DYNAMIC STUDY OF Mo/ZSM-5 CATALYST FOR CH₄
DEHYDROAROMATIZATION

Hadi Almusawa

Problem Report submitted
to the Statler College of Engineering and Mineral Resources
at West Virginia University

In partial fulfillment of the requirements for the degree of
Master of Science in
Chemical engineering

Hanjing Tian, Ph.D., Chair

Dr. John Hu, Ph.D.

Dr. Fernando Lima, Ph.D.

Department of Chemical Engineering

Morgantown, West Virginia

2020

Keywords: Methane dehydroaromatization, Mo/ZSM-5, zeolite catalysts, molybdenum,
membrane reactor, fixed-bed reactor

Copyright 2020 Hadi Almusawa

ABSTRACT

DYNAMIC STUDY OF Mo/ZSM-5 CATALYST FOR CH₄

DEHYDROAROMATIZATION

Hadi Almusawa

Methane dehydroaromatization (CH₄-MDA) is a highly promising venture for natural gas utilization/exploitation, i.e., direct conversion of methane (CH₄) to liquid aromatics (benzene) and hydrogen. This process is a catalytic reaction and therefore, is subject to all the advantages and constraints of catalysis. This study discussed the structure and reactivity of Mo/ZSM-5 zeolite catalysts and their effect on the active conversion of methane to valuable aromatic products such as benzene: 1) The preparation and characterization of Mo/ZSM-5, which are crucial steps in any catalytic reaction process since a better performing catalyst consequently leads to better outcomes; 2) An examination of the structure and properties of the prepared and characterized molybdenum zeolite catalyst (Mo/ZSM-5) reveals that the MoO_x sites are responsible for the performance of the catalyst, as discussed in surface-active structure performance relationship subsection. In addition, there are some studies compared the reaction performance of Mo/ZSM-5 with other catalytic system such as molybdenum carbide; 3) The performance of this catalyst is essentially determined by the nature of surface desorption, the propensity of mass diffusion of benzene and naphthalene by-products across active sites, and the propensity for coking. These three factors are influenced by multiple parameters such as molybdenum content, the reaction temperature, the space velocity and the reaction time, which have been discussed in detail in this study. In order to overcome the challenge of coking, which impedes the effectiveness of the MDA process, fundamental discoveries have been explored by the researchers, along with their major impacts. 4) The final section of this paper explores the best reactor design by comparing the structure and performances of a fixed-bed reactor (FR) and a membrane reactor (MR).

ACKNOWLEDGEMENTS

I wish to direct my truthful gratitude to my advisor Dr. Hanjing Tian for his guidance and encouragement during this work. I am also very grateful to the members of my advisory committee. Dr. John Hu and Dr. Fernando Lima and Dr. Charter Stinespring for their helps.

I must especially thank department chair on Graduate Student Service, Dr. Charter Stinespring for his help, and guides throughout my entire graduate program.

I am thankful to all graduate students and faculties in the Chemical Engineering Department for their friendliness and warmth that has made my stay in Morgantown pleasant and productive.

I must thank my home University “Jazan University” for giving me the chance to study abroad with full scholarship.

Last, I wish to thank my family in Saudi Arabia for their love and support throughout the course of my education in the United States.

TABLE OF CONTENTS

Title Page	i
Abstract	ii
Acknowledgements.....	iii
Table of Contents	iv
1: Introduction	1
2: Catalyst Preparation and Characterization	3
2.1 ZSM-5 Zeolite (Preparation and Structure)	5
2.2 Mo/ZSM-5 Catalyst Preparation Methods	12
2.3 Surface MoO _x Structure of Prepared Mo/ZSM-5 Catalyst	16
3: Surface Active Structure-Performance Relationship.....	17
3.1. The location and Active Structure of Mo Carbide	18
3.2 Surface Desorption and Mass Diffusion of Aromatics	20
3.3 Parameters for Catalytic Performance	23
3.4 Carbon Deposition Species and Catalytic Deactivation	27
4: Reactor Design	30
4.1 Membrane reactor.....	31
4.2 Fluidized bed reactor.....	35
Conclusion	39
References	41

1. INTRODUCTION

Methane dehydroaromatization, commonly known as MDA, is one of the prime technological innovations for decades and shows great promise and potential in the process of methane (CH_4) conversion to liquid aromatics and benzene. Methane (CH_4) is the simplest alkane and quintessentially the main component of natural gas, which can thus be converted into aromatic products in the process of dehydroaromatization and provided three main conditions; (1) Mo/ZSM-5 catalyst; (2) temperatures about 700°C and (3) non-oxidizing environmental conditions [32]. Large-scale/commercial MDA is yet to be achieved since the Mo/ZSM-5 zeolite catalyst tends to deactivate due to coking. This is a significant challenge in MDA since the formation of coke in the coking process essentially cannot be avoided under the MDA conditions [14]. However, significant progress has been made to reduce the coking rate in order to use the Mo/ZSM-5 catalysts, which have short lifespan but are the most efficient synthesizers of the desired light polycyclic aromatic products [15]. One of the main examples is the use of oxygen-permeable ceramic membranes that inject small amounts of oxygen (in pulses) into the processes without necessarily compromising the non-oxidizing conditions, which helps the decomposition of excess coke. The main aspects that will be discussed include; Mo/ZSM-5 catalyst preparation methods and characterization; ZSM-5 Zeolite (Preparation and Structure); Surface MoO_x Structure of Prepared Mo/ZSM-5 Catalyst; Surface active structure-performance relationship; the location and active structure of Mo carbide and the surface desorption and mass diffusion of aromatics.

1.1 Definition of Main Terms and Concepts

Methane Dehydroaromatization (MDA): this is the process by which methane (CH_4) is directly converted into valuable materials such as benzene, toluene and xylene in industrial chemical productions.

Zeolites: these are mineral structures occurring naturally and consisting of highly ordered microporous crystalline aluminosilicate molecular sibs. They are mainly applied in industries as molecular sieves, ion exchangers, catalysts, and commercial adsorbents.

ZSM-5 (Zeolite Socony Mobil-5): this is one of the aluminosilicate zeolites, constituent members of the pentasil zeolite family. The chemical formula is $\text{NaAl}_n\text{Si}_{96-n}\text{O}_{192}\cdot 16\text{H}_2\text{O}$. Figure 1 below shows the molecular structure of the ZSM-5 molecule, which will be the primary focus of this paper.

FIGURE 1: THE MOLECULAR STRUCTURE OF ZSM-5 ZEOLITE, WITH WELL-DEFINED PORES AND CHANNELS IN THE ZEOLITE

2. CATALYST PREPARATION AND CHARACTERIZATION

Preparation –An Overview

Scientists and engineers find catalyst preparation to be the most important step in achieving catalysts with the correct texture, attrition resistance, and shape for industrial applications [8]. Catalyst preparation is guided by advanced knowledge in scientific laws and principles relating to the chemistry of both chemical and physical transformations and the experience-based empirical observations. There are three broad types of laboratory prepared catalysts: bulk catalysts and respective supports, Impregnated catalysts from preformed supports, and Mixed-agglomerated catalysts. Table 1 below shows the typical unit operations in the industrial manufacture of catalysts. The schematic representation of the typical catalyst preparation process is as follows.

1.precipitation	8. forming and/or shaping operation
2. Gelation and flocculation	9. Impregnation.
3.Hydrothermal transformation	10. crushing and grinding
4. decantation, filtration, centrifugation	11. mixing
5. washing	12. Activation, reduction (to the desired
6 drying	oxidation state
7. calcinations	

TABLE 1: UNIT OPERATIONS IN TYPICAL CATALYST PREPARATION

The main methods for catalytic preparation are listed below:

- Ceramic based catalysis method

- Precipitation and co-precipitation method
- Impregnation method
- Sol-gel method
- Ion exchange method
- Adsorption method
- Deposition–precipitation methods
- Plasma method
- Micro-emulsion method
- Combustion method
- Electro -spinning methods

Characterization –An Overview

Remarkable improvements in characterization techniques have been applied for catalysis research [17]. The major characterization techniques include the following:

- ☑ Structural based characterization techniques: x-ray diffraction and absorption spectroscopy and electron microscopy technique
- ☑ Thermal adsorption and desorption techniques: pore structure and surface area, temperature-programmed desorption and temperature-programmed reaction, thermal analysis and thermogravimetry techniques, and microcalorimetry [11].
- ☑ Optical spectroscopic methods: infrared spectroscopy, Raman spectroscopy, UV-visible spectroscopy, electron spin resonance, and Nuclear magnetic resonance. [17, 22, 37].
- ☑ Surface-sensitive spectroscopic techniques; X-ray and UV-photoelectron spectroscopy, auger-electron spectroscopy, low energy ion scattering, and secondary, Ion-mass spectroscopy [17].

2.1 ZSM-5 ZEOLITE (PREPARATION AND STRUCTURE)

Structure of ZSM-5 Zeolite

First synthesized ZSM-5 zeolite was dated back to 1969 by scientists Argauer and Landolt [2]. The structure is described as a medium pore zeolite with channels characterized by 10-membrane rings. It is composed of pentasil chains formed by the systematic linkage of pentasil units by oxygen bridges. Each pentasil unit consists of eight, 5-membered rings with aluminum (Al)/ silicon (Si) and oxygen (O) vertex. The linked pentasil chains, therefore, form corrugated sheets consisting of 10-ring holes, each with Si or Al vertices bonded by O bridges. Additionally, the oxygen bridges connect each system of the 10-ring corrugated sheets to form straight 10 ring channels that run parallel to the corrugated sheets (pore size estimated at 5.4–5.6 Å) and sinusoidal 10-ring sheets that run orthogonal to the corrugated sheets. Inversion points relate to two adjacent sheets. The unit crystal cells of ZSM-5 consist of 96 Si/Al sites and 192 O sites. Depending on the Si to Al ratio, there are several compensating cations.

FIGURE 2: THE MOLECULAR STRUCTURE OF ZSM-5 ZEOLITE, SHOWING WELL DEFINED PORES AND CHANNELS IN THE ZEOLITE

Preparation of a ZSM-5 zeolite catalyst

Zeolite catalysts are the most effective catalysts to date known for methane dehydroaromatization. Their general chemical formula is $(M^{n+})_{x/n} (AlO_2)_x (SiO_2)_y mH_2O$, where M=cation, m= number of moles of water of crystallization, x and y are the number of Al-O and Si-O channels in the unit tetrahedral structure. The main steps for preparing molybdenum Zeolite Socony Mobil-5 (Mo/ZSM-5) catalysts are hydrothermal synthesis, ionic exchange, ad binding, and shaping. The following is a summary schematic diagram of the ZSM-5 synthesis.

2.1.1 Conventional ZSM-5 Preparation

Conventional ZSM-5 is subjected to specifically, conventional hydrothermal treatment.

Silica source for the catalyst was tetraethyl orthosilicate (TEOS, 98%), and alumina source was aluminum isopropoxide ($\text{Al}(\text{O-i-Pr})_3$). 1M sodium hydroxide pellets were added to form an aqueous solution of tetra propylammonium hydroxide (TPAOH, 40 wt. %).

The preparation steps are presented below:

- Step1: preparation of the silicate solution: half of the TPAOH, TEOS (all of it), and water (half also) are added to a polypropylene bottle and left in a shaker for 24 hours to hydrolyze TEOS.
- Step 2: preparing of aluminate solution: when 22 hours have passed in the hydrolysis of the TEOS timeline, add all $\text{Al}(\text{O-i-Pr})_3$, NaOH, and the remaining TPAOH, to a glass beaker. Stir the mixture for 25 hours till a clear aluminate solution form.
- Step 3: preparing synthesis mixture: add all the silicate solution to the aluminate solution and stir the resulting clear mixture vigorously for about 10 minutes.
- Step 4: hydrothermal treatment: fill the treatment mixture to a level of about 2/3 within a Teflon lined autoclave enabled with magnetic stirring. Seal the autoclave and place it in an oil bath at 150°C for a minimum of 3 hours and a maximum of 72 hours.
- Step 5: Purifying the product: cool the autoclave at room temperature and remove the mixture containing dispersed crystals, which are then purified by centrifugation accompanied by re-dispersion in water. This is done 4 times repeatedly.
- Step 6: calcination: calcinated the freeze-dried crystals at 500°C for 16 hours

The resulting product is ZSM 5 with a hollow structure, the aluminum and silicon are distributed in heterogeneous form where the aluminum is at the surface and the silicon is at the core. The silicon-rich core in the interior of the ZSM-5 zeolite crystal can be selectively

dissolved in alkali and re-crystallized on the exterior. However, this may not be very viable when it comes to industrial-purpose synthesis since much aluminosilicate is dissolved anyway [39].

2.1.2 Nonconventional Preparation of ZSM-5

Depending on the quantity and composition of the ZSM-5, the process can take several hours days or even weeks to complete the crystalline ZSM-5 product, which is an improvement given that the formation of natural zeolites takes hundreds of millennia to complete. Artificial synthesis through hydrothermal synthesis is a major turntable but time-consuming given the long hours of hydrolysis, crystallization, and purification. In industrial use, it becomes costly and inefficient in terms of energy use and burdening operators [13]. To overcome these hurdles, researchers have developed other nonconventional means to zeolite ZSM-5 production using alternative but ultra-fast routes [25].

One of these new techniques, contrary to the hydrothermal technique, is the continuous flow method, which synthesizes ZSM-5 by employing pressurized hot water under enormously high temperature (370 °C) as the primary heating medium [21]. Industrial synthesis of ZSM-5, in the continuous reactor contrary to the autoclave, proceeds to completion significantly faster, with crystallization rate also happening remarkably faster. The continuous flow reactor, in combination with the pressurized hot water as a heating medium, provides a feasible method to reduce the time limit of zeolite crystallization.

Materials: TPAOH (40% aqueous solution) colloidal silica 40 wt % suspension in (H₂O), aluminum hydroxide (100%), and sodium hydroxide (pellets).

Synthesis mixture preparation: TPAOH solution, an aqueous solution of NaOH (20 wt %), and aluminum hydroxide are mixed and vigorously stirred for 5 min, after this add colloidal

silica and continue stirring for an additional 30 minutes. Age this mixture in a plastic bottle at 90 °C placed in an oven rotating at 20 revolutions per minute to obtain a gel-like solution.

Synthesis of ZSM-5 under continuous flow: the apparatus is connected, as shown in the figure above. Preheat the water circulating in the system gradually to the desired temperature and sets the pressures accordingly to 23,000Pa using the pressure regulator. Feed the synthesized gel to replace the water in circulation, as shown in the figure above. At the outlet of the flow, cooling water is fed to cool the resultant slurry solution, which is at 260 °C. The purpose of the vibrator is to shake the solution and to prevent precipitation of solids at approximately 100 Hz. The slurry flowing out is centrifuged, washed and dried to obtain ZSM-5 crystals. Under optimum operating conditions, the of ZSM-5 is 260g per day.

2.1.3 Solid-State Preparation of ZSM-5

Solid-state crystallization as a method of synthesis of ZSM-5 is a novel technique that offers significant advantages over the conventional preparation technique. It generally involves introducing an aluminosilicate nanogels containing a structure-directing agent into a solvent and allowing this solvent to evaporate, hence forming dried nanogels of approximately 30% solvent by weight. This is followed by the process of heating the dried nanogels until crystallized ZSM-5 crystals of diameter 200nm and 2um are synthesized. The process is described in detail below.

Materials: Tetrapropyl ammonium hydroxide (TPAOH, 1M solution in H₂O), sodium aluminate (NaAlO₂, 8% wt. in H₂O) tetraethylorthosilicate (TEOS, >99%), and lignin (0.1 M NH₄NO₃)

Preparation (Experimental)

To prepare mesoporous ZSM-5 by solid-state crystallization, sodium aluminate (NaAlO_2), tetrapropyl ammonium hydroxide (TPAOH), tetraethylorthosilicate (TEOS), and water (H_2O) were mixed in the following ratio; $0.03\text{NaAl}_2\text{O}_3:0.25\text{TPAOH}:\text{SiO}_2:80\text{H}_2\text{O}$. For efficacy, PAOH and NaAlO_2 were dissolved in water first, followed by the subsequent addition of TEOS subjected to strong centrifugation at 600 revolutions per minute at room temperatures (ranging between 20°C . and 25°C .). After adding TEOS, the mixture of the three was removed from the centrifuge and incubated at higher temperatures of 80°C for approximately 12 hours until a clear solution was formed. This mixture was additionally; left overnight at room temperature to allow solvent evaporation. The dry gel was gathered and grounded into powder and transferred to a pre-heated Teflon-lined autoclave (140°C) for crystallization. The mixture was left in the autoclave for 12 hours without the addition of any water. Despite its use, an autoclave is not required in solid-state crystallization technique as no significant pressure is generated as compared to the conventional hydrothermal crystallization of ZSM-5 where the autoclave as a result of steaming generates a significant pressure of 1-4 MPa; depending on the filling volume of the solution used. Therein this technique also used containers such as air-tight glass bottles, which can provide a tight-seal at elevated temperature and are also resistant to basic liquids. The autoclave was used to compare the efficiency of this technique with that of traditionally prepared ZSM-5. Next, the fully crystallized ZSM-5 was removed from the autoclave, and containers; and without washing, the crystals were dried at 100°C , to additionally remove all water of adsorption and then calcinated at high temperatures of 500°C for 6 hours (heating rate= $1^\circ\text{C}/\text{minute}$). The traditional zeolites were simultaneously synthesized using the conventional hydrothermal technique described above at 140°C for 48 hours. The ZSM-5 samples were ion-exchanged thrice overusing 0.1 M NH_4NO_3 solution at 90°C or approximately 1hr 30mins (liquid: solid ratio if 10) and agitated at 500 rpm. After this, ZSM-5

samples were filtered, washed thoroughly with distilled water, and then dried at 100° C for approximately 4 hours [34].

2.2 Mo/ZSM-5 CATALYST PREPARATION METHODS

2.2.1 Wet – Impregnation Method

Sodium silicate (Na_2SiO_3) consisting of 53 %wt. SiO_2 , and 47 %wt. Na_2O) tetra propylammonium hydroxide (TPAOH, 20% vol.), aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3$], sulfuric acid, (H_2SO_4 , 95% vol.), deionized water and fumed silica. Preparation was carried out by the conventional wet impregnation technique. A certain amount of ZSM-5 was added with impregnated ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), at various concentrations from 0.5% -5% wt. based on ZSM-5 weight.

The wet-impregnation technique used is as follows; dissolve the suspension by adding distilled water and stirring the mixture for approximately 2 hours at room temperature. Next, evaporate the solvent (distilled water) from the mixture to obtain the crude. After this, the next step is to dry the obtained crude using a rotating oven, i.e., Heat to a constant weight. The final step is to heat the Mo/ZSM-5 powder for 5 hours at 550°C during calcination using nitrogen, hydrogen, and oxygen gas flow.

2.2.2 Ionic – Exchange Method

The catalyst is prepared using an aqueous solution of metal compound loaded on ZSM-5 zeolite. For this experiment, the metal loaded zeolite was Mo/ZSM-5. The ion exchange method procedure is as follows. Dissolve $(\text{NH}_4)_6\text{Mo}_7 \cdot 4\text{H}_2\text{O}$ in 25ml (or more depending on the desired quantity) of the aqueous solution with 5g of ZSM-5 zeolite. See the table below.

Experiment	Molybdenum weight	ZSM-5 weight	Name of zeolite
1	0	5	ZSM-5
2	0	5	ZSM-5
3	0.5	5	0.5Mo/ZSM-5
4	0.25	5	0.25 Mo/ZSM-5
5	0.5	5	0.5 Mo/ZSM-5
6	0.75	5	0.75 Mo/ZSM-5
7	0.25	5	0.25 Mo/ZSM-5
8	0.5	5	0.5 Mo/ZSM-5
9	0.15	5	0.15 Mo/ZSM-5
10	0.85	5	0.85 Mo/ZSM-5
11	0.5	5	0.5 Mo/ZSM-5
12	0.5	5	0.5 Mo/ZSM-5
13	0.5	5	0.5 Mo/ZSM-5
14	0.75	5	0.75 Mo/ZSM-5
15	0.5	5	0.5 Mo/ZSM-5

The mixture should be stirred vigorously at 30 °C for approximately 5 hours and then dried in a rotating oven preheated at a constant 110°C for 24 hours. The dried Mo/ZSM-5 should finally be calcined inside a box furnace at high temperatures 550 °C for 3 hours.

Catalysis Characterization

The prepared catalysts should be characterized by crystallinity using the X-ray diffraction technique. The variables affecting this experiment include the amount of catalyst used, the temperature of the reaction, and the flow rate of hydrogen. X-ray diffraction results reveal that ZSM-5 and Mo/ZSM-5 have similar patterns, with the only difference being in the level of intensity at certain points of 2θ . These differences in intensity on the X-ray spectra of Mo/ZSM-5 zeolite is on account of the different amounts of Molybdenum loaded on the ZSM-5 samples. When Mo metal is added to the ZSM-5 zeolite, an amorphous structure of Mo/ZSM-5 is formed. Additionally, the X-ray diffraction spectra of the ZSM-5 and that of Mo/ZSM-5 catalysts, as shown in the figure below, reveal that Mo loaded into ZSM-5 has a crystallinity of 84.25%.

FIGURE 3: STANDARD Mo/ZSM-5 XRD SPECTRUM

FIGURE 4: STANDARD ZSM-5 XRD SPECTRUM

Loading of molybdenum onto ZSM-5 reduces its crystallinity because metal loading on the catalyst sample usually cover the surface pores of the catalysts which finally alter the characteristics, structure, and performance of the zeolite crystals as revealed by the decreasing intensity which may also be due to the partial loss of structural cations of zeolite during the ion exchange [1].

2.2.3 Solid-State Preparation of Mo/ZSM-5

The successful loading of metals in zeolite catalysts for DMA has been explored by multiple types of research. The section below describes how solid-state ion-exchange method could be used to introduce molybdenum (from MoCl_3 or acetylacetonate) into zeolites and to synthesize novel Mo/ZSM-5 catalysts for CH_4 aromatization. It has been argued that molybdenum loaded zeolite catalyst Mo/ZSM-5 exhibits high activity in the action as well as

high stability in nonoxidative aromatization of methane. Estimated yields of converted methane from Mo/ZSM-5 catalysts assisted DMA 13.1% and aromatics yield of 7.5%.

Factors that affect ion-exchange behavior of zeolites include: the nature of the zeolite species (anhydrous or hydrous); the reaction temperature, the concentration of the zeolite cation species; the nature of the associated anion species; the solvent; and the structure of the zeolite.

PREPARATION

Molybdenum loaded ZSM-5 catalyst is the most active catalyst reported to date.

Materials: Molybdenum salts (i.e., 325.90 g/mol of molybdenum (VI) acetylacetonate $\text{MoO}_2(\text{C}_2\text{H}_7\text{O}_2)_2$) and 143.94 g/mol of molybdenum (VI) oxide (MoO_3) by Merck, and ZSM-5 zeolite powder.

To prepare the Mo/ZSM-5, the zeolite powder (ZSM-5) with a Si:Al ratio of 26 was mixed intimately with the desired Mo salt and ground in a mortar subject to desired quantity of Mo/ZSM-5 required (theoretically 1M Mo/Al ratio consisting of 6 wt. % of Mo and 0.2 g/mol of Molybdenum acetylacetonate mixture). Agitation at 500rpm was done for 5 hours at with solvent consisting of NH_4 ions was done using a solid-state ion-exchange technique [23]. Treatment of zeolite (ZSM-5) with molybdenum (VI) acetylacetonate at 250° C allows for selective catalyst reduction of NH_4 ions for 5 hours to synthesize molybdenum ion-exchanged zeolite (Mo/ZSM-5). The exchange was carried out in microwave with a frequency of 2.45 GHz and Microwave radiation power of 1.2 KW for 2 hours. The respective safety pressure (120 psi), temperature (80 °C), and power 300 watts) of the microwave were set. The molybdenum exchanged zeolite samples were then washed thoroughly with distilled water to remove NH_4 cations, dried in an oven at 100 °C, and left in a desiccator overnight [6].

2.3 SURFACE MoO_x STRUCTURE OF PREPARED MO/ZSM-5 CATALYST

The structure and role of surface MoO_x contained in solid-state prepared Mo/ZSM-5 catalyst can be investigated using infrared, UV-visible, and X-ray absorption (XAS) spectroscopy characterization techniques, and by the time-resolved mass spectrometric measures of the initial quantity of methane reaction products. UV-visible spectra of MoO₃ loaded on the ZSM-5 mixture reveal a spike in energy during airflow treatment at 773 K, which indicates that MoO₃ crystallizes as smaller domains [20]. OH, infrared band intensity decreases when temperatures are above 773 K, which thus indicates that Mo exchanges occur only after MoO₃ dispersion on the external Mo/ZSM-5 zeolite surface. The amount of H₂O incumbent of the process during the exchange and the infrared intensity diminish for the OH band and gives similar value measures for the residual OH density [20]. These values indicate that each Mo unit replaces one H⁺. Infrared OH bands lose energy during this process, which indicates that the reduction and/or carburization process does not result in the removal of Mo species from their respective exchange sites to re-model the OH groups [20].

FIGURE 5: CRYSTAL STRUCTURE OF MOLYBDENUM TRIOXIDE (MoO₃)

3. SURFACE ACTIVE STRUCTURE-PERFORMANCE RELATIONSHIP

The active Mo/ZSM-5 catalyst can be analyzed and tested for performance. In this case, performance would be based on the CH₄ (methane) yields under varying conditions of various samples. Powdered catalysts should be characterized to test their textual and chemical properties, and order to gain more insights on the MoO_x structures formed after characterization by impregnation.

The table below shows results from previous experimental research that tested the catalytic performance of various ZSM-5 mixtures. The conditions held WHSV 2 hours at 700° C [15].

Mixture	Pretreatment	Total amount of converted methane (μmol/m-2)	Coke yield (%)
HZSM-5	SiC	<0.01	100
Mo/C+ HZSM-5	SiC	11.7	97.6
	0	13.0	81.1
	1	13.3	78.2
	3	13.7	79.8
	6	14.0	75.9
Mo/ Al ₂ O ₃ + HZSM-5	SiC	13.0	95.3
	0	13.7	86.2
	1	16.3	74.9
	3	17.0	72.2
	6	18.3	72.5
Mo/SiO ₂ + HZSM-5	SiC	11.7	92.6
	0	19.7	75
	1	30.7	28.9
	3	15.3	51.6
	6	5.3	85.3
Mo/ ZSM-5+ HZSM-5	SiC	22.7	21.8
	0	28.7	32.5
	1	31.0	29.2
	3	21.3	39.3
	6	16.3	44.7

Table 3: Results from previous experimental research that tested the catalytic performance of various ZSM-5 mixtures.

The performance of Mo/ ZSM-5+ HZSM-5 is better than the performance of the other mixtures (Mo/C+ HZSM-5, Mo/Al₂O₃+ HZSM-5, and Mo/SiO₂+ HZSM-5) in terms of converted methane and rate of coking as indicated in the table above.

3.1. THE LOCATION AND ACTIVE STRUCTURE OF Mo CARBIDE (Mo/C or Mo₂C)

History: Molybdenum carbide (MoC or Mo₂C) is one of the hardest ceramic refractory materials with an estimated molar mass of 107,961 g/mol for MoC and 203,911 g/mol for Mo₂C and density of up to 8900kg/m³. Its melting point is very high at 2,687 °C. The industrial applications include drill bits (due to hardness and high melting point) and can also be used as catalysts, which will be the focus of this discussion [7]. The catalytic applications of Mo carbide were pioneered by Boudart's group who posited that molybdenum carbide could be synthesized through direct carburization process and controlled by TPR of bulk MoO₃ by passing a gas mixture of 20 vol. % CH₄ in H₂ at 700 °C. The result of this process is the yielding of Mo₂C. Mo₂C is a non-metallic catalyst and a prime alternative for metallic catalysts in fuel cells and bio-oils [27]. Synthesis and characterization: Ammonium heptamolybdate are the main precursor used in the synthesis of molybdenum carbide in a carburization process. MoO₂ is reduced by flowing H₂, which is then followed by O removal and insertion of C in a simultaneous fashion. This is done at high temperatures. The product resulting from this process is Mo₂C, which has a hexagonal close-packed structure. To understand the structural differences, it becomes imperative to prepare another sample of Mo₂C under the same conditions but now using an oxide precursor [7]. Thus, the first sample shall be Mo₂C-A and the second shall be Mo₂C-B. Using different precursors also helps understand how a structural difference in the Mo carbide catalysts affects the catalytic performance. The differences between the crystallographic structure of Mo₂C-A and Mo₂C-B were slight, with both samples exhibiting an hcp structure on a broader outlook. The crystallite size and pore sizes were also

estimated, and the noted differences in crystallite shape are an indicator that. See the figures below.

FIGURE 6: COMPARISON OF XRD PATTERNS FOR THE TWO Mo_2C SAMPLES (A AND B) [7].

Structural differences are strongly influenced by the precursors used during synthesis. For instance, these differences at grain level indicate that $\text{Mo}_2\text{C-B}$ grains have sharper corners and edges with flat phases as compared to the grains of $\text{Mo}_2\text{C-A}$.

Active sites: the destiny of active sites in the Mo carbide structure affects the performance of the catalyst; hence its discussion becomes imperative. The density of active sites can be determined from the CO uptake rate and the BET surface area measures. For more reliable active site density results, residue oxygen deposition should be minimized, carbon insertion during carburization must be done to completion, and in addition, carbon deposition in the reaction chamber must also be minimized. Conclusive results show that $\text{Mo}_2\text{C-B}$ has lower active site density as compared to $\text{Mo}_2\text{C-A}$ could have resulted from greater blockage of both pores and active sites. The shape of $\text{Mo}_2\text{C-B}$ is the main contributor to this blockage propensity [7].

Catalyst	BET surface area (S _g /m ² g ⁻¹)	Pore volume (cm ³ /g)	Pore size (nm)	CO uptake (μmol g ⁻¹)	Active Site density	Particle size/nm	Crystallite size nm
Mo ₂ C -A fresh	36	0.08	8	186	0.31	18	11/11
Mo ₂ C -A aged	64	0.5	36	26	0.02	10	10/11
Mo ₂ C -B fresh	6	0.03	23	5	0.05	110	13/19
Mo ₂ C -B aged	15	0.02	4	12	0.05	44	12/16

Table 4: Weight changes as a result of oxidation in Mo carbide samples

The surface area increases for active sites despite blocking in Mo₂C-B is owing to the increase in surface roughness of the carbide. Additionally, Mo₂C-B structure exhibited superior oxidation resistance as compared to that of Mo₂C-A. This is noted in a TGA that was performed in the air (see figure below) in which Mo₂C-B revealed oxidation onset temperatures (i.e., temperatures at which significant weight gain as a result of oxidation started) to be at least 100 °C higher than Mo₂C-A.

FIGURE 7: WEIGHT CHANGES AS A RESULT OF OXIDATION IN MO CARBIDE SAMPLES, [7].

3.2 SURFACE DESORPTION AND MASS DIFFUSION OF AROMATICS

Surface Desorption of Aromatics

In an MDA reaction, the most difficult step is the formation of the H₂ molecule and the [MoC₂H₂]²⁺ site with an energy barrier of 208 kJ/mol. This is where desorption comes in.

surface desorption of H_2 provides considerable stabilization of the entire reaction system. Dehydrogenation of CH_4 to form H_2 molecules is an energy-demanding step (106 kJ/mol energy barrier). But once the H_2 is formed, surface desorption of ethylene from the Mo site now becomes possible with an energy barrier of only 64KJ/mol. Following ethylene desorption, the active site is regenerated, and the catalytic cycle of Mo/ZSM-5 is closed. Considering methane dehydrogenation in an MDA reaction through C-C coupling to the desorbed ethylene can lead us to the realization that it is a simple method to produce aromatic products from radical alkylation [33].

FIGURE 8: REACTION MECHANISMS OF METHANE CONVERSION TO AROMATICS VIA ETHYLENE, [18].

FIGURE 9: REACTION ENERGY DIAGRAM OF ETHYLENE FORMATION, [18].

Mass Diffusion of Aromatics

As already discussed, mesoporous zeolites such as ZSM-5 are prone to higher catalytic activity and longer lifetime and better performance as compared to other traditional catalysts [36]. The two main reasons for this superiority are the improved diffusivity of the substrate molecules and improved access to active sites for better reactions. Diffusion is critical in mass transfer during catalysis, product separation, and selectivity. For example, simulation research on the diffusiveness of benzene in mesoporous H-ZSM-5 zeolite catalyst at 300K over pore sizes of 20 Å is a stunning $1.7 \pm 0.4 \times 10^{-10} \text{ m}^2/\text{s}$. These simulated experiments also give an outlook that diffusion within the micropores and the external surfaces of the hierarchical mesoporous H-ZSM-5 is dominant at low temperatures only, whereas diffusion along the mesopores only becomes significantly enhanced at pyrolysis temperatures relevant to the reaction [4]. See the figures below.

FIGURE 10: SUPERIMPOSITION OF BENZENE, MOLECULES DIFFUSING IN MESOPOROUS H-ZSM-5 ZEOLITE WITH A PORE SIZE OF 20 Å AT 300K, [4].

FIGURE 11: SUPERIMPOSITION OF BENZENE, MOLECULES DIFFUSING IN MESOPOROUS H-ZSM-5 ZEOLITE WITH A PORE SIZE OF 20 Å AT 700K, [4].

3.3 PARAMETERS FOR CATALYTIC PERFORMANCE

The performance and effectiveness of the zeolite catalyst Mo/ZSM-5 during the methane dehydroaromatization (MDA) is influenced by several parameters that have been explored at length by researchers in the field studies related of aromatization of methane. Most parameters in catalyst action are usually responsible for the activation and deactivation of the catalyst hence relatively tend to shape the performance path. In the case of Mo/ZSM-5, performance is measured in terms of the total conversion rate for methane and resultant yields of benzene, factors such as coking can be considered as impediments to the performance of Mo/ZSM-5. For this section, we will evaluate important the effects of 5 main parameters on Mo/ZSM-5 performance during methane dehydroaromatization (MDA). It is important to remember that catalytic performance, in this case, involves the quantity of benzene yield from total methane conversion and the content and condensation degree (C/H ratio) of the carbonaceous deposits during say coking. The parameters include molybdenum content (Mo content ranging from 1-10 wt. %), the reaction temperature (in the range of 720 °C -780 °C), the space velocity (ranging from 405/h-1620/h), and the reaction time (ranging from 0.5-20 h). Operating optimally, Mo/ZSM-5 catalysts generate up to 70% of aromatic selectivity and a consequent total resultant methane conversion of up to 14% at 720 °C. The main challenge with this process is the formation of carbonaceous by-products during methane

dehydroaromatization. A carbonaceous deposit affects catalytic performance. The contents of the carbonaceous deposits depend on both the contents of Mo/ZSM-5 catalysts used and the reaction condition (temperature, velocity, and reaction time).

Content/ composition of Molybdenum content in Mo/ZSM-5: According to Matus et al. [24], the formation of carbonaceous deposits increases linearly as the molybdenum content in Mo/ZSM-5 increases from 0-2 wt. % and thereafter remains relatively constant from 2-10 wt. %. The table below reflects the effects of Mo content on the activity of Mo/ZSM-5 catalyst studied in the methane DHA reaction.

Molybdenum content (wt. %)	1	2	5	10
Total methane conversion irrespective of products (%)	10.5	13.8	12.2	7.0
Methane conversion to benzene (%)	6.3	9.6	9.5	3.7
Benzene formation rate ($\mu\text{molC}_6\text{H}_6/(\text{gMo}\cdot\text{s})$)	13.9	10.9	4.1	0.5

Table 5: Total methane conversion as a result of an increase in Mo content

This data indicates that total methane conversion as a result of an increase in Mo content from 1-2 wt. %, while simultaneously, the rate of benzene conversion also grows as Mo content increases from 1 to 2 to 5. Increase in Mo content from 5 wt. % to 10 wt. % results in a substantial decline of both total methane conversion and benzene selectivity. This sharp decline is due to the product additional carbonaceous deposits aside from the main hydrogen, and benzene products wanted. These are carbon monoxide, ethylene, ethane, toluene, and naphthalene. See the graph below.

FIGURE 12: EFFECT OF THE MOLYBDENUM CONTENT (1) AND THE CONTENT OF CARBONACEOUS DEPOSITS (2) FOR THE Mo/ZSM-5 CATALYSTS

Reaction time: reaction time affects the performance of the zeolite Mo/ZSM-5 catalyst by altering the size of the zeolite micropore surface area. The specific pore volume and pore surface area decrease after the catalyst has been on stream. Reaction time is a coupled effect dependent on the Mo content in the zeolite. According to Matus et al. [24], 10 wt. % Mo content receives the largest and most pronounced effect when considering reaction time. During an MDA reaction, the surface area of zeolite Mo/ZSM-5 with Mo content of 2 wt. % decreases by 15% after 6 hours of reaction time. When the Mo content is increased to 10 wt. %, it results in a huge decline in surface area by approximately 65%. When the reaction time is increased, the surface area and pore volume continue to decrease. For example, experimental results show that specific surface area of a 2% Mo/ZSM-5 sample decreased by 35% after being on stream for 20 hours. See the figure below. Researchers argue that a decrease in pore volume and pore surface area may be as a result of excessive and continuous carbonaceous deposit accumulation on the pores during the reaction, thus effectively blocking the zeolite's micropores [24].

FIGURE 13: REACTION ACTIVITY OF 2% Mo /ZSM-5 CATALYST IN THE DHA OF (REACTION CONDITIONS: 90%CH₄, 10%Ar, 810 /h, 720°C)

Space velocity: space velocity in catalysis refers to the rate at which gas is allowed to flow through the reactor bed during a catalytic reaction. In general, an increase in the space velocity (in this case, heated Argon gas flow rate) leads to an increase in carbonaceous deposits, which in turn affects the performance of the catalysts. For example, assume that the space velocity is increased from 405/h to 1620/h will grow by approximately 7.0 units. Similar to the methane flow rate in an MDA reaction behaves in the same manner, although total rate is subjective to reaction time.

The figure below summarizes the effect of the reaction temperature (T), reaction time (t) and space velocity (V) on both the content of carbonaceous deposits (measured in wt. %) and the position of exothermic effect maximum (TDTA) for the 2%Mo/ZSM-5 catalysts after 6 h on stream.

FIGURE 14: THE EFFECT OF EFFECT OF THE REACTION TEMPERATURE (T), REACTION TIME (T) AND SPACE VELOCITY (V) ON BOTH THE CONTENT OF CARBONACEOUS DEPOSITS (MEASURED IN WT. %).

3.4 CARBON DEPOSITION SPECIES AND CATALYTIC DEACTIVATION

As discussed earlier, carbon deposits are by-products from processes such as methane dehydroaromatization, which can result in catalyst deactivation and declining performance. This section will examine these two application areas with consideration to the quantity weight of carbon deposits under specific conditions using a comparative approach.

Carbon Deposition and Catalytic Deactivation during Methane Dehydroaromatization

According to Matus et al. [24], highly effective catalysts such as Mo/ZSM-5, which provide for catalytic conversion of hydrocarbons into valuable products, are the key to resolving problems linked to environmental protection as well as efficiency in resource utilization. Methane dehydroaromatization into benzene, naphthalene, and other valuable products is one such efficiency example. Mo/HZSM-5 zeolite catalyst provides up to 70% selectivity in benzene synthesis during MDA and 14% methane conversion at temperatures of 720 °C. However, this process results in carbon deposits, which in some capacity assist in the

reaction but majorly contribute to catalytic deactivation. Studying the nature of the carbon deposits formed during MDA is instrumental in preventing its formation as well as determining the best intervention course for catalyst regeneration/activation. From the above information, data and graphs, it was revealed that the properties of carbon deposits in Mo/ZSM-5 catalytic MDA reaction is determined by; (1) the content of Molybdenum in Mo/ZSM-5 whereby the amount of carbon deposits linearly increases as the composition on Mo increases up to a certain degree (2wt%) after which it remains constant. (2) The reaction temperature which affects oxidation and consequent carbon deposition. (3) The reaction time whereby the longer the reaction time, the more the carbon deposition and the more deactivated the catalyst becomes. (4) Finally, carbon deposition is also affected by the space velocity/ flow rate of argon in the reaction, which, if increased, results in a consequent increase in carbon deposits in the active sites of the zeolite catalysts are thereby deactivating it effectively. Contrary arguments hold that consecutive mechanism of carbon deposit formation during MDA allows the active catalysts in reaction to produce monoaromatics in higher quantities and higher concentrations [30]. The figure below illustrates that, as the content of carbon deposits increases benzene formation rate also increases.

FIGURE 15: CORRELATION BETWEEN ACTIVITIES OF Mo/ZSM-5 VS. CD CONTENTS FORMED AFTER 6 H ON STREAM. REACTION CONDITIONS: 90 VOL. % CH₄ + 10 VOL. % AR, 810/H, 720°C.

Carbonization deposits are also affected by temperatures that cause oxidation (i.e., concentration and burn out temperatures). Lower temperatures of approximately 470°C 503°C cause carbonaceous deposits along Mo surfaces while high temperature of above 543°C result in carbonaceous deposit formation along with the zeolite *Bronsted* acid sites. The role of temperature on carbonization consequently results in the deactivation of Mo/ZSM-5 catalysts. Additionally, a thermal analysis using a Q-1500 D instrument with measures of TG (thermogravimetry), DTG (Differential thermal gravity) and DTA (Differential thermal analysis) can help explain the effect of temperature on catalytic performance. Results show that higher temperatures of between 370°C and 600°C result in an exothermic reaction, which causes weight gain consequential of oxidation. Additional weight loss is observed at temperatures of 450-600°C due to the burning of the carbonaceous deposits as temperature increases.

FIGURE 16: TG, DTG AND DTA CURVES FOR 2%Mo/ZSM-5 CATALYST AFTER 20 H OF THE DHA OF CH₄.

4. REACTOR DESIGN

Major processes in engineering and other scientific-based research in physics and chemistry are pegged on ubiquitous chemical reactions. The use of catalysts is integral in these processes; hence process engineers in these processes must be in a position on how to design not only the correct catalysts for the reactions but also the reactors required for the catalysis process. A reactor is defined as a machine, structure, or apparatus that allows the control of conditions ideal for a specific reaction process to occur optimally. There are several types of reactors namely: bioreactors (which control reaction within a bio-reactive environment), chemical reactors (which provide controlled chemical reactions), fusion reactors (contain and regulate an atomic fusion reaction), fission reactors (contain and regulate an atomic fission reaction), inductors, current limiting reactors (control motor current in varied frequency drivers), and nuclear reactors (contain and control energy generated from a nuclear reaction).

Effective reactor designs combine material balance, kinetic rate expression, and energy balance to achieve optimum reaction conditions as well as determine the ideal size of the reactor. Material balance implies how any given reaction species are distributed in space and time. Energy balance describes how temperature varies in space and time across the duration of the reaction, and kinetic rate expression spells out how each reaction species is dependent on concentration, temperature, and catalyst properties. Sterling catalytic reactor designs, therefore, allow for astute integration of the reactor and catalysts. See the figure below that describes the considerations in catalytic reactor designs. In recent times direct methane aromatization has yielded positive results in the conversion of abundant natural gas into valuable products such as benzene. The above section describes how rapid coking/ carbon

deposition results in deactivation of the Mo/ZSM-5 catalyst, thus being a major impediment in this process.

FIGURE 17: RELATIONSHIP BETWEEN REACTOR DESIGNS, CATALYST DESIGNS AND CATALYTIC REACTOR DESIGNS

The viability of methane conversion to benzene can be improved depending on the reactors used in the process. There are two main reactor models that have shown promise in removing the impediment, i.e., Membrane reactor and Fluidized bed reactor, as discussed below.

4.1 MEMBRANE REACTOR

A membrane reactor is a device or equipment used to simultaneously perform reactions of varying nature including steam reforming, auto thermal reforming, dry reforming, as well as a membrane-based separation of products in the same physical device. This is to say that the membrane in the reactor not only acts as a separator in the reactor but also takes part in the reaction. There are several types of membranes used in membrane reactors and can be classified depending on the factors of their nature, geometry and separation regimes; in simpler terms, classification of the membrane is based on whether they are organic, inorganic or hybrids of the two versions. Choosing a good membrane type for the membrane reactor depends on the production capacity required, the separation selectivity, the membrane life span, the operating

conditions, the mechanical and chemical integrity subject to operating conditions, as well as the cost. Membrane reactors are increasingly gaining popularity in the catalysis field as will be discussed below. First, it is important to discuss the types of membranes in brief.

TYPES OF MEMBRANES

Membranes are broadly classified into two categories; that is, biological membranes and synthetic membranes.

Biological membranes

These are easy to manufacture but are not widely applied due to many inherent disadvantages culminating from limited underlying temperatures (should not exceed 100 °C), limited pH range, hard to maintain (clean up), as well as, microbial attacks owing to their natural origin

Synthetic membranes

These are categorized into polymeric membranes and inorganic membranes:

Polymeric membranes: limited to a temperature of between 100 -300°C. All polymers can be used as polymeric membranes if the underlying chemical and physical properties are relevant to the reaction, i.e., its specific properties. Many industrial processes today involve high temperatures which are why polymeric membranes are not preferred.

Inorganic membranes: these are manufactured from different materials such as ceramics, carbon, silica, zeolites, oxides (titania, alumina, zirconia) palladium, silver and their alloys. This makes them stable even at high temperatures ranging from 300 – 800 °C and others are stable at 1000 °C. Unlike polymeric and biological membranes, they possess high resistance to physical and chemical degradation. Additional advantages include inertness to microbial degradation, resistance to high pressures and easy cleanability after fouling, as well as, easy catalytic activation. Disadvantages include high capital cost, low permeability, as well as,

difficulty of achieving high selectivity for the large-scale microporous membranes. The main types of inorganic membranes include metal membranes, ceramic membranes, carbon membranes, and zeolite membranes.

MEMBRANE REACTOR DESIGN FOR DMA

As we have discussed DMA involves a reaction that converts methane (CH_4) to hydrogen (H_2) and aromatic benzene (C_6H_6) products. It is usually performed over molybdenum (Mo) catalyst on zeolite support (e.g., HZSM-5 or ZSM-5) as shown below:

However, this design results in low methane conversion due to high concentrations of hydrogen produced in both reactions, as shown in the equations above. To overcome this limitation, it is ideal for removing the excess hydrogen from the reactor. The membrane reactor is ideal for this task due to its separation capabilities. As defined above, membrane reactors are systems which typically enable process intensification and higher process efficiency by combining a reactor and a separator into one unit. Methane conversion is thus higher in a membrane reactor due to the selective removal of both product species through the membrane. Without the membrane reactor, the equilibrium, shifts towards the reactants while using the membrane reactor for DMA, equilibrium is pushed towards the products when hydrogen is removed via the selective hydrogen membrane as shown in the figure below.

FIGURE 18: MEMBRANE REACTOR USING Mo/HZSM-5, [10].

The main advantages of a membrane reactor in DMA include reduced downstream separation and capital costs, as well as enhanced yields (higher conversion rates) and higher selectivity.

Challenges of the membrane reactor

The shell and tube membrane reactor design shown above in Figure 18 is subject to the limitations underling coking discussed earlier in this paper. A newer improved model of the same which accounts for coking is presented below.

Coking during DMA is assumed to be caused by ethylene formation from the molybdenum carbide on the zeolite pores, thus blocking access to the BAS for methane (polyolefinic and polyaromatic cokes). Oxygen and steam suppress coke formation [5] Oxygen also inhibits the formation of molybdenum carbide [37]. The multifunctional membrane model shown above makes this possible by employing two membranes in one system targeted at separating oxygen from the air into the reaction zone and separating hydrogen from the reaction zone. The model consists of three zones;

- ☑ **Reaction zone:** this is where the feed methane is introduced and where the reactions in the DMA take place.
- ☑ **Outer shell:** here, helium gas (sweep gas) is introduced whose main task is to carry away the separated hydrogen through the hydrogen-permeable membrane (M1).
- ☑ **Inner tube:** this provides a base where air enters and the oxygen in air permeates via the oxygen-permeable membrane (M2) into the reaction zone.

A simulation of the above model yielded the following results; by slow introduction of oxygen via the oxygen-selective membrane, the catalyst deactivated within the same time span as the original model however the deactivation was to a significantly lesser degree. In addition, less coke was formed, and there was increased sensitivity. Coke production is decreased by

approximately 80% to 90% over several hours. The apparent drawback was that most of the carbon in this process went to CO_x products (CO and CO₂), as opposed to benzene.

4.2: FLUIDIZED BED REACTOR

Revolutionary fluid bed reactors have gained wide usage in many industrial processes, especially those involving gas-solids reactions. The main advantage of fluid bed reactors underlies its usage with numerous reaction gases including air, nitrogen, hydrogen, ammonia, carbon dioxide, oxygen, argon, and steam among others; and is known to be tolerant for temperatures reaching up to 1100 °C. Some of these industrial processes include; oxidation of metal powders, silicates, pigments, alumina silicates, carbon materials, organic substrates and catalysts; reduction reactions for metal oxides, mixed oxides, hydroxides, silicon and silicon compounds, ores, salts, silicates and alumina silicates, organic substances and catalysts; it is also used for gas-gas reactions on fluidized catalysts for metal oxides, mixed oxides and organic substances; used for gas to solid reactions in most chemical gas-solid reactions except those involving hydrates; it is used for surface treatment, i.e., activation and passivation; used for chemical coating of support materials with metal powders metal oxides, mixed oxides, alumina silicates, carbon material, organic substances, and catalysts. This makes the fluidized bed reactor especially attractive for DMA reactions over Mo/ZSM-5 catalyst.

FLUIDIZED BED REACTOR FOR METHANE DEHYDROAROMATIZATION

Generally, catalytic reactors are of two types; fixed bed reactors and fluidized bed reactors. Research from a two decades ago had suggested that fixed bed reactors have a superior advantage over fluidized bed reactors in that they provide easier catalyst regeneration and replacement, can handle extremely high operation pressures, foster minimum wear of catalyst and reaction equipment, have higher conversion efficiency, have lower pore diffusion rate and can allow greater variability in alteration of reaction conditions [3]. However, advancements

in R&D over the past two decades have led to better-fluidized bed design in reaction processes such as DMA/ MDA [33]. This constitutes used of fluidizable binder-free Mo/HZSM-5 catalyst in the bed reactors that generated H_2 for rapid regeneration of deactivated Mo/HZSM-5 catalyst subject to coking limitation, as well as, dual-bed circulation systems that allow continuous mixing and processing of Mo/HZSM-5 for greater efficiency and reaction stability [38].

FIGURE 19: DUAL-BED TYPE OF CIRCULATING FLUIDIZED BED REACTOR, [35].

An additional reason why this system is advantageous is that it can offer greater flexibility when one requires to independently design the capacity of each of its fluidized beds in the system. This is to mean that the gas-solid contact time of each of its two beds can independently be customized to suit the user's needs.

One major challenge however with all typical Mo/HZSM-5 catalyzed MDA reaction systems is the unbalanced catalyst deactivation and regeneration rates, which make it difficult to achieve the flexibility needed to realize a stably operable and continuous MDA reactor design. Hydrogenation and hydrogenolysis reactions can be utilized to remove the carbonaceous deposits that cause the catalyst to deactivate, provided hydrogen is present, and the temperature range is maintained at a level that is workable for Mo/ZSM-5.

This process (i.e., coke removal by Hydrogenation in the presence of hydrogen from deactivated Mo/HZSM-5) is very time-consuming. This high time-dependence of the CH_4

concentration during H₂-based regeneration of deactivated Mo/HZSM-5 sample at 1073 K is shown in the figure below.

FIGURE 20: COKE REMOVAL USING HYDROGEN IN A FLUIDIZED BED REACTOR [29].

The sample in this graph was initially coked in a cyclic 5 min (CH₄-5 min) and H₂ feed switch operation for 80 min (which represents the total cumulative CH₄-feeding time). The graph shows the slow regeneration feature of deactivated Mo/ZSM-5 catalyst [29]. Research by Zhan-GuoZhang [38], shows that this challenge can be overcome altering the exposure time and reaction condition to include longer periods of H₂-regeneration (more than a few hours at least) at conditions of temperature (1093 K), pressures 0.15 MPa and Hydrogen space velocity (3,000 mL/g/h). This assists in the recovery of the benzene formation activity lost over a shorter reaction period involving Mo/ZSM-5 at identical temperature, pressure and gas hourly space velocities.

Advantages of Fluidized Bed Reactors over Membrane Reactors

Hydrogen and oxygen in heated conditions result in steam, which in turn suppresses coke formation in both the reactor models. The degree of catalyst deactivation is also reduced

significantly under the prevailing conditions. Methane conversion curve overtime is higher for a fixed-bed reactor (FR) than in a membrane reactor (MR) as shown in the figure below.

FIGURE 21: METHANE CONVERSION CURVE OVER TIME FOR A FIXED-BED REACTOR (FR) AND A MEMBRANE REACTOR (MR).

Additional advantages of the fluidized bed reactor in comparison to the membrane reactor include the following; it has simple standard components making it easier to design and operate; it flexibly allows both batch and continuous reactions tailored to the user's needs; it has a very high gas-solid contact area subject to gas velocity making reactions optimum; most bed reactors have integrated filter and reversible flow cleaning systems that prevent particulate emissions (membrane reactors are difficult to clean); finally the fluidized bed reactor shows greater heat and mass transfer efficiency, higher efficiency in heating and cooling, excellent product consistency, temperature stability, as well as lower operating costs, energy consumption and manpower requirements in comparison to the membrane reactor [11, 28].

Conclusion

Methane dehydroaromatization (MDA) is a highly promising venture in natural gas utilization/ exploitation. Essentially, Mo/HZSM-5 catalyzed MDA reaction provides an effective path towards the production of non-petroleum aromatic products from methane, which is the most abundant hydrocarbon in the planet. The fundamental aspect of gaining this add-on value from methane lays on the synthesis or selection of a catalyst with suitable performance and good mechanical stability for methane aromatization reactions. This paper has focused mainly on molybdenum zeolites mainly Mo/ZSM-5, Mo/C, and Mo/H-ZSM-5. ZSM-5 is one of the aluminosilicate zeolites, constituent members of the pentasil zeolite family. The chemical formula is $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \cdot 16\text{H}_2\text{O}$ and is the primary focus of this paper. Catalyst preparation and characterization are important in this respect as it results in catalysts with the correct texture, attrition resistance, and shape for industrial application processes such as MDA. The performance and effectiveness of the zeolite catalyst Mo/ZSM-5 during the methane dehydroaromatization (MDA) are influenced by several parameters that have been explored at length by researchers in the field studies related of aromatization of methane. These include molybdenum content, the reaction temperature, the space velocity, and the reaction time. Additionally, carbon deposition/ carbonaceous deposits as a result of coking have presented extreme performance challenges in this process. Suppression of external coke formation has now become the center of focus for many researchers in this field. A breakthrough in this research is the acid-catalyzed polycondensation on the external surface sites of zeolite crystals, which reduces the risk of external coke formation. Additionally, the silanation process based on large organosilane reagents has also proven highly efficacious in eliminating the external acidic sites where coke and carbonaceous deposits tend to form along with the transcendent HZSM-5 zeolite (Ding et al.,). The consequence of this silanation process on the Mo/HZSM-5 catalyst was shown to be an improved catalyst activity and/or aromatic

selectivity. The type of reactor and reactor design selected also play an important role in the effectiveness of the MDA process. More specifically, the types of reactor model chosen whether membrane or bed reactor has a direct effect on the efficacy of the MDA process. Thermal pyrolysis, catalytic pyrolysis as well as radical chain polymerizations, for example, being three of the most common methods for coke formation, can be reduced or effectively eliminated using a fluidized bed reactor with a dual-bed reactor system. This paper has provided an in-depth understanding of the comparative role of Mo/ZSM-5 catalyst for CH₄ dehydroaromatization process with an examination into its underlying affluent aspects such as preparation, characterization, performance, structure, active site location, reaction parameters, desorption and mass diffusion, as well as the catalytic reactor designs in use.

References

- [1]. Anggoro, Didi Dwi, et al. "Effect of Co and Mo Loading by Impregnation and Ion Exchange Methods on Morphological Properties of Zeolite Y Catalyst." *Bulletin of Chemical Reaction Engineering & Catalysis* 11.1 (2016): 75-83.
- [2]. Argauer, Robert J and Landolt, George R (1972) "Crystalline zeolite zsm-5 and method of preparing the same" *U.S. Patent* 3,702,886.
- [3]. Bartholomew, Calvin H., and William C. Hecker. "Catalytic reactor design." *Chemical Engineering*. McGraw Hill Publication (1994): 70-75.
- [4]. Bu, Lintao, et al. "Diffusion of aromatic hydrocarbons in hierarchical mesoporous H-ZSM-5 zeolite." *Catalysis Today* 312 (2018): 73-81.
- [5]. Cao, Zhengwen, et al. "Natural gas to fuels and chemicals: improved methane aromatization in an oxygen-permeable membrane reactor." *Angewandte Chemie International Edition* 52.51 (2013): 13794-13797.
- [6]. Chandrasekhar, Sathy, and P. N. Pramada. "Microwave assisted synthesis of zeolite A from metakaolin." *Microporous and Mesoporous Materials* 108.1-3 (2008): 152-161.
- [7]. Choi, Jae-Soon, et al. "Structural evolution of molybdenum carbides in hot aqueous environments and impact on low-temperature hydroprocessing of acetic acid." *Catalysts* 5.1 (2015): 406-423.
- [8]. Deraz, N. M. "The importance of catalyst preparation." *J Ind Environ Chem.* 2018; 2 (1): 16 18.2 (2018).
- [9]. Ding, Weiping, George D. Meitzner, and Enrique Iglesia. "The effects of silanation of external acid sites on the structure and catalytic behavior of Mo/H-ZSM-5." *Journal of Catalysis* 206.1 (2002): 14-22.

- [10]. Fouty, Nicholas, Juan Carrasco, and Fernando Lima. "Modeling and Design Optimization of Multifunctional Membrane Reactors for Direct Methane Aromatization." *Membranes* 7.3 (2017): 48.
- [11]. Gallucci, Fausto, Angelo Basile, and Faisal Ibney Hai. "Introduction-A review of membrane reactors." (2011): 1.
- [12]. Haber, Jerzy, Jochen H. Block, and Bernard Delmon. "Methods and Procedures for Catalyst Characterization." *Handbook of Heterogeneous Catalysis: Online* (2008): 1230-1258.
- [13]. Ji, Yajun, Honghui Yang, and Wei Yan. "Strategies to enhance the catalytic performance of ZSM-5 zeolite in hydrocarbon cracking: A review." *Catalysts* 7.12 (2017): 367.
- [14]. Julian, Ignacio, et al. "Non-oxidative methane conversion in microwave-assisted structured reactors." *Chemical Engineering Journal* 377 (2019): 119764.
- [15]. Kosinov, Nikolay, et al. "Methane dehydroaromatization by Mo/HZSM-5: mono-or bifunctional catalysis?" *ACS Catalysis* 7.1 (2016): 520-529.
- [16]. Kosinov, Nikolay, et al. "Reversible Nature of Coke Formation on Mo/ZSM-5 Methane Dehydroaromatization Catalysts." *Angewandte Chemie International Edition* 58.21 (2019): 7068-7072.
- [17]. Leofanti, G., et al. "Catalyst characterization: characterization techniques." *Catalysis today* 34.3-4 (1997): 307-327.
- [18]. Li, Guanna, et al. "Structure and Reactivity of the Mo/ZSM-5 Dehydroaromatization Catalyst: An Operando Computational Study." *ACS Catalysis* 9.9 (2019): 8731-8737.
- [19]. Li, Jianwei, Jun Li, and Qingshan Zhu. "Carbon deposition and catalytic deactivation during CO₂ reforming of CH₄ over Co/MgO catalyst." *Chinese Journal of Chemical Engineering* 26.11 (2018): 2344-2350.

- [20]. Li, Wei, et al. "The location, structure, and role of MoO_x and MoC_y species in Mo/H-ZSM-5 catalysts for methane aromatization." *Studies in Surface Science and Catalysis*. Vol. 130. Elsevier, 2000. 3621-3626.
- [21]. Liu, Zhendong, et al. "Continuous flow synthesis of ZSM-5 zeolite on the order of seconds." *Proceedings of the National Academy of Sciences* 113.50 (2016): 14267-14271.
- [22]. Ma, Zhen, and Francisco Zaera. "Characterization of heterogeneous catalysts." *Surface and Nanomolecular Catalysis* (2006): 1-37.
- [23]. Mannei, Emna, et al. "Solid-state ion exchange of molybdenum (VI) acetylacetonate into ZSM-5 zeolite." *Thermochimica Acta* 652 (2017): 150-159.
- [24]. Matus, E. V., et al. "Deactivation and regeneration of Mo/ZSM-5 catalysts for methane dehydroaromatization." *Eurasian Chemico-Technological Journal* 12.1 (2010): 1-8.
- [25]. Munnik, Peter, Petra E. de Jongh, and Krijn P. de Jong. "Recent developments in the synthesis of supported catalysts." *Chemical reviews* 115.14 (2015): 6687-6718.
- [26]. Pawar, Vivek, et al. "Study of short-term catalyst deactivation due to carbon deposition during biogas dry reforming on supported Ni catalyst." *Energy & Fuels* 29.12 (2015): 8047-8052.
- [27]. Rostrup-Nielsen, J. R., and J. Bøgild Hansen. "Steam reforming for fuel cells." *Fuel Cells: Technologies for Fuel Processing*. Elsevier, 2011. 49-71.
- [28]. Son, Seong Yong, Dong Hyun Lee, and Sang Done Kim. "Effect of uniformity of gas distribution on fluidization characteristics in conical gas fluidized beds." *Studies in surface science and catalysis* (2006): 557-560.
- [29]. Song, Y., Zhang, Q., Xu, Y., Zhang, Y., Matsuoka, K., & Zhang, Z. G. (2017). Coke accumulation and deactivation behavior of microzeolite-based Mo/HZSM-5 in the non-oxidative methane aromatization under cyclic CH₄-H₂ feed switch mode. *Applied Catalysis A: General*, 530, 12-20.

- [30]. Tempelman, Christiaan HL, and Emiel JM Hensen. "On the deactivation of Mo/HZSM-5 in the methane dehydroaromatization reaction." *Applied Catalysis B: Environmental* 176 (2015): 731-739.
- [31]. Velebná, Klaudia, et al. "The influence of molybdenum loading on activity of ZSM-5 zeolite in dehydroaromatization of methane." *Microporous and Mesoporous Materials* 212 (2015): 146-155.
- [32]. Wang, Dingjun, Jack H. Lunsford, and Michael P. Rosynek. "Catalytic conversion of methane to benzene over Mo/ZSM-5." *Topics in Catalysis* 3.3-4 (1996): 289-297.
- [33]. Wong, Kae S., et al. "Methane aromatisation based upon elementary steps: Kinetic and catalyst descriptors." *Microporous and Mesoporous Materials* 164 (2012): 302-312.
- [34]. Wang, Shengnian, and Yuxin Wang. "Synthesis of hierarchical zeolites by solid state crystallization of aluminosilicate nanogels." U.S. Patent No. 10,343,926. 9 Jul. 2019.
- [35]. Yan, Peng, et al. "Development of a CH₄ dehydroaromatization–catalyst regeneration fluidized bed system." *Chinese Journal of Chemical Engineering* 26.9 (2018): 1928-1936.
- [36]. Yu, Weiting, et al. "Theoretical and experimental studies of C–C versus C–O bond scission of ethylene glycol reaction pathways via metal-modified molybdenum carbides." *ACS Catalysis* 4.5 (2014): 1409-1418.
- [37]. Yuan, Shandong, et al. "The effect of oxygen on the aromatization of methane over the Mo/HZSM-5 catalyst." *Catalysis letters* 63.1-2 (1999): 73-77.
- [38]. Zhang, Zhan-Guo. "Process, reactor and catalyst design: Towards application of direct conversion of methane to aromatics under nonoxidative conditions." *Carbon Resources Conversion* (2019).
- [39]. Zhou, Ming, Ali A. Rownaghi, and Jonas Hedlund. "Synthesis of mesoporous ZSM-5 zeolite crystals by conventional hydrothermal treatment." *RSC advances* 3.36 (2013): 15596-15599.