

Methanol to Hydrocarbons Reaction Mechanism over Zeolite Catalyst

Jaikishor Mavai^{*}

Department of Chemical Engineering, Aligarh Muslim University, Aligarh, India

ABSTRACT

Methanol as an alternative source of fossil fuel reduced carbon emissions like carbon dioxide, NOX, and other hazardous pollutants, etc. which created air pollution and affected the environment and human beings. Methanol is obtained from alternative feed stocks, such as carbon dioxide, biomass, municipal waste, or natural gas through the intermediate formation of synthesis gas. The most recent advances in mechanistic understanding including direct C-C bond formation during the induction period and the promotional effect of zeolite catalyst topology and acidity on the alkene cycle and discussed the reaction mechanism of the conversion of Methanol to Olefins (MTO), Methanol to Hydrocarbons, (MTH) Methanol to Gasoline (MTG) and Methanol to Aromatics (MTA). Keywords: Methanol; Hydrocarbons; Zeolite; ZSM-5; Olefin

INTRODUCTION

Mobile was awarded the first Methanol to Hydrocarbons (MTH) patent methane, ethylene, propylene, butylene, C_5^+ gasoline range hydrocarbons, and aromatics were the main products of the MTH process. These products were produced over the crystalline aluminosilicate zeolite catalyst surface ZSM-5 under reaction conditions of 673 K, 1 atm, and WHSV (hour space velocity) 1-20 1/hr [1-3]. Direct C-C bond formation during the induction stage and the stimulation of the alkene cycle by zeolite catalyst structure and acidity are two of the most recent developments in mechanistic knowledge [4]. Discussed the process by which methanol is converted to a variety of carbon containing (Figure 1).

 Industrially mature process
 Current topics of review
 Industrially immature process

 CH
 Syngas
 Olefins

 Coal
 CC4
 CC4

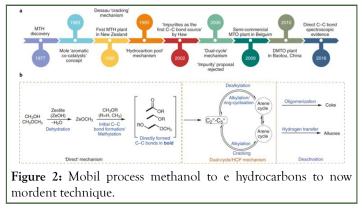
 Syngas
 CH4
 CH4

 Biomass
 Mtg
 Gasoline

 Methanol-mediated
 CO2
 Aromatics

 Figure 1:
 Sources, such as biomass, waste, coal, natural gas, or even carbon dioxide.
 CO2

As longer hydrocarbons grow inside the zeolite pores, the direct C-C bond continues to develop. Here, methane, coal, biomass, and carbon dioxide are converted into syngas by pyrolysis, thermal decomposition, and gasification techniques at higher temperatures (400-1000°C). Syngas is then converted into methanol by the Fisher-Tropsch process, which makes use of catalytic conversions such as Ni, Al, Zn, and Mo (Figure 2). Methanol is transformed into olefins, aromatics, and hydrocarbons in the gasoline range [5].



Correspondence to: Jaikishor Mavai, Department of Chemical Engineering, Aligarh Muslim University, Aligarh, India; E-mail: jaikishormavai@gmail.com

Received: 12-Sep-2022, Manuscript No. ACE-22-17981; Editor assigned: 15-Sep-2022, PreQC No. ACE-22-17981 (PQ); Reviewed: 29-Sep-2022, QC No. ACE-22-17981; Revised: 17-Jan-2023, Manuscript No. ACE-22-17981 (R); Published: 27-Jan-2023, DOI: 10. 35248/2090.4568.23.13.266

Citation: Mavai J (2023) Methanol to Hydrocarbons Reaction Mechanism over Zeolite Catalyst. Adv Chem Eng. 13:266.

Copyright: © 2023 Mavai J. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Figure 2 depicts the discovery of the mobil method in the 1970's and the broad conversion of methanol into hydrocarbons using a zeolite catalyst in the same decade. After that, a synfuel facility was developed in New Zealand by Dassu and colleagues. The production of gasoline range hydrocarbons dates back to 1986. Methanol created a carbon pool on the catalyst's active surface thanks to the methoxy group. First C-C bond mechanism by Haw and his research team was reported in 2002 [6].

The use of methanol as an alternative liquid fuel, which may be used directly to power Otto engines or fuel cells and achieve high thermodynamic efficiency and relatively minimal environmental implications, has attracted increasing interest in recent years (Figure 3). Coal and biomass are both viable fuels for gasification, while syngas is another option. Syngas production leads to methanol synthesis [7].

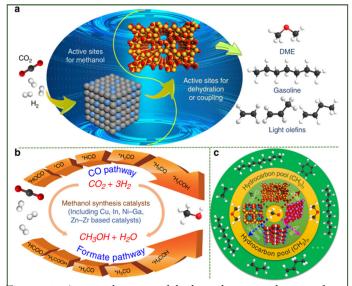


Figure 3: A typical route of hydrocarbons production from natural feed stocks.

Figure 3 shows the catalytic conversion of carbon dioxide into methanol initially, followed by the catalytic conversion of zirconium oxide and indium oxide into hydrocarbons and some catalyst zeolite forging. There are many theatres here because they help the environment by reducing damaging carbon dioxide emissions and raising global temperatures. An alternative method involves using a catalyst, such as indium oxide, zirconium oxide, aluminium oxide, etc., to convert carbon dioxide into methanol. The catalyst was given active sites to convert CO_2 into methanol, which was subsequently transformed into a hydrocarbon with the aid of a zeolite catalyst. [8]

LITERATURE REVIEW

The most recent developments in mechanistic knowledge are described in this article, including direct C-C bond formation during the induction stage and the encouraging effects of zeolite catalyst structure and acidity on the alkene cycle (Figure 4).

Reaction mechanisms of methanol to hydrocarbons mechanism conversion of methanol to hydrocarbons

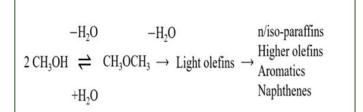


Figure 4: Methanol converted into DME as an intermediate product then converted into first olefins then aromatics.

Illustration: Reactions dehydrating methanol produces Dimethyl Ether (DME) initially. The light olefins produced from the equilibrium mixture of methanol, DME, and water are then transformed into higher hydrocarbons *via* hydrogen transfer, alkylation, isomerization, and other secondary reactions, while DME serves as an intermediate product for the transformation of light olefins into isoparaffin and alkyl aromatics (Figure 5) [9].

Hydrocarbon pool mechanism

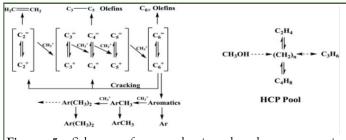


Figure 5: Scheme of a mechanism based on successive methylation and cracking.

During an induction time, the methoxy group on the active sites of the zeolite catalyst, which is formed of carbon pool, converted methanol into hydrocarbons directly. However, after early olefins are created and after it olefins are transformed into aromatics, a more effective method through olefin chain development and cracking takes over (Figure 6).

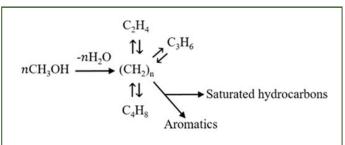


Figure 6: Phenomenological scheme of the hydrocarbon pool mechanism for MTO.

Their labeled methanol co feeding tests with ethene or propene over SAPO-34 demonstrate that the formation of propene/ butene products is not primarily caused by methylation of ethene/propene. Methane and water as well as dimethyl ether and water are concurrently produced from methanol. Here, DME interacts as an intermediary product; as the reaction progressed, hydrocarbon conversion rose while DME conversion declined (Figure 7). Gasoline, aromatics, and higher hydrocarbons produced at 573 K and 673 K-873 K, respectively, at the catalyst surface into the reacting pore [10].

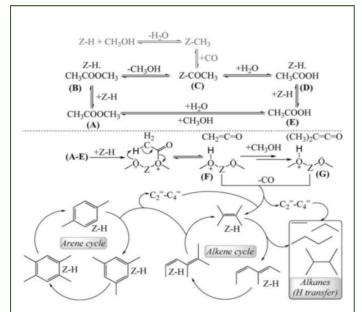


Figure 7: Methanol to hydrocarbon in the presence of zeolite catalyst.

By repeatedly methylating and oligomerizing the formed alkenes, olefins were created. Additionally, in the delicate dual cycle model, both the alkene and aromatic based cycles were engaged in the synthesis of olefins; ethene is mostly created from the aromatic based cycle, whilst C_3^+ alkenes are primarily produced from the alkene based cycle (Figure 8). The organic compounds were captured in zeolites when the reacting zeolite was dissolved in HF [11].

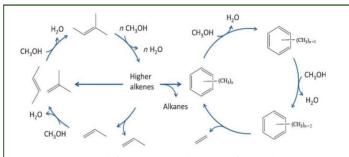
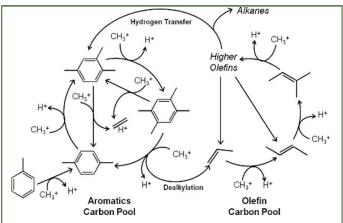
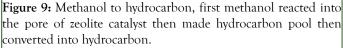


Figure 8: Methanol first converted into olefins in between DME as an intermediate product finally converted into hydrocarbons.

Olefin methylation, olefin cracking, hydrogen transfer, cyclization, aromatic methylation, and aromatic dealkylation are the six main chemistries that take place inside the dual cycle mechanism for MTH. Based on the observed catalytic induction time, during which the rate of methanol/DME conversion rose significantly as hydrocarbon content increased, MTH proposed an autocatalytic process. As opposed to the reaction of methanol alone over H-ZSM-5 at 512 K, co-processing ethene and cis-2butene with methanol first demonstrated the co catalytic effect, lowering the catalyst induction duration by a factor of 2 and 4, respectively. On H-ZSM-5, it was shown that by feeding higher alcohols and methanol together, linear olefins that are progressively methylated and then break are produced. Olefins that are successively methylated and then crack to generate smaller olefins or take part in hydrogen transfer reactions to make alkanes and aromatics can be produced by co feeding methanol with higher alcohols that quickly dehydrate to linear olefins under reaction conditions on H-ZSM-5. However, cyclic species as well as olefins are important in MTH (Figure 9). Using the "hydrocarbon pool" method, light olefins, alkanes, and aromatics are created when methanol creates a pool of (CH_2) n species inside the pores of zeolite [12].





DISCUSSION

Mechanistic analysis of the longer catalyst lifetime caused by co feeding n-butane during MTA conversion as previously indicated, the role of HZ-5 catalysts during the MTA conversion is explained. The first active species for the spread of higher alkene chains can be an alkene that is produced during the induction phase of the MTO conversion. In accordance with the olefin based cycle mechanism, the long chain alkenes can then function as active hydrocarbon species and be cracked to lower olefins. Long chain alkenes can also be further methylated and transformed into dienes at the same time. When the H-O bond breaks in this instance, O' has a negative charge while H⁺ becomes higher olefins. OH eliminates oxygen from the zeolite catalyst in methanol. Here, water molecules are removed from methanol to dehydrate it; methanol OH⁻ possesses a negative charge over a zeolite catalyst, a charge greater than the link between carbon and oxygen breaks. The oxygen of the zeolite catalyst bond is coupled to the CH3 of methanol in zeolite catalyst. Once more, CH₃ added a carbon chain to the zeolite catalyst and created hydrocarbon oxygen's negative charge and carbon's positive charge, another process removes water molecules. The bond brake then adds a CH₃ chain to create hydrocarbon oxygen's negative charge and carbon's positive charge, another process removes water molecules. The bond brake then adds a CH₃ chain to create a hydrocarbon (Figures 10 and 11).

OPEN ACCESS Freely available online

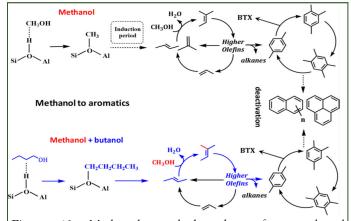


Figure 10: Methanol to hydrocarbon, first methanol reacted into the pore of zeolite ZSM-5 catalyst active sites then made hydrocarbon.

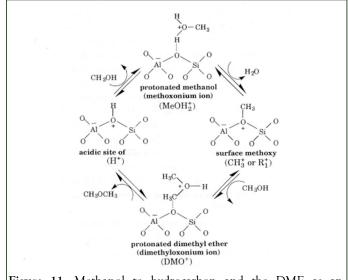


Figure 11: Methanol to hydrocarbon and the DME as an intermediate product.

Figure 8 shows the dehydration of methanol by removing the water molecules from the compound. Next, carbon and oxygen bonds are broken over a zeolite catalyst. The oxygen in the zeolite catalyst forms a connection with the CH₃ of the methanol. Once more, CH₃ was added to the zeolite catalyst, creating a carbon chain and a hydrocarbon. Due to oxygen's negative charge and carbon's positive charge, another way for removing water molecules adds a CH₃ chain to create hydrocarbon [13-15].

Figure 9 shows the mechanism for the methanol to hydrocarbons process, which uses a dual aromatic and olefin catalytic cycle (Figure 12). MTH reactions are carried out *via* a "hydrocarbon pool" mechanism that uses two catalytic cycles, the first of which yields methylbenzenes and ethylene and the second of which yields C_3^+ olefins. There are six significant phases in the reactions that take place inside this dual cycle: Olefin methylation, olefin cracking, hydrogen transfer, cyclization, aromatic methylation, and aromatic dealkylation are among the chemical reactions that are discussed [16,17].

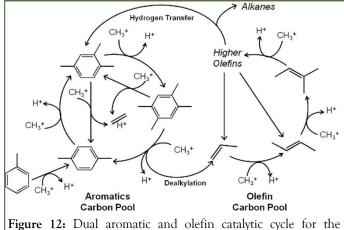


Figure 12: Dual aromatic and olefin catalytic cycle for the methanol to hydrocarbons reaction mechanism.

To create the tri coordinated carbenium ion, hydrogen transfer cracking primarily happens between CH3⁺ from methanol and an alkane in naphtha. This procedure prevents the creation of the penta coordinated carbonium ion, whose adsorption at the Brnsted acid sites is immediately protonated or H-transfer with CH3. Cracked dehydrogenation Zn species were introduced, which resulted in novel active sites and reaction pathways for naphtha conversion. Alkanes are activated differently by zinc sites than they are by B acid sites. Alkanes were dehydrogenated as a result of the C-H bond dissociating over the zinc sites, which aided in the production of hydrogen and olefins. This is a considerably more effective way to encourage the use of Brnsted acid sites than protonation. In order to generate the tricoordinated carbonium ion dehydrogenation by the zinc sites, this is far more effective in promoting the use of the Brnsted acid sites than protonation of olefins (Figure 13). The carbonium ion that has been tricoordinated then undergoes bscission to produce light olefins.

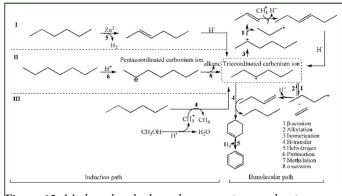


Figure 13: Methanol to hydrocarbons reaction mechanism over Zn modified zeolite ZSM-5 catalyst.

Methanol to Olefins (MTO), Methanol to hydrocarbons (MTH), Methanol to Gasoline (MTG), and Methanol to Aromatics (MTA) are all processes that use methanol as the starting material. As a fossil fuel substitute, methanol decreased carbon emissions such as carbon dioxide and other harmful pollutants like NO_x that have an impact on the environment and people. Methanol is produced by first forming synthesis gas from different feed stocks such carbon dioxide, biomass, trash, or natural gas. We describe the most recent developments in mechanistic knowledge in this review, including the stimulation

Mavai J

of the alkene cycle by zeolite catalyst structure and acidity and the chemical mechanism that transforms methanol to hydrocarbons during the induction stage.

CONCLUSION

The most recent advances in mechanistic understanding including direct C-C bond formation during the induction period and the promotional effect of zeolite catalyst topology and acidity on the alkene cycle and discussed the reaction mechanism the conversion of Methanol to Olefins (MTO), Methanol to Hydrocarbons (MTH) Methanol to Gasoline (MTG) and Methanol to Aromatics (MTA). A sophisticated understanding of the complicated processes driving C-C bond formation, chain expansion, and the deposition of carbonaceous species is required to identify them in the zeolite catalyzed conversions of methanol and methyl chloride. It is possible to do this because of operating Photoelectron Photo Ion Coincidence (PEPICO) spectroscopy. The direct experimental proof provided by the isomer selective discovery of routes to hydrocarbons up to C_{14} in size of ketene in the methanol to hydrocarbons process and methyl radicals in both reactions. Both paths eventually meet at C5 molecules, which change into aromatics. Differentiations in the predominance of coke precursors are highlighted by Operando PEPICO, which is backed up by studies of electron paramagnetic resonance, showing changes in the representative density, distribution, and molecular composition of accumulating carbonaceous species. Methyl cycle routes mediated by radicals.

ACKNOWLEDGEMENT

I thank full Aligarh Muslim University provided me research environment.

REFERENCES

- Hadi N, Niaei A, Nabavi SR, Farzi A, Navaei Shirazi M. Development of a new kinetic model for methanol to propylene process on Mn/H-ZSM-5 catalyst. Chem Biochem Eng Q. 2014;28(1):53-63.
- Johansson R, Hruby SL, Rass-Hansen J, Christensen CH. The hydrocarbon pool in ethanol to gasoline over HZSM-5 catalysts. Catal Lett. 2009;127(1):1-6.
- Esquius JR, Bahruji H, Bowker M, Hutchings GJ. Identification of C₂-C₅ products from CO₂ hydrogenation over PdZn/TiO₂-ZSM-5 hybrid catalysts. Faraday Discuss. 2021;230:52-67.

- Liu Y. Catalytic ethylene oligomerization over Ni/Al-HMS: A key step in conversion of bio-ethanol to higher olefins. Catalysts. 2018;8(11): 537.
- Kim S, Park G, Kim SK, Kim YT, Jun KW, Kwak G, et al. Gd/ HZSM-5 catalyst for conversion of methanol to hydrocarbons: Effects of amounts of the Gd loading and catalyst preparation method. Appl Catal B Environ. 2018;220:191-201.
- Chowdhury AD, Paioni AL, Houben K, Whiting GT, Baldus M, Weckhuysen BM. Bridging the gap between the direct and hydrocarbon pool mechanisms of the methanol to hydrocarbons process. Angew Chem Int Ed. 2018;57(27):8095-8099.
- Teixeira IF, Lo BT, Kostetskyy P, Ye L, Tang CC, Mpourmpakis G, et al. Direct catalytic conversion of biomass-derived furan and ethanol to ethylbenzene. ACS Catal. 2018;8(3):1843-50.
- Nawaz S, Kolboe S, Stocker M. Conversion of Methanol to Light Olefins over Sapo-17 Molecular Sieve. Stud Surf Sci Catal. 1994;81:393-398.
- Hadi N, Niaei A, Nabavi SR, Farzi A, Navaei Shirazi M. Development of a new kinetic model for methanol to propylene process on Mn/H-ZSM-5 catalyst. Chem Biochem Eng Q. 2014;28(1):53-63.
- Li Z, Li F, Zhao T, Yu H, Ding S, He W, Song C, Zhang Y, Lin H. The effect of steam on maximizing light olefin production by cracking of ethanol and oleic acid over mesoporous ZSM-5 catalysts. Catal Sci Technol. 2020;10(19):6618-6627.
- Wang S, Cai Q, Chen J, Zhang L, Zhu L, Luo Z. Co-cracking of biooil model compound mixtures and ethanol over different metal oxidemodified HZSM-5 catalysts. Fuel. 2015;15:160:534-43.
- 12. Ilias S, Bhan A. Mechanism of the catalytic conversion of methanol to hydrocarbons. ACS Catalysis. 201;3(1):18-31.
- Shetsiri S, Thivasasith A, Saenluang K, Wannapakdee W, Salakhum S, Wetchasat P, et al. Sustainable production of ethylene from bioethanol over hierarchical ZSM-5 nanosheets. Sustain Energy Fuels. 2019;3(1):115-26.
- Johansson R, Hruby SL, Rass-Hansen J, Christensen CH. The hydrocarbon pool in ethanol to gasoline over HZSM-5 catalysts. Catal Lett. 2009;127:1-6.
- Takahashi A, Fujitani T. Conversion of bioethanol to propylene over ZSM-5 zeolites. J Jpn Pet Inst. 2018;61(1):20-7.
- Li N, Meng C, Liu D. Deactivation kinetics with activity coefficient of the methanol to aromatics process over modified ZSM-5. Fuel. 2018;233:283-90.
- Arora SS, Shi Z, Bhan A. Mechanistic basis for effects of high pressure H₂ cofeeds on methanol-to-hydrocarbons catalysis over zeolites. ACS Catal. 2019;9(7):6407-6414.