



Methanol to Hydrocarbons Reaction Mechanism over Zeolite Catalyst

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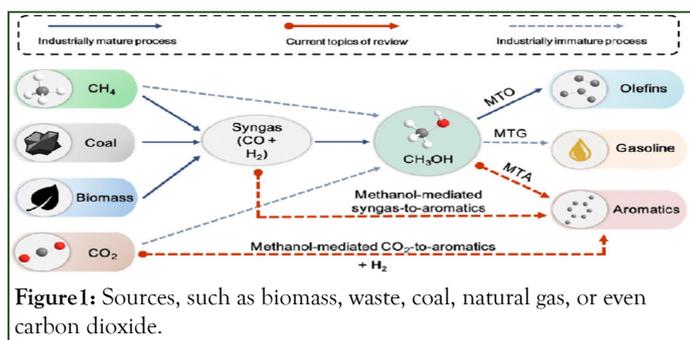
ABSTRACT

Methanol as an alternative source of fossil fuel reduced carbon emissions like carbon dioxide, NO_x, 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).

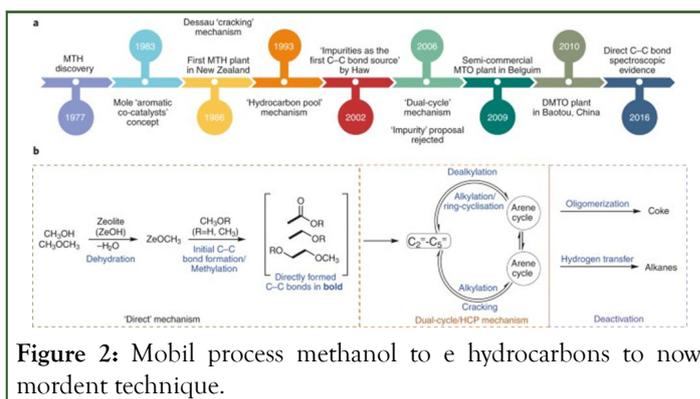
Keywords: Methanol; Hydrocarbons; Zeolite; ZSM-5; Olefin

INTRODUCTION

Mobile was awarded the first Methanol to Hydrocarbons (MTH) patent methane, ethylene, propylene, butylene, C₅⁺ 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).



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].



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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].

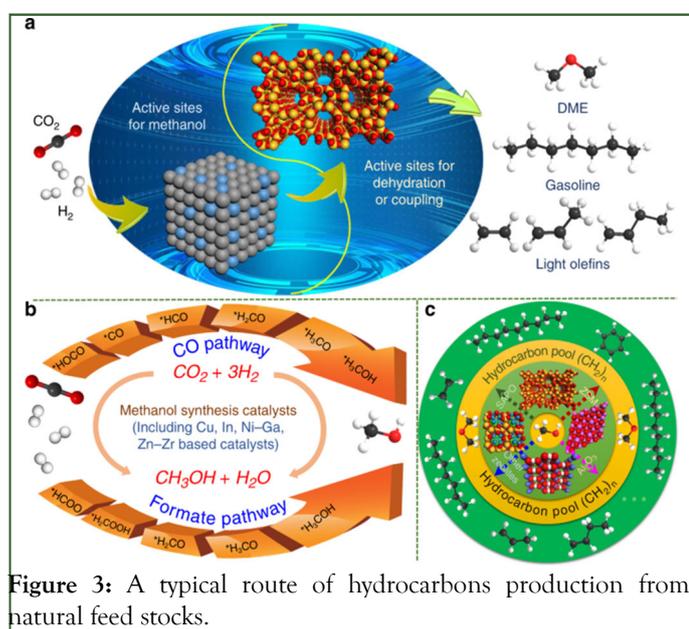


Figure 3: A typical route of hydrocarbons production from natural feed stocks.

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

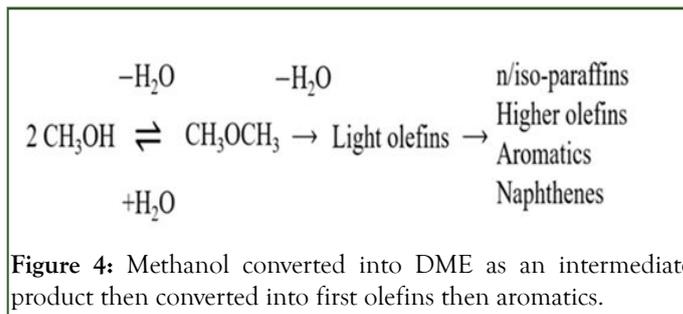


Figure 4: Methanol converted into DME as an intermediate product then converted into first olefins then aromatics.

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

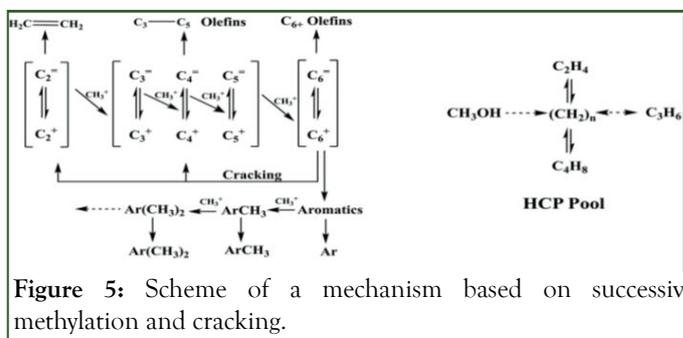


Figure 5: Scheme of a mechanism based on successive methylation and cracking.

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).

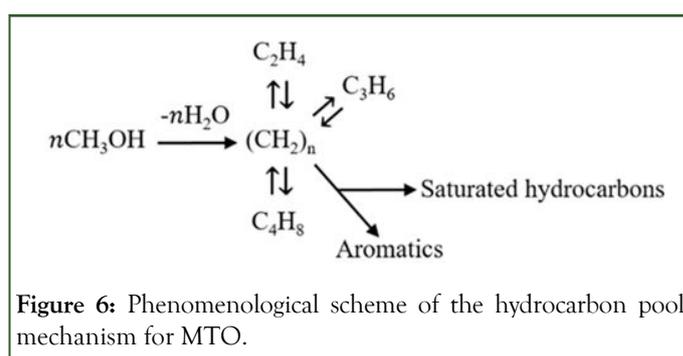


Figure 6: Phenomenological scheme of the hydrocarbon pool mechanism for MTO.

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].

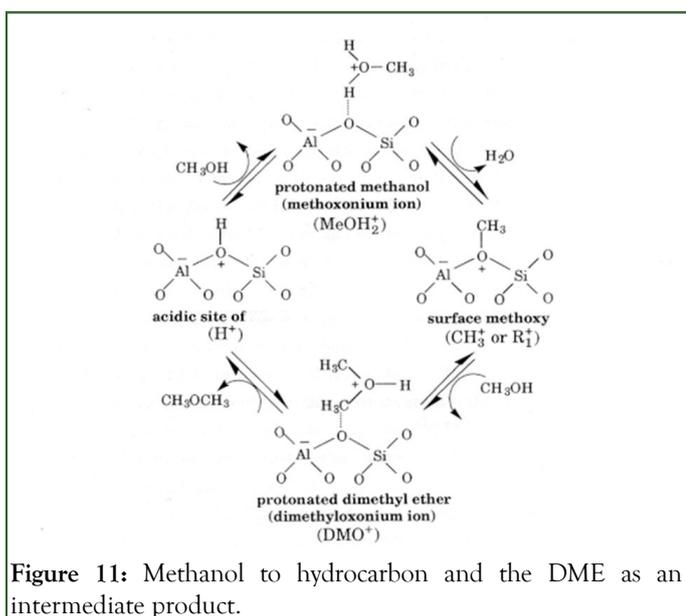
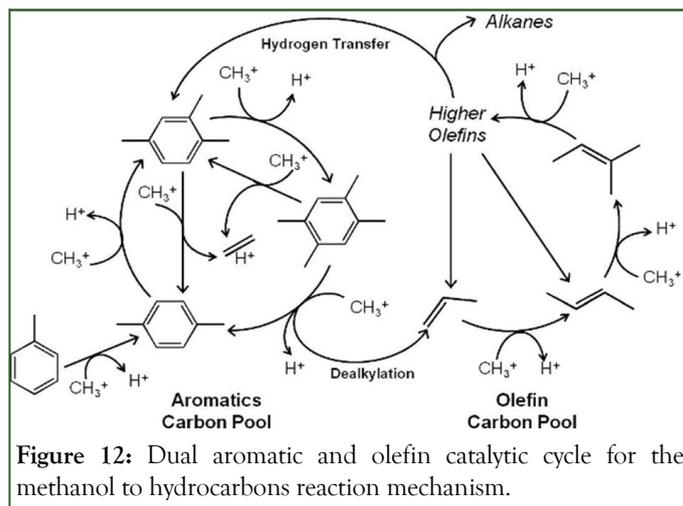
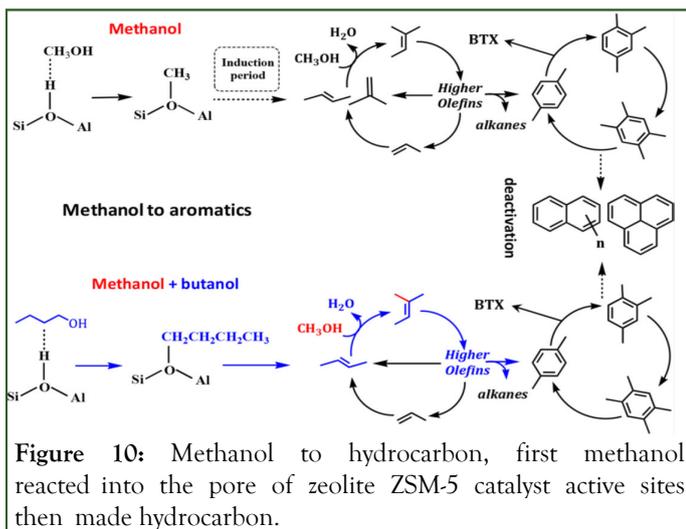


Figure 11: Methanol to hydrocarbon and the DME as an intermediate product.

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 CH_3 of the methanol. Once more, CH_3 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 CH_3 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].

To create the tri coordinated carbonium ion, hydrogen transfer cracking primarily happens between CH_3^+ 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 CH_3 . 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 β-scission to produce light olefins.

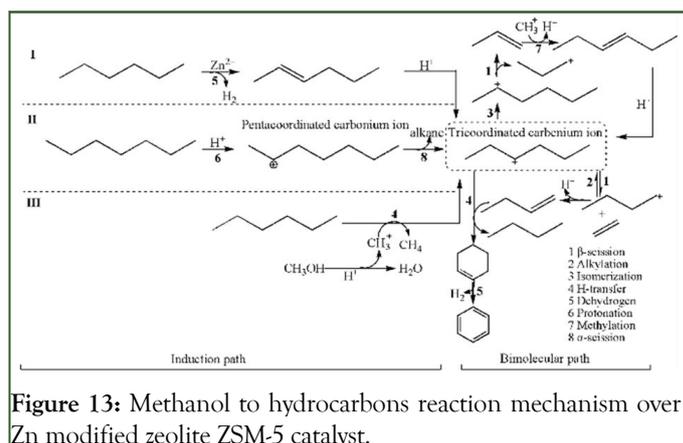


Figure 13: Methanol to hydrocarbons reaction mechanism over Zn modified zeolite ZSM-5 catalyst.

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

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 C₁₄ 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.

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