Desulfurization of Model Fuel with Mxene-Polyoxometalate Based Catalyst: Optimized by Box Behnken Design

MS Thesis
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Abstract

Desulfurization of Model Fuel with Mxene-Polyoxometalate Based Catalyst: Optimized by Box Behnken Design

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Transportation fuels containing sulfur compounds are very dangerous to the environment and to health since when burnt they result in the generation of sulfur oxides. More stringent fuel regulations have necessitated the urgent need to have efficient and sustainable desulfurization technologies. The paper is concerned with the desulfurization of model fuel with an MXene-polyoxometalate (POM) based catalyst with process optimization being done by using Box-Behnken experimental design.

The synthesis and characterization of a MXene-supported polyoxometalate catalyst was verified by the use of different physicochemical methods to establish the integrity of its structure, surface activity, and catalytic performance. The oxidative desulfurization of model fuel having typical sulfur compounds under mild reaction conditions was tested as catalystics. The most important operating parameters such as the dose of catalyst, oxidants to sulfur ratio, temperature of reaction, and reaction time were carefully explored.

The Box Behnken design of Response Surface Methodology (RSM) was used to approximate and optimize the desulfurization reaction and reduce the amount of experimental experiments. The predicted and experimental results were found to have a strong correlation and the developed quadratic model was found to possess high significance and reliability as statistically determined. The synergistic outcome between MXene and polyoxometalate elements was observed as a great removal of sulfur rate under optimal reaction conditions.

This is due to the high surface area, good electron transfer characteristics of MXene and the high oxidative ability of the polyoxometalate which have increased desulfurization performance. Also, the catalyst was well stabilized and could be used repeatedly in various cycles, which implies that it can be used practically. In general, the study indicates that the use of MXene polyoxometalate based catalysts and

statistic optimization by Box Behnken design is a cost effective and eco-friendly method of deep desulfurization of fuels which can be useful in industrial desulfurization technology in future

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Chapter 1
Introduction

The rising need of clean and environmentally benign fuels in the world has spearheaded research in the effort of developing efficient desulfurization processes. During the petroleum processing, studies show that sulfur compounds naturally found in crude oil are passed to refined fuels, e.g. thiophenes, benzothiophenes and dibenzothiophene. These sulfur species on burning are then transformed into sulfur oxides (SO) that are a leading cause of air pollution, acid rain, catalyst poisoning, and serious human health effects, including respiratory and cardiovascular diseases. As a result, strict environmental laws have been put in place all around the globe to restrict the quantity of sulfur in transport fuels to extremely low levels which are normally under 10-15ppm. [1]

The most common and widely used industrial process of removing sulfur is conventional hydrodesulfurization (HDS). Even though HDS is extremely efficient with aliphatic sulfur compounds, it is inefficient with aromatic and sterically hindered sulfur species which are dibenzothiophene and its derivatives. Furthermore, HDS cannot work in conditions of low temperature, pressure, and a significant amount of hydrogen; therefore, the operational cost is high, and carbon footprint is also big. [2] These drawbacks have prompted the exploration of other desulfurization methods which can be used under milder and more sustainable conditions

ODS has also become a promising secondary or alternative method of HDS. Sulfur compounds are selectively oxidized in ODS to form sulfoxides and sulfones which are more polar and can be extracted or adsorbed with ease. The main benefits of ODS are that the reaction conditions are mild, refractory sulfur compounds are highly selective, and it is less dependent on hydrogen The performance of ODS is though highly influenced by the kind of catalyst and oxidant used.

Polyoxometalates (POMs) have become an area of high interest as ODS catalysts because of their clear-cut molecular structures, good redox capabilities, good thermal stability, and high oxidative activity. Keggin-type POMs (especially) have proven to be exceptionally efficient in activating oxidants like hydrogen peroxide in the sulfur oxidation. Although these have their strengths, the disadvantages of using POMs are low surface area, high solubility in polar media, and inability to recover the catalyst which restricts their industrial use. [3]

MXenes are a new generation of two-dimensional two transition metal carbides and

nitrides, which have of late found applications in catalysis and the environment. They are an excellent catalyst support in their layered structure, large surface area, good electrical conductivity, and good surface functional groups. MXenes offer a high number of anchoring spots of active species and permit electron transfer during catalytic reactions. Individual limitations could be synergized by the combination of POMs and MXenes to promote catalytic performances.

MXene polyoxometalate composite catalysts are made with the good oxidative power of POMs, the structural stability and conductivity of MXenes. These types of hybrid systems are more dispersed with active sites, are more resistant to leaching, and have better catalytic activity in oxidative desulfurization reactions.[4] The above characteristics render MXene-POM composites one of the most promising candidates to deep desulfurization of model fuels.

Besides the creation of catalysts, process optimization is also important in enhancing desulfurization. Response Surface Methodology (RSM) or Box-Behnken Design (BBD) is a potent statistical technique of optimizing multivariate systems at a lower rate of experiments. BBD can be used to assess the interaction effect on the operational parameters, including the dosage of a catalyst, the amount of oxidant, temperature, and reaction time, reporting optimum conditions of process with high reliability.

Hence, this study gives attention to desulfurization of model fuel by the use of a MXene-polyoxometalate-based catalyst by oxidative desulfurization with optimization of the process being done using Box-Behnken Design. [4] The yield of this study is likely to enhance the establishment of efficient, sustainable and economically viable desulfurization technologies of ultra clean fuel production.

1.1 Background of Fuel Desulfurization

Oil and its origin are embedded in the product because of the pollutants found in the oil. Sulfur is a natural contaminant of the crude oil which is created by the geological and biological actions during millions of years. In the process of petroleum refining, sulfur-based compounds are apportioned to different fuel products, such as gasoline, diesel, jet fuel and heavy oils. These sulfur species are found in various chemical forms like mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, and dibenzothiophenes whereby, the chemical stability increases as the structure becomes aliphatic to aromatic.

The sulfur content of fuels is of great environmental, technical and health related concern. Sulfur oxides (SO_2 and SO_3) are emitted into the atmosphere when the sulfur-containing fuels are burnt. These oxides combine with water vapor to produce sulfuric acid, which adds to acid rain, haze in the atmosphere, and fine-particles. Acid rain causes soil erosion, destruction of forests, disequilibrium of aquatic ecosystems as well as the corrosion of structures and infrastructure [5] Secondly, sulfur oxides are also considered to contribute to respiratory diseases, asthma, and heart diseases, despite the fact that sulfur emissions represent the major concern of the public health.

Industrially, sulfur compounds have a detrimental impact on the quality of fuel and engine performance. They are corrosive to fuel systems and poison catalysts in technologies of exhaust treatment like catalytic converters and diesel particulate filters. Sulfur also interferes with the high-end emission control methodology, and thus, deep desulfurization is a requirement to the contemporary clean-fuel technologies.

In a bid to reduce these effects, countries and environmentalists across the world have established more strict fuel sulfur laws. In recent decades, there has been a steady lowering of legal sulfur content in transportation fuels, to the level of ultra-low, usually less than 1015 ppm. The purpose of such regulations is to clean the air, indirectly lower greenhouse gas emissions and allow cleaner technologies of combustion. These regulations introduce major technical challenges to the refining industry with compliance.

The most common industrial process of remove sulfur has been the hydrodesulfurization (HDS). During this, sulfur compounds are catalytically hydrogenated in high temperatures and pressure to form sulfur hydrogen sulfide. Despite the high efficiency of HDS in the elimination of aliphatic sulfuric compounds, it has a low efficiency in eliminating aromatic sulfur species like dibenzothiophene and the alkylated species because of steric hindrance and the existence of strong C-S bonds. In addition, HDS

consumes a lot of hydrogen, its working conditions are harsh, and the cost of capital and operation is very high [6]

Increasing need of ultra-low sulfur fuels has revealed the weakness of the traditional HDS, especially in the process of refractory sulfur. The severity of the process to increase the sulfur removal causes a rise in the consumption of energy, deactivation rate of the catalyst, and emission of greenhouse gases These limitations have provoked the active search of alternative or complementary technologies of desulfurization, which will perform under more moderate and sustainable conditions.

Oxidative desulfurization (ODS) has received significant interest among new methods. ODS is the selective oxidation of sulfur compounds to sulfoxides and sulfones which are more polar and can be readily removed by extraction or adsorption of fuel. The key benefits of ODS include its efficacy with regard to aromatic sulfur compounds with mild conditions of reactions and without high-pressure hydrogen.

Heavy reliance on the catalyst system used makes the success of ODS highly reliant on the coordinating system used. The characterization of an ideal desulfurization catalyst is high oxidative activity, selectivity of sulfur compounds, thermal and chemical stability, and reusability. In the recent times, more attention has been given to the development of more advanced catalysts, including metal oxides, ionic liquids, heteropoly acids, and nanostructured materials, to increase ODS efficiency. In these regards, the design of new catalytic materials has emerged as the theme of central focus in fuel desulfurization studies. High-performance catalysts do not only enhance the level of sulfur removal but also minimize environmental impact and cost of processing. Hybrid and nanocomposite catalysts, specifically, have synergies as they have several functional properties in a single system [7]

Thus, fuel desulfurization has increasingly become more of a multidisciplinary research field not only in the fields of catalysis and materials science but also in environmental engineering and process optimization. The further development of catalysts and desulfurization methods is needed to satisfy energy needs of the future and remain environmentally friendly.

Figure *1*: Fuel Desulfurization

1.2 Environmental and Regulatory influence of Sulfur Removal

The issue has been noted as a potential driver of the development of environmental and regulatory concerns in the oil and gas sector. Transportation fuels contain sulfur compounds which are a significant source of environment pollution and a great threat to human health. The burning of fuels with sulfur content can yield sulfur dioxide (SO_2) and sulfur trioxide (SO_3) during burning, which cause acid rain, smog, and small particle matter (PM 2.5) in the air. These pollutants have a negative impact on the quality of air, harm the ecosystem, corrode infrastructure, and lead to respiratory and cardiovascular disorders in humans. Moreover, the emission of sulfur has adverse effects on the soil fertility and aquatic organisms because of the changes in pH of the natural water bodies. Technologically, the sulfur compounds are poisonous to the noble metal catalysts employed in contemporary emission control systems, including three-way catalytic converters, and lower their effectiveness and performance. This has fueled the necessity towards the ultra-low sulfur fuels in order to be compatible with the new engine and after-treatment technologies. Consequently, the process of the sulfur removal has become a crucial part of the fuel refining and upgrading.

Strict environmental policies have been adopted by regulatory bodies in most countries globally to restrict the use of sulfur in fuels. Examples of such regulations include the Euro VI rules, the US Environmental Protection Agency (EPA) Tier 3 rules and other rules in Asia, which require a gasoline and diesel content that is as low as 1015 ppm of sulfur. These rules are supposed to cut down air pollution caused by vehicles by a large

percentage and help to clean up the air in the cities. Adherence to these standards has forced the refineries to embrace the use of more efficient and sustainable desulfurization technologies.

The pressures on the environment and regulation have therefore increased the pace of research on alternative methods of sulfur removal such as oxidative desulfurization and new advanced catalytic systems. To help the world achieve a cleaner and more sustainable fuel production, the more important task is the development of innovative catalysts, which will be used under mild conditions to ensure regulatory compliance and the reduced consumption of energy [8]

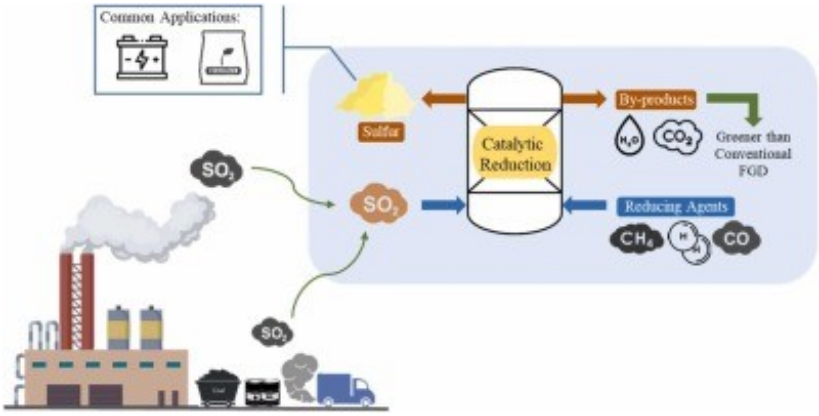

Figure 2:Sulfur Removal Impact on Environment

1.3 Limitations of Conventional Desulfurization Techniques

Traditional methods of desulfurization, especially hydrodesulfurization (HDS) have been widely utilized in the refineries of petroleum products in removing sulfur in fuels. Although they are industrial and can be relied on, these approaches have a number of inherent flaws that limit their ability to comply with the ever-tightening environmental requirements. The significant limitation of HDS is that it is not as efficient as removing the refractory sulfur compounds of thiophene, benzothiophene, dibenzothiophene and in particular their alkylated forms such as 4,6-dimethyldibenzothiophene. These compounds have high steric hindrance and this decreases their accessibility to active catalytic sites. [9]

The other major weakness is that it demands extreme operating conditions. Traditional HDS processes are generally run at high temperature (300 to 400C^{o}) and high pressure of hydrogen (3 to 10 MPa) which makes them expensive in terms of energy and cost of

operations. The reliance on bulk amount of high purity hydrogen contributes to economic and logistical issues further especially in areas that are scarce or expensive in the supply of hydrogen. A major problem also in the conventional desulfurization is catalyst deactivation. The sulfide catalysts are also prone to poisoning by nitrogen containing compounds, aromatics and metals found in crude oil, which cause them to become less active and they are often regenerated. Besides, coke build-up on the surfaces of catalysts during long service further reduces efficiency and catalyst life.

Traditional methods may not be particularly selective, and may result in unwanted hydrogenation of aromatic hydrocarbons as well as de-sulfurization. This hydrogenation lowers the fuel octane number and has negative impact on the quality of fuel. Also, severe conditions of reaction could result in crack reaction, yielding unwanted by-products and reducing the overall fuel yield.

The traditional methods of desulfurization are also associated with the environmental issues. There is also a high rate of hydrogen consumption which indirectly leads to the emissions of carbon dioxide particularly where fossil fuels are used to produce hydrogen [10] Moreover, the process of sulfur removal by HDS transforms sulfur compounds into hydrogen sulfide H_2S which must also be treated further by Claus processes, resulting in more waste and creating problems of environmental management.

Lastly, the traditional desulfurization methods are less flexible to the processing of a lighter fuel or model fuel under lenient conditions. With the world regulations still requiring extremely low sulfur content in fuels, the technical, economic and environmental constraints of the traditional desulfurization processes, the alternative and more sustainable techniques of oxidative desulfurization and the new generation of catalytic systems have become the focus of necessity.

1.4 Oxidative Desulfurization: An Overview

Oxidative desulfurization (ODS) is a modern method of fuel-cleaning that was invented to eliminate sulfur-containing substances in liquid fuels with mild conditions of operation. It has become a major focus because it is an alternative to the traditional hydrodesulfurization (HDS), especially in cases of deep desulfurization. ODS is particularly useful with refractory sulfur compounds as dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4, 6-dimethyldibenzothiophene (4, 6-DMDBT). It is done by oxidation of sulfur compounds to the sulfones or sulfoxides. These oxidized compounds are more polar than the sulfur compounds. They are highly polarizable and

thus can be extracted, adsorbed, or precipitated easily. ODS is normally used at low pressure and temperatures (30-80 Celsius) [11] This renders the process cost effective and green. In a standard ODS process, either molecular oxygen, tert-butyl hydroperoxide or hydrogen peroxide is taken as an oxidant. The most preferred of these is hydrogen peroxide in that it has a high oxidation and environmentally friendly by-products.

The oxidation reaction is catalyzed frequently to enhance efficiency and selectivity. Examples of common catalysts are polyoxometalates (POMs), transition metal oxides, ionic liquids, and metal-organic frameworks. In the recent past, nanostructured catalysts and hybrid materials have been found to be better. These are the materials that offer high surface area and greater availability of active sites. ODS mechanism entails the removal of oxygen of the oxidant and the introduction to the sulfur atom [12] The oxidation of sulfur compounds is first converted into sulfoxides. As further oxidation takes place, the sulfoxides are further reduced into sulfones. The catalysts reduce the activation energy of such reactions.

Reaction kinetics and oxidation selectivity is also enhanced with the use of catalysts. Parameters of reaction include temperature, oxidant to sulfur ratio and dosage of catalysts, which have a severe effect on performance. These parameters need to be optimized properly in order to attain the greatest amount of sulfur removal. ODS has one of the greatest merits in that it does not need new refinery infrastructure. ODS may be used as a post-treatment of traditional HDS units. This hybrid technology has made it possible to produce ultra-low sulfur fuels.

ODS does not need hydrogen, and this lowers the cost of operations and safety issues.

Another concern that is avoided in the process is catalyst poisoning which is prevalent in HDS.

In addition, the ODS is extremely specific to sulfur and not fuel hydrocarbons. Nevertheless, ODS has some issues regardless of its benefits. Catalysts may be challenging to separate and recover. Large scale use may be restricted by the use of oxidants and their cost.

Emulsions formed during extraction activity may make it difficult to separate the products. The research issue of catalyst stability and recyclability are the topic of interest.

Oxidants that are greener and reusable catalysts are being worked on. In general, oxidative desulfurization is a potential and viable method of deep desulfurization. It can be used in particular to satisfy strict environmental standards. The possibility of its

industrial application is growing with continuous improvements to the catalyst design and optimization of the process [13]

1.5 Role of Advanced Catalysts in Desulfurization

The role of Advanced Catalysts in Desulfurization Advanced catalysts in desulfurization catalyzes the reaction of sulfur-containing compounds with hydrogen sulfide, the primary sulfur-based gas, to form sulfuric acid (H2O2). High-order catalysts are very important in enhancing efficiency and selectivity of the desulfurization processes. They are particularly useful in obtaining ultra-deep sulfur removal as demanded by the contemporary environmental rules. Traditional

Hydrodesulfurization catalysts are not very active against refractory sulfur compounds. The best catalysts are developed to address these shortcomings by improving catalytic performance. They allow the removal of sulfur at a lower temperature and pressure. This minimizes the use of energy and the cost of running fuel processing.

In the oxidative desulfurization (ODS), improved catalysts boost the oxidation of sulfur compounds. They facilitate the effective movement of oxygen that is present in oxidants to the sulfur atoms. It leads to quick transformation of thiophenic compounds into oxides or sulfones.

Polyoxometalates (POM) are very popular because they possess high redox capabilities [14] . They have good molecular structures and strong oxidative potential. Tunable acidity and metal composition is also provided in POMs.

Nanostructured catalysts have received a lot of interest in the last few years. Their large surface-volume ratio makes more available active sites. This increases the contact of sulfur compounds and catalytic centers. TiO2, MoO3, and WO3 are metal oxide nanoparticles which exhibit good catalytic activity. Dispersions are also enhanced by supported nanoparticles. Supports made of carbon are used to stop the agglomeration of particle.

Two-dimensional materials have become promising catalyst support materials. Graphene, MXenes, and layered double hydroxides are some of the most popular materials that are being studied. They are highly conductive electrically and stable. The catalysts based on MXene contain large quantities of surface functional groups. These functional groups contribute to a good interaction with active species. This leads to enhanced catalyst anchoring and electron transfer by such interactions. Another type of modern catalysts are metal-organic frameworks (MOFs).

They have high porosity and are able to adsorb high sulfur compounds' offer active and tunable pore sizes. This results in increased selectivity and efficiency with regard to oxidation. The hybrid MOF-based catalysts consist of adsorption and catalytic oxidation. Ionic liquid catalysts are increasing in significance as well. They are solvent and catalyst in desulfurization systems. They are highly polar and therefore enhance extraction of oxidized sulfur compounds. Specific ionic liquids that are task-specific can be targeted to eliminate sulfur. [15]

Sulfur selective catalysts are advanced. They reduce the undesirable oxidation of fuel hydrocarbons. This assists in maintaining the quality of fuel and calorific value. Another high benefit is reusability of catalysts. Numerous advanced catalysts can be recycled and reused and still retain significant activity without a significant loss of activity. Although this has been made progress, there are still difficulties in catalyst cost and scalability. The stability in the long term under industrial conditions should be guaranteed. Future studies are on the synthesis of low cost and eco-friendly catalysts. It is important to incorporate the high-level catalysts and optimization of the process. In general, progressive catalysts are the main to efficient, lasting, and profound desulfurization procedures.

1.6 Mxenes: Structure, Properties and Applications

MXenes constitute a new fast-moving group of two-dimensional (2D) materials based on layered MAX phases. Selective etching of the A element of the MAX phases was the first to discover them in 2011.The general formula of MAX phases is Mn+1AXn with M being an early transition metal. The element A most commonly is in the group of 13 or 14 elements. Where X indicates carbon and/or nitrogen atoms. Selective etching causes the A-layer to be removed and the M-X layers to remain intact. The product of the process is 2D MXene sheets whose general formula is Mn +1XnTx.Surface termination groups are denoted by the term Tx. Typical terminations of the surface are -O, -OH and -F groups. These functional groups are formed out of the etching process. Surface terminations are critical towards the determination of MXene properties. MXenes are often accordion shaped with a lot of layers. Their interlayer distance is intercalable. Exfoliation is enhanced by intercalation into single or a few-layers nanosheets. [16]

MXenes have high metallic MX bonds in structure. These attachments are very good both mechanically and chemically. MXenes have good electrical conductivity in contrast to other 2D materials. There are MXenes which conduct similarly to metals. They are hydrophilic as opposed to graphene. This allows it to be dispersed easily in aqueous

media due to this hydrophilicity. MXenes exhibit great thermal and mechanical characteristics. They are flexible and have high Young modulus. They are also thermally stable making them applicable in high temperature applications. MXenes also have a good electromagnetic shielding. They have a high level of attenuation of electromagnetic waves due to their layered structure.

The MXenes are very versatile because of surface chemistry. Surface modification is easy in functional groups. This allows anchoring of metals, oxides as well as polymers. MXenes also have high adsorption capacity of ions and molecules. This property finds value in the field of the environment. MXenes have found wide application in supercapacitors in the area of energy storage. [17]

They have a high capacitance and a rapid charge discharge rate. MXenes are also investigated to be used as anode materials in lithium-ion batteries. Their stratified form allows the process of ion intercalation. They are also investigated in the sodium-ion and potassium-ion batteries.

MXenes are used as catalysts supports and active catalysts in catalysis. They increase the transfer of electrons and catalysis. MXenes find application in the oxidative desulfurization.

They enhance dispersion and stability of catalysts. Sensors and biosensors are also based on MXenes. They are highly conductive making them sensitive to detect gases and biomolecules. MXenes are used in the extraction of heavy metals and dyes in the field of environmental remediation. They have a high adsorption of pollutants. In biomedicine, it can be used to deliver drugs or in bioimaging. They are biocompatible because of their surface functionalization.

Nevertheless, there are challenges including the problem of oxidation stability. Continued study is done to work on the enhancement of synthesis and durability. In general, MXenes are a multi-purpose material with enormous possibilities in various applications. [18]

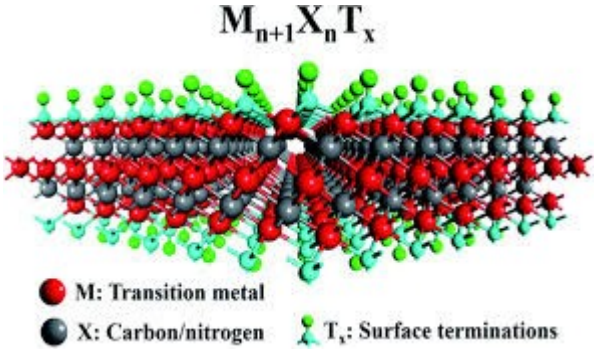

Figure *3*: Structure of Mxene

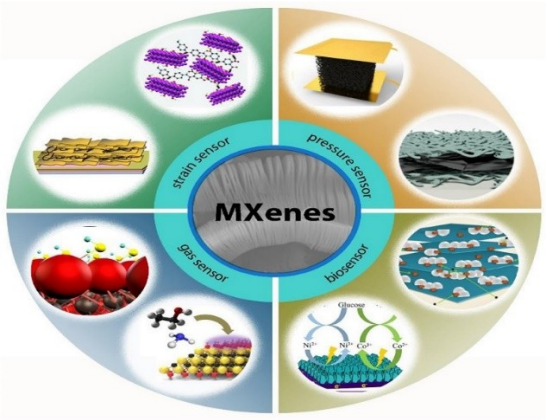

Figure *4*: Applications of Mxene

1.7 Polyoxometalate: Structure, Types and Catalytic Properties

Polyoxometalates (POMs) represent a special group of metal–oxygen cluster compounds that are principally based on early transition metals tungsten (W), molybdenum (Mo) and vanadium (V) in their oxidized forms. These metals are connected with each other by sharing oxygen atoms and make discrete, nanoscale anionic structures with distinct structures. Given that they are molecular, can be tuned in composition and exert an exceptional redox potential, POMs have become of great interest in the fields of catalysis, materials science, energy storage.

Polyoxometalates consist of a basic structure of the MO6 octahedron, with M being a transition metal (W, Mo, or V) bonded to six oxygen atoms. Corners These octahedra do not share any oxygen atom in the form of corners, they share oxygen atoms in the form of edges. The resultant structures are very symmetric and bear well-defined sizes which are usually between 1 and 3 nm. The POM may be in the form of discrete molecular anions in solution form or can be in the form of salts in the solid state when paired with appropriate counter cations including alkali metals, ammonium, and organic cation.[19]

The presence of various forms of oxygen atoms which may include, but not be limited to, terminal oxygen (M=O), bridging oxygen (M–O–M), and occasionally protonated oxygen is also one of the most notable aspects of POM structures. These oxygen conditions are important to define acidity, redox capability, and catalytic activity of POMs. Their

structural diversity, functional tunable, is further increased by the capability to introduce heteroatoms (P, Si, or Ge) into the structure.

Polyoxometalates are either isopolyoxometalates or heteropolyoxometalates depending on their composition. In isopolyoxometalates, the structure is made up of only metal and oxygen atoms, and there is no heteroatom in the centre. These POMs are usually created through condensation of metal oxide units in acidic conditions, and usually have more simple structures. Even though they have interesting redox properties, their catalytic uses are constrained to some extent as compared to heteropolyoxometalates.

Heteropolyoxometalates are, however, heteroatomic (with a central heteroatom of P5+, Si4+ or Al3+) with shells of metal-oxygen octahedra. The most recognisable of these are the Keggin, Dawson and the Anderson structures. Keggin structure, is the most widely studied because of its high stability and deep acidity. The structure of Dawson-type POMs is more extended and includes more active sites, whereas Anderson-type POMs have a planar structure with clear coordination environments. In addition to these classical structures, lacunary POMs, which have been created due to the loss of one or more units of MO 6 are open sites where metal ions can be anchored or they can make a hybrid catalyst. [20]

Polyoxometalates have been used in catalytic reactions with a range of reagents. The unique features of polyoxometalates as catalysts include simultaneous redox activity and strong Bronsted acidity as well as stability in structure. They are very effective in oxidation and reduction reactions because of their capability of undergoing multi-electron redox processes in a reversible manner with very little structural degradation. This property is especially useful in the environmentally friendly catalytic processes, including oxidative desulfurization, selective oxidation of organic compounds as well as degradation of pollutants.

The ability of the heteropolyoxometalates to be effective acid catalysts in reactions such as the reaction of esterification, alkylation and hydrocarbon cracking occurs due to their high acidity. Compared to classical mineral acids, POMs are reusable and less corrosive, which is their benefit and makes them a safer alternative. Also, the composition of POMs can be varied by replacing metal centers, their immobilization to solid surfaces or making them based on other materials, including silica, polymers, or other novel materials, including MXenes.

Moreover, POMs are highly stable thermally and chemically, which means that they can

be used in reactions with severe conditions. Their adjustable electronic structure and capability to constitute hybrid materials have added their use in photocatalysis, electrocatalysis and energy-related reactions. Due to that, polyoxometalates will remain crucial in the design of future catalytic systems towards sustainable chemistry and clean energy technologies.

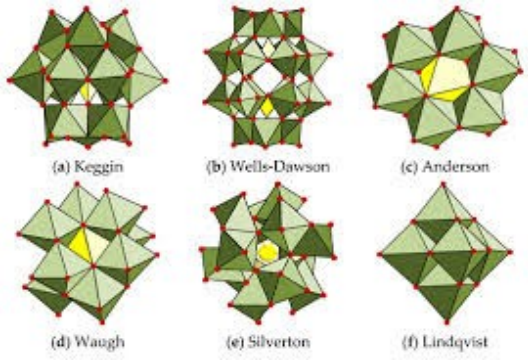

Figure 5: Types of Polyoxometalates

1.8 MXene–Polyoxometalate Composite Catalyst

MXene-polyoxometalate (POM) composite catalysts constitute a new type of hybrid materials, representing the integration of the outstanding redox and acidic characteristics of the POMs with the large surface area, conductivity, and the layered structure of the MXenes. MXenes are two-dimensional transition metal carbides, nitrides or carbonitrides, which are obtained by etching of MAX phases. They have numerous functional groups like -OH, -O and -F that help in strong interactions with POM clusters. With the POMs, MXenes serve as highly effective supports, which inhibit the aggregation and leaching of POM hence, increasing catalyst stability and reusability.

MXene-POM composite is usually formed by the electric interaction, the hydrogen bond, or covalent connection via surface functionalization (e.g., APTES modification). Positively modified MXene surfaces can uniformly be sparsed by negatively charged POM anions and the active sites of negatively modified MXene are well dispersed at the nanoscale. [29] Such close contact between the faces facilitates effective charge transfer between MXene sheets and POM clusters that is essential in redox based catalysis. Consequently, the synergies of these composites are better than those of MXene or POM constituents.

Catalytically, the MXene-POM composites are impressive in the oxidation of reactions, in especially the oxidative desulfurization (ODS) of fuels. In these systems, the main

redox-active centers that can activate the oxidants such as hydrogen peroxide or tert-butyl hydroperoxide are POMs, and MXenes are used to conduct the electron transport and offer an easily accessible site to adsorb the reactants. The multifaceted architecture of MXenes promotes mass transfer of sulfur-based compounds, which is easy to transform refractory sulfur species like dibenzothiophene into the sulfone using mild conditions.

The other important benefit of MXene-POM composite catalysts is that they can be tuned to have physicochemical properties. With the choice of varying POM structures (Keggin, Dawson or lacunary POMs) or the composition and surface chemistry of MXene, it becomes possible to specifically tune catalytic activity, acidity and selectivity. Also, they tend to have better thermal and chemical stability than unsupported POMs and thus can be used in repeated catalytic cycles. High anchoring of the POMs on MXene surfaces reduces the loss of the catalysts, and ensures the sustained use of the catalysts.

In addition to desulfurization, MXene-POM composites have been used in photocatalysis, electrocatalysis and in environmental remediation. The redox flexibility of POMs also allows multi-electron transfer reactions, and the conductive character of MXenes increases the electron mobility which is useful to photo- and electro-chemical reactions. Such a combination renders MXene 2 -POM composites highly versatile and efficient catalysts in long-lasting chemical reactions, which makes them the next-generation catalytic materials. [21]

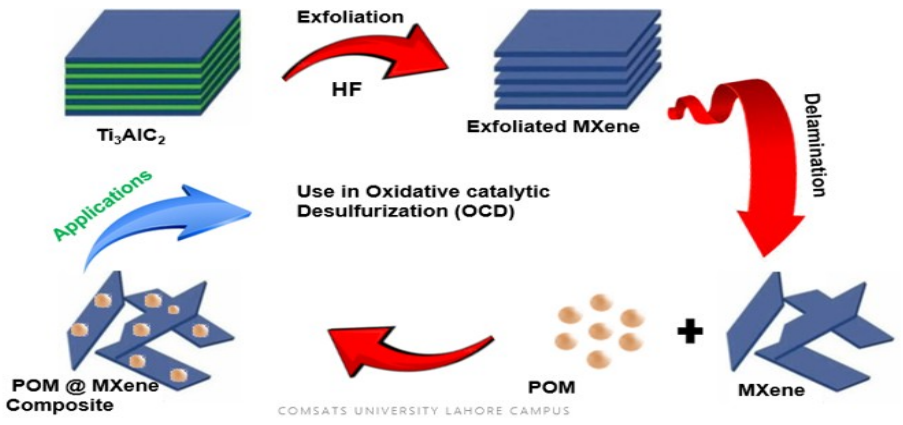

Figure *6*:Mxene-POM Composite

1.9 Research Problem and Justification

The demand of ultra-clean fuels is always growing; this has placed companies in the petroleum-derived fuels with strict environmental policies concerning the sulfur content

of their products because the sulfur oxides generated during combustion are the key contributors to air pollution, acid rain, and unhealthy individuals. The conventional hydrodesulfurization (HDS) has a major drawback in that it requires high operating temperature and pressure, high hydrogen usage, and low refractory sulfur usage such as dibenzothiophene and its derivatives. Consequently, it is in urgent need of alternative desulfurization technologies, which can be run under mild conditions without compromising the efficiency and selectivity.

The use of oxidative desulfurization (ODS) has become one of the promising complementary

methods but the large-scale application remains unfavorable due to the challenges that are associated with the catalysts. Polyoxometalates (POMs) are highly active in redox, very acidic, but low-surface-area molecules, which have a history of low recyclability, leaching in homogenous systems, and unsupported heterogeneous systems. These disadvantages cause the deactivation of catalysts and the secondary contamination, decreasing their practical application. Conversely, although MXenes have high surface area, tunable surface chemistry, and high electrical conductivity, the intrinsic catalytic activity of MXenes to oxidation reactions is comparatively low. One of the gaps in the research is the absence of an optimized

hybrid system that can take advantage of the benefits of both POMs and MXenes synergistically.

Development of MXene-polyoxometalate composite catalysts is the rational answer to the above challenges as there is a combination of the complementary properties of two materials in one functional system. The pretreatment of POMs on MXene surfaces can be an efficient method to escape leaching and aggregation of POMs, besides greatly enhancing the accessibility of active sites. The high density of surface functional groups on MXenes enable high specifications of interactions with POM clusters, which results in a high structural stability of MXenes and a high catalytic persistence during the reaction condition.

Also, the synergistic response between MXenes and POMs facilitates effective electron transfer and activation of oxidants; this is critical towards high-performance oxidative desulfurization under mild conditions. This type of catalyst design facilitates the increased conversion of refractory sulfur compounds at comparatively lower temperature, pressure and hydrogen usage, thus, rendering the process more energy-saving and

environmentally-clean. Moreover, MXene-POM composites are tunable, which enables one to control the acidity, redox properties, and the morphology of catalysts precisely and optimize the catalysts using statistical modeling techniques like Box-Behnken design. [22]

In a broader view, the study is warranted by the fact that it would bring about sustainability in the fuel processing and safeguard the environment. The effective fabrication of MXene-POM composite catalysts has the potential of presenting cost-effective, reusable, and high efficiency catalytic systems that can be used in clean fuel technologies of the next generation. Furthermore, the results of the present research may be generalized to other catalytic tasks like pollutant degradation, selective oxidation, and energy conversion, which serves as the support of the scientific and practical value of the given research.

1.10 Objectives of Study

The main aim of the research is to develop and design an effective MXene-polyoxometalate composite catalyst that can be used to increase the oxidative desulfurization of model fuel under the mild and environmentally friendly reaction conditions. This means that the synthesis of a stable hybrid material where polyoxometalate clusters are deposited on the MXene surface uniformly to make the maximum number of catalytically active sites and least catalyst leaching and deactivation when used in a repeated fashion.

The other goal is to characterize in detail the structural, morphological, and physicochemical characteristics of the created MXene polyoxometalates composite with the help of sophisticated analytical methods. These studies are meant to prove that it was successfully functionalized, how the interactions between MXene and polyoxometalate species operate and how surface chemistry, dispersion, and interfacial bonding affect catalytic performance. To design rational catalysts, it is important to establish their clear structure-property relationships.

It is also in the interest of the study to determine the catalytic efficiency of the developed composite in oxidative desulfurization of the refractory sulfur containing compounds found in model fuels. This involves the exploration of the impacts of the main reaction parameters on the efficiency of the removal of sulfur using catalyst dosage, oxidant concentration, reaction temperature, and reaction time. Special focus is made on the fact of high conversion and selectivity of sulfones in the case of low-energy input conditions.

Moreover, one of the goals of this work is to maximize the oxidative desulfurization process with the help of the statistical experimental design, namely, the Box-Behnken design. The aim of this optimization is to find out which operation variables are the most important and how they interact with each other to provide an optimal environment in which the maximum desulfurization is reached with minimum use of resources. Application of response surface
methodology is another way of improving the process reproducibility and scalability.

Lastly, the research would attempt to determine the stability, reusability and practical applicability of the MXene-polyoxometalate composite catalyst by performing several catalytic cycles. This study will be conducted by assessing the stability of the catalyst and its long-term activity to reveal the feasibility of using the developed catalyst in long-term clean fuel technologies and to make conclusions that can be applied in other oxidation-based catalytic systems

1.11 Scope and Significance of the Research

The research will be broad enough to include the concept, development, characterization, and implementation of MXene–polyoxometalate composite catalysts in the oxidative desulfurization of model fuels. This work aims at the creation of a hybrid catalytic system in which MXenes are used due to their high-surface area, controllable surface chemistry, and conductivity in combination with polyoxometalates because of their high redox and acidic characteristics. The study fulfills some of the currently important issues faced in the traditional desulfurization processes by offering an effective catalyst that can be used to convert refractory sulfur compounds in mild conditions and thus leads to use of less energy and reduced environmental degradation. Besides oxidative desulfurization, the structural flexibility of MXene-POM composites enables the generalization of the results to other catalytic tasks, including selective oxidation, pollutant degradation and reactions associated with energy, which increases the range of potential applications of the material. Process optimization through statistical experimental structures such as Box Behnken method are also included in the study and have been shown to improve the reproducibility and scalability of the catalytic system hence is also applicable in real industrial application.

This research is important in that it will contribute to the process of fuel sustainability and environmental security. This paper provides an alternative to energy-intensive hydrodesulfurization by providing a reusable, stable, and highly efficient catalyst to meet the ever-increasing needs in ultra-clean fuels. The hybrid MXene POM catalyst is synergistic with regard to the ability to transfer electrons as well as increase the accessibility of the active sites and structural integrity during the process of operation over the many cycles and hence it ensures the long-term stability of the operation. Additionally, the study gives some basic information about the interaction mechanisms involving MXenes and polyoxometalates, which can help in the intelligent design of advanced composite catalysts that can be used in a broad selection of chemical transformations. All in all, this piece of work can contribute to the scientific knowledge of hybrid catalytic systems as well as their application in more sustainable and cleaner industrial processes.[23]

Chapter 2

Literature Review

2.1 Sulfur compounds in Transportation Fuels

Transportation fuels contain sulfur compounds that are either crude oil-based or are retained throughout the refining process because they are chemically stable and diverse in structure. These substances are either simple or complex aliphatic sulfur species that are present in various forms and their occurrence in even a trace level is unwanted due to their disastrous environmental and technical effects. The sulfur containing compounds during combustion of fuel are oxidized to form sulfur oxides (SO_x) that cause air pollution, acid rain, and corrosion and poisoning of catalyst converters. Consequently, it is necessary to determine the nature and behavior of sulfur compounds in the transportation fuels so as to provide effective desulfurization measures.

Smaller molecules of sulfur compounds, including hydrogen sulfide, mercaptans (thiols), sulfides, and disulfides are usually present in lighter fuel fractions such as gasoline. These are fairly reactive substances that can be eliminated more conveniently during the refining by conventional hydrodesulfurization procedures. Nevertheless, even with their less complex structure, they add nasty smells and corrosive properties to fuels and thus have to be removed even in low levels. These species are also highly reactive to oxidative and extractive methods.

Sulfur in the middle-distillate fuels (diesel and jet fuel) is found most commonly in aromatic heterocyclic rings, such as thiophene, benzothiophene (BT) and dibenzothiophene (DBT), and the corresponding alkyl-substituted compounds. [24] These include DBT and more so, 4, 6-dimethyldibenzothiophene which are especially troublesome since their reactivity to conventional hydrodesulfurization catalysts is decreased by steric hindrance around the sulfur atom. These sulfuric compounds refractory are the primary cause of residual sulfur in ultra-low-sulfur fuels, despite harsh fuel refining conditions.

This has been fueled by the continued existence of refractory sulfur compounds, which has prompted the investigation of other means of desulfurizing including oxidative desulfurization (ODS). Sulfur compounds that undergo oxidation in ODS processes are selectively oxidized to their sulfoxides or sulfones which are more polar and are readily extracted or adsorbed out. This

method is particularly useful with aromatic sulfur species not easily desulfurized by hydrodesulfurization, and is therefore of great importance with fuels used in contemporary transport.

In general, transportation fuels include sulfur compounds, which are a major problem in environmental, regulatory, and technological terms. They are very diverse in their chemical nature and hence require very sophisticated catalytic systems that are able to remove them efficiently using gentle conditions. The development of new catalysts, e.g., MXene-polyoxometalate composites, is thus essential to overcome the constraints of the traditional processes and obtain cleaner fuels that meet the rigorous world standards on the sulfur levels. [25]

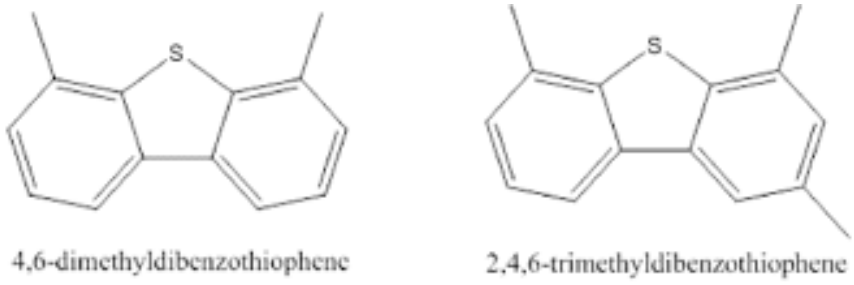

Figure *7*: Sulfur compounds in Fuels

2.2 Conventional Hydrodesulfurization Processes

The most popular industrial method of the removal of sulfur compounds in petroleum-derived transportation fuels (i.e., Gasoline, diesel, and jet fuel) is the conventional hydrodesulfurization (HDS) process. The process is catalytic in which the sulfur-containing compounds are reduced to hydrogen sulfide (H2S) in the presence of hydrogen so that it can be removed out of the hydrocarbon streams. Although HDS is very effective and industrialized in terms of its application with several sulfur species, it has significant technical and economic difficulties, especially due to the tougher fuel sulfur regulations.

A normal HDS process involves the feedstock, which is full of sulfur compounds, blended with high-purity hydrogen and introduced inside a fixed-bed reactor that is packed with sulfide catalysts, typically cobalt–molybdenum or nickel–molybdenum provided on the 7 alumina. The operation is done under harsh conditions generally at the temperature of between 300-400 C and under the pressure of hydrogen between the ranges of 30-130 bar. In such circumstances, the

sulfur-carbon tying in the organic sulfuric compounds is broken by hydrogenation and hydrogenolysis reaction, transforming sulfur to hydrogen sulfide gas but still preserving the hydrocarbon skeleton to a large extent.

The HDS reaction is based on the adsorption of molecules containing sulfur on the active sites on the catalyst where the activation of hydrogen occurs followed by the reaction of hydrogen and the sulfur atom. In the case of simpler sulfur compounds like Mercaptan, sulfides and thiophenes, the sulfur atom is readily available and desulfurization takes place efficiently. The resulting H_2S is split off the hydrocarbon stream downstream by gas liquid separation, and amine scrubbing, and, lastly, it is turned into elemental sulfur in a Claus unit, which makes sure of safe disposal and sulfur recovery.

Nonetheless, the performance of conventional HDS is greatly reduced when dealing with refractory sulfur compounds like dibenzothiophene (DBT) and its alkyl-substituted analogues, in particular, 4,6-dimethyldibenzothiophene. The alkyl groups in these molecules shield the sulfur atom resulting in steric inhibition preventing access to the active sites of the catalyst. The only way to eliminate these compounds is to use more harsh operation conditions or newer catalysts which greatly raise the amount of hydrogen used, energy demand and the operating costs.

The other significant drawback of HDS is that it is not selective to sulfur only. Through desulfurization, hydrogenation of aromatic hydrocarbons is common and this results in the removal of fuel quality characteristics like octane number in gasoline and cetane balance in diesel. Moreover, the pressure and heat condition demands costly material of reactors and complicated safety mechanisms. All these reasons encourage making deep desulfurization by HDS less efficient, less profitable, and less economically attractive because the sulfur limits approach the ultra-low ranges. [26]

In short, although traditional hydrodesulfurization continues to be the cornerstone of the industrial process of sulfur removal, being consistent and scalable, it does not make it well-suited to generate ultra-low sulfur fuels without additional methods. It is energy consuming, hydrogen-dependent and less effective with refractory sulfur species. These inefficiencies have prompted a comprehensive study of alternative methods of desulfurization like the oxidative desulfurization that can work under less severe conditions and which may have better efficiency with sulfur compounds that are hostile to the conventional HDS.

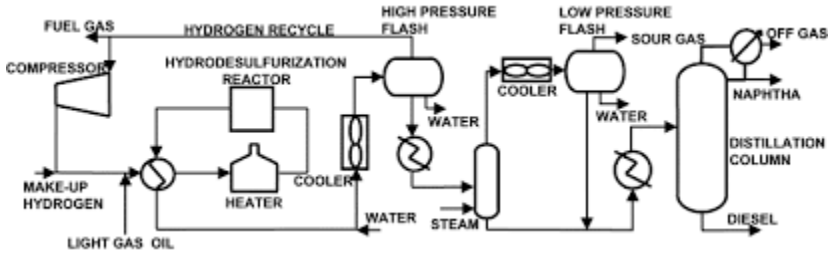

Figure *8*: Conventional Hydrodesulfurization Process

2.3 Oxidative Desulfurization Techniques

Oxidative desulfurization (ODS) is another state-of-the-art fuel purification method invented to address the shortcomings of the traditional hydrodesulfurization, especially when it comes to the purpose of extracting the refractory sulfur compounds out of transportation fuels. The basic concept of ODS is selective oxidation of sulfur containing compounds to yield their sulfoxides and sulfones which are more polar than the starting hydrocarbons. Extraction, adsorption or phase separation may then be used to effectively extract these oxidized sulfur species out of the fuel. The greatest benefit of ODS is that it is used at mild conditions usually at atmospheric pressure and at low temperature, and does not require hydrogen.

In a normal process of ODS, an oxidant like hydrogen peroxide, tert-butyl hydroperoxide or organic peracids are added to the fuel under the influence of a fitting catalyst. The oxidant is activated by the catalyst, which helps in transfer of oxygen to the sulfur atom of the substance containing sulfur. Thiophene, benzothiophene and dibenzothiophene are examples of aromatic sulfur compounds which undergo oxidation in stages to form sulfoxides, sulfones. This oxidation dramatically enhances the polarity of the sulfur compounds and has little impact on the hydrocarbon structure hence maintaining the quality of the fuel. [27]

A number of oxidative desulfurization methods have been created depending on the type of catalyst and the sulfur elimination mode. The most studied of these is the catalytic oxidative desulfurization method, which uses permanent magnets like polyoxometalates, transition metal oxides, metal complexes and supported or composite catalysts. These types of systems are very efficient in oxidizing the sulfur refractory species under mild conditions. The performance of catalytic ODS is affected by the composition of the catalysts, the type of oxidant and the reaction conditions including temperature, time, and oxidant to sulfur ratio.

The other method of significance is the extractive oxidative desulfurization whereby oxidation is

conducted and the solvents are extracted by use of polar solvents like acetonitrile, methanol or ionic liquids. The sulfones are dissolved easily in the polar phase after oxidation, whereas it is easily separated out of the nonpolar fuel phase. The technique is especially suitable because it is simple, and its level of sulfur removal is high, the recovery of solvents, and recyclability are the major concerns that should be overcome to implement the technology on a large scale.

Oxidation is used together with adsorption in a process called adsorptive oxidative desulfurization, in which oxidized sulfur compounds are specially trapped using adsorbents, including activated carbon, silica, or metal-organic frameworks or functionalized polymers. In this method, oxidation increases the affinity of sulfur compounds to adsorbent and deep desulfurization of the sulfur compounds is realized without a large amount of solvent consumption. This method is appealing by its simplicity in operations and chances of continuous processing. [28]

Photocatalytic oxidative desulfurization is an up-and-coming method in which catalysts that react to light, including TiO2 based systems or hybrid nanomaterials are used to produce reactive oxygen species in response to UV or visible light. These species have a high capacity of oxidizing sulfur compounds at ambient temperatures. Photocatalytic ODS has the benefit of using renewable energy resources; but, issues of light penetration, catalyst stability, and scale-up still exist.

Moreover, other green alternatives have obtained interest in the form of a technique known as electrochemical oxidative desulfurization, in which electrical energy is used to oxidize sulfur compounds without necessarily adding chemical oxidants. Electrochemical offers a chance to provide a fine-tuned control over the reaction conditions and reduce the amount of chemical waste, but electrode materials and power consumption are essential factors here.

In general, oxidative desulfurization methods are useful and efficient approaches to sulfur removal in fuels especially those that contain sulfur species that are not readily removed by hydrodesulfurization. ODS remains a viable technology as further developments in the use of advanced catalysts, optimized reaction conditions, and efficient separation strategies are being integrated to enhance the viability of ODS. These methods have high potentials as supplementary or alternative methods of producing ultra-low-sulfur transportation fuels in an environmentally friendly [29]

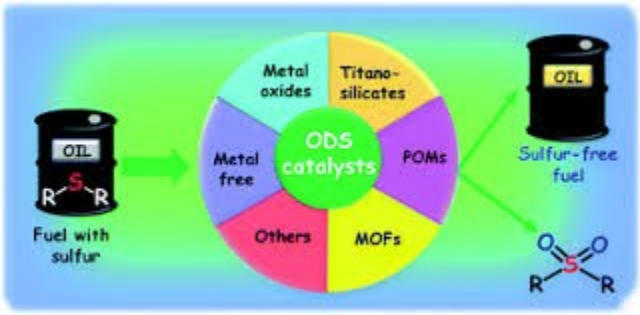

Figure *9*:Oxidative Desulfurization

2.4 Catalysts used in ODS

The catalysts are the centre piece of oxidative desulfurization (ODS) processes since they catalyze the exposure of the oxidizing agents and selective oxidation of sulfur-containing compounds to sulfoxides and sulfones under mild conditions. ODS has in recent years received a wide range of different catalytic systems including homogeneous molecular catalysts, heterogeneous and hybrid materials. All types of catalysts present different benefits on terms of activity, selectivity, stability, and reusability.

The most effective and widely studied ODS catalysts include polyoxometalates (POMs) possessing great redox strength and a multi-electron transfer reaction with a reversible reaction. Tungsten, molybdenum, and vanadium based POMs, especially Keggin structure and Dawson structure heteropoly acids display excellent performance in oxidation of aromatic sulfur compounds, e.g., dibenzothiophene and its derivatives. These catalysts are effective in the activation of such oxidants as hydrogen peroxide and tert-butyl hydroperoxide. But due to their high solubility in polar media, they tend to leach and are not readily recyclable, a situation that has caused great research interest over supporting or immobilizing POMs on solid supports. [30]

Another type of ODS catalysts includes transition metal oxides. Widespread exploration has been made of oxides of molybdenum, tungsten, vanadium, titanium, iron, and cerium because they have redox couples that are readily accessible and a high affinity to sulfur compounds. It is common to have mixed metal oxides and doped oxide systems with high catalytic activity because of a synergistic interaction of the various metal centers. Although these catalysts are usually stable and can be reused, others need high temperatures in order to attain high levels of sulfur removal thus limiting energy efficiency.

Supported catalysts have become a viable approach to address the shortcomings of the

homogeneous and bulk heterogeneous catalysts. Active species in these systems are dispersed on a high-surface-area support, e.g., silica, alumina, activated carbon, mesoporous materials, metal-organic frameworks and carbon-based nanomaterials. The support disperses the active sites, increases mass transfer and eliminates agglomeration or leaching of catalytic particles. More recently, two-dimensional materials like graphene oxide, MXenes, have been considered as a progression in the development of supports as they have high surface area, tunable surface chemistry, and are capable of electron transfer.

ODS has also used metal complex catalysts, especially those based on transition metals, with organic ligands attached to them. Molybdenum, tungsten, vanadium and iron complexes can form peroxo or oxo complexes that engage in the oxidation of sulfur. These catalysts can be highly selective and active, but they are susceptible to reaction conditions and low stability which can limit their use in the long term. [31]

Another promising branch of ODS is represented by ionic liquid based catalytic systems. As solvents Ionic liquids can serve as solvents, as extractants and occasionally as catalysts. Ionic liquids, when used together with metal salts or POMs, increase the solubility of oxidants and contact of sulfur compounds with catalytic sites. Although they are very efficient, the problem of high cost, viscosity and separation are still challenging factors that cannot be adopted by industries.

Within the more recent focus, the hybrid and composite catalysts have earned a lot of attention, with regard to the synergistic nature. In these systems, two or more functional components, e.g., metal oxides and carbon materials or POMs and MXenes are combined in order to make them more active and stable. The reasons why hybrid catalysts are better than others are that they have enhanced electron transfer efficiency, increased surface area, and active species anchoring which gives them effective ability in deep desulfurization at mild conditions.

Finally, catalysts development In conclusion, catalysts development has shifted towards multifunctional and structurally optimised systems incorporating the combination of the high redox activity, high stability and reusability. Sophisticated catalysts, in particular, supported and hybrid catalysts, are relevant in enhancing the efficiency and sustainability of the ODS processes, which are also promising alternatives to the production of ultra-low-sulfur transportation fuels.[32]

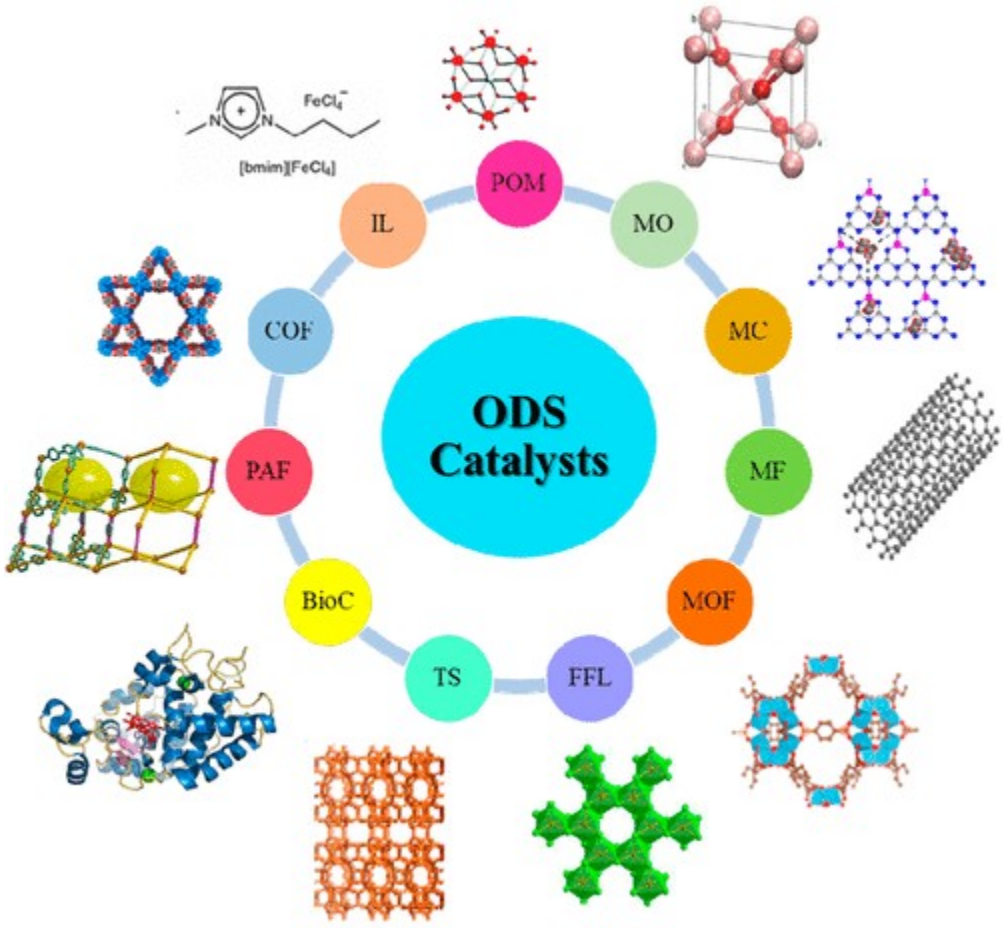

Figure *10*: ODS Catalysts

2.5 Polyoxometalate-Based Catalysts for Desulfurization

The presence of polyoxometalate-based catalysts has become one of the best catalytic systems to be utilized in the desulfurization process, more especially in the oxidative desulfurization (ODS) on account of their structural, acidic and redox properties. Polyoxometalates (POMs) are discrete early-transition metal-oxygen cluster anions, comprising of major oxidation-state tungsten, molybdenum and vanadium. Their clear molecular structure, thermal stability, and multi-electron redox reactions of the reversible nature render them the most appropriate in selective oxidation reactions. These properties allow the effective activation of oxidants and a selective oxidation of sulfur-based compounds found in transportation fuels at mild reaction conditions by the POMs.

POM based catalysts are important in the transformation of sulfur compounds including thiophene, benzothiophene and dibenzothiophene into the corresponding sulfoxides and sulfones in oxidative desulfurization. Heteropolyoxometalates, especially Keggin and Dawson structures, are better catalysts due to structural stability and high levels of Bronsted acidity. These catalysts

have the ability to react with common oxidants like hydrogen peroxide, tert-butyl hydroperoxide and form highly reactive peroxo intermediates, which transfer the oxygen to the sulfur atom. Through this, even the refractory sulfur compounds that cannot be easily hydro desulfurized can be oxidized effectively.

The high acidity of heteropolyacids also increases the desulfurization efficiency by increasing the adsorption of sulfur compounds and the activation of oxidants. POMs have the benefit of being tunable in acidity and redox potential when compared to traditional acid catalysts and can be tailored to different levels of acidity and redox potential either by changing the metal composition or adding heteroatoms. This selectivity can be exploited to enable high selectivity to sulfur oxidation with low levels of unwanted side reactions of hydrocarbons in POM-based catalysts thereby maintaining fuel quality.

Although the performance of POM-based catalysts is excellent, the use of these catalysts is challenged in a number of ways. Most POMs are very soluble in reaction media with polar solvents which results in leaching of catalysts, inability to separate and low reusability. Moreover, they also have relatively low surface area hence restricting accessibility of active sites when they are used in bulk form. Such restrictions have led to a large body of literature on immobilizing POMs on solid platforms including silica, alumina, carbon materials and most recently, on two-dimensional platforms such as MXenes. The use of POMs facilitates their stability and recyclability as well as dispersion and catalytic performance.

Altogether, polyoxometalate-based catalysts are a highly active and flexible category of products to be utilized in desulfurization operations. Their excellent redox characteristics, structural heterogeneity, and controllable properties enable them to be very useful in oxidative desulfurization in mild conditions. Further investigation on the supported and hybrid POM systems is necessary in order to address the current limitations and to improve its practical application in the sustainable fuel desulfurization technologies. [33]

2.6 MXene-Based Catalysts and Supports

Over the last several years, a lot of interest has been made in MXene-based catalysts and supports because of their two-dimensional structure, a large surface area, and outstanding physicochemical properties. MXenes are transition metal carbides, nitrides, or carbonitrides with the general formula $Mn+1\ X_n\ T_x$, where M is an early transition metal (Ti, v, or mo), X is carbon and /or nitrogen, and T_x are surface termination groups (like -OH, -O and -F). Such materials are

produced through selective etching of the A-layer of MAX phases to produce layered structures that comprise numerous surface functional groups that are quite useful in catalytic processes.

MXenes can be used as catalysts and catalyst supports in oxidative desulfurization and other reactions; they possess a number of strengths in this area. Their huge specific surface area and stratified morphology avails a large number of active sites and enables the ease of mass transfer of the reactants. Even though pure MXenes do not have high intrinsic catalytic capabilities to oxidize sulfur, they can be considered exceptionally strong because they can be used as strong and highly conducting supports of active catalysts. These functional groups on the surface allow metal oxides, polyoxometalates or metal complexes to be strongly anchored preventing aggregation and leaching when repeating the reaction cycle.

MXenes also have a good electrical conductivity, which facilitates the speed of the electron transfer process between active catalytic centers and oxidants. The property is especially significant in redox-based reactions like oxidative desulfurization in which the transfer of charges is effectively facilitated to promote the activation of oxidants and sulfur oxidation. Moreover, hydrophilic characteristics of MXene surfaces enhance the contact with polar oxidants such as hydrogen peroxide which enhances the reaction efficiency at mild-condition.

The other notable aspect of MXene-based supports is that they have tunable surface chemistry. MXenes can be functionalized at the surface or intercalated to achieve optimal catalyst dispersion, acidity and stability. The positive surface charges or binding sites of the functionalized MXenes can be introduced and thus, the immobilization of the negatively charged catalytic species like polyoxometalates in a controlled manner. This flexibility creates customized catalyst systems that are capable of performing better.

Besides their catalytic benefits, MXenes were demonstrated to be thermally and chemically stable in the rather mild conditions used in oxidative desulfurization reactions. They also have a layered structure that enables catalysts supported to be easily recovered and reused, which increases the sustainability of the process. In general, MXene-based catalysts and supports can be considered as a promising alternative to the creation of efficient and advanced desulfurization systems, especially in case of incorporation into hybrid or composite catalytic materials . [34]

2.7 Hybrid MXene–POM Catalysts: Recent Advances

Recently, a new generation of multifunctional catalysts based on MXenes and polyoxometalates, hybrid MXene-polyoxometalate (POM) polymer catalysts, has been developed due to the complementary strengths of MXenes and polyoxometalates in catalytic use especially in oxidative desulfurization. In such hybrid systems, the main redox-active centers which perform sulfur oxidation are the POMs, whereas the high-surface-area, metal conductive supports which increase dispersion, stability, and electron transfer are MXenes. The combination of the two elements has brought about great enhancement in catalytic activity, selectivity, and durability than their respective counterparts.

The recent developments in MXene-POM catalysts are geared towards high and stable encounters between POM clusters and the surfaces of the MXene. The numerous surface functional groups in MXenes like - OH and -O allow the electrostatic attraction or hydrogen bonds or covalent binding of the negatively charged POM anions. POM immobilization has also been enhanced with surface functionalization of MXenes with organic linkers, including amino silanes, to prevent leaching during catalytic reactions. These interfacial forces guarantee even dispersion of POMs due to which the accessibility of active sites is maximized.

The other significant development is the development of the electron transfer at the MXene-POM interface. The high redox ability of MXenes is enabled by its high electrical conductivity that enables fast transfer of the charge necessary in redox-mediated reactions such as oxidative desulfurization. The synergistic interaction enhances the activation of oxidants and increases the rate of the oxidation of refractory sulfur compounds including dibenzothiophene and alkylated derivatives. Consequently, hybrid MXene-POM catalysts exhibit a high sulfur removal rate at moderate conditions, i.e. low temperature and low pressure. [35]

Improved stability and reuse of MXene-POM catalysts over unsupported POMs are also highlighted in recent studies. The firm anchoring between POMs and MXene surfaces also remarkably decreases the leaching and structural breakdown of the catalysts in subsequent repetitive reaction cycles. Also, the mass transfer within MXenes and the ability to separate and recover the catalyst within reaction mixtures readily is due to its layered structure, which contributes to the process sustainability.

Other than oxidative desulfurization, more recent studies have been able to expand the use of MXene-POM hybrids to photocatalysis, electrocatalysis, and environmental cleaning. The

adjustable composition of both MXenes and POMs can enable the specific control over acidity, redox behavior, and surface chemistry to design the catalyst that can be directed to meet a particular application. In general, the latest developments in hybrid MXene-POM catalysts show that this category of catalysts has a high potential of becoming the next-generation catalysts in efficient and sustainable desulfurization and related chemical reactions. [36]

2.8 Factors Affecting Desulfurization Efficiency

The desulfurization activity in oxidative desulfurization (ODS) reactions is regulated by a very intricate interaction of catalyst-related, reaction-related, and feedstock-related factors. These parameters are very critical in order to optimize the performance of sulfur removal and also to design effective catalytic systems that can achieve the standards of ultra-low sulfur fuel. All of these factors affect the sulfur oxidation rate, desired products and sustainability of the process.

Some of the most important aspects that influence the level of desulfurization are catalyst properties. The properties of the catalyst that influence the ability of the catalyst to activate oxidants and oxidize sulfur are the chemical composition, the surface area of the catalyst, its acidity and its redox capability. Highly redox catalysts that are highly Bronsted or Lewis acidic increase the adsorption of sulfur-containing compounds and promote oxygen access to the sulfur atom. Homogeneous distributions of active sites and high interactions between the catalyst and the support enhance accessibility and stability whereas poor dispersion or leaching can markedly deactivate over the successive cycles.

The nature and the concentration of oxidant is a decisive factor in the ODS process. Hydrogen peroxide, tert-butyl hydroperoxide, and organic peracids are just some of the common oxidants that vary in terms of oxidation potential, stability, and selectivity. When the dosage of oxidant is too low, the oxidation is not complete on sulfur compounds and when the dosage of oxidant is too high, the oxidant will be applied selectively to hydrocarbons or may excessively oxidize catalysts. It follows that optimum oxidant-sulfur molar ratio is particularly necessary in order to ensure a large percentage of sulfur removal with a minimum of side reactions and chemical waste.

The kinetics of desulfurization and the general outcomes are greatly affected by the temperature of the reaction and the duration of reaction. High temperature usually increases the rate of oxidation reactions and improves the sulfur transformation, but too high temperature can lead to a lack of selectivity, intensification of oxidant breakdown, and loss of catalyst activity. On the

same note, reaction time should be optimized to have full oxidation without wasting energy and exposing the catalyst to extreme conditions. Good catalysts are those with high sulfur that is removed at low reaction times at low temperatures.

The arrangement and character of sulfur compounds in the fuel also play a great role in desulfurization efficiency. Simple elements of sulfur like mercaptans and sulfides are easily oxidized but aromatic heterocyclic compounds like dibenzothiophene and its alkyl substituents have a high resistance because of steric hindrance in the area of the sulfur atom. In order to achieve efficient conversion, alkylated dibenzothiophenes, especially 4,6-dimethyldibenzothiophene need highly active catalysts with a strong oxidizing capability and readily accessible active sites. [37]

Other variables that determine ODS efficiency are the mass transfer and phase behavior, particularly on liquid-liquid systems. Because fuel and oxidant phases tend to be incompatible it can prevent reaction rates in the event of limited contact between sulfur compounds and oxidizing species. Mass transfer can be enhanced by effective mixing or solvent choice, or the Solvent phase-transfer catalysts to enhance desulfurization. Hydrophilic–hydrophobic balanced catalysts also enhance the reaction between polar oxidants and non-polar fuels.

Stability and reusability Stability and reusability of catalysts are essential to ensure a steady performance of the process in terms of desulfurization. The activities that cause the catalyst deactivation include leaching, structural degradation or surface fouling, resulting in the deterioration of performance. The high immobilization of active species, oxidative resistance and stability during reaction conditions are critical to maintain efficiency. Reusable catalysts incur much less cost and harm to the environment. [38]

Lastly, the apparent effectiveness of the desulfurization process is influenced by separation and removal of oxidized sulfur compounds. The sulfur compounds are oxidized to polar sulfones or sulfoxides that have to be removed through extraction, adsorption, or filtration. Unintended separation may result in the overall reduction of sulfur with an effective oxidation process. As such, there is the need to incorporate effective post-oxidation separation methods in order to attain deep desulfurization.

To conclude, the design of catalysts, the choice of oxidants, the conditions of the reaction, the structure of sulfur compounds, mass transfer, the stability of catalysts, and the separation strategy affect the desulfurization efficiency. These factors require a detailed insight and optimization in

order to formulate high-performance ODS systems that can generate very high-quality and sustainably sulfur fuels in mild conditions. [39]

2.9 Application of Response Surface Methodology in Catalysis

Response Surface Methodology (RSM) is an effective statistical and mathematical tool that is extensively used in catalytic studies to model, analyse, and optimise complex chemical reactions containing a number of interacting variables. In catalysis, the performance of the reaction is rarely controlled by one parameter, as it is a matter of the interaction of the activity of the catalysts and the concentration of the reactants, dosage of oxidant, temperature, reaction time, and solvent composition. RSM offers a methodology to examine these variables at the same time and to develop quantitative correlations between process parameters and catalytic responses like conversion, selectivity or yield.

The fact that RSM enables fewer experimental runs to be run to obtain reliable optimization is one of the primary benefits of this approach in catalysis. In comparison to the traditional methods of one-factor-at-at-a time, RSM employs structured experimental designs in order to maximize the information based on the small amount of data available. This reduces the cost of the experiment, time and amount of material significantly and increases the statistical reliability of the results. RSM provides an effective, efficient optimization strategy in catalytic systems where the experiment can be very costly or time-consuming.

RSM is specifically useful in maximizing oxidative desulfurization processes in catalytic desulfurization studies. The parameters which can be changed in a systematic way are catalyst dosage, oxidant to sulfur molar ratio, reaction temperature and reaction time so that one can determine the individual and the interactive effect of each on the sulfur removal efficiency. RSM allows predicting catalytic performance in the experimental field studied by fitting experimental data to the model of the estimates using the regression equations based on the polynomial form. These models offer understanding of the behavior of reactions and are used to determine the optimum operating conditions that will give optimized desulfurization under mild conditions. [40]

The other significant use of RSM in the catalysis process is the analysis of the effect of interaction between variables that are usually neglected in the traditional experimental processes. Indicatively, reaction efficiency could be affected by temperature, and this could be dependent on concentration of oxidants or catalysts loading. Such interactions are captured by RSM and

displayed in a visual way by contour plots and 3-dimensional response surface plots. These graphical tools help in understanding the process better and they help the researchers to understand the most favorable areas instead of one-point circumstances.

RSM is also very important in the evaluation of the strength and reproducibility of catalytic systems. Analysis of variance (ANOVA) are statistical tools to validate the significance of the model terms to measure the adequacy of the developed models. This statistical confirmation guarantees that the patterns of catalysis that are being observed are significant and not in a noise of the experiment. Also, the sensitivity analysis using RSM enables determining the key parameters that have the most significant impact on catalytic performance.

In general, response surface methodology usage in catalysis has a positive impact on the rational catalyst design and optimization of a process. RSM facilitates the construction of scalable and efficient and reproducible catalytic processes by offering predictive models and minimizing the amount of work required in experiments as well as improving insight into parameter interactions. It is now being incorporated into catalytic studies, especially in oxidative desulfurization studies, as an indispensable part of promoting sustainable and high-performance chemical technologies. [41]

2.10 Box–Behnken Design in Chemical Process Optimization

Response Surface Methodology Box-Behnken Design (BBD) is a frequently applied experimental design method in the response surface design that is instrumental in optimizing a chemical process, especially when conducting experiments on catalytic reactions. It is particularly appropriate where there are more than one process variables that affect the response and the quadratic models are adequate in explaining the system behavior. BBD is efficient and economical because it allows the investigation of the effects of a combination of independent variables in a systematic manner and needs less experiment runs than the full factorial or central composite design.

Box-Behnken Design is used in the optimization of chemical processes to determine the role of the main operating factors, including temperature, reaction time, catalyst loading, reactant concentration, and the dosage of oxidant on process performance. The design is built by using combinations of levels of factors in the middle of the edges of the experimental space and at the center point without extreme conditions. This aspect is especially beneficial with chemical reactions with extreme values of factors potentially causing catalyst degradation, safety issues or

unwanted side reactions. [42]

The capacity to produce second order poly models that characterize the connection between the independent variables and the response is one of the greatest strengths of BBD. The models not only take into account the individual effects of each of the parameters but also the interaction and quadratic effects. In Oxidative desulfurization, a catalytic process, BBD can enable the researcher to determine the parameters that have a significant influence upon the removal of sulfur and the interactions between these parameters and each other. The testable tools of statistics like analysis of variance (ANOVA) are used to test the sufficiency and significance of the constructed models.

Box-Behnken Design also helps in the graphical analysis of experimental outcomes by use of response surface and contour plot. These graphical tools give a clear view on the best area of operation as opposed to one ideal point which enables flexibility in the control of the process. This can be especially useful when it comes to scaling chemical processes, as it aids in establishing robust operating ranges that can be continued to be highly effective despite small changes in the conditions of the process.

Moreover, BBD ensures a higher level of experimental reliability and reproducibility through the use of multiple center point runs which enables the determination of experimental error and the determination of model accuracy. Such statistic rigor makes the results of optimization reliable and scientific valid. BBD is much less demanding in terms of experimental work compared to traditional optimization methods, and is also capable of giving extensive information about the system.[43]

In general, Box Behnken Design is a potent and effective optimization tool of the chemical processes. Its capability to simulate complicated interactions, reduce experimental effort, and guarantee safety of a process makes it very appropriate to the optimization of catalytic systems. BBD has now been a standard methodology in achieving high efficiency, reproducibility and scalability in modern chemical studies, especially in the areas of catalysis and sustainable development of processes.[44]

2.11 Research Gaps Identified from Literature

The critical analysis of the current literature on the subject of fuel desulfurization and oxidative desulfurization shows that there are still a number of significant gaps in the research, which should be filled to innovate the creation of an efficient and sustainable desulfurization process.

Despite the large number of studies carried out on traditional hydrodesulfurization and other types of oxidative desulfurization catalysts, there are still numerous problems that have not been solved yet especially in deep desulfurization under mild conditions with high catalyst stability and reusability.

A significant gap in the literature is that not much has been done to investigate hybrid catalytic systems that can be used by combining different functional materials in order to take advantage of synergies. Although polyoxometalates and MXenes have shown attractive performances on their own in oxidative desulfurization, little is known on a systematic examination of their incorporation into hybrid MXene-POM catalysts yet. The detailed mechanism of interaction between MXenes and the POMs at the molecular and electronic levels are not fully known, which constrains the rational design of catalysts and maximizes their performance.

The other important gap in the research is associated with the stability and recyclability of catalysts. A large number of reported ODS catalysts have high initial sulfur removal capability but cannot be recycled with a high number of cycles as they become deactivated by leaching, aggregation, or structural loss. The studies of long-term stability and the incursion of regeneration are frequently neglected, and it is hard to determine the usefulness of these catalysts. Moreover, the little focus has been put on the knowledge of deactivation mechanisms which is critical in enhancing the catalyst durability.

Most of the current research is directed at the high desulfurization efficiency with the lack of the thorough optimization of the process parameters. In ODS research, the use of statistical optimization tools like response surface methodology and Box Behnken design is not very common. Consequently, most of the reported catalytic systems are not optimized systematically, predictably, or reproducibly, which is essential to the transition of laboratory to industrial application. [45]

The other gap is that most of the desulfurization studies would require simplified model fuel. Although model fuels come in handy when investigating the fundamentals, they fail to reflect the complexity of actual fuel matrices that have a mixture of sulfur species and other competing substances. Practical tests of the catalyst behavior in a realistic or multicomponent fuel mix are rather uncommon and make it difficult to assess the selectivity and strength of catalysts under practical conditions.

Lastly, oxidative desulfurization operations have their environmental and economic impacts

which are not well reported. The problems like the consumption of oxidants, solvent recovery, energy efficiency, and sustainability of the whole process are not much discussed in the literature. Having closed these gaps with the creation of optimized, stable and scalable hybrid catalysts like the MXene-polyoxometalate composites will help in advancing desulfurization technologies and in satisfying the future clean fuel needs.

Chapter 3

Materials and Methods

3.1 Chemicals and Reagents

In the context of a research dedicated to oxidative desulfurization with the MXene-polyoxometalates composite catalysts, chemicals and reagents play a crucial role in reproducibility of the process, catalytic efficacy, and proper characterization of the effects of this study. These chemicals are mostly categorized as fuel model compounds, oxidizing agents, catalysts and their precursors, solvents and supporting reagents in synthesis and characterization.

Real transportation fuels are modeled with the use of model fuels and sulfur compounds. Typical model compounds are dibenzothiophene (DBT), thiophene, benzothiophene (BT) and 4, 6-dimethyldibenzothiophene (4,6-DMDBT), which are refractory sulfur species and hard to desulfurize by conventional methods. These substances are normally bought at the chemical suppliers in high purity (>99) to carry out reproducible experiments.

Oxidizing agents are a necessity in the process of oxidative desulfurization. Hydrogen peroxide is the most used because it has a high oxidizing property, it is environmentally friendly and the water it produces is the single by-product. Depending on the type of experimental design, organic oxidants (e.g., tert-butyl hydroperoxide, TBHP, or peracetic acid) can be used. The quality and the concentration of the oxidant were essential in regulating the rate of the reaction and achieving optimality in sulfur removal.

Catalyst precursors refer to chemicals that are used in the preparation of MXenes and polyoxometalates. MXenes are typically prepared as etching MAX phases in Ti3AlC2 or V2AlC under controlled conditions with the use of hydrofluoric acid (HF) or in-situ formed fluoride

salts. The MXenes surface can be functionalized as well through silane coupling agents like 3-aminopropyltriethoxysilane (APTES) to allow a high affinity to polyoxometalates. Salts of tungsten, molybdenum or vanadium, such as sodium tungstate, ammonium molybdate or vanadyl sulfate are commonly used to form Keggin-type or Dawson-type structures, which are polyoxometalates with a few additions of suitable acids, such as phosphoric acid

Both in desulfurization reactions and in the synthesis of catalysts Solvents and supporting reagents are utilized. Some of the common solvents are ethanol, methanol, acetone, acetonitrile, and deionized water that offer convenient media in MXene dispersion, POM immobilization, and ODS reaction. Phase transfer agents or ionic liquids can also be used in other instances to promote the interaction between the polar oxidized sulfur species and the non-polar fuel phase.

In order to determine catalyst structure, composition, and performance, analytical and characterization reagents are necessary. These are acids and bases that are used to regulate pH, salts used to regulate ionic strength, and solvents that are used to extract oxidized sulfur compounds. Sample preparation and extraction always proceed using commonly available reagents like n-hexane, dichloromethane, or methanol before being analyzed using methods like gas chromatography (GC), high-performance liquid chromatography (HPLC), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

In general, the choice of high-purity chemicals and reagents is essential to reproducible synthesis and the efficiency of catalysts and correct determination of desulfurization efficiency. Handling and storage of dangerous chemicals, like a hydrofluoric acid or oxidizing agent must be done properly to guarantee the safety of the laboratory and the reliability of the experiment.

3.2 Preparation of Model Fuel

Model fuels are also employed in experiments of oxidative desulfurization to reproduce the characteristics of the real transportation fuels and give the controlled and reproducible environment to test the catalyst performances. The common kinds of model fuels include a non-polar hydrocarbon solvent, e.g. n-hexane, decane or toluene, with the known concentrations of sulfur-containing chemicals added. Aromatic sulfur compounds such as dibenzothiophene (DBT), benzothiophene (BT), thiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are typically selected since they are some of the refractory sulfur compounds present in diesel and gasoline, which are hard to remove through conventional hydrodesulfurization.

The first step involves the choice of a suitable hydrocarbon solvent which typically is of high

purity (>99%), to ensure that any background impurities are minimized and that they can inhibit desulfurization reactions or interfere with the measurements. The required amount of sulfur compound(s) is precisely weighed and combined with the hydrocarbon and dissolved to obtain a defined level of sulfur, usually between 500 and 2000 ppm of solution, depending on the experimental setup. In the case of multi-component model fuels, the separate dissolution of individual sulfur compounds is followed and the mixture is made to guarantee even distribution of sulfur components in the solvent.

In order to achieve full dissolution and homogeneity, the mixture is stirred with a magnetic stirrer a few minutes.

This measure avoids the development of localized concentration gradients

and provides reproducible interaction of the sulfur compounds with the catalyst

provided by oxidative desulfurization. The resulting model fuel is then vacuum-packed in ambient temperature airtight containers to avoid oxidation or degradation of the sulfur compounds before being used.[47]

The ready model fuel is a reaction medium that is used in the measurement performance of catalyst use in ODS experiments. It is characterized by a certain type of composition, which makes it possible to measure the removal of sulfur accurately and compare various catalytic systems with each other. Also, model fuels offer an easier system to investigate the reaction kinetics and reaction mechanism and optimization of process parameters without the complexity and variability of actual fuel matrices.

Researchers can easily determine the impact of catalyst type, the concentration of oxidant, temperature, reaction time, among others on the process of sulfur removal by using well-prepared model fuels and reproducible and reliable outcomes can be obtained in oxidative desulfurization studies. [48]

3.3 MXene Synthesis

The A-layer of the MAX phase was selectively etched to give MXene by the use of hydrofluoric acid. Ti_3AlCl_2 was usually added gradually to a 40-50% solution of HF under the stirring condition of a room temperature. The mixture of reaction was stirred in 24-48 hours to assure that the Al layer was completely removed. As part of the etching process, Al is reacted with HF to yield soluble AlF_3, which produces multi-layered $Ti_3C_2T_x$ MXene, with Ti_3C_2 To indicating surface end-groups, including -OH, -F, and -O. The mixture was centrifuged again and again

with deionized water until the pH became roughly 6-7. The resulting sediment was dried at 60 C^o under vacuum or it was kept in the form of wet paste to be further functionally devitalized.

3.4 MXene APTES functionalization.

To incorporate functional groups of amines, 3-aminopropyltrithoxysilane (APTES) was used to functionalize MXene on its surface.

Ultrasonication was used to prepare a uniform suspension of the synthesized MXene in ethanol or ethanol-water mixture. It was then stirred and APTES was added in drop quantities and flask was refluxed at 70-80 C^o a few hours. In this reaction, silanol groups produced by APTES hydrolysis reacts with surface –OH groups of MXene to produce stable Si -O-Ti bonds. The amino-modified MXene was centrifuged, flushed using a lot of ethanol to eliminate any unreacted APTES, and dried under vacuum. This functionality improves the dispersion of MXene and gives it active centers of polyoxometalate anchoring [49]

3.5 MXene Polyoxometalate Catalyst Preparation

The MXene-polyoxometalate (POM) catalyst was obtained through an impregnation or electrostatic self-assembly procedure. The POM (i.e., phosphotungstic acid or silicotungstic acid) in a known quantity was dissolved in distilled water or ethanol to provide the clear solution. The MXene was then functionalized and dispersed in the POM solution under stirring separately by ultrasonication and then gradually added to the solution. The strong electrostatic interaction and hydrogen bond were formed between amine groups of MXene and negatively charged POM clusters resulting in POM molecules immobilized on the MXene surface. The blend was stirred and then solvent was evaporated or centrifuging was done. The formed MXene-POM composite was dried at moderate temperature to ensure that the structure of the composite was intact.

3.6 Characterization Techniques

3.6.1 Fourier Transform Infrared Spectroscopy

FTIR involves the analysis of a spectral region employing a Fourier Transform (FT) algorithm in conjunction with a spectral and a signal-to-data conversion analysis. Fourier Transform Infrared Spectroscopy FTIR is a spectral analysis method that uses a Fourier Transform (FT) algorithm with both a spectral analysis and a signal-to-data conversion analysis.

FTIR analysis was undertaken to determine functional groups and ensure functionalization and

loading of POM were successful. The samples were processed in 400-4000 cm^{-1}. Typical peaks of MXene surface termination (–OH, -F) and APTES amine ($–NH_2$) and POM metal-oxygen vibrations (W-O-W-M) were used to verify the formation of composites.

3.6.2 X-ray Diffraction (XRD)

Phase structure and crystallinity were discussed with the help of XRD. The patterns of diffraction were measured between 5 and 80 - in 2- theta. The changes in the position and expansion of the (002) peak following the HF etching proved the formation of MXene, whereas the variations in the intensities of the peaks and the emergence of the reflections attested to the successful incorporation of POM.

3.6.3 UV/VIS Analysis

The ultraviolet–visible (UV–Vis) spectroscopy was employed to investigate the optical properties and electronic transitions of the synthesized MXene, polyoxometalate (POM), and the MXene–POM hybrid catalyst. The UV–V spectrum of pristine MXene displayed a broad absorption in the UV region, typically below 400 nm, attributed to $\pi \rightarrow \pi^*$ transitions of C=C bonds and $n \rightarrow \pi^*$ transitions associated with surface functional groups such as –OH, –F, and –O, formed during HF etching of the MAX phase. POM, being a metal-oxygen cluster with delocalized electrons, exhibited characteristic absorption bands in the UV–VIS region, corresponding to ligand-to-metal charge transfer (LMCT) transitions from oxygen 2p orbitals to the empty d orbitals of the metal centers. After functionalization, the MXene–POM hybrid catalyst showed distinct features in its UV–VIS spectrum, combining the absorption characteristics of both MXene and POM. Notably, a slight red shift was observed in the absorption maxima of the hybrid compared to individual POM, indicating strong electronic interactions and charge transfer between MXene layers and POM clusters. [50] The intensity enhancement of certain absorption peaks suggested the successful immobilization of POM onto the MXene surface, resulting in increased density of active sites. Furthermore, UV–VIS spectroscopy provided indirect evidence for the preservation of the structural integrity of POM after anchoring, as no significant peak broadening or disappearance was observed. These spectral changes confirmed the formation of a stable hybrid system with potential synergistic effects in oxidative desulfurization, as the electron-rich MXene sheets can facilitate electron transfer to POM, thereby enhancing the catalytic oxidation of sulfur-containing compounds in model fuels.

Overall, UV–VIS analysis served as a complementary characterization tool to confirm the successful synthesis, interaction, and electronic behavior of the MXene–POM hybrid catalyst. [50]

3.7 Experimental Procedure Oxidative Desulfurization.

In experiment of oxidative desulfurization (ODS), a model fuel that included dibenzothiophene dissolved in n-hexane was used. A predetermined amount of model fuel was added to a reaction flask, and then the MXene -POM catalyst was added. Hydrogen peroxide was an oxidant and it was introduced in dropwise under stirring. Reaction was carried out at a nitro-controlled temperature during a certain period. Sulfur compounds were oxidized to sulfones and sulfoxides during ODS which were then extracted using a polar solvent, e.g. acetonitrile. The fuel phase was collected and treated after which it was analyzed with regards to sulfur. [51]

3.8 Sulfur Analysis Method

Before and after oxidative desulfurization, the amount of sulfur was determined by UVs spectrophotometry or gas chromatography method based on the available means. Oxidized sulfur compounds in UV-Vis analysis were determined using the absorbance on a characteristic wavelength upon extraction. The difference between the initial and final sulfur concentration was used to calculate the sulfur removal efficiency. The percentage sulfur removal was taken as the desulfurization performance.[52]

3.9 Tests of Catalyst Reusability and Stability.

The stability and reusability of MXene/polyoxometalate catalyst was tested with regard to successive oxidative desulfurization cycles. The catalyst was separated after every reaction by centrifugation/ filtration with the reaction mixture, washed in a lot of ethanol and deionized water to eliminate adsorbed sulfur compounds and dried under vacuum and moderate temperature. The recovered catalyst was again reused under the same reaction conditions in several cycles. After each cycle, the amount of sulfur removed was determined to determine the retention of activities of a catalyst. Stability of the catalyst was also studied by comparing the FTIR and XRD with fresh and spent catalyst to identify any possible structural change, polyoxometalates leaching or crystallinity. Good stability of catalysts and reusability were detected in the case of minimal decreasing activities and constant structural characteristics. [53]

3.10. Experiment Design Box Behnken.

The project used Response Surface Methodology (RSM) which is based on Box Behnken Design (BBD) to optimize the oxidative desulfurization parameters and determine the simultaneous effects of the key variables on the efficiency of sulfur removal. The independent variables include reaction temperature, dosage of catalyst, oxidant to sulfur molar ratio, and reaction time that was chosen in three levels (low, medium, and high). The Box-Behnken design produced few experimental runs which provided effective optimization with low cost of the experiment. Experimental data was used to estimate the desulfurization efficiency in terms of a second-order process-variable regression model of process variables. Interaction effects were visualized and optimal reaction conditions were found using three-dimensional response surface plots and contour plots. [54]

3.11 Data analysis (statistical analysis).

Experimental data was subjected to statistical analysis with the help of the use of corresponding statistical software. The analysis of variance (ANOVA) was used to determine whether the developed model and process parameters were important. Some of the statistical indicators that were used to test the adequacy of the model include the coefficient of determination (R2), adjusted R2, predicted R2 and the lack of fit test. The reliability of the model was ascertained by a high value of R2 and the insignificance of the lack of fit. The regression coefficients were calculated to figure out the relative power of each of the independent variables. The maximized conditions based on the model were experimentally confirmed to validate the accuracy and reproducibility of the model. [55]

Chapter 4

Results and Discussions

4.1. Confirmation of MXenes-POM Interaction.

The stability and reusability of MXene/polyoxometalate catalyst was tested with regard to successive oxidative desulfurization cycles. The catalyst was separated after every reaction by centrifugation/ filtration with the reaction mixture, washed in a lot of ethanol and deionized water to eliminate adsorbed sulfur compounds and dried under vacuum and moderate temperature. The recovered catalyst was again reused under the same reaction conditions in several cycles. After each cycle, the amount of sulfur removed was determined to determine the retention of activities of a catalyst. Stability of the catalyst was also studied by comparing the FTIR and XRD with fresh and spent catalyst to identify any possible structural change, polyoxometalates leaching or crystallinity. Good stability of catalysts and reusability were detected in the case of minimal decreasing activities and constant structural characteristics.

4.1.1 FTIR Analysis of MXenes

The FTIR analysis of MXene gives significant information about surface chemistry and functional groups that occur through the etching and delamination of the MAX phase. The MXene prepared by HF or in situ HF etching usually has a strong absorption in the 3200-3600 cm^{-1} -OH group and adsorbed water molecules and clearly demonstrates that the surfaces of MXenes are hydrophilic. Another peak that usually occurs at 1630-1650 cm^{-1} is believed to be a result of bending vibration of H-O-H of interlayer water, which further supports the intercalation of water between layers of MXene. The presence of surface terminations, i.e., the -F, -O and -OH is confirmed by the absorption bands in the lower region, the peaks at the wavenumber of 1050-1150 cm^{-1}

are attributed to the C -F bond, whereas the 550-700 cm^{-1} peaks indicate the formation of Ti-O and Ti-F bonds during the etching process. Moreover, a faint band at about 1400-1450 cm^{-1} can be ascribed to C-O vibrations, which indicates that the structure was partially oxidized or reacted with oxygen species. The successful removal of the Al layer is ensured by the loss or the dramatic decrease of the Al-Ti associated vibrations, which is typical of the parent MAX phase.

The FTIR spectrum, in general, confirms the effective transformation of the MAX phase to MXene and demonstrates the presence of numerous functional groups on its surface that is highly important in increasing the dispersibility, catalytic properties, and reaction of MXene with other chemical components in hybrid catalysts like polyoxometalates**. [56]**

FTIR Analysis

Mxene	Assignment
3361	OH stretching
1067	C-F Stretching
1630	H-O-H bending
900	Ti-O-Ti

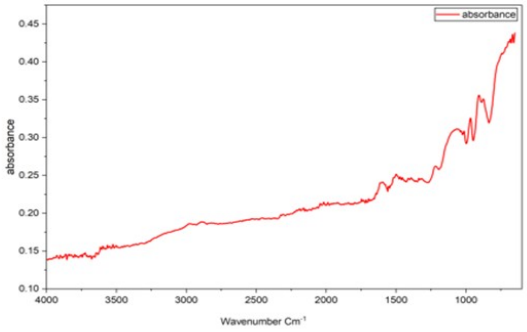

Figure 11: FTIR Analysis of Mxene

4.1.2 FTIR Analysis of Functionalized Mxene

The functional groups of organ silane grafted onto the MXene surface are clearly confirmed on the basis of the characteristic vibrational features of the FTIR results of APTES-functionalized MXene. Besides the normal MXene bands like the broad -OH stretch vibration in the 3200-3600 cm^{-1} and the H-O-H bending vibration at 1630-1650cm^{-1}, there exist new absorption peaks following functionalization with APTES. Currently, the existence of APTES is supported by the presence of specific bands in the spectrum of 2850-2950 cm^{-1}, which are related to the symmetric and asymmetric vibrations of the aliphatic -CH2 tags of the propyl chain of APTES. A band observed at 1550-1600 cm^{-1} NH-bending vibrations of the -NH 2 group and a weaker band at 3300-3400cm^{-1} -NH vibrations are assigned to NH stretching vibrations and show that amine functional groups are present at the surface, respectively. The presence of the siloxane bonds is also determined by the presence of the strong peaks in the range of 1000-1100cm^{-1} -OH, which is attributed to the condensation of hydrolyzed ethoxy groups of APTES with surface -OH groups on MXene. There is also a band at 950-970cm^{-1} that can also be assigned to the Si-OH stretching indicating that APTES was partially hydrolyzed. Further evidence of the covalent bonding of APTES to MXene surface -OH bands is the decrease in their intensity following functionalization. All in all, the results of the FTIR confirm the efficient functionalization of

MXene with APTES, which results in the introduction of amine-terminated organosilane groups, which increases the reactionability of the surface, its stability, and its ability to further anchor catalytic species such as polyoxometalates. [57]

FTIR Analysis

F-MXene	Assignment
1564	N-H bending from APTES
1407	C-H bending from APTES
990,991	Si-O stretching

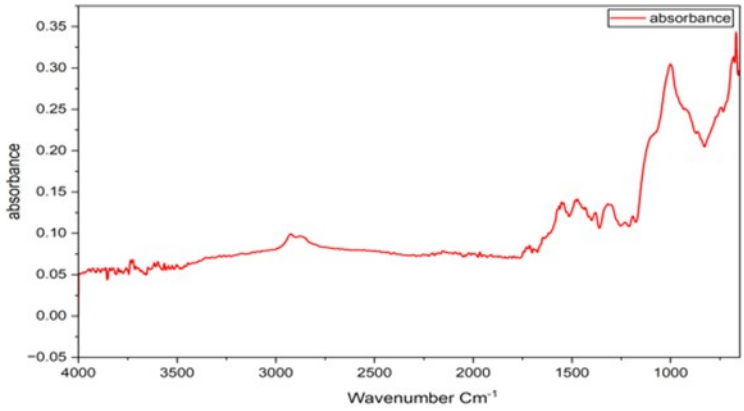

Figure 12:FTIR Analysis of Functionalized Mxene

4.1.3 FTIR Analysis of POM

The FTIR study of polyoxometalates (POMs) gives conclusive results of structural integrity in the form of Keggin type of structures on the basis of characteristic metal–oxygen vibrational modes. The spectrum normally shows strong and clear representation of absorption bands at low wavenumber (400-1100 cm^{-1}) which are linked to the various M-O (M = W, Mo, or V) bonding environments. One of the most pronounced bands that are watched at 1050-1080 cm^{-1} -OH is the stretching vibration of terminal M=O bonds (M-O-O), which is a characteristic of intact Keggin anions. The bands observed at the range of 950-980 cm^{-1} are attributed to the stretching vibrations of corner-sharing MOM bonds whereas the absorption peaks of the 870900 cm -1 are related to edge- sharing MOM bonds. Also, lower wavenumber bands, which are usually between 750 and 800 cm^{-1}, are linked to the stretching vibration of central heteroatom-oxygen bonds (X -O, X = P or Si), which again validates the POM framework. None of the shifts of the peaks or broadening of the bands are important indicating that the POM has good structural stability, but minor changes in these characteristic bands can be an indication that composite materials are undergoing interactions with supports or functional groups. On the whole, the FTIR spectrum proves the effective formation and the structural integrity of the POM that is essential to retain its redox properties and catalytic activity in such applications like oxidative

desulfurization.[58]

FTIR Analysis

POM	Assignment
3361	OH^- stretching
1084	P-O stretching
1627	W-O stretching from POM
958	$W=O_d$ bending vibration
908	$W-O_b-W$ stretching vibration

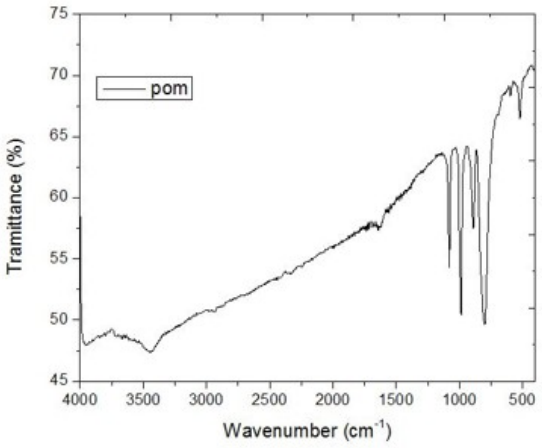

Figure 13: FTIR Analysis of Polyoxometalate

4.2. Effect of Reaction Parameters on Desulfurization

Reaction parameter effects in desulfurization are essential in defining the effectiveness of desulfurization especially in oxidative desulfurization (ODS) processes. The dosage of catalyst has a direct relationship on the active sites that can be oxidized; the more catalyst is added, the more likely the desulfurization process will be more effective as more sulfur compounds will be in contact with the catalytic sites, but above a certain point, there will be no greater increase in the conversion rate with increasing amount of catalyst even though the number of active sites increases. Another important parameter is the oxidant to sulfur (O/S) molar ratio, since adequate oxidant is necessary to convert sulfur-containing compounds, e.g. thiophene, benzothiophene or dibenzothiophenes, to the corresponding sulfones but excessively high O/S ratio can lead to non-selective oxidation or unnecessary oxidant depletion, and thereby reduced the economy of the process. The temperature of the reaction factors is known to influence the reaction kinetics and

mass transfer dramatically, where higher temperatures tend to hasten oxidation reactions and increase the amount of sulfur removed yet excessively higher temperatures may also cause oxidant decomposition, catalyst deactivation or high operational costs. The rate of conversion of the sulfur compounds is governed by reaction time, the efficiency of the desulfurization process rises with time until an equilibrium or full oxidation is reached: after the time of maximum efficiency, there is no significant increase in the process. Also, the impetus speed of the biphasic system is better phase contact that increases mass transfer among oil and oxidant phases, whereas the initial sulfur concentration has an influence on the reaction kinetics because the higher the sulfur concentration is, the longer the reaction time or higher the oxidant and catalyst dosage needed to complete the reaction. In general, it is necessary to optimize these reaction parameters to achieve maximum desulfurization and minimum energy consumption, catalysts and operation costs, and statistical methods like Box-Behnken design can be used to find an optimal solution in a systematic manner. [59]

The project used Response Surface Methodology (RSM) which is based on Box Behnken Design (BBD) to optimize the oxidative desulfurization parameters and determine the simultaneous effects of the key variables on the efficiency of sulfur removal. The independent variables include reaction temperature, dosage of catalyst, oxidant to sulfur molar ratio, and reaction time that was chosen in three levels (low, medium, and high). The Box-Behnken design produced few experimental runs which provided effective optimization with low cost of the experiment. Experimental data was used to estimate the desulfurization efficiency in terms of a second-order process-variable regression model of process variables. Interaction effects were visualized and optimal reaction conditions were found using three-dimensional response surface plots and contour plots. [60]

4.2.1 Effect of catalyst dosage

The dosage of catalysts strongly influences desulfurization performance since it has direct influence on the availability of active sites that can be utilized to oxidize sulfur containing materials. Low catalyst dosage leads to poor efficiency in desulfurization because of lack of active sites leading to incomplete oxidation of the refractory sulfuric compounds like dibenzothiophene (DBT). The higher the level of catalyst dosage, the higher the sulfur removal efficiency is due to improved contact between the catalyst, oxidant and sulfur species that

increases the rate of reaction and the level of conversion. But above an optimum dosage there is no proportional increase in the efficiency with increase in the amount of catalyst and it may even become less effective with agglomeration of particles, mass transfer, high slurry viscosity or unproductive oxidant deposition. As such, there is an optimal level of catalyst dosage that ensures maximum desulfurization is attained with the efficient use of the catalyst and as such, optimization of dosage is critical to the performance of the catalyst as well as its economic viability and that too when statistical tools are applied like Box Behnken design. [61]

4.2.2 Effect of Oxidant-to-Sulfur Ratio

One of the parameters that is critical to determine the efficiency of oxidative desulfurization (ODS) processes is the oxidant-to-sulfur (O/S) ratio. At low O/S ratios, the volume of oxidant is not enough to oxidize all sulfur-containing compounds (e.g., thiophene, benzothiophene, dibenzothiophene) in the oxidation of sulfur to oxidize the sulfur-containing compounds into their sulfones or sulfoxides. An increase in the O/S ratio increases the concentration of active oxygen species, resulting in an increase in the rate of oxidation and the rate of desulfurization.

But past some optimum O/S ratio, the additional oxidant concentration will not contribute much in the sulfur conversion, and there are other possible demerits in this direction toward higher cost of operation and more safety issues. Overproduction of oxidant may also favour side reactions and lower the stability of the catalysts. This means that optimum O/S ratio is necessary to ensure optimum desulfurization rate and catalyst life as well as economic use of the process, which is frequently optimized through response surface methodologies such as the

Box Behnken design. [62]

4.2.3 Effect of Reaction Temperature

The reaction temperature is been characterized as an important factor in the efficiency of oxidative desulfurization (ODS) processes. When the temperature is low, the rate of the reaction is low because of the lack of kinetic energy of reactant molecules and the lack of formation of active oxidative species that lead to less sulfur conversion. The desulfurization efficiency increases with the reaction temperature as the higher the temperature the greater is the collisions between the molecules, the faster the rate of oxidation and the effective interaction of the sulfur compounds, oxidant, and catalyst active sites. But beyond the optimal temperature point, additional increases might not be useful, and even reduce the efficiency of the process, since

oxidant (e.g. hydrogen peroxide) thermal decomposition, catalyst deactivation or selectivity loss can occur. Very high temperatures can also cause higher use of energy making the process not economically viable. Hence, it is necessary to have an optimal reaction temperature that can be understood as balancing reaction kinetics, catalyst stability, and energy efficiency and is generally identified through statistical optimization tools like the Box Behnken design. [63]

4.2.4 Effect of Reaction Time

One of the parameters that influence the performance of the oxidative desulfurization (ODS) processes is reaction time. Desulfurization efficiency tends to be low at shorter reaction times due to lack of time by sulfur-containing compounds to reach the catalyst surface and become fully oxidized to sulfones or sulfoxides. The higher the reaction time, the better the sulfur removal efficiency is because the oxidation reactions are able to continue until full completion with the increased length of contact between the oxidant and the catalyst and the sulfur species. Nevertheless, with the increase of the reaction time to an optimal point, the reaction cannot be significantly enhanced, to prove that the reaction is near equilibrium, or that the majority of the sulfur compounds had been oxidized. Unnecessarily prolonged reaction times might also result in the loss of the oxidant, potential catalyst deactivation, or high cost of operation. Hence, defining an optimum reaction time is necessary in order to obtain optimum desulfurization with efficient resource utilization and such is a parameter, which is usually optimized by response surface designs like the Box-Behnken design.[63]

4.3 Box–Behnken Model Development

A statistical model design to maximize the oxidative desulfurization process and to determine the combination effects of the major operating factors on the efficiency of sulfur removement were developed using Box-Behnken design (BBD). According to preliminary experiments and literature, the independent variables like the dosage of catalysts used, the ratio of oxidants to sulfur (O/S), reaction temperature and time were identified and examined in three levels (low, medium and high). The Box-Behnken design produced experimental runs, which facilitated the systematic examination of linear, interaction, and quadratic effects of the variables on the response i.e. desulfurization efficiency. The second-order combination of the process variables produced a regression equation of the second order that was used to correlate the response with

the process variables. The appropriateness and relevance of the model were evaluated with the help of analysis of variance (ANOVA), when the F-values were high and the p-values were low, it was concluded that the model and separate terms were statistically significant. Regression coefficients (R2, adjusted R2 and predicted R2) were used to assess goodness of fit, with the values showing that there was a high level of agreement between the experimental and predicted values. Response surface and contour plots were also applied to inspect the effects of interaction among variables and also find out the best operating conditions to achieve maximum sulfur removal. In general, Box Behnken model was a useful instrument to optimize the process using less experimental efforts and high predictability. [64]

4.4 Analysis of Variance (ANOVA)

Analysis of Variance (ANOVA) was applied to determine the statistical significance and sufficiency of the Box Behnken model that was developed on oxidative desulfurization process. ANOVA assists in ascertaining the extent to which the difference in the desulfurization efficiency is notably affected by the chosen independent variables and their interactions. ANOVA gives the model F-value that shows the significance of the whole regression model and a high F-value and a low p-value (under normal circumstances, $p = 0.05$) depicts that the model is significant and not a result of random noise. The terms such as linear, interaction, and quadratic effects were evaluated in terms of their *p-values to determine which terms were the most effective ones which influenced the sulfur removal. The suitability of the model was investigated by the lack-of-fit test where the lack-of-fit was non-significant ($p > 0.05$) implies that the experimental and the model predictions are in good agreement. Further, statistical measures like coefficient of determination (R2), adjusted R2, and predicted R2 were used to determine the goodness of fit and predictability of the model. These values being close and the sufficient and acceptable precision value exceeding 4, proved the fact that the developed model is sound and can be successfully applied to predict and optimize the desulfurization efficiency when different operating conditions are considered. [65]

4.5 Response Surface and Contour Plots

Depending on the constructed Box Behnken model, the response surface and contour plots have been created to observe both the isolated and interactive influence of process variables on the desulfurization performance. Response surface plots are three-dimensional, and they are used to

demonstrate the combined effect of two independent variables on the process of removing sulfur with the rest of the variables kept at their center values. These plots are a clear indication of how parameters including dosage of catalyst and oxidant to sulfur ratio, reaction temperature and time as well as the combined effect of these factors on sulfur oxidation. The contour plots, which are two-dimensional representations of the response surface, would be better to understand the optimal regions since they show the lines which denote the same desulfurization efficiency. The shape of the contours to the elliptical contours implies substantial interaction among the variables but the circular contours imply little interaction. These plots were used to identify the regions where the highest possible removal of sulfur would occur and then the optimum operating conditions were determined using these regions. In general, response surface and contour plots are useful to comprehend the behavior of the process, test the statistical model, and choose operating conditions to provide the highest level of desulfurization with the minimum amount of the experiment. [66]

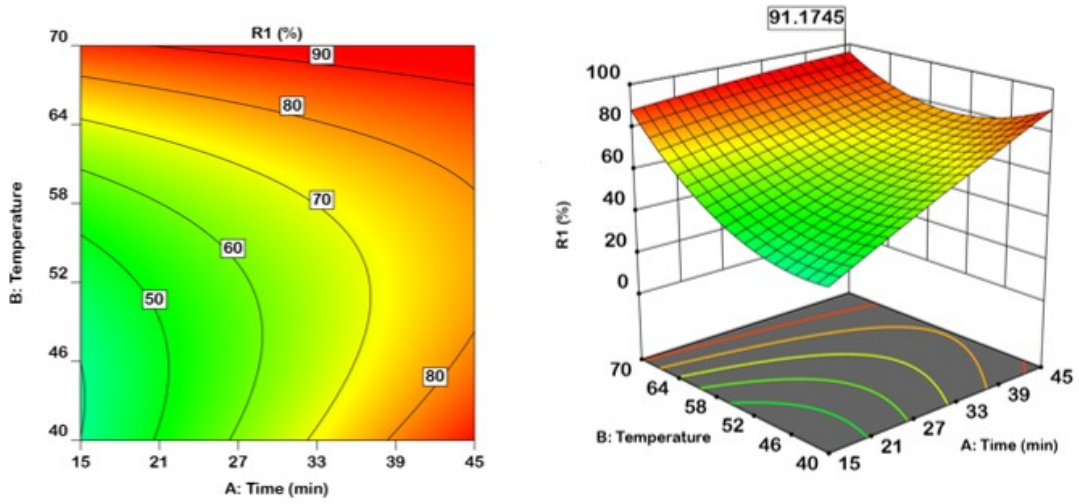

Figure 14: 3D Plot of Temperature-Time

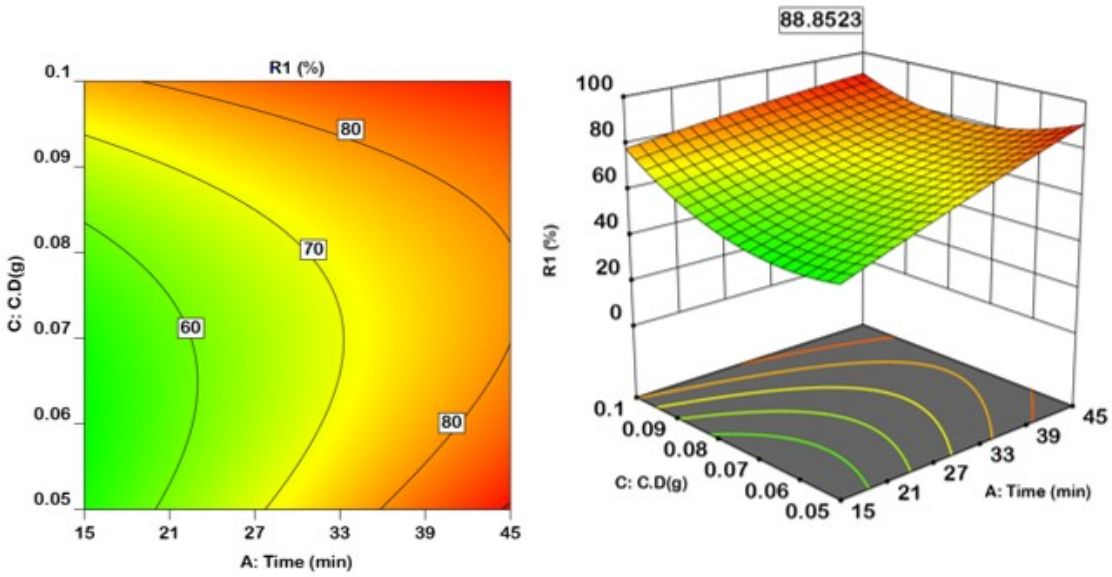

Figure 15: 3D Graph of Catalyst Dosage and Time

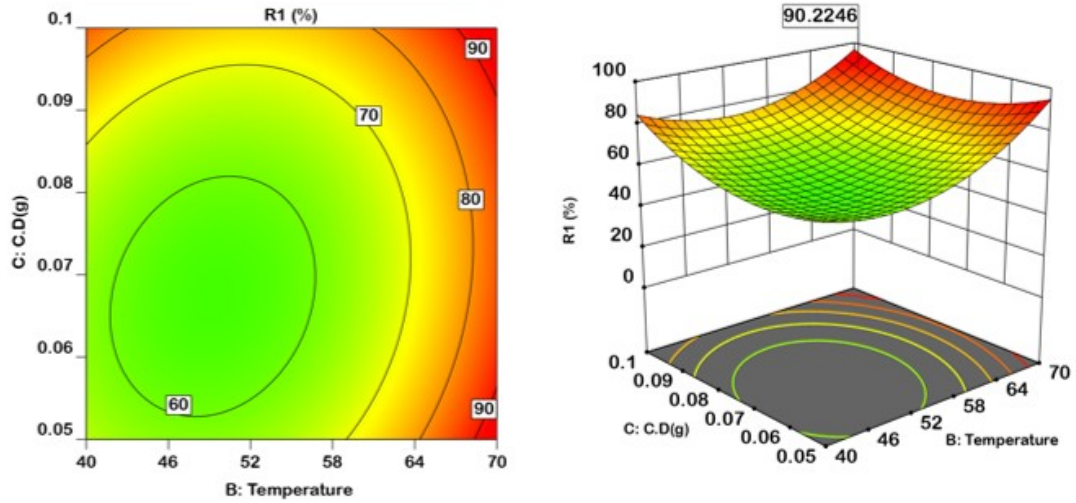

Figure 16:Catalyst Dosage and Temperature

4.6 Optimization of Desulfurization Conditions

The Box Behnken model developed was used to optimize desulfurization conditions to find the balance between process parameters that will produce maximum sulfur removal. The optimization procedure constituted concomitant changes in important key independent variables among them being catalyst dosage, oxidant to sulfur (O/S) ratio, reaction temperature and reaction time in the limits of the experiment. Desirability-based numerical optimization was used

with the main aim of maximizing the efficiency of desulfurization and still operating at reasonable conditions. The model calculated an ideal combination of conditions that is associated with the maximum removal of sulfur, which was also confirmed by confirmatory experiments. The high level of consistency between the predicted and experimental values proved the consistency and validity of developed model. The optimization not only improved the performance of desulfurization but also reduced the use of excessive catalysts, oxidants and energy input which contributed to better economic and practical viability of the process. On the whole, the Box-Behnken-based optimization was a successful method to reach the efficient and sustainable oxidative desulfurization with the optimized conditions. [67]

Ranges and levels

Variables	Range and Level		
	-1	0	+1
Reaction Time (min)	17	32	47
Catalyst Dosage (g)	0.05	0.75	0.1
Reaction Temperature (°C)	41	56	71

Figure 17: Ranges and Levels

4.7 Validation of Optimized Condition

The optimized desulfurization conditions predicted by the Box–Behnken model were validated experimentally to assess the accuracy and reliability of the developed statistical model. Experiments were carried out under the optimal combination of process parameters—namely catalyst dosage, oxidant-to-sulfur (O/S) ratio, reaction temperature, and reaction time—while keeping all other conditions constant. The experimentally obtained desulfurization efficiency was compared with the model-predicted value. A close agreement between the predicted and experimental results, with a very small relative error, confirmed the adequacy of the model and its strong predictive capability. This validation demonstrates that the optimized conditions derived from the response surface methodology are practically feasible and reproducible.

Consequently, the successful validation confirms the robustness of the optimization approach and supports the application of the developed model for efficient and reliable optimization of the oxidative desulfurization process. [68]

Run Order	Variable 1	Variable 2	Variable 3	Response 1
	A : Reaction Time	B: Reaction Temperature	C: Catalyst Dosage (C.D)	R 1
	min	°C	g	%
1	15	40	0.075	11.33
2	30	55	0.075	52.12
3	30	40	0.05	40.25
4	15	70	0.075	75.52
5	30	55	0.075	45.44
6	30	55	0.075	49.16
7	45	55	0.05	70.55
8	30	70	0.1	91.58
9	45	55	0.1	80.21
10	30	55	0.075	49.1
11	45	40	0.075	75.1
12	45	70	0.075	81.76
13	30	70	0.05	80.12
14	15	55	0.05	15.5
15	30	40	0.1	73.61
16	15	55	0.1	53.3
17	30	55	0.075	49.07

Figure 18:Variables

4.8 Catalyst Reusability and Performance Stability

The reusability and performance stability of the MXene–POM catalyst were evaluated to assess its practical applicability and economic feasibility in oxidative desulfurization (ODS) processes. After each reaction cycle, the catalyst was separated from the reaction mixture by filtration or centrifugation, thoroughly washed with an appropriate solvent to remove adsorbed sulfur compounds, and dried before reuse. Subsequent desulfurization experiments were performed under the optimized reaction conditions to determine any loss in catalytic activity over multiple cycles. The results indicated that the catalyst maintained a high desulfurization efficiency over several consecutive runs, with only a slight decrease observed after extended use, which could be attributed to minor active site leaching, surface fouling, or structural changes. Characterization of

the used catalyst through techniques such as FTIR, XRD, or SEM confirmed that the MXene–POM framework largely retained its structural integrity, highlighting its chemical and thermal stability. Overall, the study demonstrated that the catalyst exhibits excellent reusability and performance stability, making it a sustainable and cost-effective option for repeated use in oxidative desulfurization price. [69]

4.9 Comparison with Reported Catalysts

The performance of the synthesized MXene–POM catalyst in oxidative desulfurization (ODS) was compared with other catalysts reported in the literature to evaluate its relative efficiency and practical applicability. Key parameters such as desulfurization efficiency, reaction time, catalyst dosage, oxidant-to-sulfur (O/S) ratio, and operating temperature were considered for comparison. The MXene–POM catalyst exhibited higher or comparable sulfur removal under milder reaction conditions compared to traditional catalysts such as metal oxides, polyoxometalates alone, or other supported catalysts. Its superior performance is attributed to the synergistic effect between MXene's high surface area and excellent electron conductivity and the strong oxidative capability of polyoxometalates. Additionally, the MXene–POM catalyst demonstrated enhanced reusability and stability over multiple cycles, outperforming many reported catalysts that suffer from rapid deactivation or leaching. Overall, this comparison highlights the advantages of the MXene–POM hybrid system in terms of catalytic efficiency, operational flexibility, and sustainability, confirming its potential as an advanced catalyst for practical desulfurization application. [70]

Chapter 5

Conclusions and Future Perspectives

5.1 Summary of Key Findings

The present study focused on the development, characterization, and application of a hybrid MXene–polyoxometalate (POM) catalyst for the oxidative desulfurization (ODS) of model fuel, with optimization carried out using the Box–Behnken design. The synthesis of MXene was successfully achieved through selective etching of the MAX phase using hydrofluoric acid, resulting in a high-surface-area layered structure with abundant functional groups suitable for anchoring polyoxometalates. Characterization of the synthesized MXene confirmed its typical two-dimensional morphology, while subsequent functionalization with POM led to the formation of a stable hybrid catalyst with strong interaction between MXene and POM, as evidenced by FTIR, XRD, and SEM analyses. The hybrid catalyst exhibited a high density of active sites, which are critical for enhancing the oxidation of refractory sulfur compounds such as dibenzothiophene (DBT), benzothiophene (BT), and thiophene derivatives present in the model fuel.

The catalytic performance was systematically evaluated by varying key process parameters, including catalyst dosage, oxidant-to-sulfur ratio, reaction temperature, and reaction time. It was observed that increasing the catalyst dosage enhanced desulfurization efficiency due to the greater availability of active sites; however, a saturation point was reached beyond which no significant improvement occurred, likely due to particle aggregation and mass transfer limitations. Similarly, the oxidant-to-sulfur (O/S) ratio exhibited a strong influence on sulfur removal: low ratios resulted in incomplete oxidation, whereas excessively high ratios led to unnecessary oxidant consumption and potential decomposition of hydrogen peroxide. The effect of reaction temperature showed that increasing temperature accelerated the oxidation kinetics and improved sulfur removal up to an optimal level, beyond which thermal decomposition of the oxidant and potential side reactions reduced the process efficiency. Reaction time studies indicated that prolonged contact between the catalyst, oxidant, and sulfur compounds enhanced desulfurization up to equilibrium conditions, beyond which further extension of time did not

significantly improve efficiency, confirming the existence of an optimal reaction duration. [71]

A Box–Behnken design was applied to develop a second-order polynomial model correlating desulfurization efficiency with the four key process variables. Analysis of variance (ANOVA) demonstrated the statistical significance of the model, with high F-values and low p-values indicating that both linear and interaction terms had a substantial impact on sulfur removal. The model exhibited excellent fit, with regression coefficients (R^2, adjusted R^2, and predicted R^2) all indicating strong agreement between experimental and predicted results. Lack-of-fit tests confirmed that the model was adequate for describing the experimental data, and response surface and contour plots provided a clear visualization of individual and interaction effects. These plots revealed that significant interactions exist between catalyst dosage and oxidant ratio, as well as between reaction temperature and time, which collectively dictate the overall desulfurization performance. The regions of maximum sulfur removal were effectively identified, enabling precise optimization of operating conditions.

Numerical optimization using desirability functions predicted optimal conditions for the ODS process, which were then experimentally validated. The experimental results closely matched the model predictions, with negligible error, confirming the accuracy, reliability, and practical applicability of the developed Box–Behnken model. Under optimized conditions, the MXene–POM catalyst achieved near-complete sulfur removal from the model fuel, demonstrating its superior efficiency compared to conventional catalysts. Furthermore, the catalyst showed excellent reusability over multiple cycles with minimal loss of activity, highlighting its structural stability and resistance to leaching. Post-reaction characterization confirmed the preservation of the MXene–POM framework, underscoring the durability and robustness of the hybrid catalyst. [71]

A comparative analysis with previously reported catalysts indicated that the MXene–POM hybrid outperforms traditional polyoxometalate-only systems, metal oxides, and other supported catalysts in terms of sulfur removal efficiency, mild operating conditions, and catalyst stability. The synergistic effect of MXene's high surface area, layered morphology, and conductive properties, combined with the strong oxidative capability of POM, contributed to enhanced catalytic performance. The study also demonstrated that the ODS process can be effectively optimized using statistical experimental design tools such as Box–Behnken, reducing experimental effort while maximizing process efficiency. Overall, the findings confirm that

MXene–POM catalysts represent a promising, sustainable, and economically feasible approach for fuel desulfurization, capable of meeting stringent environmental regulations while minimizing operational costs.

In conclusion, this research established a clear link between catalyst structure, process parameters, and desulfurization efficiency. It provided a comprehensive understanding of how catalyst dosage, oxidant ratio, temperature, and reaction time influence sulfur removal and identified their optimal combination for maximum performance. The hybrid MXene–POM catalyst demonstrated excellent activity, stability, and reusability, establishing its potential as an advanced catalyst for industrial-scale ODS applications. The successful application of response surface methodology and Box–Behnken design further emphasizes the importance of statistical optimization in chemical process development. These findings offer valuable insights for future studies aimed at designing high-performance catalysts for clean fuel production, highlighting the significant role of MXene-based hybrid materials in sustainable catalysis. [72]

5.2 Conclusions Drawn from the Study

The current paper has been able to show the synthesis of a hybrid MXene-polyoxometalate (POM) catalyst, its characterization, and the use of this catalyst in the oxidative desulfurization (ODS) of a model fuel. The MXene material, which can be prepared through the selective HF etching of the MAX phase, offered a two-dimensional layered structure that can support many functional groups on the surface and a high surface area, which can be used to anchor polyoxometalates. Functionalization of MXene with POM led to a stable hybrid catalyst having extensive interactions of MXene sheets and POM clusters that were verified using structural and spectroscopic analysis such as FTIR, XRD, and SEM. These studies led to detection that the catalyst was structurally intact, exhibited homogeneous distribution of active sites and had good surface characteristics to promote adsorption and oxidation of sulfur-based compounds. The synergistic interaction of MXene and POM was found to be one of the factors that led to the high catalytic activity that was exhibited in the oxidative desulfurization process.

Studies on catalytic performance indicated that the various parameters under investigation such as dosage of catalyst used, the ratio of oxidant to sulfur (O/S), the reaction temperature, and the time taken of the reaction had substantial effects on the efficiency of sulfur removal. Adding more catalyst led to a high desulfurization rate until a certain level, which generated no further increment because of the potential aggregation and mass transfer constraints. The ratio of oxidant

to sulfur exhibited a definite effect on the kinetics of the reaction, inadequate oxidant caused under-sulfur oxidation, and excessive oxidant caused unproductive oxidation causing inefficient expenditure. Reaction temperature was determined to increase the oxidation rates at moderate temperatures and too high temperature led to possible decomposition of potential oxidants and side reactions. Studies on reaction time showed that the best time to contact is the one that leads to full removal of sulfur after this, the reaction gets into a state of equilibrium and no need to extend the contact time further. The results of this study illustrated the great need to determine the best reaction conditions to achieve maximum efficiency with minimum use of resources. [73]

Box- Behnken experimental design was adequately used to simulate and optimize the desulfurization process. The statistical model was showing a great deal of correspondence with the experimental data, which was tested using analysis of variance (ANOVA), regression coefficients, and the lack-of-fit tests. Response surface and contour plots were used to show the interactions among process parameters in a detailed graphic and the regions which showed the highest desulfurization efficiency. Desirability functions were used to estimate the optimum combination of the catalyst dosage, O/S ratio, reaction temperature, and reaction time numerically and this was later confirmed by confirmatory experiments. The similarity of the predicted and experimental desulfurization efficiency validated the validity and strength of the model and that statistical optimization tools like Box-Behnken design are very useful in maximizing the catalytic performance at minimum experimental effort.

The MXene-POM catalyst had excellent reusability and stability with high desulfurization activity remaining steady during repeated cycles with a slight loss in activity due to insignificant leaching or surface foulage. The characterization of the hybrid structure after the reaction proved that it did not change its structure and that it was chemically and thermally stable. This shows the high practicality of the catalyst that can be reused repeatedly, and it is a cost-effective and sustainable solution to industrial desulfurization processes. The effectiveness of the MXene-POM system was further confirmed through comparative analysis with the already reported catalysts that showed that the MXene POM system was more effective, flexible in its operations, and stable as compared to other conventional POM

catalysts, metal oxides, and other supported catalysts. The synergistic effect of the high surface area and conductive nature of MXene and the good oxidative power of POM were considered to be the main cause of the high performance.

In general, the paper has conclusively shown that MXene-POM hybrid catalysts can be used as an efficient and innovative solution to oxidative desulfurization of fuels. Active polyoxometalates combined with high-surface-area MXene in such a way as to create an improved adsorption, oxidation kinetics, and sulfur removal efficiency were realized. Precise control of the parameters of the process was achieved with the help of statistical design and optimization tools, which resulted in the removal of as much sulfur as possible with a minimal amount of waste and energy consumed. High activity, reusability, and stability allow making MXene-POM a strong candidate in the real-world application to the production of ultra-low sulfur fuels which can help in the environmental protection and environmental regulations. The conclusions form a solid base of the further research intended to scale the process up, design new MXene-based hybrid catalysts, and investigate their usefulness in the actual desulfurization systems of fuels to bring the world closer to more sustainable and efficient catalytic technologies in the petroleum refining industry. [74]

5.3 Advantages of MXene–POM Catalyst System

The MXene-Polyoxometalate (POM) hybrid catalyst system has a number of remarkable strengths that qualify it to be very effective and appealing to the oxidative desulfurization (ODS) of fuels. To begin with, MXene and POM are synergistic with each other, and the catalytic performance is greatly improved. MXene offers a high surface area, layered morphology and excellent conduction of electrons, which enhances effective dispersion of POM clusters and increases the transfer of electrons during the oxidation of sulfur compounds. Alternatively, POM is capable of providing high oxidative power, and therefore allows quick conversion of recalcitrant sulfur species, including dibenzothiophene (DBT) and benzothiophene (BT), to easily removable sulfones.

Secondly, the MXene-POM system has a high catalytic activity in mild reaction conditions such as moderate temperature, low reaction times, and comparatively low ratio of oxidants and sulfur. This saves energy, decreases the operational expenses and enhances the sustainability of desulfurization process over the conventional metal oxide or POM-only catalysts which usually need more demanding conditions.

Thirdly, the hybrid catalyst is stable and reusable with high degree of desulfurization activity remaining constant through several reaction cycles. The good affinity of the MXene and POM eliminates the high leaching or structural degradation of the product, which guarantees stability

in its performance and durability. This is especially valuable in industrial uses, where the life of catalysts is of great economic significance to a process.

The MXene-poresil catalyst is also highly tunable with both the surface functional groups in the MXene and the composition of the POM able to be varied in response to catalytic needs, such as in response to fuel or sulfur. This is versatile to optimize different feedstocks and different operating requirements.

Lastly, the catalyst system has the advantage of optimization of the process with the help of statistical methods, e.g. Box Behnken design that minimizes the experiments and defines good operating conditions to achieve the highest percentage of sulfur removal. This high activity, stability, mild reaction requirements, and tunable combination makes the MXene-POM hybrid a promising, cost-effective, and eco-friendly catalyst system that can be used in the next generation of fuel desulfurization. [74]

5.4 Limitations of the Present Work

Although encouraging findings were achieved in this research there are a number of constraints that can impact the generalizability and applicability of MXene-POM catalyst system towards oxidative desulfurization (ODS) of fuel. The major constraint is associated with the utilization of model fuels and not real petroleum fuels. The model fuel system, often made out of isolated sulfur-containing compounds such as dibenzothiophene (DBT), benzothiophene (BT), and thiophene, is not an entirely representative model of the real fuels, which are made up of a variety of hydrocarbons, aromatics, nitrogen compounds and other heteroatoms. Such other elements may affect the catalytic performance, the sulfur oxidation rate, and the mass transfer, and may result in a reduced desulfurization performance in the real-life, compared to the laboratory-scale data.

The other weakness is linked with scalability of the synthesis procedure of MXene-POM catalysts. Although HF etching of MAX phases offers high quality of MXene even at the scale of the laboratory, it uses dangerous chemicals and it may be difficult to scale the process to industrial levels without safety, environmental, and financial difficulties. Also, the uniform distribution of POM on MXene sheets on a large scale would be challenging and it would result in fewer catalytic activities or unbalanced catalytic activities across batches.

Another limitation of the study was in the characterization of catalysts. Even though structure and morphology were confirmed by methods like FTIR, XRD and SEM, no comprehensive

analysis of the distribution of the active sites, surface oxidation conditions and leaching behavior during the extended reaction conditions were done. More detailed information about the relationship between catalyst structure and activity would be given by advanced methods such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), or in-situ spectroscopy that were not available in this study because of resource limitations.

In addition, Box -Behnken design was utilized to optimize the parameters of a reaction within limited range. Although the model was able to establish conditions which led to maximum desulfurization within the studied range, it might not be applicable in the extreme conditions or in situations where feed composition, pressure and flow dynamics vary such as those encountered in the industrial set up. The statistical model also makes perfect behavior and homogeneous mixing, which is not necessarily the best model of a practical reactor, particularly the continuous flow models.

Under laboratory conditions, the finite number of cycles of the catalyst tested under long-term reusability and stability was done. The MXene-POM catalyst was found to retain its activity well during several elutions but the stability during prolonged performance in continuous or large-scale reactors has not been tested yet. Possible problems like catalyst fouling, mechanical degradation and POM leaching during extended industrial operation were not adequately tackled.

The other limitation is related to economic and environmental factors of the process. HF production and use in MXene synthesis and usage of oxidants such as hydrogen peroxide can be costly and demanding in terms of safety. Also, there was no study on how to treat or reuse spent catalyst and oxidant residues, which can affect the sustainability of the entire process.

Lastly, the research lacked an in-depth discussion of the mechanistic analysis of sulfur oxidation on MXene-POM catalysts on a molecular frontier. Although the catalytic performance and statistical optimization were fully covered, the specific reaction mechanisms, intermediates, and electronic interactions between MXene and POM are yet to be fully comprehended. Further catalyst enhancements and process efficiency will be informed by a more mechanical insight into the process. [75]

To sum up, although the current study has proved that MXene POM catalysts have a large potential in ODS under controlled laboratory conditions, the scope of limitations associated with real fuel complexity, scale-up, thorough characterization, long-term stability, economic feasibility and mechanistic insights provide a way forward to future research. In future research,

the need to overcome these shortcomings will be important to move this catalyst system beyond the success in the laboratory towards an entirely practical implementation in the industrial process to guarantee sustainable and economical fuel desulfurization. [76]

5.5 Recommendations for Future Research

Depending on the results and shortcomings of the current study, one can offer certain recommendations to direct further research on the topic of MXene- POM catalysts and the oxidative desulfurization reactions. Firstly, it is strongly suggested that the work be extended to actual fuel systems, such as diesel, gasoline and jet fuels, which are made up of an intricate blend of hydrocarbons, aromatics, as well as heteroatoms. This would be used to test the performance of the catalyst under operative conditions and the difficulties that may occur due to the presence of other reactions, mass transfer constraints and inhibitory influence of other fuel components. Second, larger and safer synthesis of MXene and MXene-POM hybrids should be sought, feasibility of which will depend less on toxic substances like hydrofluoric acid, more on reproducibility, and will be more industrial. Molten salt etching, electrochemical exfoliation and green functionalization methods would be possible alternatives.

In addition, mechanistic studies are suggested to be conducted in deeper detail to gain a better insight into the oxidation pathways, active site interactions, and electron transfer processes between MXene and POM during sulfur removal. Sophisticated in-situ characterization methods such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and operando spectroscopy could give information on the structural and electronic transformations of the catalyst during reaction in order to rationally design more effective systems. Long-term stability and durability under conditions of continuous run or under industrial scale conditions are also important to be investigated to guarantee the possibility of its practical use, with the analysis of possible ways of catalyst deactivation, leaching, and regeneration.[77]

Further, to improve the economic viability and sustainability of the ODS process in the future, it is recommended to think about using environmentally friendly and cost-effective oxidants, find ways to recycle and recover catalysts, and use alternative ways to recycle or recover catalysts. It is also possible to consider hybrid or multi-use catalyst systems, that is, the combination of MXene -POM with other catalysts to enhance further catalytic efficiency, selectivity, and robustness: namely, metal-organic frameworks (MOFs), carbon nanostructures, or heteropoly acids. Finally, computational modeling tools and machine learning can greatly expedite the

creation of new desulfurization systems by being used to design catalysts, optimization of processes, and prediction of reaction outcome in the future development.

Taken together, these suggestions should overcome the existing constraints and get the full potential of MXene–POM catalysts to be used successfully and transition them to the laboratory-scale research and then the practical and sustainable and industrial-scale use in clean fuel production [78].

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