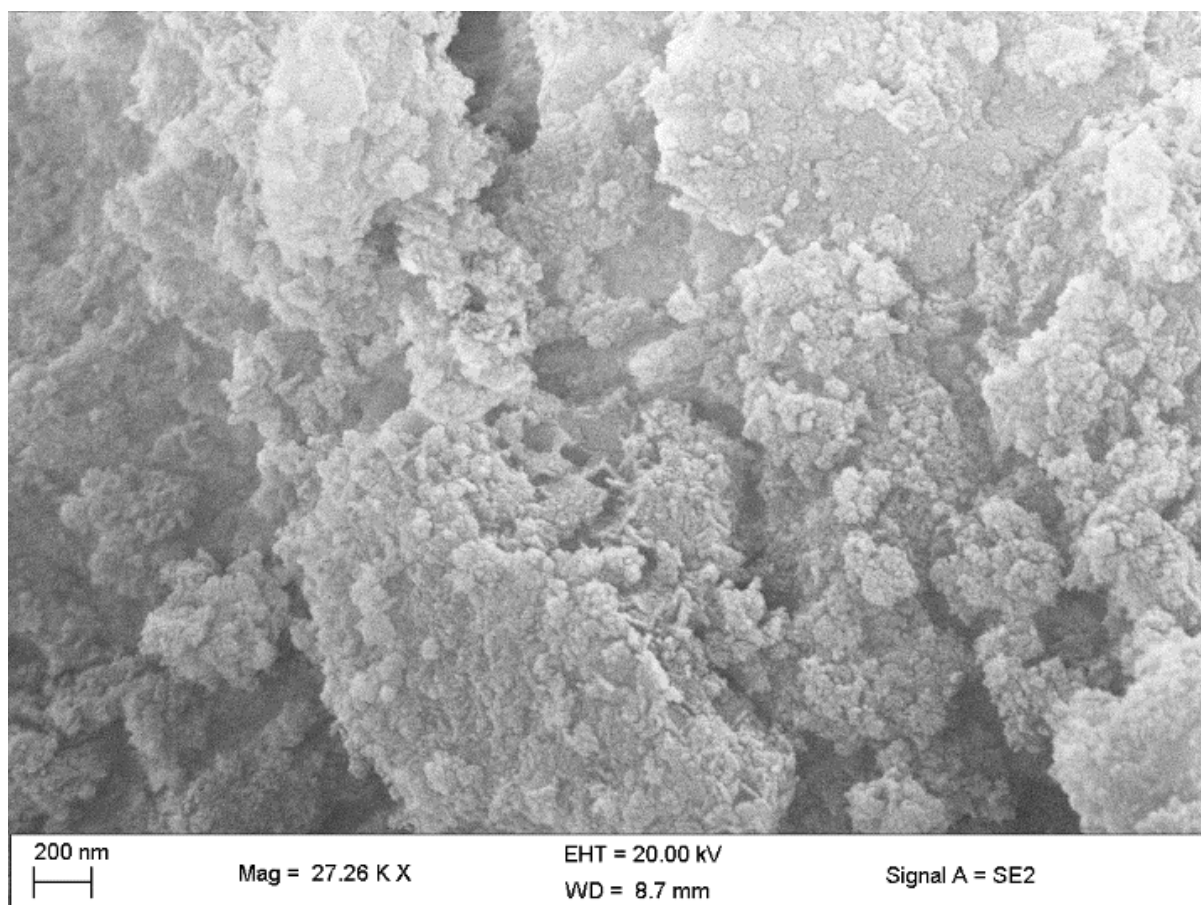


Figure B.10: SEM images of a 5wt% CuO/Al₂O₃ catalyst, used catalyst image.

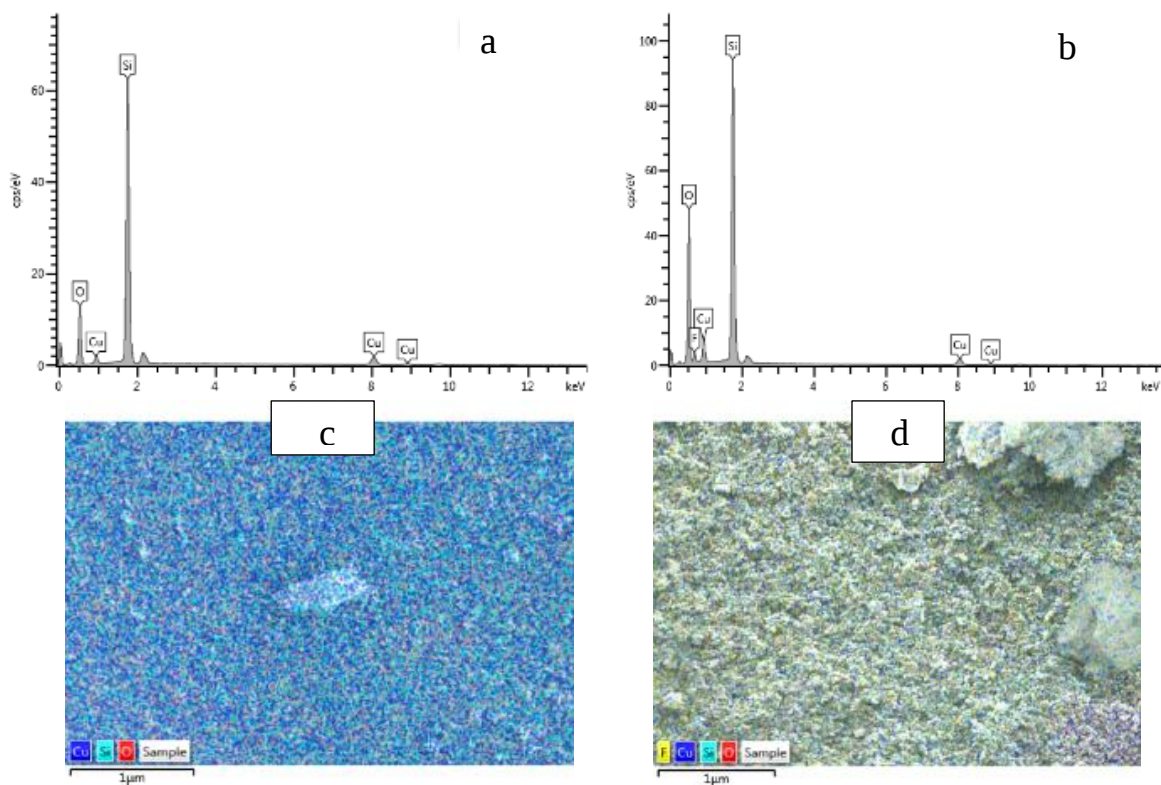


Figure B.11: SEM-EDX elemental identification/mapping indicating CuO dispersion on SiO₂ (a) Fresh catalyst, (b) Used catalyst, (c) Fresh catalyst, (d) Used catalyst

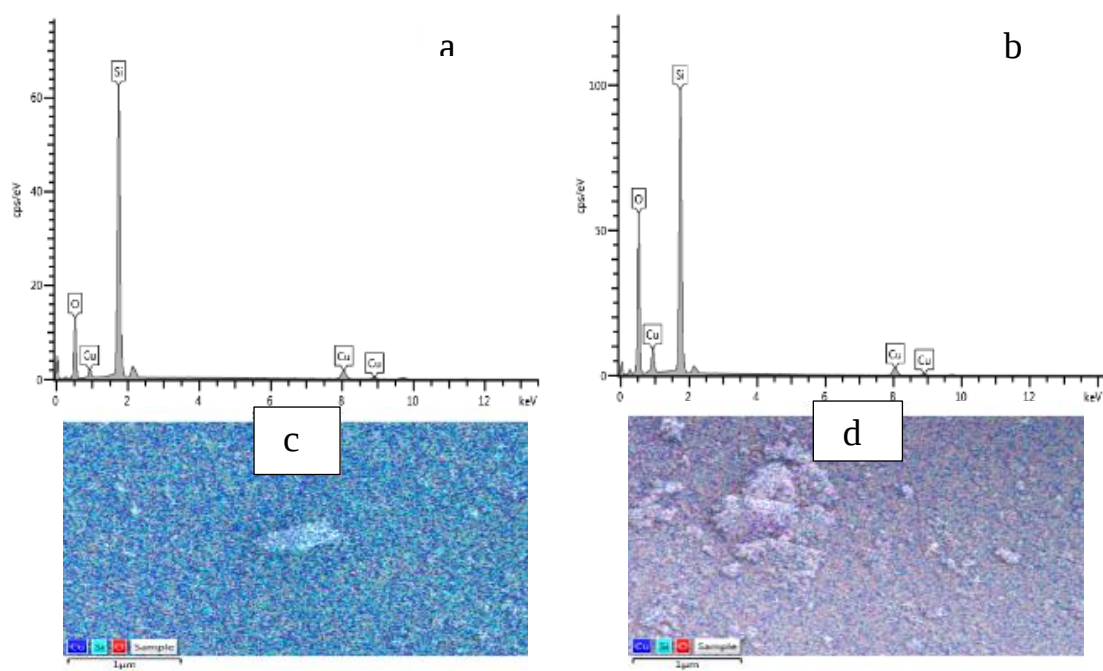


Figure B.12: SEM-EDX elemental identification/mapping indicating CuO dispersion on SiO₂ (a) without Cs, (b) with Cs, (c) without Cs, (d) with Cs

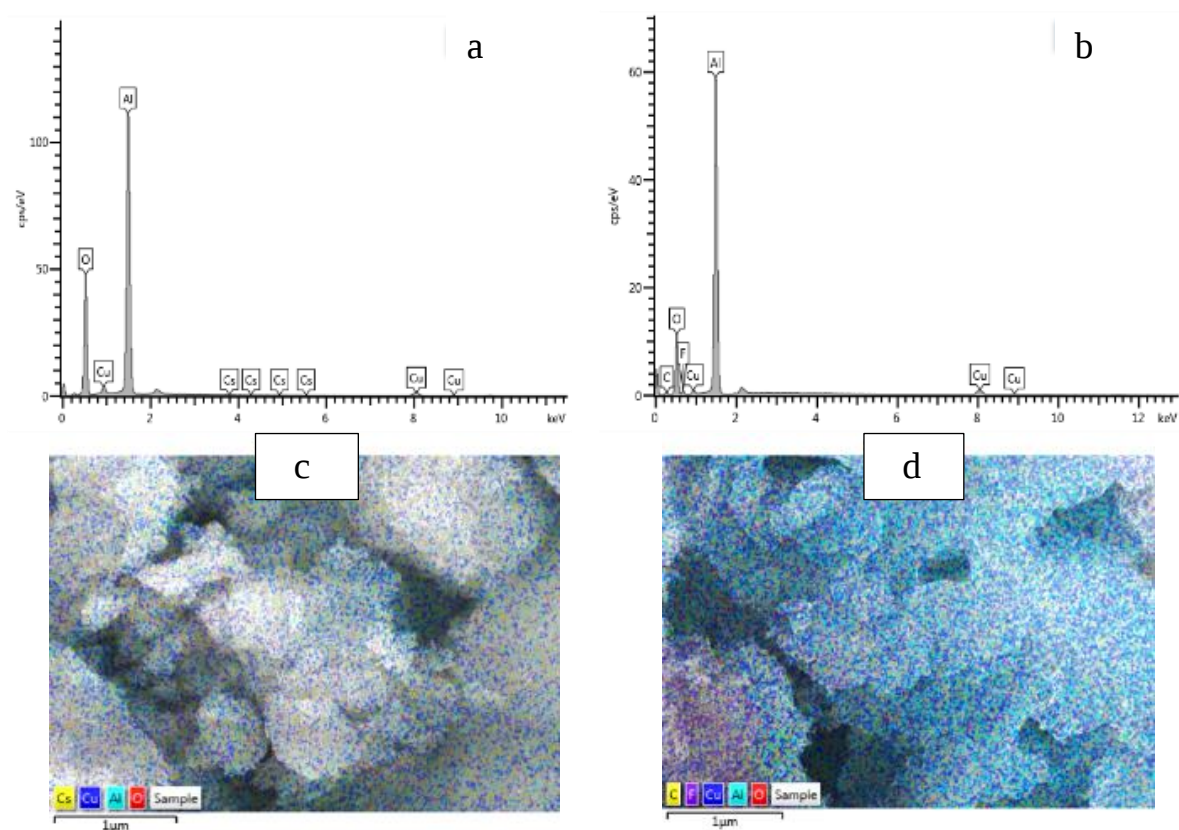


Figure B.13: SEM-EDX elemental identification/mapping indicating CuO dispersion on Al_2O_3 (a) Fresh catalyst, (b) Used catalyst, (c) Fresh catalyst, (d) Used catalyst

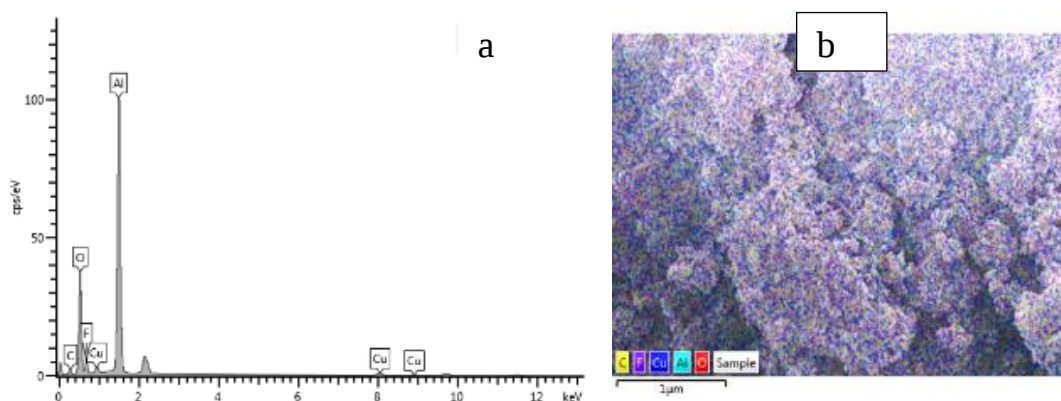


Figure B.14: SEM-EDX elemental identification/mapping indicating CuO dispersion on Al_2O_3

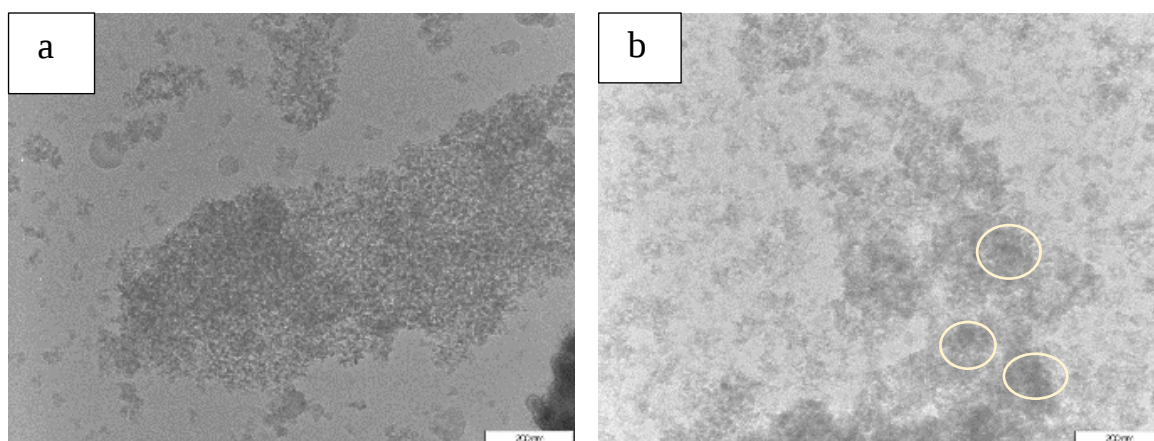


Figure B.15: TEM micrographs of 10%CuO/SiO₂ catalyst (a) fresh (b) used

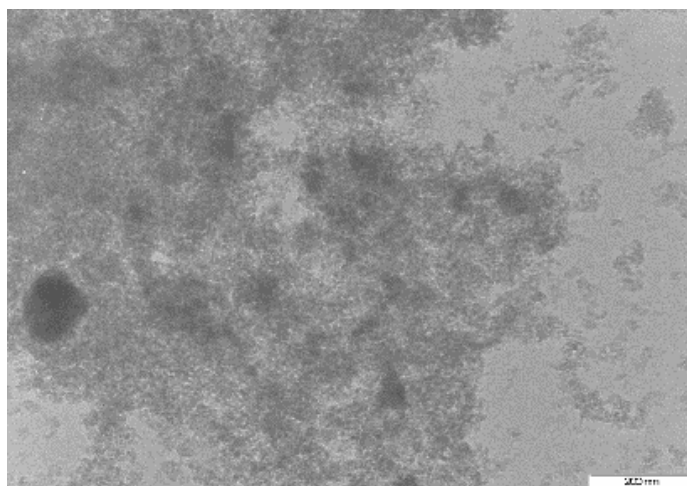


Figure B.16: TEM micrographs of 10%Cs_CuO/SiO₂ catalyst

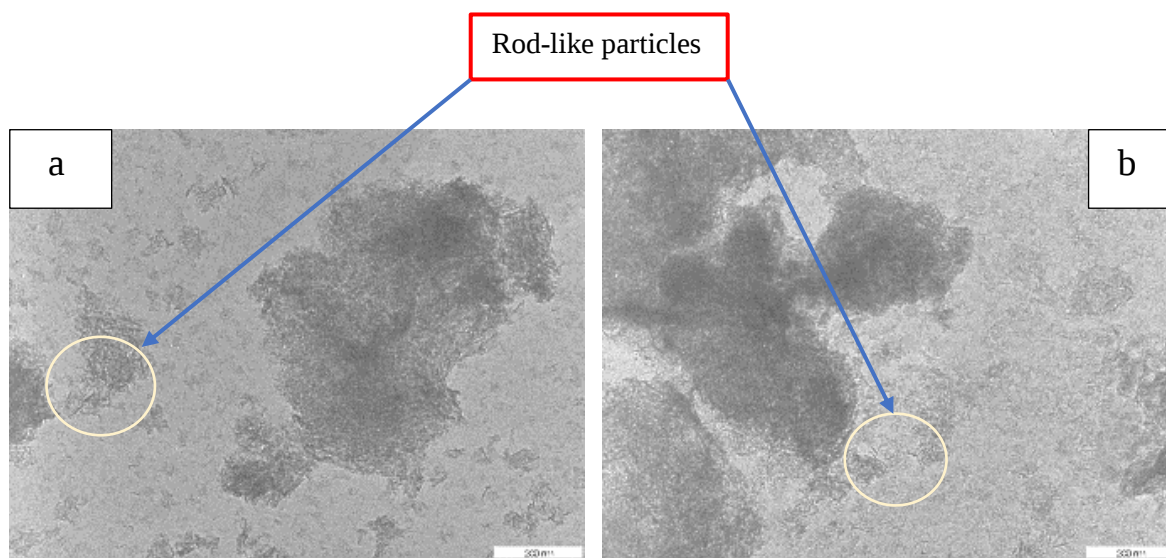


Figure B.17: TEM micrographs of 5%Cs_CuO/Al₂O₃ catalyst (a) fresh (b) used

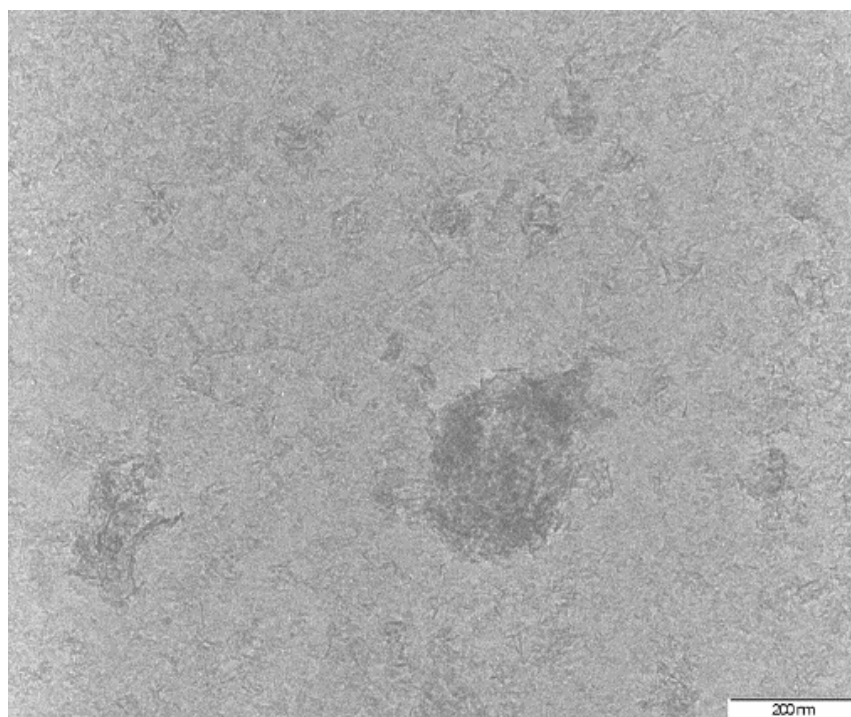


Figure B.18: TEM micrographs of a used 5%CuO/Al₂O₃ catalyst

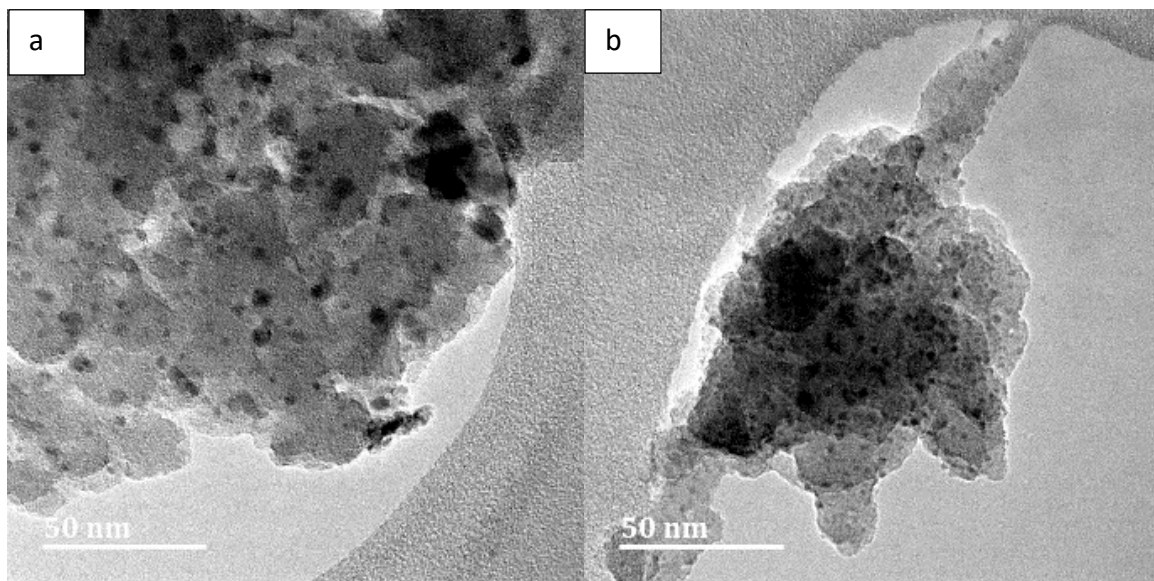


Figure B.19: HR-TEM images of the fresh 10wt% CuO/SiO₂ catalysts. IWI prepared (a) without a dopant and (b) with 0.5 wt% Cs dopant

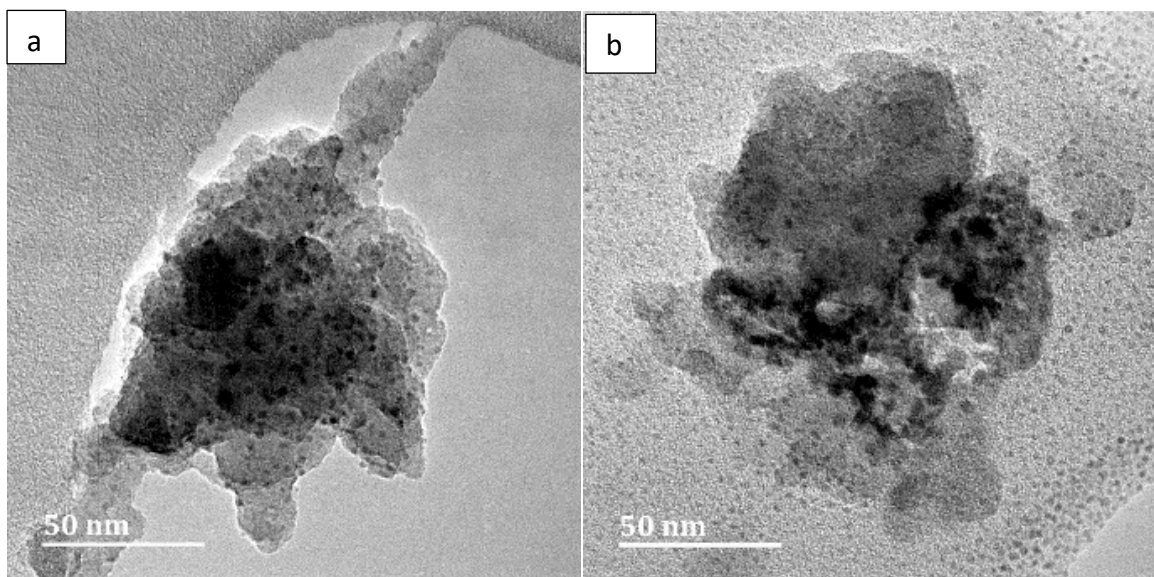


Figure B.20: HR-TEM images of the 10wt% Cs-CuO/SiO₂ catalysts. 0.5 wt% Cs dopant IWI prepared (a) fresh catalyst (b) used catalyst

Table B.1: BET surface areas, pore volume, and pore sizes of the catalysts

Catalyst	Surface Area m^2/g	Pore Volume cm^3/g	Pore Size nm
Fresh 10wt% Cs-CuO/SiO ₂ 0.5%Cs (IWI)	258	0.26	3.39
Used 10wt% Cs-CuO/SiO ₂ 0.5%Cs (IWI)	51	0.19	5.21
Fresh 10wt% Cs-CuO/SiO ₂ 0.2%Cs (WI)	291	0.28	3.47
Used 10wt% Cs-CuO/SiO ₂ 0.2%Cs (WI)	81	0.15	5.93

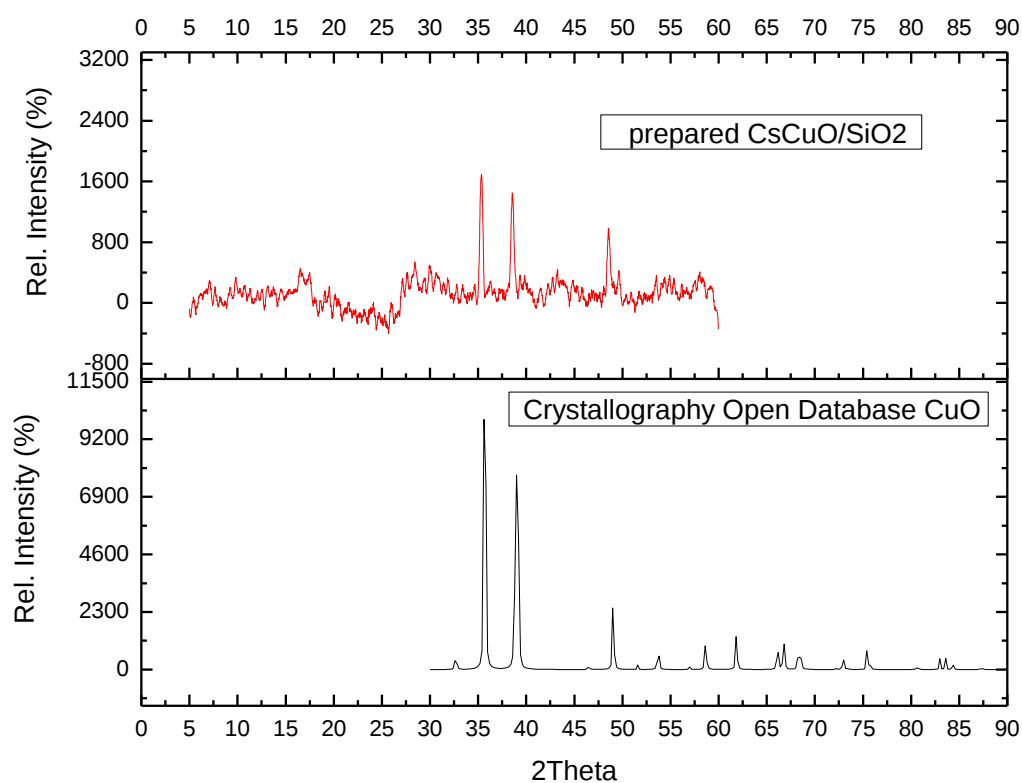


Figure B.21(a): XRD pattern of fresh 10wt%Cs-CuO/SiO₂ catalyst, 0.2% Cs content, synthesized from smaller particle size (higher grade) silica compared with a database constructed CuO pattern.

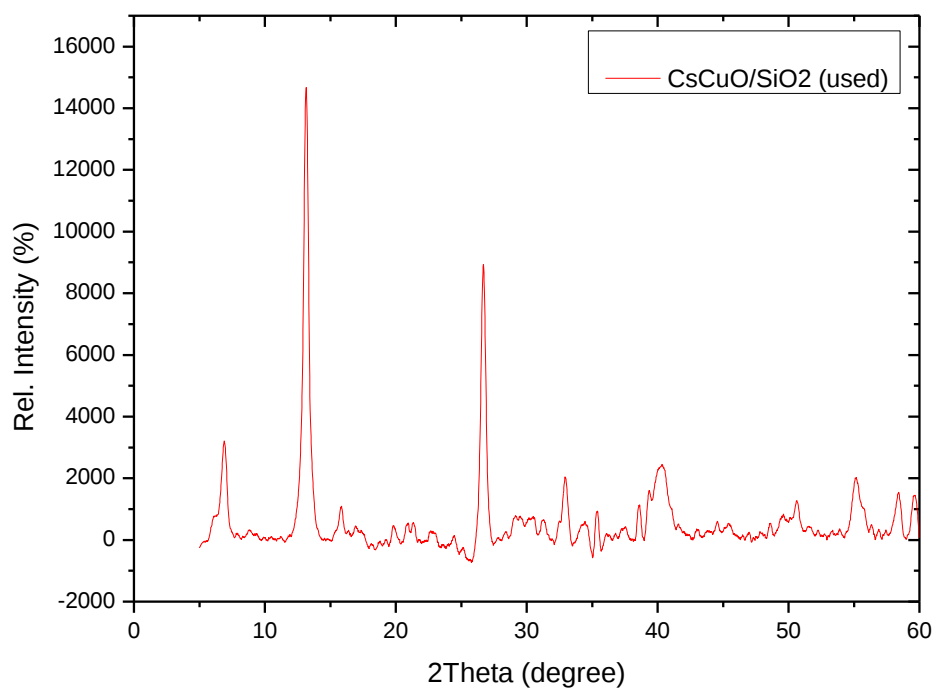


Figure B.21(b): XRD pattern of used 10wt%Cs-CuO/SiO₂ catalyst, 0.2% Cs content, synthesized from smaller particle size (higher grade) silica

Table B.2: TEM Average particle sizes of the catalysts

Catalyst	Average particle size (nm)
10%Cs-CuO/SiO ₂ (lower grade silica. 0.1%. Fresh catalyst)	1.59
10%Cs-CuO/SiO ₂ (lower grade silica. 0.1%. Fresh catalyst)	2.65

Table B.3: Assignment of Miller indices

Catalyst nature	Peak number	2θ	<i>i</i>	<i>h</i>	<i>k</i>	<i>l</i>
Fresh	1	35,5	100	1	1	-1
	2	38,7	99	1	1	1
	3	48,7	30	2	0	-2
Used	1	7,2	999	1	1	0
	2	13,5	163	1	3	0
	3	27,2	167	0	4	1
	4	33,8	31	4	2	1

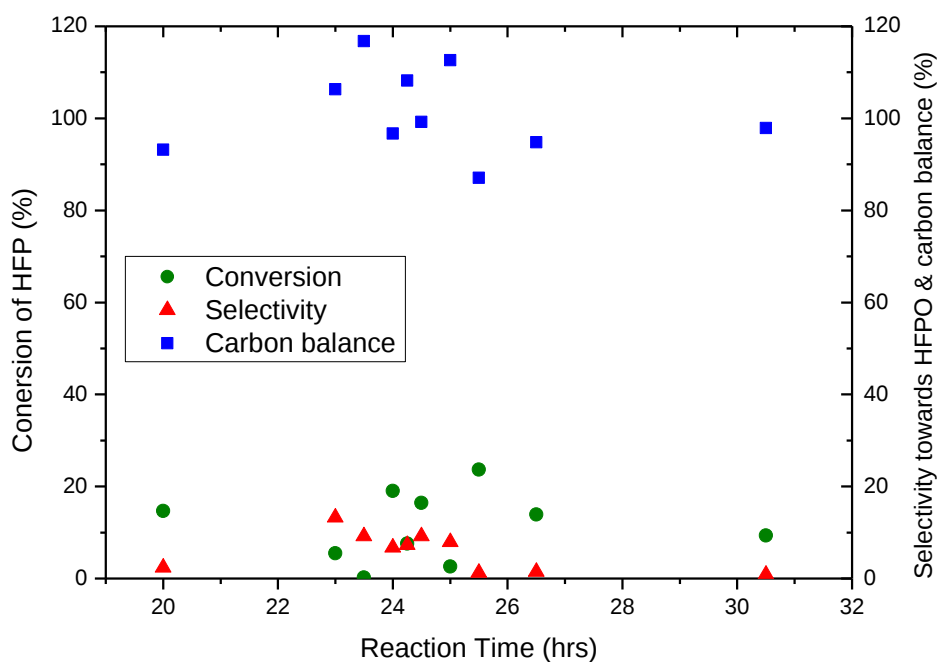


Figure B.22(a): Conversion, carbon balance, and selectivity towards HFPO as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. WI prepared.

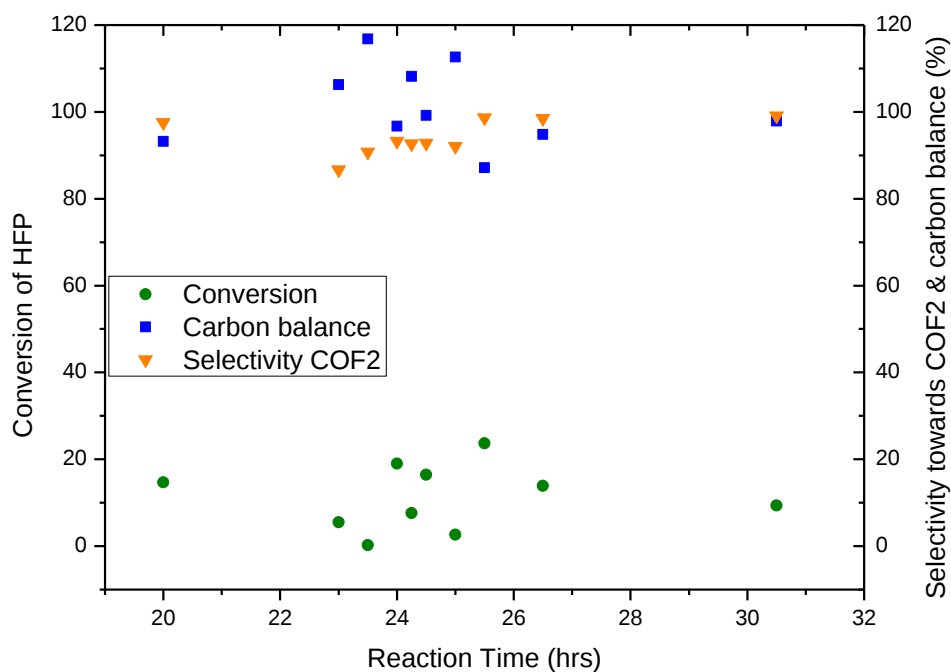


Figure B.22(b): Conversion, carbon balance, and selectivity towards COF₂ as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. WI prepared.

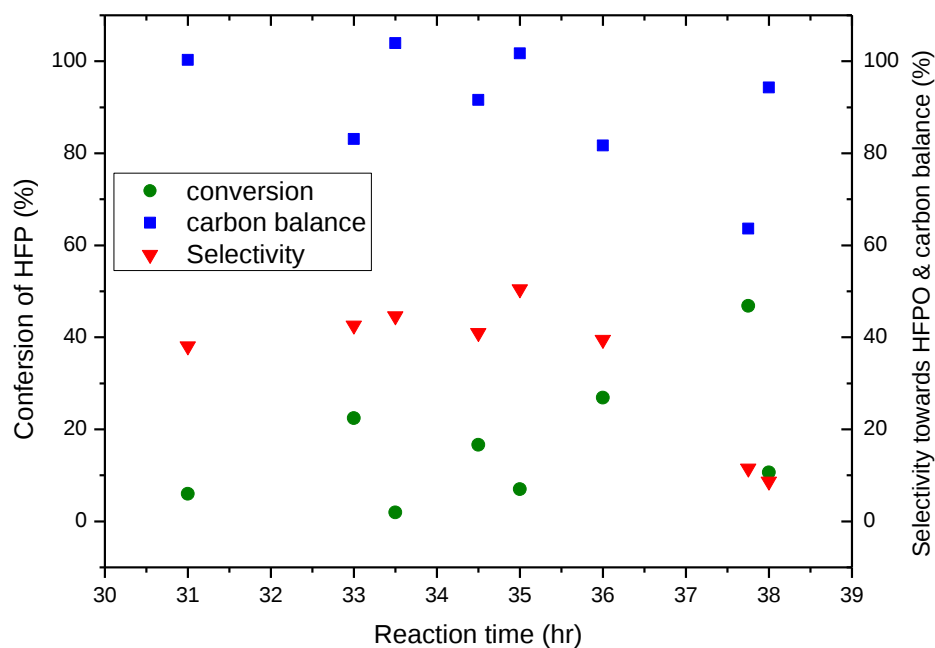


Figure B.23(a): Conversion, carbon balance, and selectivity towards HFPO as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. IWI prepared.

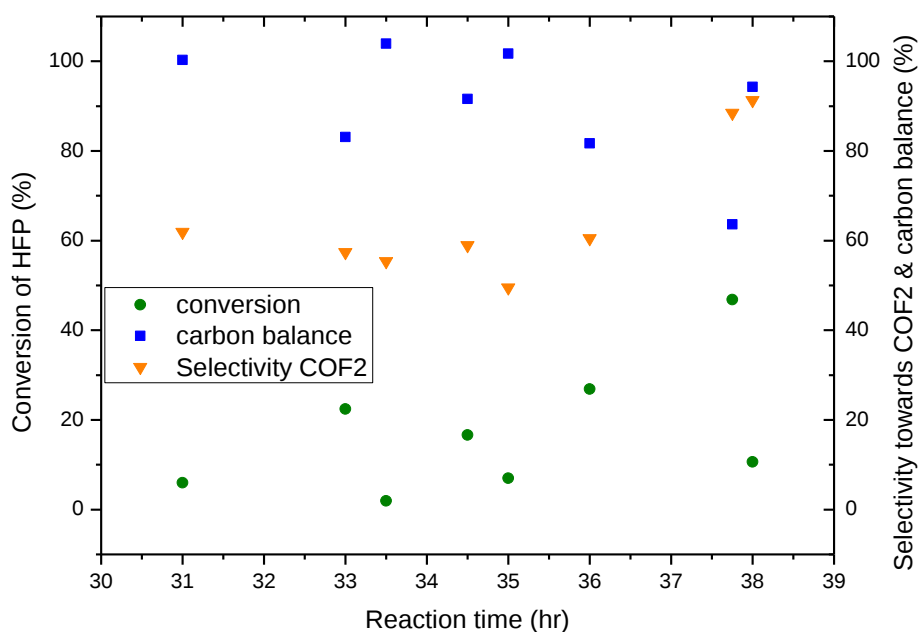


Figure B.23(b): Conversion, carbon balance, and selectivity towards COF₂ as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. IWI prepared.

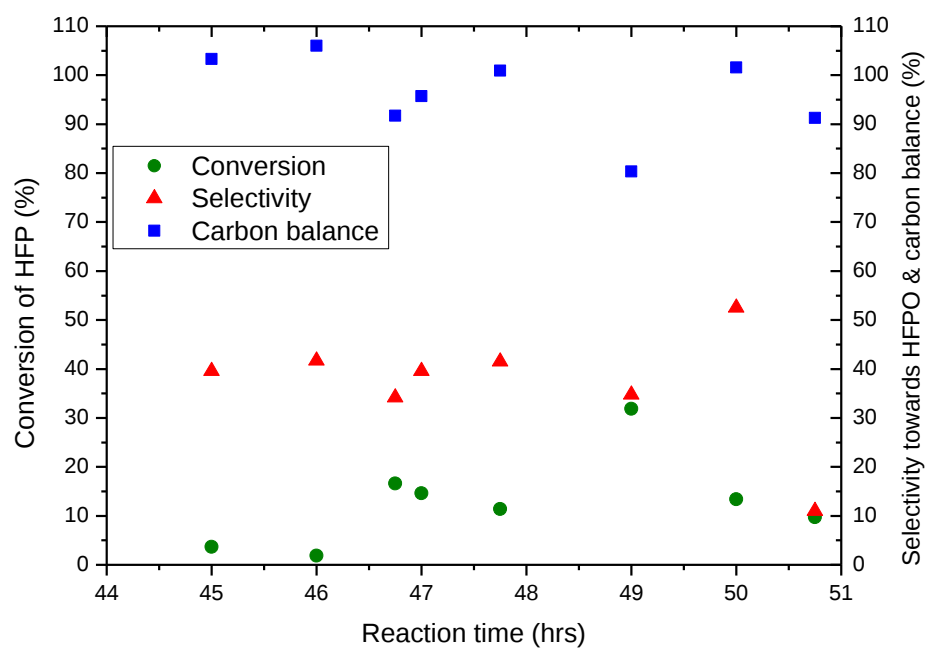


Figure B.24(a): Conversion, carbon balance, and selectivity towards HFPO as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. WI prepared.

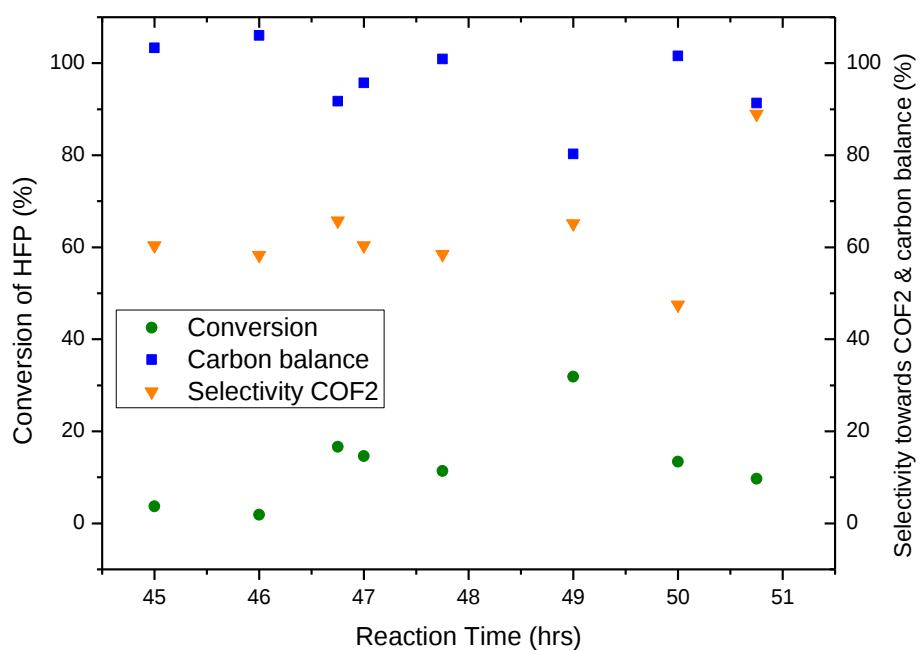


Figure B.24(b): Conversion, carbon balance, and selectivity towards COF₂ as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. WI prepared.

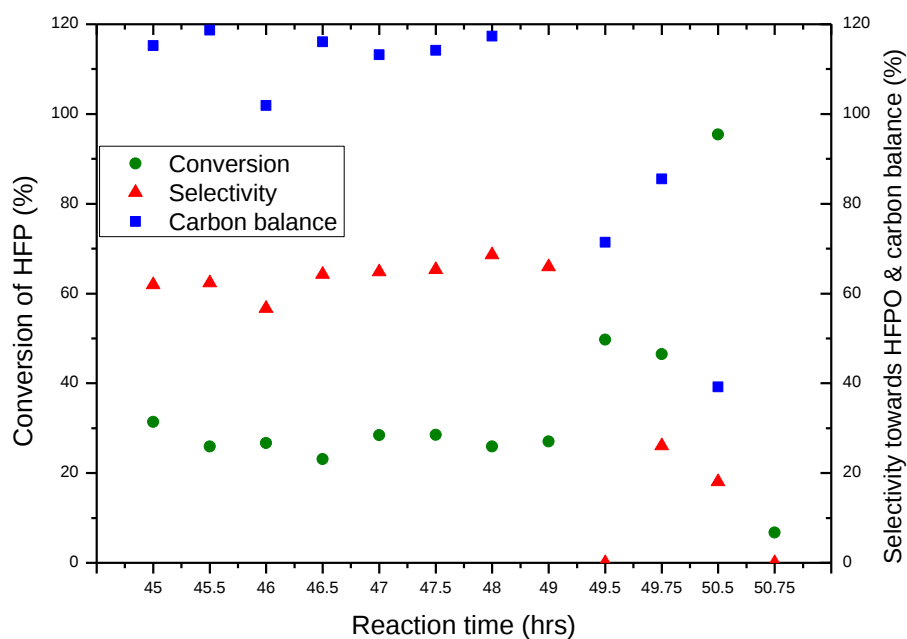


Figure B.25(a): Conversion, carbon balance, and selectivity towards HFPO as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. IWI prepared.

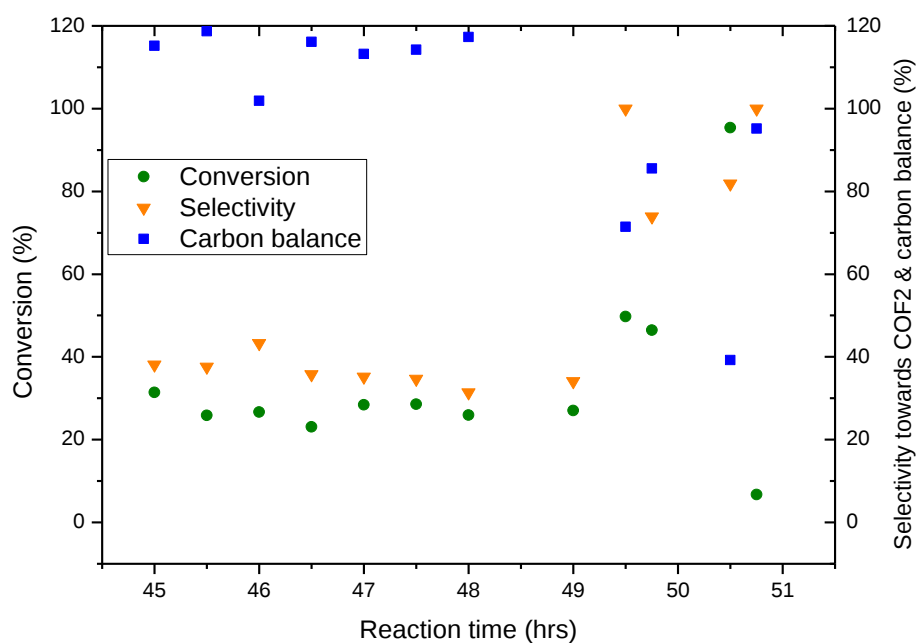


Figure B.25(b): Conversion, carbon balance, and selectivity towards COF₂ as a function of time over 10 wt% Cs-CuO/SiO₂ catalyst, 0.1 wt% Cs content. IWI prepared.

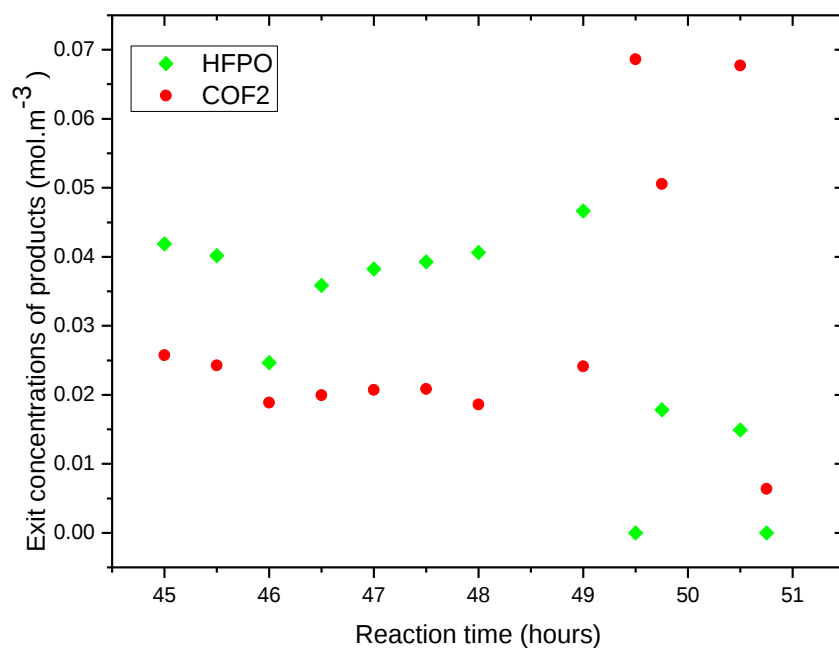


Figure B.26: Exit concentrations of HFPO and COF₂ as a function of time over IWI prepared 10wt% Cs-CuO/SiO₂ catalyst, 0.1wt% Cs content.

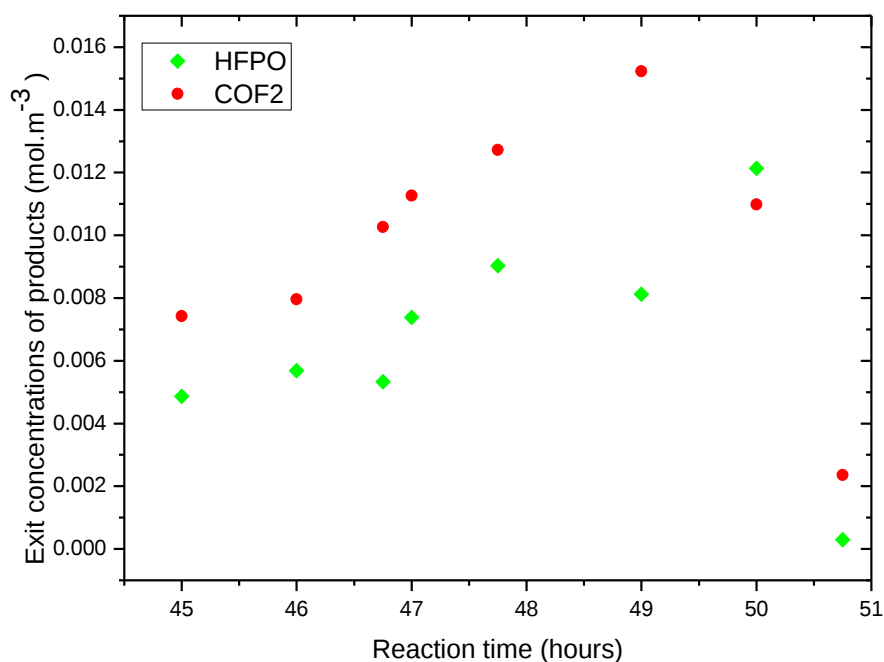


Figure B.27: Exit concentrations of HFPO and COF₂ as a function of time over WI prepared 10wt% Cs-CuO/SiO₂ catalyst, 0.1wt% Cs content.

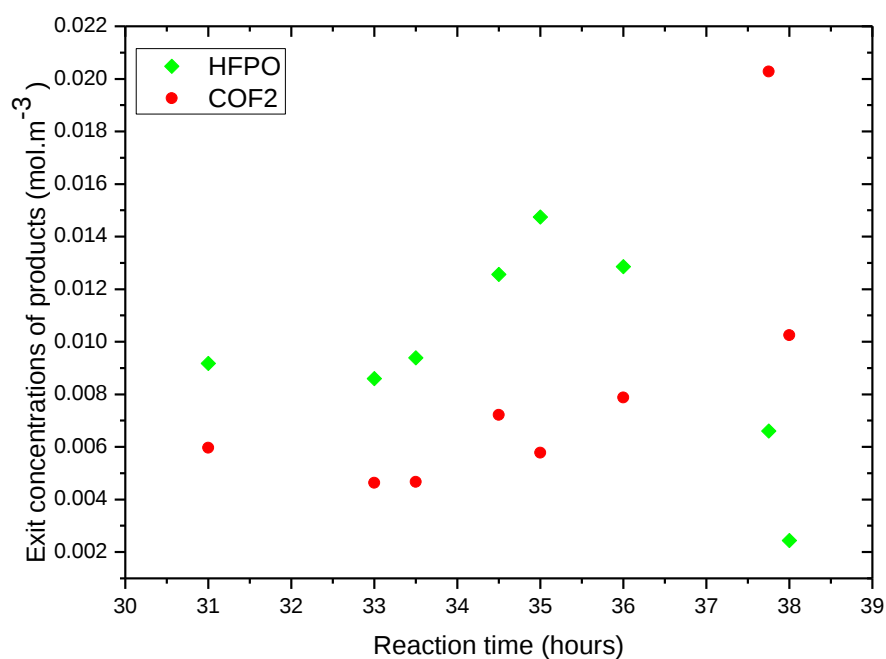


Figure B.28: Exit concentrations of HFPO and COF₂ as a function of time over IWI prepared 10wt% Cs-CuO/SiO₂ catalyst, 0.1wt% Cs content.

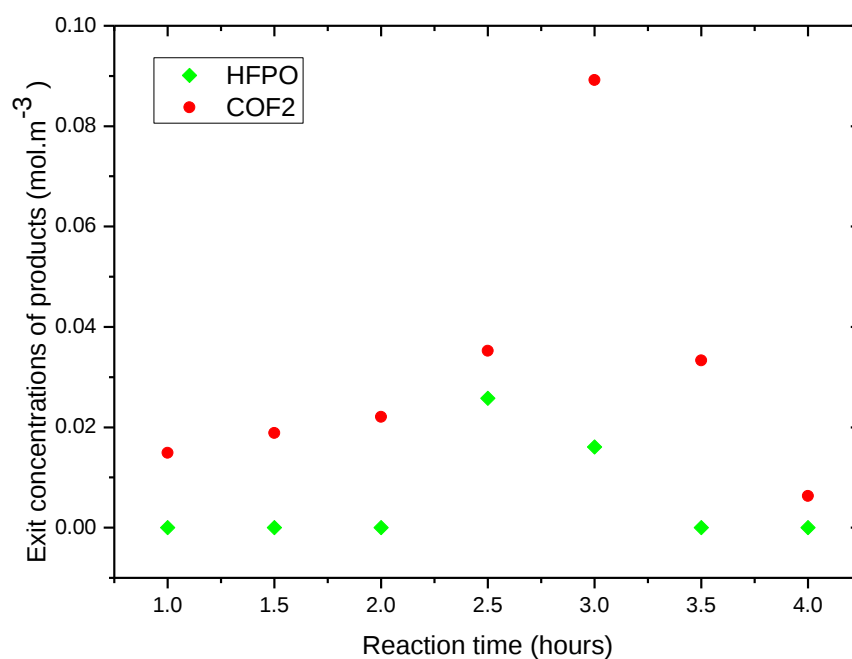


Figure B.29: Exit concentrations of HFPO and COF₂ as a function of time over WI prepared 10wt% Cs-CuO/SiO₂ catalyst, 0.1wt% Cs content.

Appendix C. Raw experimental data

Table C.1: Raw experimental data for the catalytic oxidation of HFP

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles of effluent components injected into the GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.2%Cs) - WI	HFPO	33.25	8.21699E-08	0.000811735	0.00010123	119.4429468	0.0120909
		33.5	9.47283E-08	0.000811735	0.0001167	119.4429468	0.01393881
		34	1.0666E-07	0.000811735	0.0001314	119.4429468	0.015694554
		34.25	1.09728E-07	0.000811735	0.00013518	119.4429468	0.01614589
		34.75	1.10899E-07	0.000811735	0.00013662	119.4429468	0.016318325
		35.75	1.38382E-07	0.000811735	0.00017048	119.4429468	0.02036231
		36.75	1.36107E-07	0.000811735	0.00016767	119.4429468	0.020027495
		37	1.7786E-07	0.000811735	0.00021911	119.4429468	0.026171256
		37.25	1.99117E-07	0.000811735	0.0002453	119.4429468	0.029299051
		37.5	1.90088E-07	0.000811735	0.00023417	119.4429468	0.027970513
		38.25	1.73386E-07	0.000811735	0.0002136	119.4429468	0.025512852
		38.75	1.6392E-07	0.000811735	0.00020194	119.4429468	0.024119965
		39	1.8043E-07	0.000811735	0.00022228	119.4429468	0.026549474
		39.5	2.08523E-07	0.000811735	0.00025689	119.4429468	0.030683224
		40.25	2.78439E-07	0.000811735	0.00034302	119.4429468	0.040970901
		41.75	2.66274E-07	0.000811735	0.00032803	119.4429468	0.03918086
		42	3.36217E-07	0.000811735	0.00041419	119.4429468	0.049472671
		42.5	2.4924E-07	0.000811735	0.00030705	119.4429468	0.036674491
		42.75	2.7444E-07	0.000811735	0.00033809	119.4429468	0.040382544

Table C.1. (continued)

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles of effluent components injected into the GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.2%Cs) - WI	COF ₂	33.25	1.4666E-07	0.002029339	7.227E-05	119.4429468	0.008632142
		33.5	1.51188E-07	0.002029339	7.4501E-05	119.4429468	0.008898611
		34	1.68734E-07	0.002029339	8.3147E-05	119.4429468	0.009931336
		34.25	1.74741E-07	0.002029339	8.6108E-05	119.4429468	0.010284944
		34.75	1.83946E-07	0.002029339	9.0643E-05	119.4429468	0.010826722
		35.75	1.97086E-07	0.002029339	9.7118E-05	119.4429468	0.011600082
		36.75	2.1627E-07	0.002029339	0.00010657	119.4429468	0.01272926
		37	2.21814E-07	0.002029339	0.0001093	119.4429468	0.013055558
		37.25	2.23418E-07	0.002029339	0.00011009	119.4429468	0.013149959
		37.5	2.32306E-07	0.002029339	0.00011447	119.4429468	0.013673109
		38.25	2.52934E-07	0.002029339	0.00012464	119.4429468	0.014887216
		38.75	2.55726E-07	0.002029339	0.00012601	119.4429468	0.015051549
		39	2.66881E-07	0.002029339	0.00013151	119.4429468	0.015708092
		39.5	2.69359E-07	0.002029339	0.00013273	119.4429468	0.015853956
		40.25	2.88257E-07	0.002029339	0.00014204	119.4429468	0.016966243
		41.75	3.60039E-07	0.002029339	0.00017742	119.4429468	0.021191228
		42	3.80302E-07	0.002029339	0.0001874	119.4429468	0.022383866
		42.5	3.63137E-07	0.002029339	0.00017894	119.4429468	0.021373557
		42.75	4.49392E-07	0.002029339	0.00022145	119.4429468	0.026450359

Table C.1. (continued)

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles of effluent components injected into the GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.2%Cs) - WI	HFP	33.25	1.43456E-06	0.000811735	0.00176727	119.4429468	0.211088476
		33.5	1.47369E-06	0.000811735	0.00181548	119.4429468	0.216845994
		34	1.42086E-06	0.000811735	0.00175039	119.4429468	0.209072232
		34.25	1.50094E-06	0.000811735	0.00184905	119.4429468	0.220856408
		34.75	1.39382E-06	0.000811735	0.00171709	119.4429468	0.205093913
		35.75	1.49106E-06	0.000811735	0.00183688	119.4429468	0.219402284
		36.75	1.54084E-06	0.000811735	0.0018982	119.4429468	0.226726667
		37	1.34223E-06	0.000811735	0.00165353	119.4429468	0.197502356
		37.25	1.3884E-06	0.000811735	0.00171041	119.4429468	0.204296181
		37.5	1.41335E-06	0.000811735	0.00174114	119.4429468	0.207966983
		38.25	1.374E-06	0.000811735	0.00169267	119.4429468	0.202177946
		38.75	1.27988E-06	0.000811735	0.00157672	119.4429468	0.188327986
		39	1.10773E-06	0.000811735	0.00136464	119.4429468	0.162996647
		39.5	1.24464E-06	0.000811735	0.0015333	119.4429468	0.183142457
		40.25	1.41955E-06	0.000811735	0.00174878	119.4429468	0.208879344
		41.75	1.11064E-06	0.000811735	0.00136823	119.4429468	0.163425712
		42	1.16278E-06	0.000811735	0.00143246	119.4429468	0.171096906
		42.5	1.00016E-06	0.000811735	0.00123213	119.4429468	0.147168901
		42.75	1.02409E-06	0.000811735	0.0012616	119.4429468	0.150689797

Table C.1. (continued)

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles of effluent components injected into the GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.2%Cs) - WI	O ₂	33.25	6.3858E-07	0.002029339	0.00031467	119.4429468	0.037585589
		33.5	6.55142E-07	0.002029339	0.00032284	119.4429468	0.03856042
		34	6.31809E-07	0.002029339	0.00031134	119.4429468	0.037187073
		34.25	6.2456E-07	0.002029339	0.00030777	119.4429468	0.036760385
		34.75	6.32333E-07	0.002029339	0.0003116	119.4429468	0.037217901
		35.75	6.39339E-07	0.002029339	0.00031505	119.4429468	0.037630238
		36.75	5.98533E-07	0.002029339	0.00029494	119.4429468	0.035228508
		37	5.93372E-07	0.002029339	0.0002924	119.4429468	0.034924738
		37.25	5.78471E-07	0.002029339	0.00028505	119.4429468	0.034047709
		37.5	5.76975E-07	0.002029339	0.00028432	119.4429468	0.033959608
		38.25	5.64842E-07	0.002029339	0.00027834	119.4429468	0.033245494
		38.75	5.48803E-07	0.002029339	0.00027043	119.4429468	0.032301492
		39	5.52479E-07	0.002029339	0.00027225	119.4429468	0.032517826
		39.5	5.28834E-07	0.002029339	0.00026059	119.4429468	0.031126141
		40.25	5.17426E-07	0.002029339	0.00025497	119.4429468	0.030454683
		41.75	5.00082E-07	0.002029339	0.00024643	119.4429468	0.029433875
		42	5.43981E-07	0.002029339	0.00026806	119.4429468	0.032017654
		42.5	4.55662E-07	0.002029339	0.00022454	119.4429468	0.026819399
		42.75	5.31074E-07	0.002029339	0.0002617	119.4429468	0.031257961

Table C.1. (continued)

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles injected into GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.5%Cs) - IWI	HFPO	28	1.42004E-07	0.000811735	0.00017494	119.4429468	0.0208952
		28.5	1.69513E-07	0.000811735	0.00020883	119.4429468	0.024942984
		29	1.87796E-07	0.000811735	0.00023135	119.4429468	0.027633295
		29.5	1.87417E-07	0.000811735	0.00023088	119.4429468	0.027577437
		29.75	2.04496E-07	0.000811735	0.00025192	119.4429468	0.030090565
		30	2.03702E-07	0.000811735	0.00025095	119.4429468	0.029973709
		30.5	1.95153E-07	0.000811735	0.00024041	119.4429468	0.028715833
		31	2.68511E-07	0.000811735	0.00033079	119.4429468	0.039510146
		31.5	1.68972E-07	0.000811735	0.00020816	119.4429468	0.024863442
		32	2.64936E-07	0.000811735	0.00032638	119.4429468	0.038984071
		32.5	2.72523E-07	0.000811735	0.00033573	119.4429468	0.040100458
		32.75	3.59764E-07	0.000811735	0.0004432	119.4429468	0.052937572
		33	3.44062E-07	0.000811735	0.00042386	119.4429468	0.050627042
		33.25	3.71262E-07	0.000811735	0.00045737	119.4429468	0.054629413
		33.5	2.01606E-07	0.000811735	0.00024836	119.4429468	0.029665315
		33.75	3.6675E-07	0.000811735	0.00045181	119.4429468	0.053965424
		34	3.6613E-07	0.000811735	0.00045105	119.4429468	0.053874319
		34.25	2.70436E-07	0.000811735	0.00033316	119.4429468	0.039793404
		34.5	3.02278E-07	0.000811735	0.00037239	119.4429468	0.044478813
		34.75	4.20104E-07	0.000811735	0.00051754	119.4429468	0.06181622
		35	2.90771E-07	0.000811735	0.00035821	119.4429468	0.042785519
		35.5	5.81102E-07	0.000811735	0.00071588	119.4429468	0.085506354
		36	1.84273E-07	0.000811735	0.00022701	119.4429468	0.027114817
		36.5	2.06558E-07	0.000811735	0.00025446	119.4429468	0.030394044
		37	1.52643E-07	0.000811735	0.00018804	119.4429468	0.022460634
		37.25	1.66063E-07	0.000811735	0.00020458	119.4429468	0.024435342
		38	4.00638E-08	0.000811735	4.9356E-05	119.4429468	0.005895191

Table C.1. (continued)

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles injected into the GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.5%Cs) - IWI	COF2	28	2.09584E-07	0.002029339	0.00010328	119.4429468	0.012335713
		28.5	2.30713E-07	0.002029339	0.00011369	119.4429468	0.01357934
		29	2.35903E-07	0.002029339	0.00011625	119.4429468	0.013884801
		29.5	2.56464E-07	0.002029339	0.00012638	119.4429468	0.015094961
		29.75	2.59433E-07	0.002029339	0.00012784	119.4429468	0.015269713
		30	2.6414E-07	0.002029339	0.00013016	119.4429468	0.015546759
		30.5	2.69464E-07	0.002029339	0.00013278	119.4429468	0.015860112
		31	3.16378E-07	0.002029339	0.0001559	119.4429468	0.018621413
		31.5	2.98695E-07	0.002029339	0.00014719	119.4429468	0.017580637
		32	3.25639E-07	0.002029339	0.00016047	119.4429468	0.019166506
		32.5	3.46205E-07	0.002029339	0.0001706	119.4429468	0.020376982
		32.75	3.62424E-07	0.002029339	0.00017859	119.4429468	0.021331566
		33	3.73141E-07	0.002029339	0.00018387	119.4429468	0.021962378
		33.25	4.0483E-07	0.002029339	0.00019949	119.4429468	0.023827502
		33.5	4.21362E-07	0.002029339	0.00020764	119.4429468	0.024800556
		33.75	4.25447E-07	0.002029339	0.00020965	119.4429468	0.025040978
		34	5.04785E-07	0.002029339	0.00024874	119.4429468	0.029710657
		34.25	4.8984E-07	0.002029339	0.00024138	119.4429468	0.028831057
		34.5	4.83462E-07	0.002029339	0.00023824	119.4429468	0.028455664
		34.75	4.65855E-07	0.002029339	0.00022956	119.4429468	0.027419308
		35	6.21562E-07	0.002029339	0.00030629	119.4429468	0.036583914
		35.5	5.50146E-07	0.002029339	0.0002711	119.4429468	0.032380556
		36	5.41223E-07	0.002029339	0.0002667	119.4429468	0.031855353
		36.5	3.22914E-07	0.002029339	0.00015912	119.4429468	0.019006119
		37	3.52672E-07	0.002029339	0.00017379	119.4429468	0.020757584
		37.25	7.22707E-07	0.002029339	0.00035613	119.4429468	0.042537159
		38	1.27796E-06	0.002029339	0.00062974	119.4429468	0.075217966

Table C.1. (continued)

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles injected into the GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.5%Cs) - IWI	HFP	28	1.62757E-06	0.000811735	0.00200505	119.4429468	0.239488672
		28.5	1.69689E-06	0.000811735	0.00209044	119.4429468	0.249688492
		29	1.70254E-06	0.000811735	0.00209741	119.4429468	0.25052064
		29.5	1.58608E-06	0.000811735	0.00195393	119.4429468	0.233383659
		29.75	1.72854E-06	0.000811735	0.00212944	119.4429468	0.254346775
		30	1.67944E-06	0.000811735	0.00206894	119.4429468	0.247120845
		30.5	1.40619E-06	0.000811735	0.00173233	119.4429468	0.206914086
		31	1.86379E-06	0.000811735	0.00229606	119.4429468	0.274247983
		31.5	1.15861E-06	0.000811735	0.00142733	119.4429468	0.170484355
		32	1.4128E-06	0.000811735	0.00174046	119.4429468	0.20788614
		32.5	1.46339E-06	0.000811735	0.00180279	119.4429468	0.215330907
		32.75	1.61618E-06	0.000811735	0.00199102	119.4429468	0.237812986
		33	1.54984E-06	0.000811735	0.00190929	119.4429468	0.228050928
		33.25	1.53355E-06	0.000811735	0.00188923	119.4429468	0.225654966
		33.5	9.40959E-07	0.000811735	0.00115919	119.4429468	0.138457503
		33.75	1.3872E-06	0.000811735	0.00170893	119.4429468	0.204119427
		34	1.28567E-06	0.000811735	0.00158385	119.4429468	0.18917958
		34.25	8.94952E-07	0.000811735	0.00110252	119.4429468	0.131687791
		34.5	9.31757E-07	0.000811735	0.00114786	119.4429468	0.137103526
		34.75	1.31738E-06	0.000811735	0.00162291	119.4429468	0.193845452
		35	1.05894E-06	0.000811735	0.00130454	119.4429468	0.155818077
		35.5	1.26456E-06	0.000811735	0.00155785	119.4429468	0.186074373
		36	1.28074E-06	0.000811735	0.00157778	119.4429468	0.1884547
		36.5	1.60224E-06	0.000811735	0.00197385	119.4429468	0.235762087
		37	9.33675E-07	0.000811735	0.00115022	119.4429468	0.137385693
		37.25	1.14428E-06	0.000811735	0.00140968	119.4429468	0.168375836
		38	7.16561E-07	0.000811735	0.00088275	119.4429468	0.105438532

Table C.1. (continued)

Catalyst	Product component	Reaction time [hours]	Product sample moles [mol]	Total no. of moles injected into the GC [mol]	Molar fraction	Total concentration [mol/dm ³]	Exit concentration of species [mol/dm ³]
10% Cs-CuO/SiO ₂ (0.5%Cs) - IWI	O ₂	28	6.77069E-07	0.002029339	0.00033364	119.4429468	0.03985098
		28.5	6.44407E-07	0.002029339	0.00031755	119.4429468	0.03792856
		29	6.33902E-07	0.002029339	0.00031237	119.4429468	0.037310255
		29.5	6.35677E-07	0.002029339	0.00031324	119.4429468	0.037414701
		29.75	6.25497E-07	0.002029339	0.00030823	119.4429468	0.036815531
		30	5.95093E-07	0.002029339	0.00029324	119.4429468	0.035025995
		30.5	6.01441E-07	0.002029339	0.00029637	119.4429468	0.035399662
		31	5.72918E-07	0.002029339	0.00028232	119.4429468	0.033720817
		31.5	5.52088E-07	0.002029339	0.00027205	119.4429468	0.032494837
		32	5.29019E-07	0.002029339	0.00026069	119.4429468	0.031137037
		32.5	5.05699E-07	0.002029339	0.00024919	119.4429468	0.029764488
		32.75	5.12737E-07	0.002029339	0.00025266	119.4429468	0.030178685
		33	4.77575E-07	0.002029339	0.00023534	119.4429468	0.028109163
		33.25	4.74277E-07	0.002029339	0.00023371	119.4429468	0.027915021
		33.5	4.62045E-07	0.002029339	0.00022768	119.4429468	0.02719506
		33.75	4.42136E-07	0.002029339	0.00021787	119.4429468	0.026023297
		34	5.02913E-07	0.002029339	0.00024782	119.4429468	0.02960051
		34.25		0.002029339	0	119.4429468	0
		34.5	4.15864E-07	0.002029339	0.00020493	119.4429468	0.024476936
		34.75	4.09741E-07	0.002029339	0.00020191	119.4429468	0.024116557
		35	6.46873E-07	0.002029339	0.00031876	119.4429468	0.038073669
		35.5	3.79944E-07	0.002029339	0.00018723	119.4429468	0.022362766
		36	5.28062E-07	0.002029339	0.00026021	119.4429468	0.031080695
		36.5		0.002029339	0	119.4429468	0
		37	5.67797E-07	0.002029339	0.00027979	119.4429468	0.033419438
		37.25	4.33955E-07	0.002029339	0.00021384	119.4429468	0.025541728
		38	2.02386E-07	0.002029339	9.973E-05	119.4429468	0.011912041

Appendix D. Sample calculations

Sample calculations for one experimental run are presented here. The conversion of measurement values using instrument calibration data is not shown.

Feed gas:

Moles of HFP entering the reactor,

$$n_{HFP} = \frac{PV}{RT} = \frac{4.5 \times 10^5 Pa \times 2 \times 10^{-5} m^3}{8.314 m^3 Pa \cdot mol^{-1} K^{-1} \times 298.15 K} = 3.633 \times 10^{-3} mol$$

These are moles per minute

This gives a molar flow rate of HFP, $F_{HFP} = 3.633 \times 10^{-3} mol \cdot min^{-1} = 6.055 \times 10^{-5} mol \cdot s^{-1}$

$$\text{The total inlet concentration} = C_{tot}^0 = \frac{P_{reaction}}{R \times T_{atm}} = \frac{4.5 \times 10^5 Pa}{8.314 m^3 Pa \cdot mol^{-1} K^{-1} \times 298.15 K} = 181.538 mol \cdot m^{-3}$$

Product gas: GC

$$\text{Total injected moles} = N_{TOT} = \frac{P_{atm} \times V_{sample}}{R \times T_{atm}} = \frac{100021 Pa \times 0.00002 m^3}{8.314 m^3 Pa \cdot mol^{-1} K^{-1} \times 296.4126 K} = 8.117 \times 10^{-4} mol$$

$$\text{Total concentration} = C_{tot} = \frac{P_{reactor}}{R \times T_{reactor}} = \frac{450000 Pa}{8.314 m^3 Pa \cdot mol^{-1} K^{-1} \times 453 K} = 119.44 mol \cdot m^{-3}$$

$$\text{Exit concentration} = X_{HFP} \times C_{tot} = \frac{\text{moles of HFP product sample}}{\text{total moles injected}} \times C_{tot} = \frac{1.5408 \times 10^{-6}}{8.117 \times 10^{-4}} \times 119.44 = 2.267 \times 10^{-1} mol \cdot m^{-3}$$

For each individual component, the mole fraction is given by the ratio of the number of moles of the particular species, obtained from the G.C. peak area and calibration data, to the total number of moles injected.

Appendix E. MATLAB® script files

E.1. Kinetic parameter identification, plug flow reactor model (Isothermal fit).

E.1.1. Main program file.

```
% Main Program to identify kinetic parameters
clc
% global variables
global Fin Ctot Xout c2 trxn

% experimental data
Fin = xlsread('ratedata.xlsx','c4:u8'); % inlet flow-rate in mol/s
Xout = xlsread('ratedata.xlsx','h22:z26'); % outlet mole fractions of all components
Ctot = xlsread('ratedata.xlsx','c12:u12'); % total inlet concentration in mol/m^3
trxn = xlsread('ratedata.xlsx','h28:z28'); % reaction times

Wlo = 0; % initial value of the catalyst length (cm) in the reactor
Wlf = 196; % final value of the catalyst length (cm) in the reactor

NN = [1 2 3 4];
c1 = size(Xout);
c2 = c1(2);

lb = [0 0 0 0 0 0];
ub = [inf inf inf inf inf inf];

k0 = [0.5 0.5 0.01 10 0.05 0.01]; % parameter estimates

options = optimset('Display','iter','MaxIter',20,'MaxFunEvals',2000,'TolFun',1e-17,'TolX',1e-17,'LargeScale','off');
```

```

[k,resnorm,residual,exitflag,output,lambda,jacobian]=lsqnonlin(@myfun,k0,lb,ub,options);

% k=k0;

% ci=nlparci(k,residual,jacobian);

FHFP_pred = zeros(1,c2);
FO2_pred = zeros(1,c2);
FHFPO_pred = zeros(1,c2);
FCOF2_pred = zeros(1,c2);
FCF3COF_pred = zeros(1,c2);

XHFP_pred = zeros(1,c2);
XO2_pred = zeros(1,c2);
XHFPO_pred = zeros(1,c2);
XCOF2_pred = zeros(1,c2);
XCF3COF_pred = zeros(1,c2);

for c3=1:c2           %cycle through data points

    Finp=Fin(:,c3);           % inlet flow-rates for one data point
    Ctotp=Ctot(:,c3);
    trxnp=trxn(c3);           % reaction time for one data point

    options=odeset('BDF','on','NonNegative',[1,2,3,4,5],'AbsTol',1e-12,'RelTol',1e-12);
    [W,F]=ode15s(@(W,F) catepox(W,F,k,Ctotp,trxnp),[Wlo,Wlf],Finp,options);

    c4=size(F);
    c5=c4(1);

    Fout_pred=F(c5,:);           % outlet flow-rates predicted by model
    Ftot_out_pred=sum(F(c5,:));   % total outlet flow-rate predicted by model

    FHFP_pred(1,c3) = Fout_pred(1); % exit molar flow-rates, predicted
    FO2_pred(1,c3) = Fout_pred(2);
    FHFPO_pred(1,c3) = Fout_pred(3);

```

```

FCOF2_pred(1,c3) = Fout_pred(4);
FCF3COF_pred(1,c3) = Fout_pred(5);

XHFP_pred(1,c3) = FHFP_pred(1,c3)/Ftot_out_pred; % exit mole fractions, calculated
XO2_pred(1,c3) = FO2_pred(1,c3)/Ftot_out_pred;
XHFP0_pred(1,c3) = FHFPO_pred(1,c3)/Ftot_out_pred;
XCOF2_pred(1,c3) = FCOF2_pred(1,c3)/Ftot_out_pred;
XCF3COF_pred(1,c3) = FCF3COF_pred(1,c3)/Ftot_out_pred;

end

% measured outlet mole fractions

XHFP = Xout(1,:); % measured mole fractions
XO2 = Xout(2,:);
XHFP0 = Xout(3,:);
XCOF2 = Xout(4,:);
XCF3COF = Xout(5,:);

%-----

% Plotting results

figure(1)

plot(XHFP,XHFP_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)

FFDx1=linspace(0,0.7,100);
FFDy1=linspace(0,0.7,100);

hold on

plot(FFDx1,FFDy1,'k-','LineWidth',1)

xlabel('Measured HFP mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')
ylabel('Predicted HFP mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')

```

```

axis square

figure(2)

plot(XO2,XO2_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)

FFDx1=linspace(0,0.3,100);
FFDy1=linspace(0,0.3,100);

hold on

plot(FFDx1,FFDy1,'k-','LineWidth',1)

xlabel('Measured O2 mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')
ylabel('Predicted O2 mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')

axis square

figure(3)

plot(XHFPO,XHFPO_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)

FFDx1=linspace(0,0.3,100);
FFDy1=linspace(0,0.3,100);

hold on

plot(FFDx1,FFDy1,'k-','LineWidth',1)

xlabel('Measured HFPO mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')
ylabel('Predicted HFPO mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')

axis square

figure(4)

```

```

plot(XCOF2,XCOF2_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)

FFDx1=linspace(0,0.6,100);
FFDy1=linspace(0,0.6,100);

hold on

plot(FFDx1,FFDy1,'k-','LineWidth',1)

xlabel('Measured COF2 mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')
ylabel('Predicted COF2 mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')

axis square

figure(5)

plot(trxn,XHFPO_pred)
hold on
plot(trxn,XHFPO,'bo','MarkerFaceColor','blue','MarkerSize',8)

xlabel('modified reaction time','FontName','Arial','FontSize',20,'FontWeight','normal')
ylabel('Experimental and model HFPO mole fraction','FontName','Arial','FontSize',20,'FontWeight','normal')

axis square

figure (6)

plot(XHFP,XHFP_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)
hold on
plot(XO2,XO2_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)
plot(XHFPO,XHFPO_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)
plot(XCOF2,XCOF2_pred,'bo','MarkerFaceColor','blue','MarkerSize',8)

```

```

FFDx1=linspace(0,0.7,100);
FFDy1=linspace(0,0.7,100);

hold on

plot(FFDx1,FFDy1,'k-','LineWidth',1)

xlabel('Measured mole fractions','FontName','Arial','FontSize',20,'FontWeight','normal')
ylabel('Predicted mole fractions','FontName','Arial','FontSize',20,'FontWeight','normal')

axis square

```

E.1.2. Objective function file

```

function Fob = myfun(k)

% Global variables
global Fin Ctot Xout c2 trxn

Wlo = 0;
Wlf = 196;

Fob=zeros(5,c2);

for c3=1:c2                % cycle through data points
    Finp=Fin(:,c3);        % inlet flow-rates for one data point
    Xoutp=Xout(:,c3);      % outlet mole fraction for one data point
    Ctotp=Ctot(c3);
    trxn timerxn(c3);      % reaction time for one data point

    options=odeset('BDF','on','NonNegative',[1,2,3,4,5],'AbsTol',1e-12,'RelTol',1e-12);
    [W,F]=ode15s(@ catexp(W,F,k,Ctotp,trxn timerxn),[Wlo,Wlf],Finp,options);

    c4=size(F);
    c5=c4(1);

```

```

Fout_pred=F(c5,:);           % outlet flow-rates predicted by model
Ftot_out_pred=sum(F(c5,:));   % total outlet flow-rate predicted by model

Xout_pred=Fout_pred./Ftot_out_pred;

for c6=1:5

    Fob(c6,c3)=sum(((Xoutp(c6)- Xout_pred(c6))/(1)).^(2));
end

end

Fob=reshape(Fob,1,[]);
Fob=Fob';

```

E.1.3 Function handle for the ODE integrator

```

function dF = catepox( W,F,k,Ctotp,txnp)
Wcat = 0.7*0.63;           % bulk density * cross sectional area g/cm^3 * cm^2
Ctot_0 = 181.538;          % total inlet concentration in mol/m^3

dF = zeros(5,1);
C = zeros(5,1);

for counterp =1:5;
    if F(counterp)<0;
        F(counterp)=0;
    end
end

% Flow-rates of all species involved
F_HFP      = F(1);
F_O2       = F(2);

```

```

F_HFPO    = F(3);
F_COF2    = F(4);
F_CF3COF  = F(5);

% Rate constants
kox  = k(1)*1e-8;    % rate constant for HFP oxidation
kred = k(2)*1e-8;    % rate constant for catalyst reduction
k2   = k(3)*1e-10;   % HFP + O2 -> CF3COF + COF2
k6   = k(4);         % CF3COF + 1/2O2 -> 2COF2
ka   = k(5);         % activation rate constant
kd   = k(6);         % deactivation rate constant

Ftot = F(1) + F(2) + F(3) + F(4) + F(5); % mol/s

C_HFP    = Ctot_0*F_HFP/Ftot;    % mol/m^3
C_O2     = Ctot_0*F_O2/Ftot;     % mol/m^3
C_HFPO   = Ctot_0*F_HFPO/Ftot;   % mol/m^3
C_COF2   = Ctot_0*F_COF2/Ftot;   % mol/m^3
C_CF3COF = Ctot_0*F_CF3COF/Ftot; % mol/m^3

r1 = (kox*kred*(C_HFP^1)*(C_O2^1)/(kox*(C_O2^1)+kred*(C_HFP^1)));

r2 = k2*(C_HFP^1)*(C_O2^1);
r6 = k6*(C_CF3COF^1)*(C_O2^1);

activation = (1+ka*trxnp);

deactivation = 1/(1+kd*trxnp^2);

% Reaction rates

r_HFP = -(activation*deactivation)*r1-(1/deactivation)*r2;
r_O2  = -0.5*(activation*deactivation)*r1-(1/deactivation)*r2-0.5*r6;
r_HFPO = (activation*deactivation)*r1;

```

```
r_COF2= (1/deactivation)*r2 + 2*r6;  
r_CF3COF = (1/deactivation)*r2-r6;
```

```
% differential balances
```

```
dF(1) = r_HFP*Wcat;  
dF(2) = r_O2*Wcat;  
dF(3) = r_HFPO*Wcat;  
dF(4) = r_COF2*Wcat;  
dF(5) = r_CF3COF*Wcat;
```

```
end
```