

SYNTHESIS OF NANO-SIZED METAL CARBIDES AND ITS APPLICATION IN METHANE DEHYDRO-AROMATIZATION

A dissertation submitted in the partial fulfillment of
the requirement for the degree of
Master of Science
in
Chemistry

Submitted by:
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DECLARATION

I declare that the thesis entitled “**Synthesis of nano-sized metal carbides and its application in methane dehydro-aromatization**” has been prepared by me under the supervision of **Professor (Dr.) Bhawna Yadav Lamba, Department of Chemistry, School of Engineering, University of Petroleum & Energy Studies, Dehradun, India** and co-supervision of **Sr. Principal Scientist (Dr.) Raja Ram Bal, CSIR-IIP, Dehradun (Uttarakhand)**.

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I, **Simratjeet Singh Saini**, hereby certify that the research dissertation titled “**Synthesis of nano-sized metal carbides and its application in methane dehydro-aromatization**” submitted for the partial fulfillment of a M.Sc. degree from University of Petroleum Energy & Studies, Dehradun, India is an original idea and has not been copied/taken verbatim from anyone or from any other sources.

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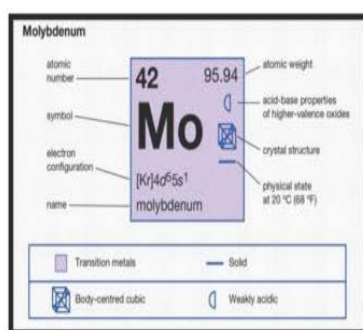
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CHAPTER 1 INTRODUCTION

Metal carbides are emerging as extraordinary entities in the rapidly changing science and catalysis. Their unique features make them invaluable applications. Among these, tungsten carbide (WC) and molybdenum carbides have a particularly interesting use in the process of methane (MDA), which is extremely important for petrochemicals and energy. This paper sheds light on the synergy between material science and catalytic engineering, aims to delve into the synthesis procedures of MoC and WC, clarify their crucial role in the catalytic conversion of methane to high



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ABSTRACT

The catalytic conversion of methane into higher hydrocarbons, particularly aromatic chemicals, has enormous potential for resolving both environmental issues and energy demands. Metal carbides have emerged as attractive catalysts for this transformation due to their distinct features, which include excellent thermal stability, tuneable surface chemistry, and strong metal-support interaction. This abstract describes metal carbide synthesis approaches and their critical involvement in methane dehydroaromatization (MDA) processes.

Metal carbides are synthesized using a variety of techniques, including carbothermal reduction, sol-gel procedures, and chemical vapor deposition (CVD). Carbothermal reduction, which uses metal oxides and carbon sources at high temperatures, remains one of the most prevalent processes, providing control over particle size and composition. Sol-gel techniques, which use metal precursors and carbon sources, enable homogenous dispersion and customized surface chemistry. Furthermore, CVD methods provide fine control over layer thickness and composition, which is essential for industrial applications.

Metal carbides, particularly transition metal carbides (TMCs) like Mo₂C and W₂C, are highly catalytic in MDA reactions. Methane is dehydrogenated and aromatized on the surface of metal carbides via complicated chemical pathways. The spillover of carbon species from metal carbides promotes the synthesis of higher hydrocarbons and aromatics. Furthermore, the existence of metal-support contact improves catalytic stability and reduces carbon deposition, hence increasing catalyst lifetime.

Metal carbides' catalytic efficiency in MDA processes is controlled by several parameters, including catalyst composition, surface shape, and reaction conditions. The metal composition and surface structure of carbide catalysts can be tuned to optimize activity, selectivity, and stability. Furthermore, operational factors like temperature, pressure, and feed composition have a major influence on reaction kinetics and product distribution.

To summarize, the production of metal carbides and their use as catalysts in methane dehydroaromatization constitute a viable route for converting methane into higher value products. Continued research efforts to understand the structure-activity correlations of metal carbides and optimize reaction conditions are critical for moving this catalytic process closer to commercialization and general use.

Keywords: Metal carbides, carbothermal reduction, chemical vapor deposition (CVD), carbon deposition, catalyst composition, methane dehydroaromatization.

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I owe heartiest gratitude to higher power, who gave me the opportunity to be a part of the noble profession of serving the humanity. The writing of this dissertation has been one of the most significant academic challenges that I have ever had to face, it has taught me time management, critical analysis, bridging theory and practice, new research techniques and how to work independently.

In bringing out the present work, the debts of gratitude that I owe are heavy and numerous, but some of them need special mention.

Firstly, I am highly indebted and will remain ever grateful to my **SUPERVISOR PROFESSOR (DR.) BHAWNA YADAV LAMBA, DEPARTMENT OF CHEMISTRY, UPES, DEHRADUN (UTTARAKHAND) and CO-SUPERVISOR SR. PRINCIPAL SCIENTIST (DR.) RAJA RAM BAL, CSIR-IIP, DEHRADUN (UTTRAKHAND)** for their relentless guidance and valuable inputs for the dissertation, despite their many other academic and professional commitments.

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Last but not the least I would like to thank my friend **MR. MANAV BALI** for his indispensable assistance whenever it is required; if they all had been not there my dissertation would have neither be completed nor successfully submitted.

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CHAPTER 1

INTRODUCTION

Metal carbides are emerging as extraordinary entities in the rapidly changing fields of materials science and catalysis. Their unique features make them invaluable in a wide range of applications. Among these, tungsten carbide (WC) and molybdenum carbide (MoC) are particularly notable due to their adaptability, robustness, and catalytic activity. These metal carbides have a particularly interesting use in the process of methane dehydroaromatization (MDA), which is extremely important for petrochemicals and energy generation. In order to shed light on the synergy between material science and catalytic engineering, this introduction aims to delve into the synthesis procedures of MoC and WC, clarify their inherent features, and examine their crucial role in the catalytic conversion of methane to higher hydrocarbons. (1)

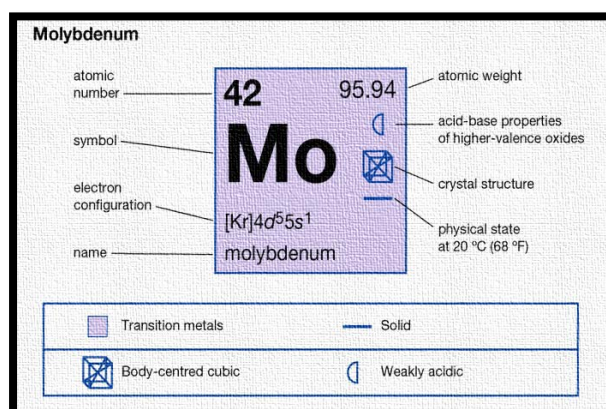


Fig.1: overview of Molybdenum

MoC and WC synthesis is a complex process that uses a variety of techniques based on conventional and sophisticated synthesis pathways. In the past, a common method for creating these metal carbides has been the controlled carburization of tungsten and molybdenum oxides. This process produces well-defined crystalline structures of MoC and WC with customized compositions and morphologies. It frequently involves the interaction of metal oxides with carbonaceous species at high temperatures. Furthermore, the synthesis of metal carbides has been refined thanks to the use of cutting-edge methods including chemical vapor deposition (CVD) and sol-gel procedures, which have allowed for exact control over the chemical characteristics, surface area, and particle size. By carefully adjusting the synthesis settings, scientists have made incredible progress in customizing the physicochemical characteristics of molecular carbons.

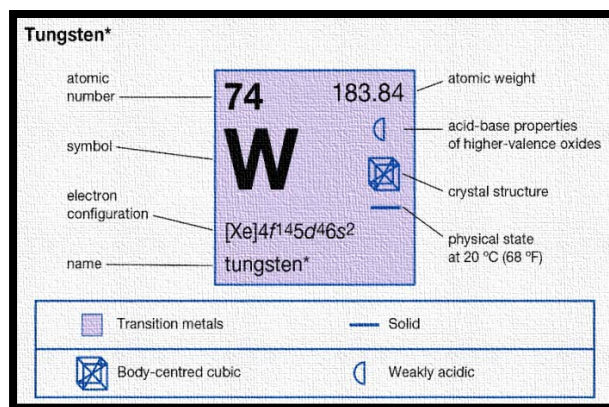


Fig.2: Overview of Tungsten

The remarkable activity and stability of MoC and WC under challenging reaction conditions can be attributed to their distinct surface chemistry and electronic structure. Because of their partially filled d orbitals, metal carbides, in contrast to ordinary metal catalysts, have a high density of active sites, making reactant molecules like methane easier to adsorb and activate. Moreover, the inherent carbide-carbide and carbide-metal interactions in the crystalline lattice provide increased resistance against sintering and catalyst deactivation, extending the lifetime of the catalyst and guaranteeing continuous activity across longer reaction cycles. These characteristics highlight the potential of metal carbides as catalysts for the catalytic process of methane dehydroaromatization, which is challenging in terms of catalyst selectivity, activity, and stability.

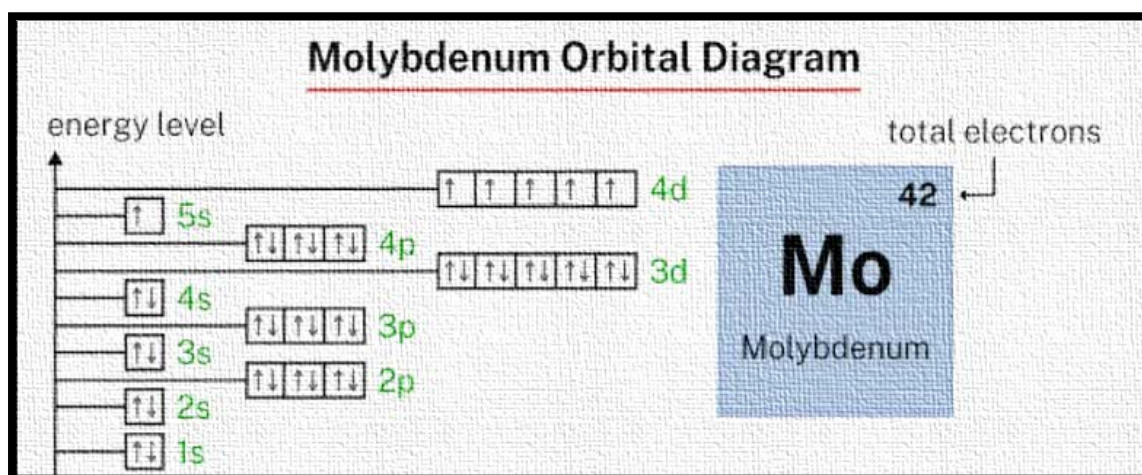


Fig.3: Molecular orbital diagram of Molybdenum

Methane dehydroaromatization (MDA) provides a catalytic method of fundamental importance in the valorization of natural gas and shale gas reserves, enabling a means to create valuable aromatic hydrocarbons such as benzene, toluene, and xylene (BTX) from methane feedstocks. More environmentally friendly and sustainable techniques must be developed in order to replace energy-intensive and energy-intensive conventional methods of producing BTX, such as steam cracking and aromatization of light hydrocarbons. In this regard, the search for more environmentally friendly and commercially feasible pathways to produce BTX through methane dehydroaromatization has placed MoC and WC catalysts at the forefront. (2)

1.1 Background

Because of their exceptional mechanical strength, great thermal stability, and distinct catalytic qualities, metal carbides have attracted a lot of interest. Mo and W carbides are particularly notable among them because to their adaptability and prospective uses in a variety of industries. These carbides have been utilized for a long time in wear-resistant coatings and cutting tools, but they have only discovered new uses in catalysis, specifically in the process of methane dehydroaromatization (MDA). Methane, is an inexpensive and plentiful source. Nevertheless, its great thermodynamic stability makes direct conversion to liquid fuels or value-added compounds more difficult. By transforming methane into higher hydrocarbons and aromatics—valuable building blocks for the chemical industry—MDA provides a viable path to overcome this obstacle. Methane is processed by dehydrogenating and aromatizing it over an appropriate catalyst, with metal carbides emerging as promising candidates due to their high activity and selectivity.

Mo and W carbide synthesis and their potential applications in MDA are important for the following reasons:

- I. **Energy and Environmental Sustainability:** With the world's energy demand only growing, it is critical to create sustainable routes for chemical synthesis and energy production. Methane is a greenhouse gas with significant climatic implications that can be valorized into higher-value products using MDA. This work advances sustainable catalytic processes by creating effective catalysts based on Mo and W carbides.
- II. **Resource Efficiency:** Transition metals Mo and W are widely available, and their carbides can be produced from low-cost precursors. The production of metal carbides, which is based on these plentiful materials, offers an affordable substitute for traditional catalysts made of rare and costly metals. This improves MDA and associated processes' scalability and economic viability.
- III. **Catalyst Design and Optimization:** To customize the catalytic performance of Mo and W carbides, it is essential to comprehend their synthesis processes and structural characteristics. In order to enable the logical design and optimization of catalysts for MDA and other processes, this research attempts to clarify the parameters impacting catalytic activity, selectivity, and stability through systematic investigations.
- IV. **Industrial Applications:** There are a lot of industrial applications that can be impacted by the effective development of Mo and W carbide-based catalysts for MDA. The chemical industry can become more diverse and less dependent on fossil fuels by incorporating these catalysts into large-scale operations for the synthesis of aromatics, olefins, and other useful compounds.

1.2 Advantages of Metal Carbide

Metal carbides, which are mixtures of metal elements and carbon, have attracted a lot of interest from a variety of industries because of their special qualities and extensive range of uses. Among them, carbides of tungsten (W) and molybdenum (Mo) are notable for their superior thermal and electrical conductivity, high melting temperatures, and remarkable hardness. We explore the synthesis, characteristics, and uses of Mo and W carbides in this overview, providing insight into their importance in contemporary materials research and engineering. The synthesis of tungsten carbide (WC) and molybdenum carbide (MoC) represents the meeting point of material science and catalytic engineering, providing exciting opportunities for the generation of chemicals and sustainable energy. Researchers have unlocked the catalytic potential of metal carbides in methane dehydroaromatization through a synergistic blend of novel synthesis approaches and mechanistic insights, opening the door to more environmentally friendly and productive pathways for the manufacture of xylene, toluene, and benzene. Metal carbides are expected to become more and more important in determining the direction of chemical synthesis and catalysis as the search for renewable energy sources heats up.

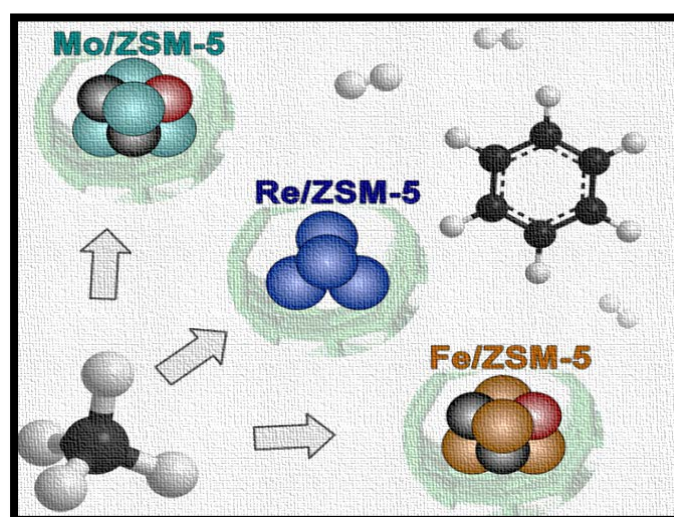


Fig.4: Different metal carbides with supported zeolites

Because of their many benefits over conventional catalysts, metal carbides—in particular, tungsten carbide (WC) and molybdenum carbide (MoC)—have attracted a lot of interest as MDA catalysts. The conversion of methane to higher-value aromatic hydrocarbons is crucial in the field of MDA, and metal carbides' special qualities provide a number of benefits that enhance process efficiency, selectivity, and sustainability.

The remarkable activity and stability of metal carbides in MDA under severe reaction circumstances is, first and foremost, one of their most notable benefits. MoC and WC show exceptional resistance to catalyst poisoning and coke production, in contrast to traditional metal catalysts like nickel or platinum, which are prone to deactivation and sintering at high temperatures. The crystalline lattice's strong carbide-metal and carbide-carbide interactions, which prevent carbonaceous deposits from building up and agglomerating active sites, are the source of this intrinsic stability and guarantee sustained catalytic activity over extended reaction cycles.

Furthermore, metal carbides have a high density of active sites due to their electrical structure, which makes it easier for methane molecules to bind and activate, which is an essential step in the MDA process. Molybdenum's and tungsten's partially filled d orbitals in MoC and WC, respectively; facilitate the easy breakage of C-H bonds in methane, starting the series of events that result in the production of aromatic hydrocarbons. This increased activity results from the cooperative interaction of carbon and metal species on the catalyst surface, which encourages the production of reactive intermediates and precisely directs methane conversion to the desired products.

Metal carbide presents a strong advantage in MDA due to its adjustable surface chemistry and composition, which can be adjusted to meet particular catalytic needs and reaction circumstances. Researchers can adjust the crystalline structure, particle size, and surface area of MoC and WC catalysts to maximize catalytic performance and product selectivity in methane dehydroaromatization by precisely controlling synthesis parameters like temperature, pressure, and precursor stoichiometry. Researchers can precisely balance the dehydrogenation, cyclization, and aromatization reactions to maximize the output of desirable aromatic hydrocarbons while reducing the generation of unwanted by-product, thanks to the adaptability of catalyst design.

1.3 Historical Development

The synthesis and characteristics of metal carbides were first studied in the late 1800s, which is when the history of these compounds began. The identification of tungsten carbide (WC) and molybdenum carbide (MoC) can be attributed to early research conducted in the late 1800s by chemists like Henri Moissan and Carl Wilhelm Scheele. The first systematic investigation into metal carbides was initiated in 1896 when Moissan created tungsten carbide by heating tungsten oxide and carbon in an electric arc furnace.

Through experimental research and theoretical analysis, the synthesis techniques and structural features of Mo and W carbides were progressively clarified at the beginning of the 20th century. To create carbides with specialized qualities for particular uses, researchers investigated a variety of synthesis techniques, such as mechanical alloying, chemical vapor deposition (CVD), and carburization of metals. The advancement of sophisticated characterisation methods, including electron microscopy, X-ray diffraction (XRD), and spectroscopic techniques, allowed for in-depth analyses of the morphology, characteristics, and crystal structure of Mo and W carbides. (8)

After Moissan's discovery, scientists started looking into other synthesis techniques to create metal carbides with unique properties for particular uses. Carburization was one of the first processes used; metal powders were heated with carbon sources present to cause solid-state reactions that resulted in the creation of carbides. By producing carbides with regulated compositions and crystal structures using this technique, more research into their characteristics and potential uses was made possible.

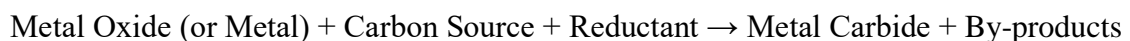
Significant advancements in synthesis techniques, including as chemical vapor deposition (CVD), mechanical alloying, and sol-gel synthesis, were made in the early to mid-20th century. CVD has become a highly versatile technique that provides accurate control over the thickness, content, and homogeneity of carbide thin films deposited onto substrates. Conversely, mechanical alloying allowed elemental metal powders to be ground into finely dispersed carbide nanoparticles by high-energy ball milling with carbon sources. Metal oxide precursors could be created by sol-gel synthesis and then carburized to create carbides with specific surface characteristics and microstructures. These improvements in synthesis techniques increased the variety of carbide materials that could be used in different industrial applications.

The evolution of metal carbides throughout history, especially those of tungsten and molybdenum, is a tale of scientific discovery, technological progress, and industrial ingenuity. Modern materials research and engineering have been greatly influenced by Mo and W carbides, from their discovery in the late 19th century to their ubiquitous uses in the 21st.

1.4 Synthesis Methods

Metal carbides are important materials with a wide range of industrial uses. They are compounds created when metal elements combine with carbon. Among them, the carbides of tungsten (W) and molybdenum (Mo) are particularly notable for their outstanding thermal and electrical conductivity, high melting temperatures, and remarkable hardness. These carbides are synthesized using a variety of techniques, each with their own benefits and drawbacks. We examine the synthesis methods of Mo and W carbides in this thorough review, providing insight into their underlying ideas, workings, and uses in contemporary materials science and engineering. (9)

- a. **Carburization Method:** One of the most popular techniques for creating metal carbides, such as Mo and W carbides, is carburization. This process involves the high-temperature reaction of pure metals or metal oxides with carbon sources in the presence of reducing agents. The following is a representation of the overall response:



The metallurgical process of carburization is essential for improving metal carbides, which are essential parts of many industrial applications, from tooling to the production of automobiles. By adding carbon to a metal's surface, this technique creates carbides, which provide the metal desired qualities including higher hardness, resistance to wear, and strength at higher temperatures. Carburization is based on the principles of thermodynamics, diffusion kinetics, and phase transitions, which coordinate a subtle atomic dance to provide metals enhanced performance properties.

Diffusion of carbon atoms into the metal substrate is the fundamental process that drives carburization. Fick's rules, which explain the flow of atoms across a solid material, control this diffusion process. First, the metal substrate is heated to high temperatures in an environment high in carbon. The concentration differential between the carbon source and the metal surface is what propels carbon diffusion. Carbon

atoms enter the lattice structure and take up interstitial locations, creating carbides, as they move in the direction of the metal.

The length of the carburization process is similarly important because it establishes the layer's depth of carbon enrichment. While longer carburization times are required for deeper penetration and homogeneous carbide distribution, shorter times may be sufficient for surface hardening purposes. Furthermore, the kinds of carbides that form and the metal substrate's aptitude for absorbing carbon are influenced by its composition. The presence of alloying materials in the metal matrix can change the microstructure and characteristics of carburization by facilitating or impeding it.

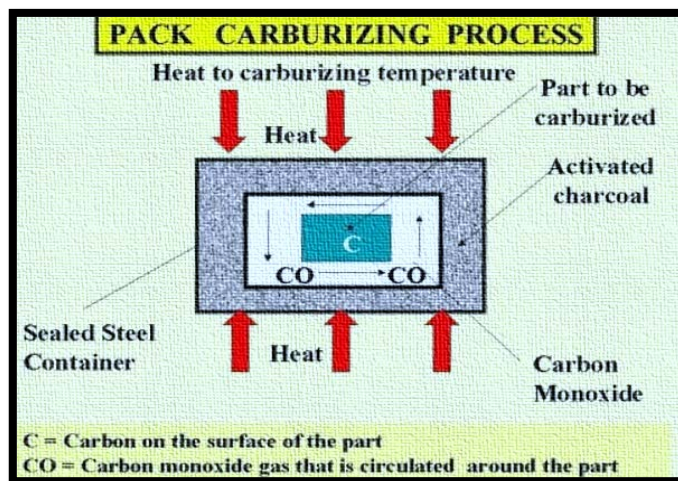


Fig.5: Explanation of Pack Carburization Process

The metal substrate goes through several phases and microstructural changes during carburization. First, depending on the alloy system, carbon atoms diffuse into the lattice and create phases of solid solution called α - and γ - phases. These phases may become more soluble as the carbon level rises, which could cause carbides like cementite (Fe_3C) or other intermetallic compounds to precipitate. By successfully pinning dislocations and preventing plastic deformation, these carbides serve as strengthening agents that improve hardness and wear resistance.

A key concept in metallurgy is the carburization principle, which allows for the precise alteration of metal characteristics by carefully regulating the diffusion of carbon. Through an understanding of the associated thermodynamics, kinetics, and phase transitions, metallurgists can utilize this process to enhance a variety of engineered materials' strength, wear resistance, and hardness. The concepts of carburization continue to drive advancements in sectors ranging from energy production to aerospace, advancing modern metallurgical processes as new materials challenges arise and technology develops.

- b. **Hydrothermal Carbonization Method:** A novel and eco-friendly process for synthesizing metal carbides, especially tungsten (W) and molybdenum (Mo) carbides, is hydrothermal carbonization (HTC). Through this method, metal precursors are converted in aqueous solutions at high pressures and temperatures to generate carbides

with special qualities and uses. This thorough investigation explores the fundamentals, workings, methods of synthesis, and uses of hydrothermal carbonization in the synthesis of Mo and W carbides.

The synthesis of metal carbides has found potential in hydrothermal carbonization (HTC) because of its ease of use, scalability, and environmental friendliness. HTC enables the controlled conversion of organic compounds into carbonaceous materials, which then react with metal species to generate carbides, by exposing metal precursors to hydrothermal conditions. HTC provides a viable and effective way to modify the characteristics of Mo and W carbides and improve their performance for a range of cross-industry applications.

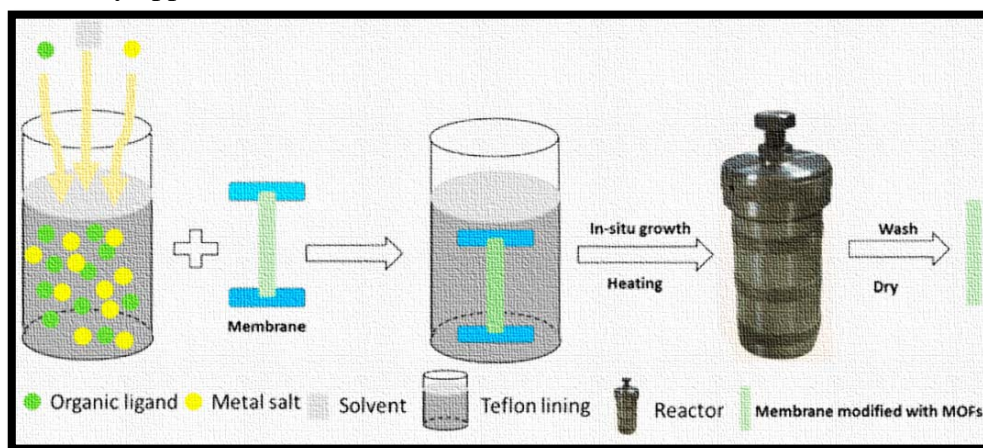


Fig.6: Synthesis via Hydrothermal Carbonization

Aqueous solutions or suspensions of organic precursors are treated at high temperatures and pressures, usually between 150 and 300 °C and 1 and 30 MPa, in the process of hydrothermal carbonization. Organic molecules undergo hydrolysis, dehydration, polymerization, and carbonization processes at these conditions, resulting in the development of hydro chars (materials rich in carbon). When these hydro chars are hydrothermally reacted with metal salts or complexes, they function as precursors for the creation of metal carbides. The hydrothermal environment promotes metal species dissolution, their migration into the carbonaceous matrix, and the chemical processes that lead to the creation of carbides. Temperature, pressure, pH, reaction duration, and reaction media composition are some of the variables that control HTC principles.

The synthesis of Mo and W carbides using hydrothermal carbonization involves a range of procedures designed to produce distinct carbide compositions, structures, and characteristics. The hydrothermal treatment of aqueous solutions containing organic precursors (such as carbohydrates, lignocellulosic biomass, or waste materials) and metal salts (such as ammonium molybdate or tungstate) is one popular technique. The organic precursors carbonize at hydrothermal conditions, forming hydro chars that combine with metal ions to form carbides. Variations in precursor composition, reaction temperature, pressure, and reaction time can all be used to modify the final carbides' composition and attributes. Further post-treatment methods, including reduction or calcination, can improve the characteristics of Mo and W carbides made with HTC. **(10)**

Under high pressure and temperature conditions, a sequence of intricate reactions involving organic precursors, water, and metal species take place to produce the mechanisms of hydrothermal carbonization. Reactive intermediates including organic acids, aldehydes, and ketones are first formed when organic molecules go through hydrolysis and dehydration processes. These intermediates undergo further processes, such as condensation and polymerization, to produce carbon-rich hydrochars with different levels of carbonization and aromaticity. In parallel, metal species dissolve in the aqueous medium and interact with the carbonaceous matrix through carbothermal reduction or other chemical processes to generate metal carbides. Conditions including temperature, pressure, pH, reactant concentration, and the presence of catalysts or additives can all have an impact on the kinetics and processes of hydrothermal carbonization.

Because of their special mix of qualities, tungsten carbide and molybdenum carbide produced by hydrothermal carbonization have wide-ranging uses in several industries. MoC and WC-based materials are effective and stable catalysts for a variety of reactions in catalysis and electrocatalysis, such as hydrodeoxygenation, hydrogenation, dehydrogenation, and electrochemical energy conversion. Green chemistry and renewable energy applications find them appealing due to their high surface areas, catalytic activity, and resistance to poisoning. Furthermore, because of their advantages in hardness, abrasion resistance, and thermal stability, MoC and WC-based materials find application in cutting tools, wear-resistant coatings, and heat management systems. Mo and W carbides are made via hydrothermal carbonization, and as more is learned about their special qualities and their uses, their importance in materials science and engineering will only increase.

A flexible and eco-friendly process for producing tungsten and molybdenum carbide with specific qualities and improved performance characteristics is hydrothermal carbonization. Researchers may create and optimize HTC procedures to fulfil the demands of a variety of applications across industries by utilizing the principles of hydrothermal chemistry. Mo and W carbides made by hydrothermal carbonization continue to be essential in moving materials science and engineering toward novel and sustainable solutions, from classic tooling and coatings to state-of-the-art catalysis and electrocatalysis. HTC is well-positioned to spearhead additional developments in the synthesis and use of metal carbides as science and technology advance, opening up fresh avenues for material innovation and industrial success. (6)

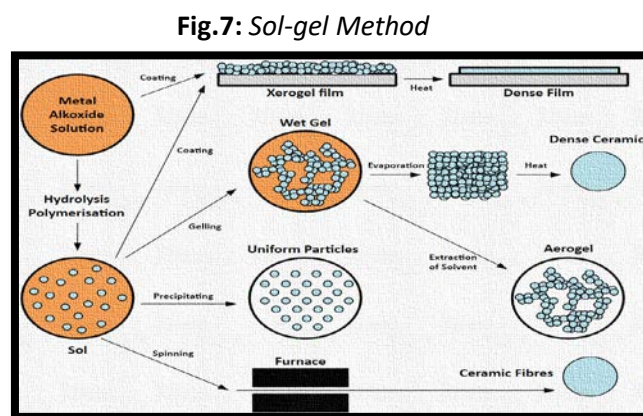
- c. **Wet Impregnation method:** The remarkable mechanical, thermal, and chemical properties of metal carbides, such tungsten carbide (WC) and molybdenum carbide (MoC), have attracted a lot of interest in materials science and engineering. Among other things, these carbides are used in electrical devices, cutting instruments, wear-resistant coatings, and catalysis. To customize metal carbides' qualities for particular uses, their morphology and composition must be carefully managed during the synthesizing process. The wet impregnation method is one of the several synthesis procedures that provides flexibility and accuracy in regulating the properties of the final carbides.

Using the wet impregnation approach, metal precursors are deposited onto a support material and then heated to cause carbide formation. The following steps are part of the standard procedure:

- **Support Material Preparation:** Because of their high surface area and porosity, which aid in the dispersion of metal precursors, porous materials such as carbon nanotubes, alumina, silica, and activated carbon are frequently employed as support materials.
- **Impregnation:** In this method, a solution comprising metal precursors—usually metal salts or organometallic compounds—is immersed in the support material. Adsorption of metal species onto the support surface is made possible by the impregnation process.
- **Drying:** To eliminate the solvent and guarantee that the metal precursors are distributed uniformly across the support surface, the impregnated support material is dried.
- **Thermal Treatment:** To break down the precursors and encourage the synthesis of metal carbides by carburization processes, the dried precursor-loaded support material is heated and exposed to an environment.

An efficient way for creating metal carbides with regulated composition, shape, and characteristics is the wet impregnation process. Tailored materials with different levels of molecular content (MoC) and WC can be generated for a variety of applications in a wide range of sectors by adjusting the synthesis parameters, such as precursor choice, characteristics of the support material, and carburization conditions. **(13)**

- d. **Sol-Gel Method:** Because of their remarkable mechanical, thermal, and chemical characteristics, metal carbides—such as tungsten carbide (WC), molybdenum carbide (MoC), and titanium carbide (TiC)—are valuable materials for a wide range of applications, including electronics, wear-resistant coatings, cutting tools, and catalysis. Because the sol-gel process allows one to regulate the composition, shape, and nanostructure of the materials that are produced. **(11)**



In the sol-gel process, hydrolysis and condensation processes are used to turn a precursor sol into a gel network. The following are the general procedures in the preparation of metal carbides using the sol-gel method:

- **Precursor Preparation:** For the sol-gel synthesis of metal carbides, metal alkoxides or metal salts are commonly employed as precursors. In order to

create a homogenous solution, or sol, these precursors are dissolved in an appropriate solvent.

- **Hydrolysis:** The metal hydroxides or oxides are formed when the metal alkoxide or salt combines with water in the precursor solution.
- **Gel Formation:** A three-dimensional network, or gel structure, is created when condensation interactions between the dissolved metal species take place.
- **Calcination and Drying:** After the solvent are extracted from the gel by drying it, it is heated to a high temperature during calcination, which causes carburization processes that turn metal oxides and hydroxides into metal carbides.

1.5 Importance of Methane Dehydroaromatization

The most basic hydrocarbon molecule found in large quantities in nature, methane, offers both possibilities and difficulties. Methane is abundant, but using it as a feedstock for the synthesis of compounds with added value is difficult due to its high stability and inert character. Methane dehydroaromatization (MDA) is a game-changing technology that unlocks methane's enormous potential for energy production and sustainable chemical synthesis by turning it into higher hydrocarbons.

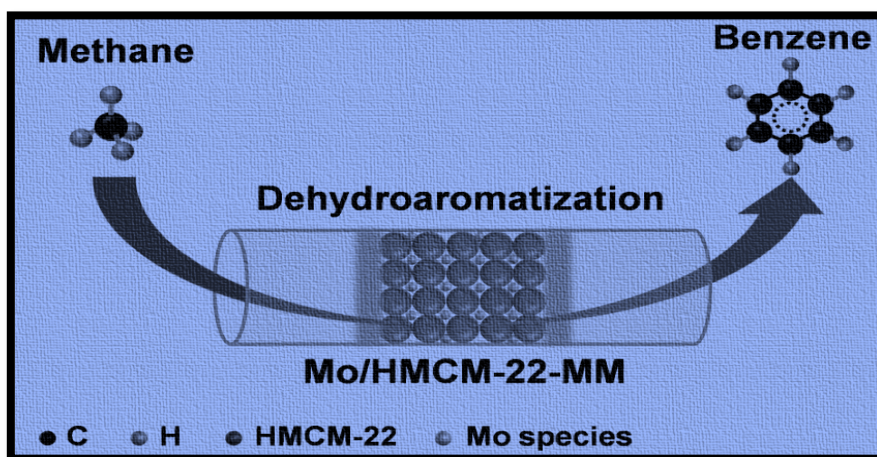


Fig.8: Methane Dehydroaromatization

Methane is a plentiful feedstock, but because of its low reactivity and limited use in conventional chemical processes, it is usually underestimated. The economic value of methane is significantly increased when it is converted into more lucrative aromatics like benzene, toluene, and xylene (BTX). These aromatics are essential components that are used to produce a wide range of fuels, polymers, and industrial chemicals. This helps to diversify sources of income and increase the profitability of methane-based processes. Aromatics, especially benzene, toluene, and xylene, are highly sought-after products in the chemical sector. They are used in the production of solvents, plastics, resins, synthetic fibres, and medications. The capacity to create these important aromatics from methane feedstocks meets market demand and lessens dependency on aromatics obtained from fossil fuels, which could be vulnerable to changes in pricing and unpredictability in geopolitics. (5)

MDA is a catalytic process that turns methane through a sequence of intricate processes into aromatic hydrocarbons. Dehydrogenation, aromatization, and the oxidative coupling of methane (OCM) are the usual processes in the process. The primary reaction in MDA is the creation of unsaturated hydrocarbons like benzene and ethylene, which then go through further reactions to produce aromatic compounds with higher value. By reducing the activation energy and offering active sites for the transformation of hydrocarbons and methane, catalysts are essential in promoting these processes.

For MDA to be successful, effective and selective catalyst development is essential. Usually, transition metals supported on oxide or zeolite supports serve as the basis for MDA catalysts. Prominent catalysts include materials based on molybdenum, nickel, and platinum; each has special benefits with regard to activity, selectivity, stability, and affordability. New catalysts with better performance and resistance to deactivation have been created as a result of recent developments in catalyst synthesis and design. These catalysts minimize unwanted side reactions such as coke formation and methane combustion while exhibiting excellent activity and selectivity towards the synthesis of aromatics.

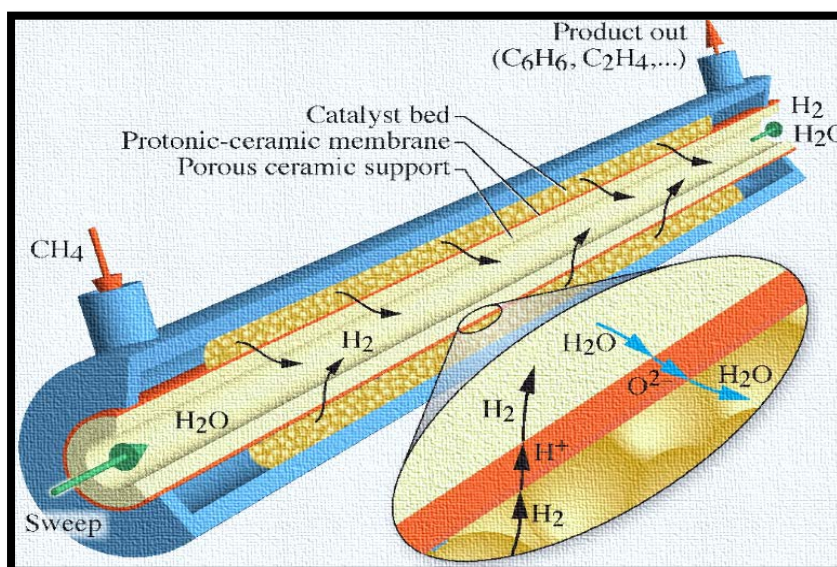


Fig.9: Illustration of a shell and tube membrane reactor used in MDA

MDA finds its application in a wide range of industries, including as materials research, petrochemicals, fine chemicals, and pharmaceuticals. Aromatic materials including benzene, toluene, and xylenes (BTX) are essential for the petrochemical industry's manufacturing of polymers, plastics, and specialty chemicals. By generating BTX from methane in a sustainable and economical manner, MDA lessens the need for fossil fuels and has a positive environmental impact. Additionally, MDA-derived aromatics are used in the production of agrochemicals, fragrances, medicines, and dyes, among other products, where their functionalization and purity are essential to the efficacy and quality of the final product.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 Materials and Method used

The molybdenum trioxide (MoO_3) provided by Sigma-Aldrich is an essential starting point for the synthesis of molybdenum carbide (MoC), a material that is highly valued for its exceptional mechanical, thermal, and catalytic characteristics. This molecule is essential for the production of molecular carbon using a variety of techniques, such as carburization procedures. Here, we explore the role that Sigma-Aldrich's MoO_3 plays in the creation of MoC and its many uses.



Fig.10: *Products used in Synthesis*

Reputable chemical reagent provider Sigma-Aldrich provides WO_3 with specifications designed for a range of industrial and research uses. Because Sigma-Aldrich WO_3 is so pure, there are few impurities present, which makes it easier to synthesize WC with predictable qualities and performance traits.

The hydrothermal carbonization (HTC) Method is used as it is a viable avenue for the production of metal carbides, such as tungsten carbide (WC) and molybdenum carbide (MoC). In this technique, carbides are formed by hydrothermally treating precursor materials that include tungsten or molybdenum at high pressures and temperatures. Among the many benefits of the HTC process are its scalability, simplicity, and compatibility with a broad variety of precursor materials, including organic compounds, metal oxides, and hydroxides.

2.2 Synthesis of Molybdenum Carbide (MoC_x)

There are many phases involved in the hydrothermal carbonization (HTC) process that yields molybdenum carbide (MoC_x). The typical process for creating MoC_x nanoparticles by hydrothermal carbonization is given below: **(4) (18)**

i. Precursor Preparation:

- A precursor solution is prepared by dissolving molybdenum Trioxide and 30% Hydrogen Peroxide Solution in water.
- Then, a carbon source is added to the precursor solution. Glucose, sucrose, and other carbohydrates are common sources of carbon and can supply the carbon required for carburization during the hydrothermal process. D-Glucose is used as carbon source in this reaction.

ii. Hydrothermal Treatment:

- Transfer the precursor solution into a hydrothermal reactor vessel also known as Autoclave.
- Seal the vessel to sustain the high pressures and temperatures required for the hydrothermal process.
- For a given amount of time, usually several hours to a day, heat the precursor solution under high pressure at temperatures between 180°C and 250°C.
- Molybdenum oxide and carbonaceous species are formed as a result of the hydrolysis of molybdenum precursors and the carbonization of the carbon source, which are encouraged by the hydrothermal environment.

iii. Washing and Drying:

- The resultant Molybdenum oxide nanoparticles are usually dried and cleaned with water after the hydrothermal process to get rid of any remaining solvent or contaminants.

iv. Carburization:

- Molybdenum oxide and carbonaceous species undergo carburization to yield molybdenum carbide (MoC_x) after hydrothermal treatment.
- Transfer the Molybdenum oxide and carbonaceous species in a Quartz vessel (Quartz Boat) and put it in Tubular Furnace for several hours at temperatures between 700°C and 900°C.
- The carbon supply for carburization is the carbonaceous species produced during hydrothermal treatment, which combines with molybdenum oxide to form MoC_x. **(13)**

v. Characterization:

- The phase composition, morphology, particle size, and elemental composition of the synthesized MoC_x nanoparticles can be ascertained by employing a variety of analytical techniques, including energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD).

2.3 Synthesis Method of Tungsten Carbide (WC_x)

There are many phases involved in the hydrothermal carbonization (HTC) process that yields molybdenum carbide (MoC_x). The typical process for creating MoC_x nanoparticles by hydrothermal carbonization is given below:

- i. Precursor Preparation:**
 - A precursor solution is prepared by dissolving Tungsten Trioxide and 30% Hydrogen Peroxide Solution in water.
 - Then, a carbon source is added to the precursor solution. Glucose, sucrose, and other carbohydrates are common sources of carbon and can supply the carbon required for carburization during the hydrothermal process. D-Glucose is used as carbon source in this reaction.

- ii. Hydrothermal Treatment:**
 - Transfer the precursor solution into a hydrothermal reactor vessel also known as Autoclave.
 - Seal the vessel to sustain the high pressures and temperatures required for the hydrothermal process.
 - For a given amount of time, usually several hours to a day, heat the precursor solution under high pressure at temperatures between 180°C and 250°C.
 - Tungsten oxide and carbonaceous species are formed as a result of the hydrolysis of tungsten precursors and the carbonization of the carbon source, which are encouraged by the hydrothermal environment. (17)

- iii. Washing and Drying:**
 - The resultant tungsten oxide nanoparticles are usually dried and cleaned with water after the hydrothermal process to get rid of any remaining solvent or contaminants.

- iv. Carburization:**
 - Tungsten oxide and carbonaceous species undergo carburization to yield Tungsten carbide (WC_x) after hydrothermal treatment.
 - Transfer the Tungsten oxide and carbonaceous species in a Quartz vessel (Quartz Boat) and put it in Tubular Furnace for several hours at temperatures between 700°C and 900°C.
 - The carbon supply for carburization is the carbonaceous species produced during hydrothermal treatment, which combines with Tungsten oxide to form WC_x. (3)

- v. Characterization:**
 - The phase composition, morphology, particle size, and elemental composition of the synthesized WC_x nanoparticles can be ascertained by employing a variety of analytical techniques, including energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD).

2.4 Synthesis of Molybdenum/Tungsten supported zeolite

In order to impregnate the metal precursors onto the zeolite support, there are many processes involved in the synthesis of metal (Mo, W) supported on zeolite (ZSM-5). The typical process for creating metal-supported zeolites employing tungsten (W) or molybdenum (Mo) as the metal precursor is given below: (7)

i. Zeolite Support Preparation:

- Either buy commercially available ZSM-5 or create it in the lab using traditional hydrothermal techniques to prepare the ZSM-5 zeolite support.
- If you're using commercially available ZSM-5, calcinate the zeolite at high temperatures (500–600°C, for example) to create active sites on the surface and remove any organic matter and water that may have been adsorbed.

ii. Metal Precursor Impregnation:

- Use a suitable solvent (such as ethanol or deionized water) to dissolve unwanted salts.
- To enhance the dispersion of metal particles on the zeolite surface, you can optionally include an appropriate binder or dispersant into the metal precursor solution.
- Submerge the zeolite support in the metal precursor solution, allowing capillary action, vacuum, or pressure-assisted techniques to saturate the zeolite pores.
- To get the appropriate loading of Mo or W on the zeolite support, modify the impregnation period and metal precursor solution concentration.

iii. Drying:

- After impregnation, dry the impregnated zeolite at a moderate temperature (e.g., 80–120°C) in a vacuum oven or under ambient pressure to eliminate excess solvent.
- Make sure the zeolite surface is thoroughly dried to avoid the forming of clusters of metal oxides.

iv. Calcination:

- To break down the metal precursor salts and create metal oxide species supported on the zeolite surface, calcine the dried zeolite-supported metal precursor at high temperatures (such as 400–600°C) in an inert environment (such as nitrogen or argon) or air.
- Additionally, the calcination process enhances the metal species' dispersion and interaction with the zeolite support by activating them. (16)

v. Characterization:

- Using methods like energy-dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), nitrogen physisorption analysis, and X-ray diffraction (XRD), characterize the synthesized metal-supported zeolite in order to evaluate its surface area, composition, structure, and morphology.
- Determine the activity, selectivity, and stability of the metal-supported zeolite by assessing its catalytic performance in pertinent processes, such as hydrocarbon conversion, hydro processing, or selective catalytic reduction (SCR).

2.5 Characterization Techniques:

i. X-Ray Diffraction:

An effective analytical method for examining the structure, orientation, and ordering of materials at low angles with respect to the incident X-ray beam is called low-angle X-ray diffraction, or LAXRD. This method is broadly relevant in subjects including materials science, physics, chemistry, and biology since it offers insightful information on the configuration of atoms, molecules, and crystalline domains inside a material. We will go over the fundamentals, tools, uses, and restrictions of low-angle X-ray diffraction in this in-depth conversation. (12)

Bragg's law, which explains the link between the angle of incidence (θ), the wavelength of the incident X-ray light (λ), and the spacing between atomic planes (d) in a crystalline material, is the foundation of low-angle X-ray diffraction. When the path difference between X-ray waves scattered from neighbouring crystal planes is an integer multiple of the X-ray wavelength, constructive interference occurs, according to Bragg's law: $2d\sin(\theta)=n\lambda$

The incident X-ray beam is focused onto the sample in LAXRD at a low angle, usually a few degrees to a few tens of degrees, with respect to the sample surface. After that, the scattered X-rays are found and examined to ascertain the diffraction angle and intensity, which reveal details on the low spatial frequency ordering and structure of the material.

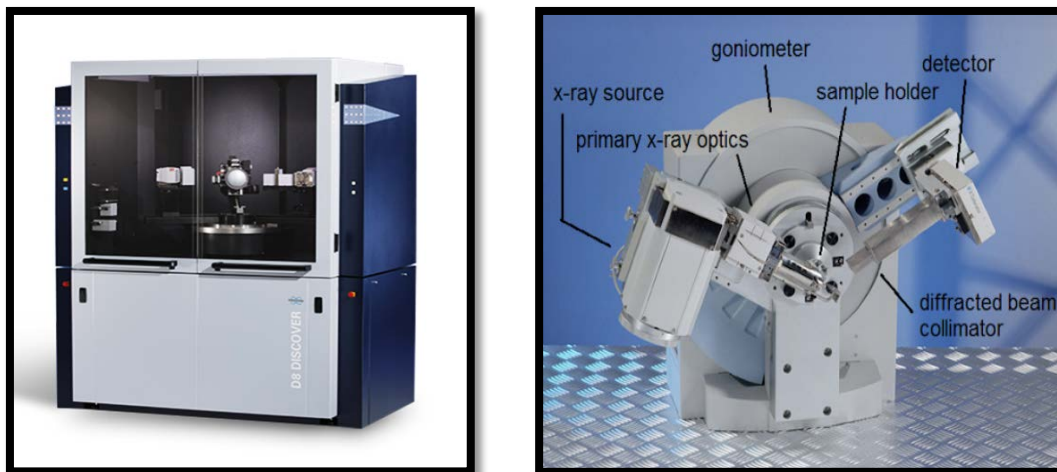


Fig.11: Photograph and Elements of X-Ray Diffraction Machine

Typically, an X-ray source, sample holding, detector, and data processing software make up the LAXRD apparatus. Rotating anode generators and sealed X-ray tubes are common sources of X-ray radiation used in LAXRD. These sources may generate monochromatic or polychromatic radiation with wavelengths ranging from 0.1 to 1 nm. The detector gauges the intensity and angle of diffracted X-rays, while the sample holder permits exact sample placement and alignment with respect to the incident X-ray beam. High-resolution characterisation of complicated materials is made easier by the quick collection and interpretation of data made possible by sophisticated detectors like area detectors and CCD cameras.

ii. Thermogravimetric Analysis:

A potent analytical method for examining the composition, stability, and thermal breakdown of materials as a function of temperature is thermogravimetric analysis (TGA). Applications for this flexible method may be found in many different domains, such as chemistry, polymers, medicines, materials science, and environmental science. We will go over the fundamentals, tools, protocols, techniques for analyzing data, applications, and constraints of thermogravimetric analysis in this in-depth conversation.

Thermogravimetric analysis works on the basis of determining how a sample's mass changes in response to temperature or time when heated under controlled circumstances. Using a very sensitive balance, the sample is continually monitored for mass while being subjected to a preprogrammed temperature ramp. The sample changes in mass over time due to thermal breakdown, oxidation, dehydration, or other chemical processes that occur when the temperature rises.

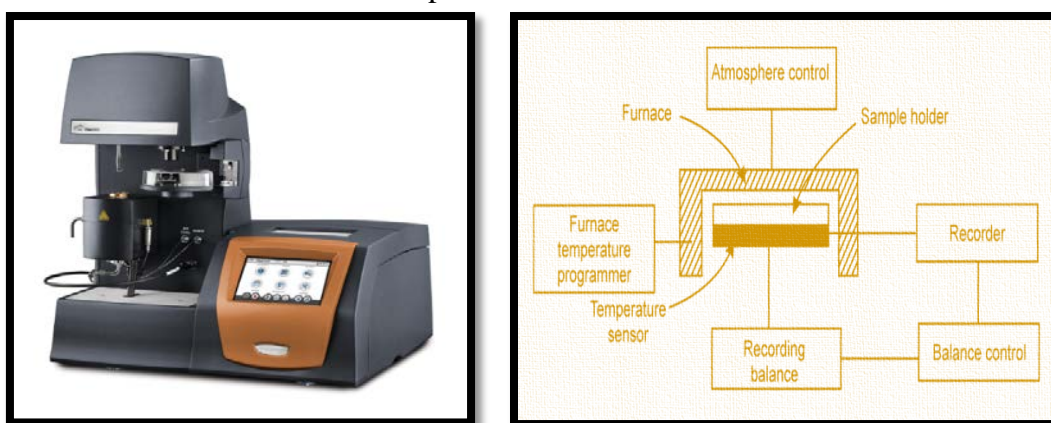


Fig.12: Photograph and explanation of TGA Machine

A thermogram, which is a representation of the thermogravimetric curve (TGA curve) that shows the sample's percentage weight gain or loss as a function of temperature or time, is used to record the mass change. Important details on the sample's composition, heat stability, decomposition rates, and reaction processes may be obtained from the TGA curve.

The following elements are commonly seen in thermogravimetric analysis instrumentation:

- **Sample Holder:** A quartz, platinum, or alumina-based crucible or pan is usually used to hold the sample. The sample holding is set up on an extremely sensitive balance that can detect even the smallest mass changes.
- **Furnace:** The sample holder is inserted into a temperature-controlled furnace that has the ability to gradually raise the sample's temperature from room temperature to a maximum of 1000°C.
- **Balance:** Throughout the experiment, the balance continually and extremely accurately monitors the mass of the sample. Various methods, like electromagnetic, piezoelectric, or optical sensors, might serve as the foundation for the balancing.

- **Gas Flow System:** To supply regulated atmospheres like air, nitrogen, oxygen, or inert gases throughout the analysis, certain TGA instruments are outfitted with gas flow systems. The study of thermal breakdown in particular environmental settings is made possible by the gas flow system.
- **System of Data Acquisition:** The data collection system records the mass change of the sample in real time and presents it as a thermogram. Usually, the thermogram is represented as a percentage of weight gained or lost in relation to time or temperature.

To sum up, thermogravimetric analysis is a useful method for researching the composition, thermal behaviour, and breakdown kinetics of materials at a variety of temperatures. Through its capacity to provide light on a material's thermal stability, degradation routes, and reaction processes, TGA helps a wide range of sectors with research, development, and quality assurance.

iii. **Transmission Electron Microscope:**

A sophisticated microscopy method called transmission electron microscopy (TEM) uses an electron beam to examine the shape, chemistry, and internal structure of materials at the nanoscale. This high-resolution imaging technique has completely changed how we think about biology, nanotechnology, materials science, and many other disciplines. We will go over the fundamentals, tools, sample preparation methods, imaging modes, applications, and constraints of transmission electron microscopy in this in-depth conversation.



Fig.13: *Transmission Electron Microscope*

The basis of transmission electron microscopy is the wave-particle duality theory, according to which electrons may act like both waves and particles. A high-energy electron beam (usually between 80 and 300 keV) is focused onto a thin object in a transmission electron microscope (TEM). The specimen's interior structure determines how the electrons scatter and diffract when they contact with its atoms during passage through it.

A sequence of electromagnetic lenses gathers the transmitted electrons, which are then concentrated onto a fluorescent screen or digital detector to create a picture depending

on the electron transmission strength. TEM gives atomic-resolution details on the morphology, crystal structure, flaws, interfaces, and elemental makeup of materials by adjusting the electron beam and examining the transmitted electrons.

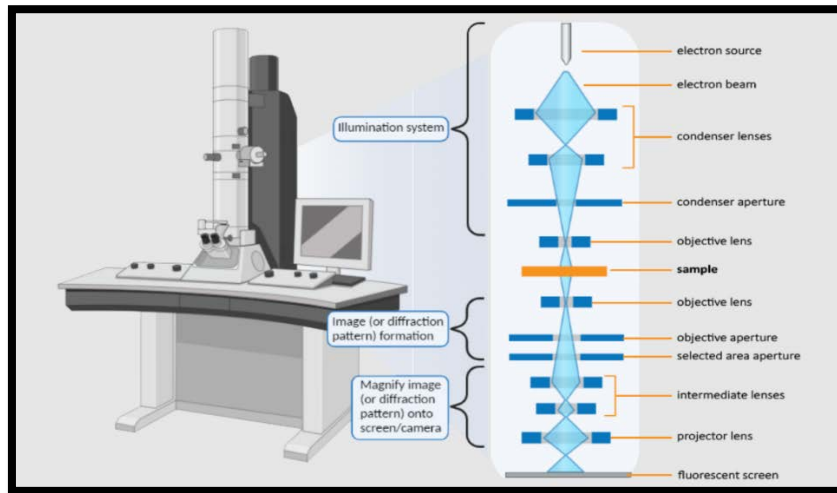


Fig.14: Diagram of Transmission Electron Microscope

The following are the main parts of a transmission electron microscope.

- **Electron Source:** The electron cannon on TEMs produces an electron beam by field emission (cold cathode) or thermionic emission (tungsten filament). Electromagnetic fields are used to accelerate the electron beam to high energies.
- **Electron Lenses:** To achieve high resolution and magnification, an array of electromagnetic lenses, such as condenser lenses, objective lenses, and projector lenses, focus and modify the electron beam.
- **Specimen Stage:** For imaging and analysis, the specimen stage precisely positions and controls the tilt of the thin sample, which is usually less than 100 nm thick.
- **Detector System:** High-resolution pictures are created by capturing the transmitted electrons using electron detectors, which include scintillation screens, photographic films, and digital cameras.
- **Vacuum System:** The TEM works in a highly vacuum environment to reduce the number of electrons that are scattered and absorbed by air molecules, resulting in the best possible picture quality and resolution.
- **Computer Interface:** In order to facilitate sophisticated imaging modes and quantitative measurements, modern TEMs are outfitted with computer-controlled interfaces for data collecting, image processing, and analysis.

To sum up, transmission electron microscopy is a flexible and essential technique for viewing, examining, and comprehending objects at the nanoscale. Through the use of TEM, which offers atomic resolution imaging and spectroscopic capabilities, scientists may investigate the links between structure and property, as well as nanoscale phenomena and the underlying principles that regulate the behaviour of materials. TEM persists in propelling progress in science, engineering, and technology in spite of its obstacles, moulding our comprehension of the nanoworld and expanding the frontiers of knowledge and creativity.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Morphologies

This process produces huge quantities of well scattered molybdenum carbide nanoparticles impregnated with carbon using inexpensive precursors such as molybdenum trioxide and glucose. Fig.15 depicts the shape, size and weight percentage of a sample produced at 180°C for 6 hours under hydrothermal conditions. (14)

- Average Particle size is observed to be 11.49 nm, with minimum particle size of 8.34 nm.
- Weight percentage of Carbon is 92.7% and Molybdenum is 5.9% with a standard Deviation of 0.3%
- The Interplanar Spacing of 0.344 nm is assigned to plane 110.
- Five separate planes at 411, 322, 213, 111 and 110 are observed when a light falls upon the sample.

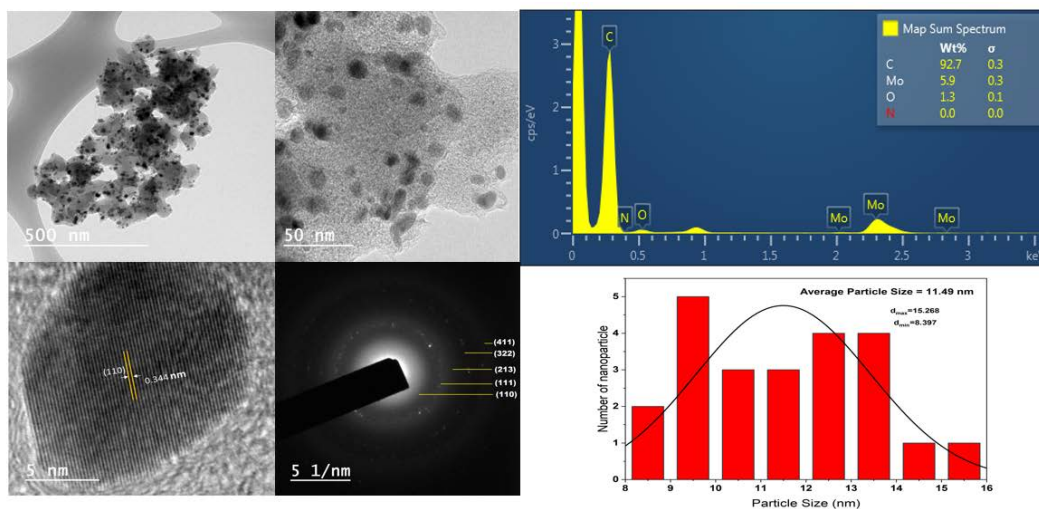


Fig.15: TEM of MoO₂

The sample has a porous structure composed of tiny particles. After 4 hours of carbonization at 700°C, the morphologies of the samples are nearly identical. (15) Although some changes have been observed in fig.16 which are mentioned below:

- Average Particle size is observed to be 12.20 nm, with minimum particle size of 6.98 nm.
- Weight percentage of Carbon is 92.4% and Molybdenum is 6.3% with a standard Deviation of 0.2%
- The Interplanar Spacing of 0.224 nm is assigned to plane 102.
- Five separate planes at 240, 040, 221, 111 and 102 are observed when a light falls upon the sample.

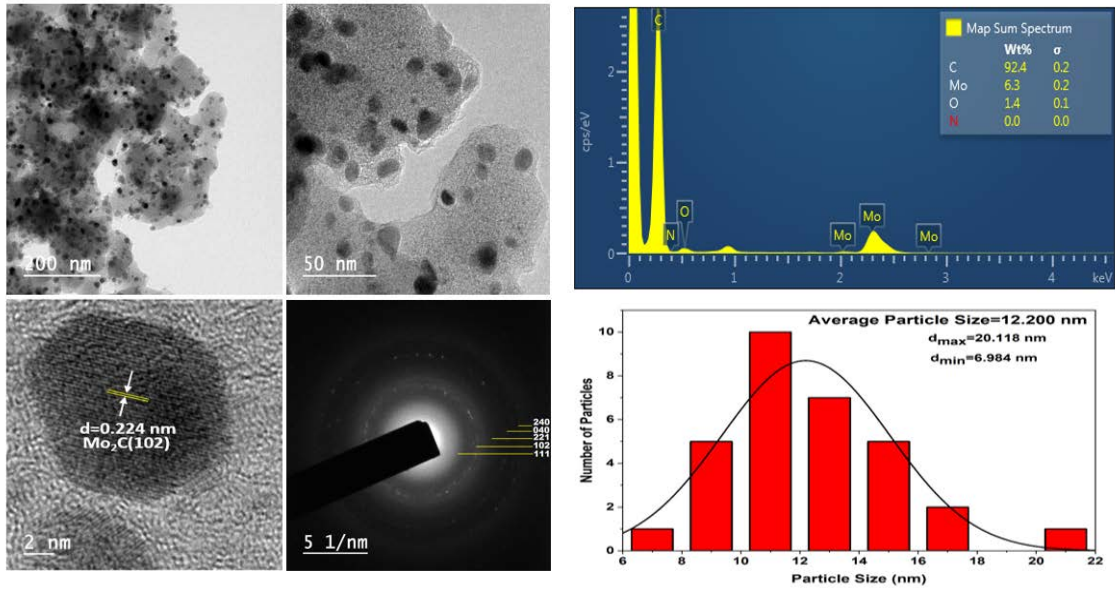


Fig.16: TEM of Mo₂C

We were unable to get dispersed nanoparticles for tungsten carbide via hydrothermal method as, particle clusters were seen in tungsten carbide nanoparticles impregnated with carbon using inexpensive precursors such as tungsten trioxide and glucose. Fig.17 depicts the shape, size and weight percentage of a sample produced at 900°C for 4 hours of carburization. (22)

- Average size of particle is not mentioned as carbide nanoparticles were grouped together (not dispersed).
- Weight percentage of Carbon is 24.7% and Molybdenum is 74.6% with a standard Deviation of 0.3%
- Two separate planes at 200 and 202 are observed when a light falls upon the sample.

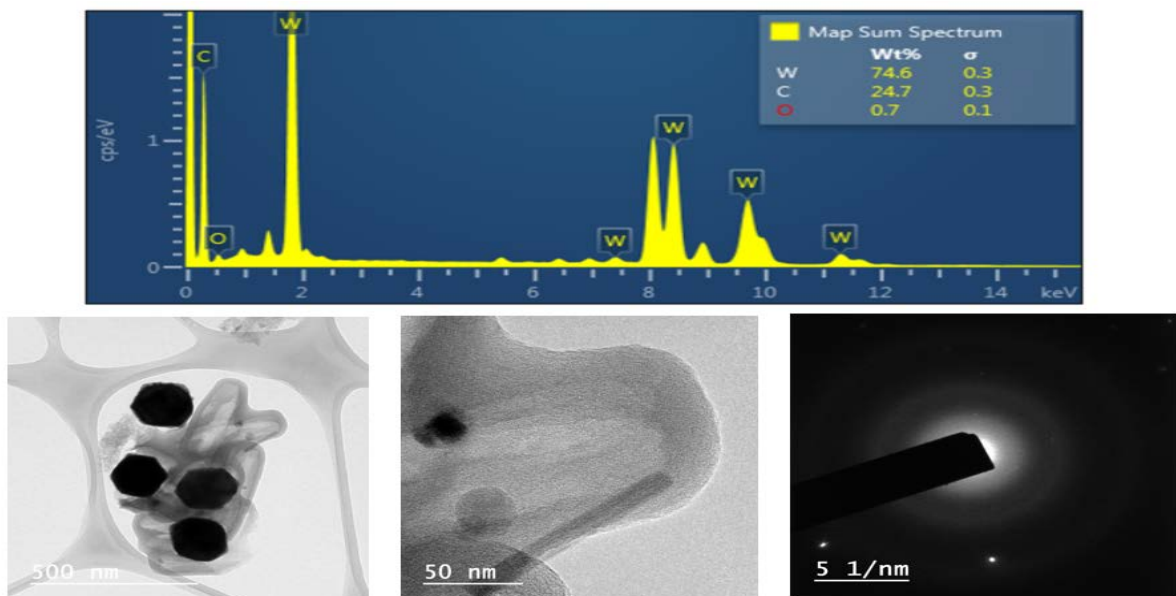


Fig.17: TEM of W₂C_x

3.2 Phase and Textural Structure

The crystalline structures of the materials were characterized using XRD (fig.18). The XRD pattern of MoO₂ shows a crystalline phase (2θ-26.2, 37.0, 41.2, 53.0, 53.5, 60.2, and 66.6, JCPDS no. 86-0135).

The composite material was identified as MoO₂ embedded in carbon. The carbonaceous phase in these samples is amorphous, with no graphitic carbon peaks seen. After carbonization in an inert environment, the principal diffraction peaks of MoO₂ changed to Mo₂C as, carbonaceous phase plays its role of carbon source.

MoO₂ has the widest lattice spacing (0.34 nm). The crystallinity of the Mo₂C phase is much enhanced in the MoC-H sample, as evidenced by diffraction peaks such as (2θ and JCPDS no. 89-2669) emerge and are being upgraded. Furthermore, Fig.18 confirms that the peak associated with MoO₂ is not visible in the sample of Mo-CH, and no peaks were ascribed to MoO₂. This suggests that MoO₂ modified the carbonization in CH₄/H₂. In Fig.17, the lattice spacings of 0.244 nm and 0.344 nm correspond to the (102) and (110) planes of MoO₂ and Mo₂C, respectively. (20)

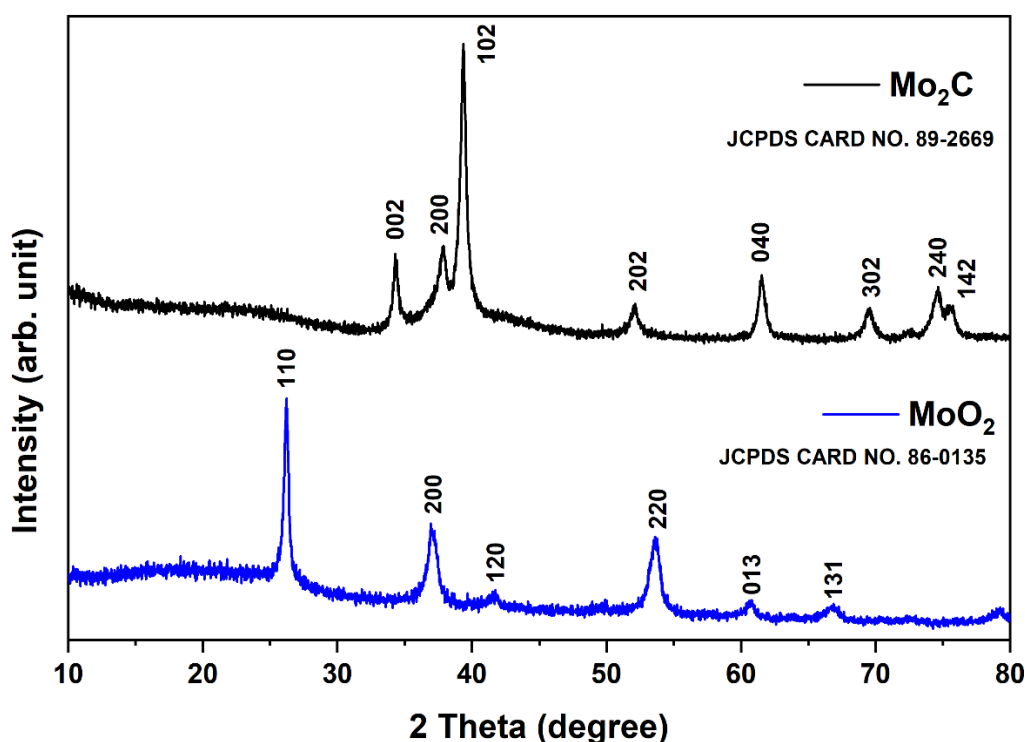


Fig.18: XRD Graph of MoO₂ and Mo₂C

The crystalline structures of the materials were characterized using XRD (fig.19). The XRD pattern of WO₃ shows a crystalline phase (2θ-26.2, 37.0, 41.2, 53.0, 53.5, 60.2, and 66.6, JCPDS no. 75-0768).

The composite material was identified as WO₃ embedded in carbon. The carbonaceous phase in these samples is amorphous, with no graphitic carbon peaks seen. After carbonization in an inert environment, the principal diffraction peaks of WO₃ changed to W₂C_x as, carbonaceous phase plays its role of carbon source. An Abnormality was seen in the XRD pattern of W₂C_x as the first two planes were matching to JCPDS no.

75-0768 and rest of the peaks matched to JCPDS no. 02-1055 so, from that we conclude that W_2C_x is in mixed phase. (21)

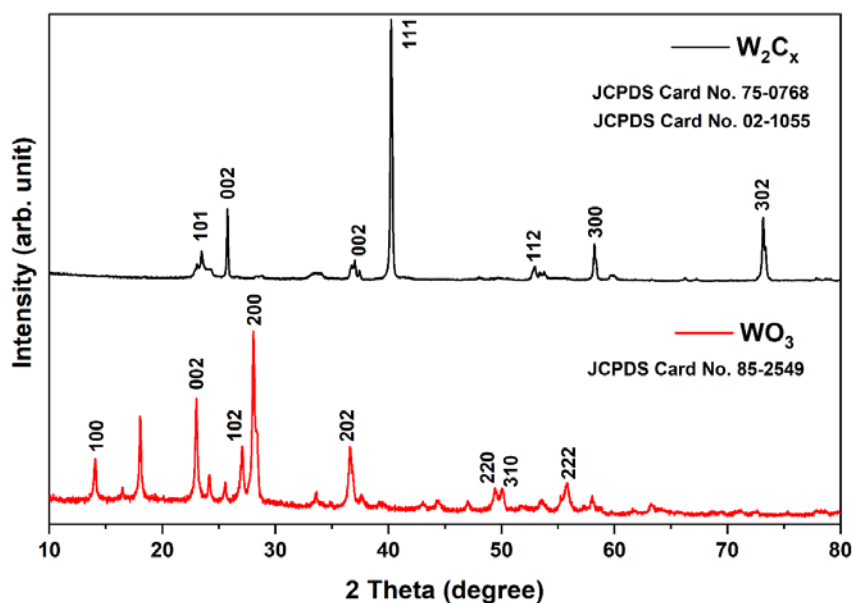


Fig.19: XRD pattern of WO_3 and W_2C_x

3.3 Catalytic Performance

Methane dehydroaromatization (MDA) has emerged as a viable technology for generating renewable energy and value-added chemicals. MDA is the conversion of methane, the primary component of natural gas, into higher hydrocarbons and aromatics, which are useful precursors for a variety of industries. Molybdenum-supported zeolites have received a lot of interest as MDA catalysts because of their unique characteristics and catalytic performance. This article investigates the catalytic properties of molybdenum-supported zeolites for methane dehydroaromatization, including their structure, activity, and potential for commercial use.

Fig.20 explains the selectivity of Molybdenum supported Zeolite over increasing temperature.

- It can be observed clearly that selectivity of Mo supported zeolite is more towards coke formation at 550°C as the catalyst is not activated yet.
- As the temperature reaches to 650°C , the selectivity of catalyst increases towards formation of Ethene to 50% and selectivity towards Benzene formation is 40%.
- Molybdenum oxide present with the supported zeolite activates as temperature reaches 700°C enabling maximum selectivity of Ethene upon 90%

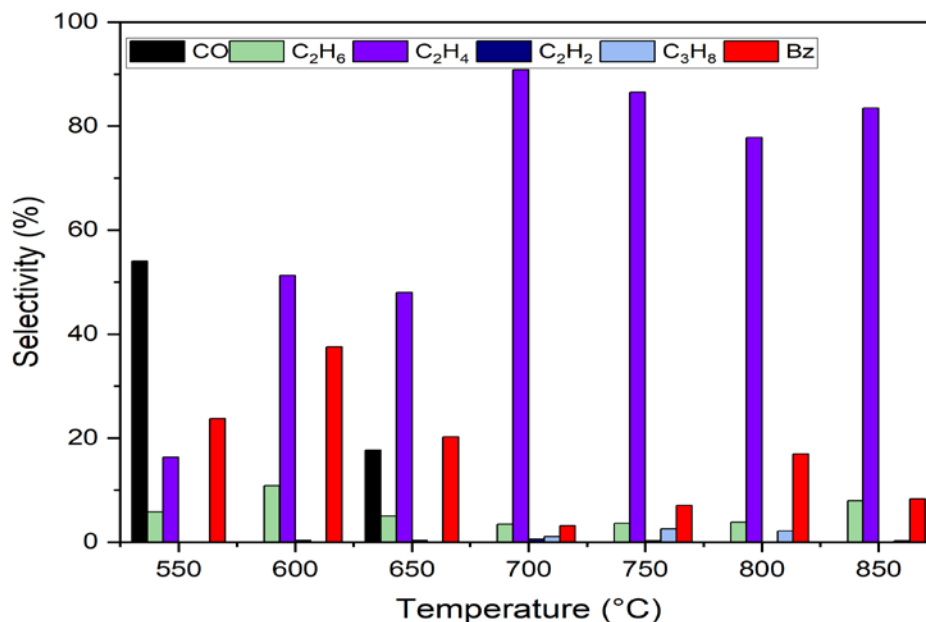


Fig.20: Selectivity Graph of Mo supported zeolite

Fig.21 explains the conversion% of Methane to Benzene using Molybdenum supported Zeolite over increasing temperature.

- It can be observed clearly that Conversion% of Methane to Benzene using Mo supported zeolite is only 5% at 550° C as the catalyst is not activated yet.
- As the temperature reaches to 650°C, the conversion % of catalyst increases to 10%.
- Conversion rate increased to 11% at 700°C. At this temperature the catalyst starts activating and enhances the conversion rate with increase in temperature.
- After the activation of catalyst, a sudden spike in conversion rate of 12% is observed at 750°C.
- Maximum conversion of benzene i.e., 23% is observed at 850°.

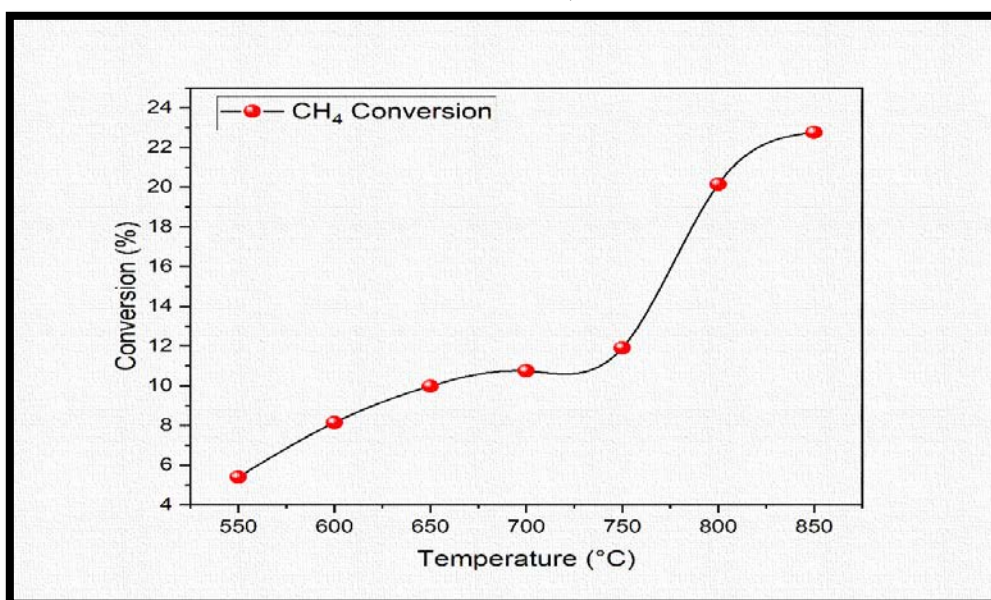


Fig.21: Methane to Benzene Conversion Graph

4. Conclusion

To summarize, the synthesis of metal carbides and their use in methane dehydroaromatization represent a viable avenue toward sustainable energy and chemical synthesis. Metal carbides have the potential to change the field of catalysis by optimizing reaction conditions, designing revolutionary catalysts, and collaborating on research. Despite existing obstacles, further research into metal carbide-based catalysts shows considerable promise for resolving critical environmental and economic problems while meeting rising global energy demand.

The synthesis of molybdenum and tungsten carbides uses a variety of processes, each with its own set of benefits and problems. Researchers have devised a variety of tactics for modifying the characteristics and uses of Mo and W carbides, including classic methods such as carburization and solid-state reactions as well as sophisticated techniques like as CVD, PVD, and hybrid approaches. **(23)**

A well dispersed Molybdenum Carbide was formed via Hydrothermal method followed by Carburization, in which we were able to attain a minimum particle size of 6.98 nm and average size of 12.20 nm. Considering the maximum selectivity, we attain is 23% at 850°C and conversion rate of 70% at 800°C. **(19)**

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