



“ METHANOL SYNTHESIS AND CONVERTED INTO HYDROCARBONS OVER ZEOLITE CATALYST A REVIEW”

JAIKISHOR MAVAI

ALIGARH MUSLIM UNIVERSITY, ALIGARH, INDIA

1. Abstract-

Methanol is an alternative source of fossil fuel that is environmentally friendly and renewable. Methanol gives low carbon dioxide emissions and other hazardous materials such as NO_x, SO_x, etc., when transformed into hydrocarbons, hence less polluting the environment. Methanol can be synthesized from different sources such as coal, CO₂, biomass, natural gas, and municipal waste. Information about the methanol-to-hydrocarbon (MTH) process over ZSM-5, ZSM-11, SAPO-34, SAPO-17, and SAPO-18 catalyst has been discussed. Also, the methanol-to-olefins (MTO) process over ZSM-5 and methanol-to-aromatics (MTA) over ZSM-5 and ZSM-11 are discussed. Modification with metals enhances the catalyst acidity. It was observed that after modification, the catalytic performance is increased and showed better conversion, selectivity/yield towards the selective product. The effects of various parameters such as surface morphology, temperature, pressure, WHSV, etc., are discussed, which give a good understanding of the catalytic activity, selectivity, and stability in the MTH, methanol-to-gasoline (MTG), MTO, MTA process.

KEY WORDS- MTH, MTO, MTA, ZSM-5

2. Introduction

Methanol is one of the top chemicals produced in the world [1], [2], which can be (1) used as a fuel in internal combustion engines [3] or direct methanol fuel cell [4] to produce power, (2) reformed to produce hydrogen [1], (3) mixed with gasoline as an additive to provide fuel blends, e.g., the M85 (15% gasoline and 85% methanol) [1], [3], [5], or (4) used as a raw material to synthesize other fuels and chemicals [1], [2], [6], [7], [8], e.g., olefins, gasoline, dimethyl ether, methyl tert-butyl ether, and acetic acid.

Methanol was produced since the early 20th century by using the BASF and ICI processes [10], [11], [12]. The state-of-the-art (SOA) commercial methanol plants use syngas (H₂ and CO) derived from fossil resources [13]. However, methanol should be more and more produced from alternative feedstocks to avoid carbon emissions. One reasonable option is to use the CO₂ captured from various sources and the H₂ produced by using renewable energy, but it is limited by the installed renewable capacity and energy intensity of CO₂ capture. An alternative option is to use biomass as the feedstock since biomass represents 14% of global renewable energy [14], [15]. Especially in recent years, methanol synthesis based on biomass gasification, i.e., biomass-to-methanol, has been intensively investigated [2], [16], [17], [18], [19], [20], [21].

Methanol synthesis-

COAL TO METHANOL

Coal is found in massive amounts worldwide and is expected to play a crucial role as an abundant energy source. However, one critical issue in promoting coal utilization controlling environmental pollution. Clean coal technologies are needed to utilize coal in an environmentally acceptable way and to improve coal utilization efficiency. But as the most abundant energy resource, it will continue to be the dominant energy supply for a long time. Therefore, the development and deployment of clean coal technologies are crucial to promoting sustainable development and coal to form methanol and then hydrocarbon (Liu et al., 2017).

As seen in **Figure 1(a)**, the proven coal reserves in the world were 984453 million tonnes (MT) in 2000, while in 2020, it was 1074108 MT. Hence a large number of coal reserves can be opted to be used for coal conversion to methanol. Therefore, clean coal technology needs to be adopted to have less harmful pollutants released into the atmosphere. Also, in Figure 1(b), the amount of coal production is greater compared to its consumption. Therefore, there is as such no scarcity of this non-renewable fossil fuel. Thus, it can be used as a feedstock for the production of methanol, which can then be converted into gasoline range hydrocarbons. Hence an alternative to conventional gasoline can be obtained.

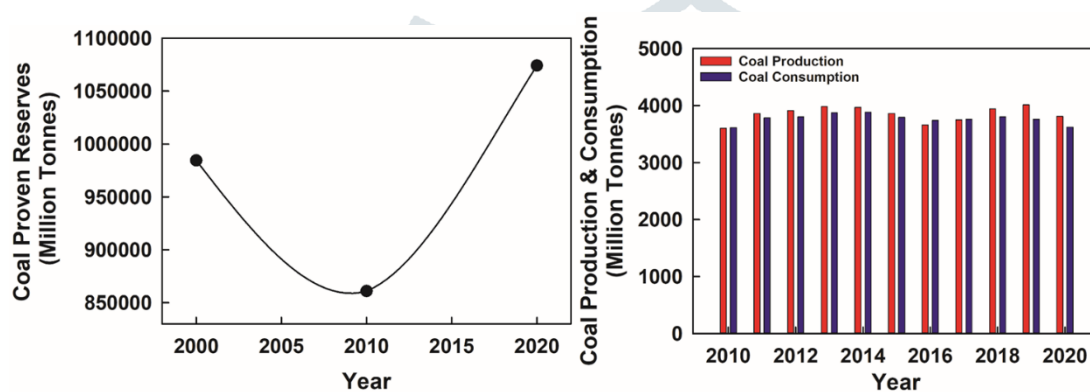


Figure 1(a) Coal proven reserves from 2000 to 2020; (b) Production & Consumption of coal in the world from 2010 to 2020.

Even though the proven oil reserves of oil from 1300.9 thousand million barrels (TMB) to 1732.4 TMB has increased (**Figure 2(a)**), but one cannot rely on these fossil reserves. There need to find another alternative, gasoline range hydrocarbons, which can be produced via methanol, which we have discussed that it can be made from coal. While from **Figure 2(b)** it can be depicted that the oil consumption was certainly on a higher side than its production. Thus, it can be assured that the oil demand has increased from 2010 to 2020. In 2020 it was declined to owe to the COVID-19 situation, because of which most all vehicles movement was stopped. Hence, overall, an alternative to present fossil fuel needs to be adopted as soon as possible to avoid the scarcity of available fossil reserves.

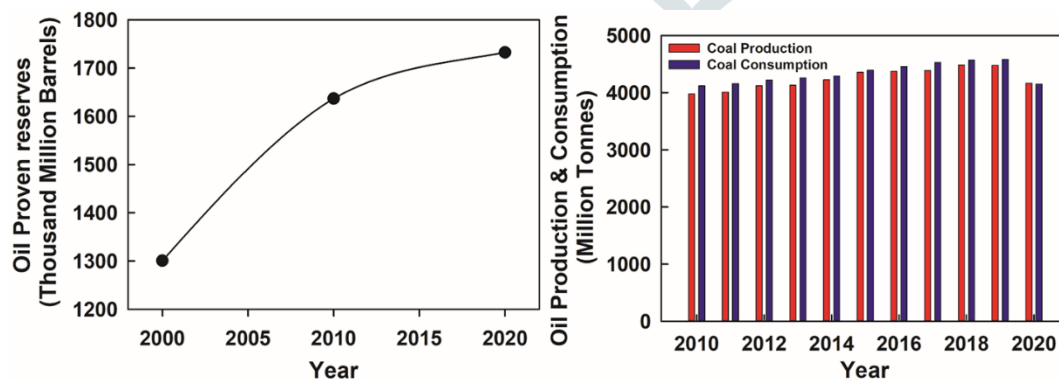


Figure 2(a) Oil proven reserves from 2000 to 2020; (b) Production & Consumption of oil in the world from 2010 to 2020.

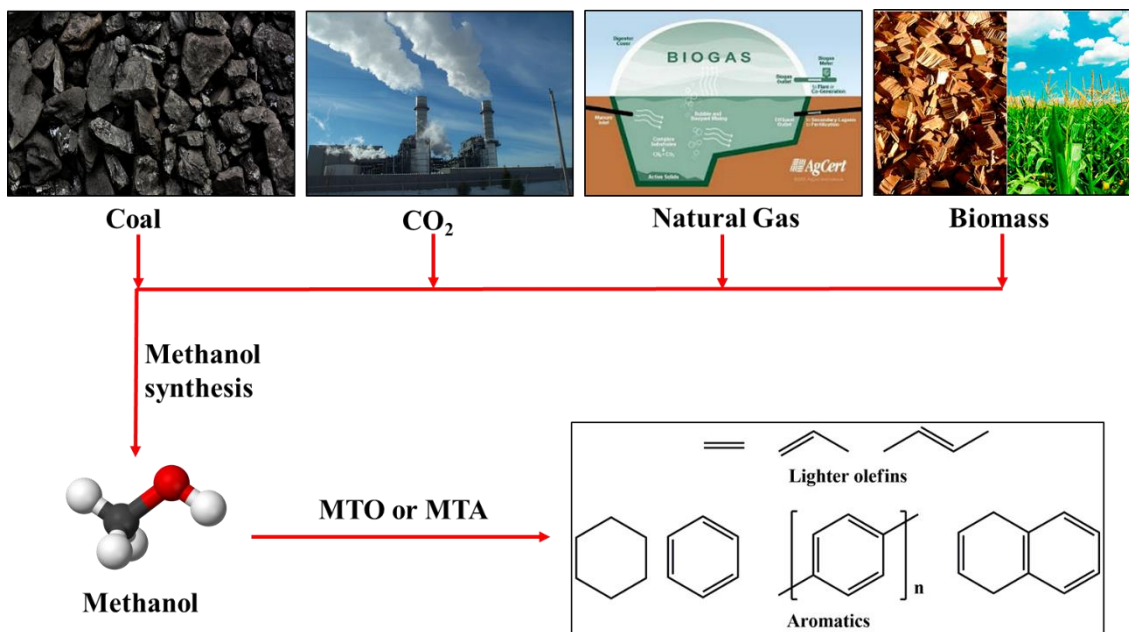


Figure 3: A typical route of hydrocarbons production from natural feedstocks.

In recent years, a growing interest has been observed in applying methanol as an alternative liquid fuel, which can be used directly for powering Otto engines or fuel cells, achieving high thermodynamic efficiencies and relatively low environmental impacts. Biomass and coal can be considered as potential fuels for gasification, and further syngas production leads to methanol synthesis (Chmielniak et al., 2003).

BIOMASS TO METHANOL

Use of abundantly available virgin and wood, energy crops, and waste from forests, yards, or farms known as biomass to methanol. Waste biomasses as feed-stock for producing gaseous (bio-gas) and liquid fuels (bio-methanol, bio-ethanol, and bio-butanol) is being considered as the sustainable and viable alternative to fossil fuels (coal, natural gas, and Petro-fuels like gasoline and diesel). Out of these bio-methanol is being considered as an attractive liquid fuel as well as feed-stock for the synthesis of enumerable valuable organic compounds currently being produced from coal, natural gas, and petroleum feedstocks. Biochemical routes that are being explored for the sustainable production of bio-ethanol from waste biomass. It focuses especially on the biochemical conversion route which utilizes microbes as biocatalysts for methanol production under normal temperature and pressure conditions. To make the process cost-effective certain improvements like the utilization of raw biogas instead of natural gas for methanol production (Gautam et al., 2020).

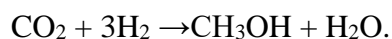
Natural gas to methanol-

The life cycle environmental performance of liquefied natural gas (LNG), liquefied biogas (LBG), methanol, and bio-methanol. A transition to the use of LNG or methanol produced from natural gas would significantly improve the overall environmental performance. However, the impact on climate change is of the same order of magnitude as with the use of heavy fuel oil. It is only the use of LBG and bio-methanol that has the potential to reduce the climate impact. The analysis did not show any significant differences in environmental performance between methane and methanol when produced from the same raw materials, but the performance of the methanol engines is yet to be validated (Brynnolf et al., 2014). Methanol production potential of Methylosinus sodium from raw biogas originated from an anaerobic digester³.

CO₂ to methanol-

Methanol, in addition to its energy storage property, is used as a convenient fuel as well as a raw material for various hydrocarbons. Moreover, methanol is used to generate electricity using direct methanol fuel cell (DMFC) technology. The conversion of CO₂ with H₂ to methanol (MeOH) over a commercial Cu/ZnO catalyst. The obtained results showed good stability of the catalytic system and a large potential for a CO₂ emission reduction with simultaneous production of MeOH as bulk chemicals or alternative fuels. If H₂ is obtained from renewable or CO₂ neutral sources (e.g. biomass, the solar, wind, or nuclear energy), respectively, a potentially CO₂-neutral cycle is possible. Compared to the conventional synthesis gas-based

technologies like the Lurgi Mega Methanol process, the CO₂-based process shows lower productivity. However, since the overall reaction is less exothermic, lower temperature peaks and lower by-product contents are found at similar process conditions. The higher purity is beneficial for further chemical conversion.



Conversion of CO₂ with hydrogen to MeOH over a commercially available standard Cu/ZnO/Al₂O₃ catalyst. (Rothaemel et al., 2011)

Municipal solid waste (MSW) uses dolomite catalysts, followed by a methanol synthesis. (AlMohamadi et al., 2020). MSW can be used in anaerobic digesters to produce biogas/biomethane. Furthermore, a fraction of Municipal Solid Waste (e.g. non-recyclable plastics, paper cardboard, etc.) can be converted to Refuse Derived Fuel (RDF). The digestate derived from anaerobic digestion, as well as CO₂ from biogas, can be used as a nutrient source to grow microalgae, which are feedstock suitable for supercritical water gasification (SWG). An integrated process is proposed, by coupling an anaerobic digestion plant for biomethane production with (i) high-temperature gasification of RDF and (ii) SWG of algae grown up with digestate and CO₂ from biogas. The biomethane is assumed to be converted in syngas by steam reforming. Considering its importance for the chemical industry chain, methanol is considered a target product. Methanol synthesis is assessed in terms of mass and energy balances and direct CO₂ emissions⁴.

The present work discusses methanol as an alternative source of fossil fuels that is environmentally friendly and renewable. Methanol gives low carbon dioxide emissions and other hazardous materials NO_x, SO_x, etc., when transformed into hydrocarbons, hence less polluting the environment. Insight information about methanol production via coal, biomass, natural gas, CO₂, and municipal waste. Insight information about the methanol-to-hydrocarbon (MTH) process over ZSM-5, ZSM-11, SAPO-34, SAPO-17, and SAPO-18 catalyst has been discussed. Also, the methanol-to-olefins (MTO) process over ZSM-5 and methanol-to-aromatics (MTA) over ZSM-5, H-SAPO-34, and ZSM-11 are discussed. ZSM-5 using various metals such as Ni, Fe, Zn, Ir, Na, Pd, Ga, Gd, Pt, Cr, etc., either by wet impregnation and ion-exchange method is also studied of various literature. It was observed that after modification, the catalytic performance is increased and showed better selectivity/yield towards the selective product. Lastly, the effects of various parameters such as surface morphology, temperature, pressure, WHSV, etc., are discussed, which give a good understanding of the catalytic activity, selectivity, and stability in the MTH, methanol-to-gasoline (MTG), MTO, MTA process also discuss modeling of MTH, MTA, MTO, MTG, in the process reaction mechanism of methanol to hydrocarbons when methanol converted the made hydrocarbon pool in catalyst surface.

Zeolite catalyst structure

ZSM-5 is a silica-rich zeolite that has been synthesized with greatly differing SiO₂/Al₂O₃ ratios; the ZSM-5 zeolite size of the pore was not more than 20 angstrom. Ion exchange capacity, catalytic activity, and water sorption are shown to vary linearly with aluminum content and extrapolate smoothly to the end member of the series, a pure silica ZSM-5^{7,8}

Zeolites are crystalline aluminosilicates with pores and channels of molecular dimensions. Zeolites can be synthesized with different chemical compositions and distinct framework topologies, and about 170 such topologies have been reported. Figure 1 shows the framework structure of four commonly used zeolites: Zeolite A, Zeolite Y, Zeolite L, and ZSM-5. Due to their ion-exchange properties, as well as adsorption and reactions of molecules within their cages, zeolites have found use in numerous applications in catalysis and separations.

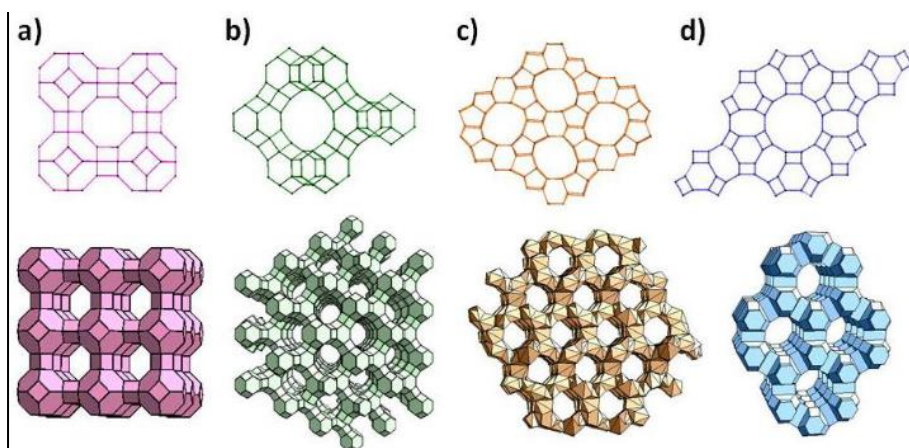


Figure 1. Representative zeolite frameworks, (with pore openings). (a) zeolite A (3D, 4.2 Å); (b) zeolite Y (3D, 7.4 Å); (c) Zeolite L (1D, 7.1 Å); (d) ZSM-5 (silicalite) (2D, 5.3 × 5.6 Å, 5.1 × 5.5 Å) D—dimensions of channel system. (Reference: Y Zheng, X Li, PK Dutta, Exploitation of unique properties of zeolites in the development of gas sensors, *Sensors* 12 (2012) 5170–5194)

The first one is located on oxygen bridges connecting silicon and aluminum atoms of the framework (Si-OH-Al) and is associated with the Bronsted acid sites, and the second one is attributed to the silanol groups terminating the zeolite lattice (Si-OH) which are mostly placed on the external surface and are regarded as non-acidic centers. It has been shown that the Si/Al ratio directly influences the Bronsted/Lewis ratio which affects the acid sites strength and distribution and therefore the selectivity toward different products increasing the Si/Al ratio in ZSM-5 zeolite from 20-60.

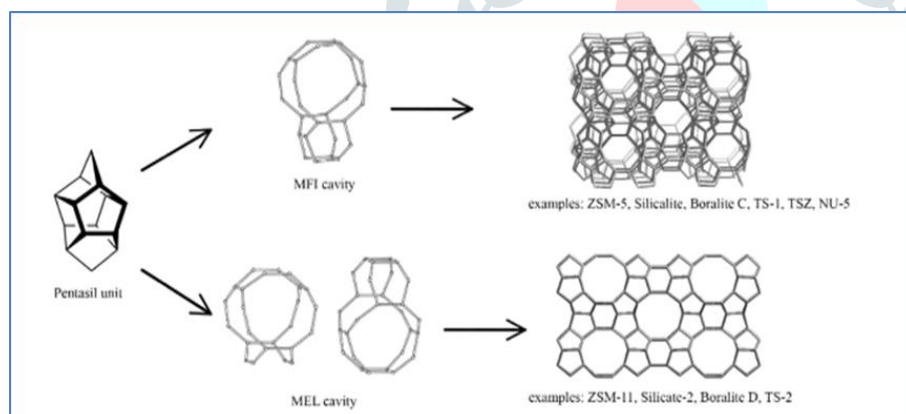


Figure 2. Structure of different zeolites made from pentasil unit. (Reference: J Weitkamp, *Zeolites and catalysis*, *Solid State Ion.* 131 (2000) 175–188)

Fig. 2 shows the structures of four selected zeolites along with their respective void systems and pore dimensions. In these commonly used representations, the T-atoms are located at the vertices, and the lines connecting them stand for T–O–T bonds. For example, if 24 tetrahedra are linked together as shown in the top line of Fig. 2, the cuboctahedron, also referred to as a sodalite unit or β -cage, results. It is an important secondary building unit from which various zeolite structures derive. If sodalite units are connected via their hexagonal faces as shown in Fig. 2, the structure of the mineral faujasite results. It is identical with the structures of the synthetic zeolites X ($1 \leq n_{\text{Si}}/n_{\text{Al}} \leq 1.5$) and Y ($n_{\text{Si}}/n_{\text{Al}} > 1.5$). Zeolite Y is of utmost importance in heterogeneous catalysis, for example, it is the active component in catalysts for fluid catalytic cracking. Its pore system is relatively spacious and consists of spherical cages, referred to as super cages, with a diameter of 1.3 nm connected tetrahedrally with four neighboring cages through windows with a diameter of 0.74 nm formed by 12 TO₄-tetrahedra. Zeolite Y is therefore classified to possess a three-dimensional, 12-membered-ring pore system. An example of a zeolite with unidimensional, 12-membered-ring pores is zeolite ZSM-12 (Fig. 2, line 2). Its pores are slightly elliptical with dimensions of 0.57 × 0.61 nm. Zeolite ZSM-5 (Fig. 2, line 3) and its all-silica analog silicalite-1 ($n_{\text{Si}}/n_{\text{Al}} = \infty$) are built from the

pentasil unit. They contain intersecting systems of ten-membered-ring pores, one being straight and one sinusoidal. ZSM-5 is another example of a zeolite that has gained huge importance in heterogeneous catalysis. It is used industrially in the synthesis of ethylbenzene, the isomerization of xylenes, and the disproportionation of toluene, and it is often looked upon as the prototype of shape-selective catalysts (vide infra). Several zeolites with unidimensional, ten-membered-ring pores exist as well, one example being Theta-1 which is isostructural to zeolite ZSM-22 (Fig. 2, bottom line). An assortment of zeolite catalysts as shown in Fig. 1 is often a good starting point for a coarse investigation of the influence of the pore width and/or dimensionality on the selectivity of the reaction to be studied.

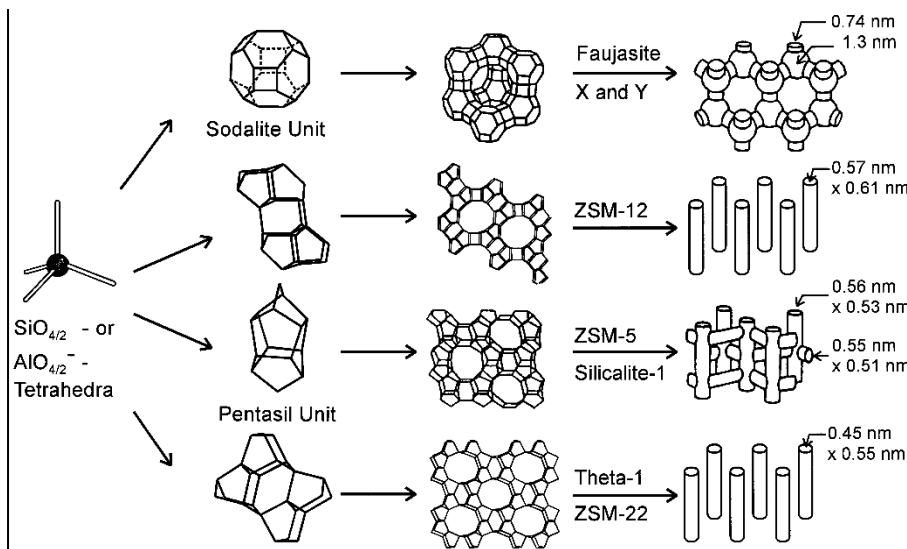


Figure 3. Structures of four selected zeolites (from top to bottom: faujasite or zeolites X, Y; zeolite ZSM-12; zeolite ZSM-5 or silicalite-1; zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions. (Reference: J Weitkamp, Zeolites and catalysis, Solid State Ion. 131 (2000) 175–188).

Methanol to olefins

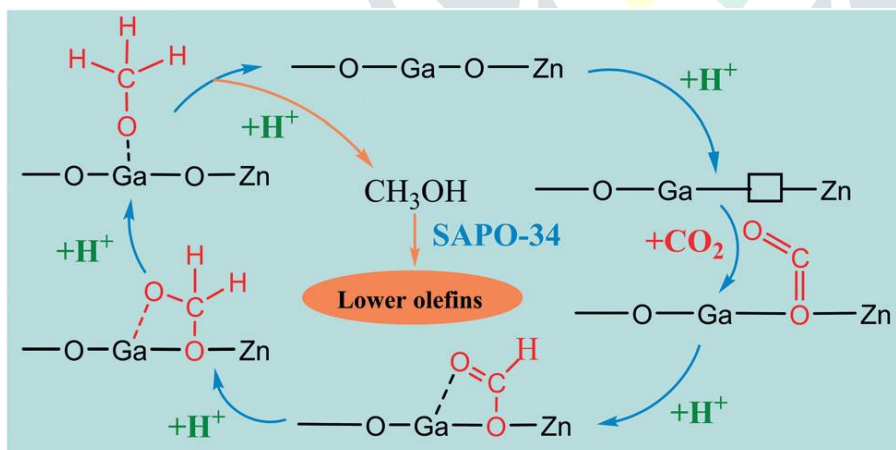
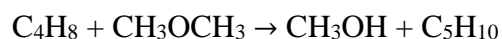
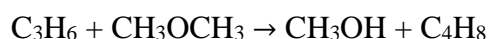
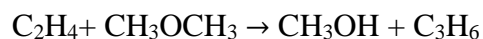


Figure 4. MTO over SAPO-34 methanol first was converted into DME by a dehydration process treated as an intermediate product. When oxygenated compound reacted at catalyst surface in the cage of pores at acid reactive sites to made hydrocarbon pool and converted into olefins and hydrocarbon product (Sharma et al., 2021).





Methanol converted into DME and formed a hydrocarbon pool after it converted into olefins (Heriyanto et al., 2020).

Selective conversion of methanol into low molecular weight olefins over high silica SSZ-13 zeolite catalyst surface at $T = 873 \text{ K}$, $P = 1 \text{ atm}$, and $\text{WHSV} = 0.1\text{-}10 \text{ h}^{-1}$. (Santilli et al., 1985)

SAPO-17 were studied concerning their catalytic behavior in the MTO process. Experiments with SAPO-17 in range 623-750K. A deactivated sample of SAPO-17 could be restored to full activity by calcination in air at 823K (Nawaz et al., 1994). The MTO process is advantages in comparison with other natural gas utilization technologies and conventional naphtha cracking processes at 573K, 1atm (Liu et al., 1999).

Natural gas utilization technologies and conventional naphtha cracking processes at 573K, 1atm. In situ MAS NMR spectroscopy investigated of the conversion of MTO on silico-aluminophosphate SAPO-34 and SAPO-18 under continuous flow reactor at the reaction conditions at $P = 1 \text{ atm}$, temperature 573 to 673 K and of olefins yield 58% (Hunger et al., 2001)

MTO reaction is performed over SAPO-34 catalyst at $T=663\text{K}$, $P= 1 \text{ bar}$, and $\text{LHSV}= 6 \text{ hr}^{-1}$ with selectivity of olefins ($\text{C}_2\text{-C}_4$) = 96%. Coke is initially formed in the triangular crystal edges at the surface of catalyst, in which straight channel openings reached directly the external crystal surface (Mores et al., 2008).

Effects of zinc incorporation on hierarchical ZSM-11 catalyst for MTO conversion in a continuous flow isotherm fixed-bed reactor at 773K, and 0.1MPa. The yield of propene and butene was enhanced through the direct synthesis method (2 % ZnZ11-C, 4 % ZnZ11-C), and the sample 4 % ZnZ11-C displayed a fast deactivation. A monotonic increase in the effluent propylene-to-ethylene molar ratio as inlet methanol pressure is varied from 0.6-52 KPa during MTH catalysis on H-ZSM-5 and conversion of catalyst 80%. (Arora et al., 2017)

MTO over HZSM-48 at $T = 723\text{-}973\text{K}$, $P = 1 \text{ bar}$, and $\text{LHSV} = 1 \text{ hr}^{-1}$ produced $\text{C}_3\text{-C}_5$ olefins. MTO reaction using Cr, Cu, Ga, La, Mg, Y, and Zn doped on 3D-printed ZSM-5 zeolite. 3-D printed ZSM-5 zeolite monolith doped with 10 wt% Mg exhibited a favorable effect on the light olefins production and showed ethylene and propylene selectivity of 24% and 33%, respectively with methanol conversion approaching 95% (Li et al., 2019).

MTO over Zn-modified high-silicon HZSM-5 (Zn/HZSM-5) catalyst. Due to the heterogeneous distribution of the protons of high silicon ZSM-5, two types of Lewis acid sites were formed by the interaction of Zn with hydroxyl groups (OH) adsorbed on HZSM-5. The comparatively high light olefins yield of 51.7 wt% was obtained on 0.3-Zn/HZSM-5 catalyst under the optimal reaction conditions of $T= 923\text{K}$, and $\text{WHSV} = 3.83 \text{ hr}^{-1}$ (Juybar et al., 2019)

Methanol dehydration is a high potential route for the production of light olefins ($\text{C}_2\text{-C}_4$). Hierarchical Si-rich [B]-ZSM-5 catalysts ($\text{Si/Al}=200$) were prepared through one-pot hydrothermal synthesis. The best catalytic performance was obtained at a temperature of 753K, $\text{WHSV}=7.2 \text{ h}^{-1}$. The optimum catalyst had the highest propylene selectivity (58%) and light olefin selectivity (85%)¹⁹

MTO, the most important catalytic process producing ethylene and propylene from non-oil feedstocks (coal, natural gas, biomass, CO_2). It is hindered by rapid catalyst deactivation due to coke deposition. Transforming coke to naphthalenic species in SAPO-34 zeolites via steam cracking at $T = 773\text{K}$, $P = 1 \text{ bar}$, and $\text{LHSV} = 5 \text{ hr}^{-1}$ and high light olefins selectivity of 85%²⁰

Methanol to hydrocarbon

Reaction mechanisms

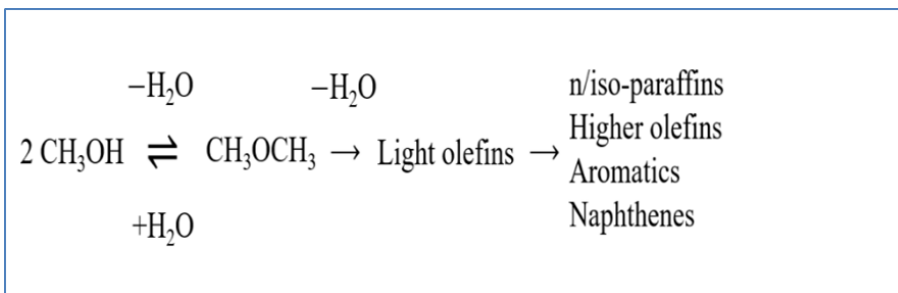


Figure 5. Methanol converted into DME as an intermediate product then converted into first olefins and aromatics (Chang et al.,1979)

The early 70s explain the above reaction steps dimethyl ether (DME) is first obtained by dehydration of methanol. The equilibrium mixture of methanol, DME, and water is then converted to light olefins, whereas DME acts as an intermediate product responsible for the conversion of light olefins into isoparaffin, and alkyl aromatics via hydrogen transfer, alkylation, isomerization, other secondary reactions (Chang et al.,1979)

Hydrocarbon pool-

[I]

The direct mechanism may operate during an induction period, but that a more efficient route through olefin chain growth and cracking dominates once initial olefins are formed. Before this, Mole and Langner had also shown independently that Toluene and cyclohexene, respectively, had a co-catalytic effect on the reaction, thus diminishing the importance of direct C-C bond formation. Their findings and theories were very insightful and likely contributed greatly to later mechanistic studies (Dessau et al., 1982)

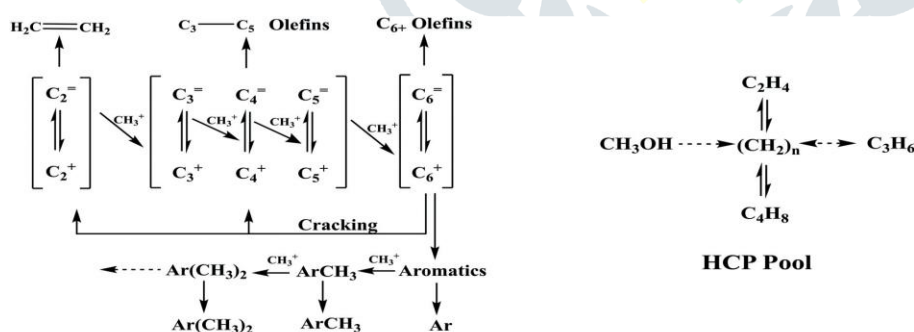


Figure 6: Scheme of a mechanism based on successive methylation and cracking. (Dessau et al., 1982)

[II]

A major advance in the mechanistic understanding of methanol conversion came about when Dahl and Kolboe suggested the concept of a hydrocarbon pool in the 1990s. Their co-feeding experiments of labeled methanol with ethene or propene over SAPO-34 show that propene/butene products are not chiefly formed by methylation of ethene/propene. (Dhal et al., 1996)

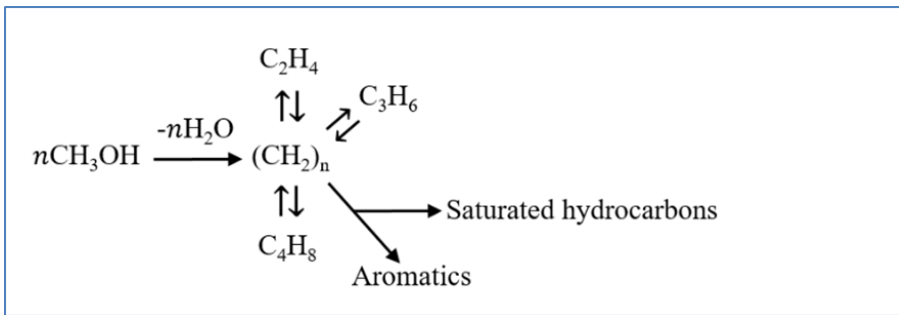


Figure 7: Phenomenological scheme of the hydrocarbon pool mechanism for MTO. (Dhal et al., 1996)

Methanol is converted into simultaneously di ethyl-ether and water and by methane and water. Here DME reacts as an intermediate product when the reaction proceeds the conversion of hydrocarbon increased and conversion of DME decreased concerning time. At the catalyst surface into the reacted pore where hydrocarbon pool formed then first formed olefins at 573 K and 673-873K gasoline, aromatics and higher hydrocarbon formed. (Dessau et al., 1982)

The acid number of hydrocarbon fraction is reduced by contacting the hydrocarbon fraction and lower alcohol such as methanol with a solid catalyst having a surface area greater than 15 m²/g at temperature 573-644 K of thermal cracking pressure 1-8 bar, WHSV= 4 h⁻¹ (Chun et al., 1973). Process for preparing hydrocarbon from methanol at T= 573K, P= 8 bar and WHSV= 1-5 h⁻¹. (Pearson et al., 1975)

The conversion of methanol and other O-compounds to hydrocarbon over ZSM-5 zeolite catalysts at T= 573-673K, P=1 atm, and WHSV= 1-9 h⁻¹. The conversion of MTH to C₂- C₁₀ hydrocarbon using a new class of shape-selective zeolite. Methanol dimethyl ether an equilibrium mixture converts the first reaction sequence to olefins range C₂-C₅. In the final step reaction path, C₂-C₅ olefins are converted to paraffin, aromatics, cycloparaffins, and C₆ olefins at conversion 100% with hydrocarbon selectivity 57% (Chang et al., 1977).

MTH process at T=573 K, P= 1 atm, and WHSV=1-20 h⁻¹ in the presence of nickel, aluminum, magnesium, silica, titanium, and zirconium metal doped on zeolite catalyst and enhanced the selectivity, yield and conversion (Pinto et al., 1980). In the mobil process, methanol is converted to mixtures of hydrocarbons consisting of olefins, paraffin, and aromatics at T = 673 K, P = 1 atm, WHSV = 9 h⁻¹. The dehydration of methanol to dimethyl ether and converted into ethene, and propane is primarily formed olefins by oligomerization and isomerization processes (Berg et al., 1981).

MTH process used carbenium ion mechanism incorporating over HZSM-5 (Dessau et al., 1982) .MTG over HZSM-5 reaction at T=673K, P=1-5 MPa, WHSV=1-9 h⁻¹(Hutchings et al., 1990).Hydrothermal treatment of silicon aluminophosphate molecular sieves at temperatures over about 973K for MTH process increased selectivity for C₂ -C₃ olefins and decreased selectivity for paraffin production than the untreated SAPO-n starting composition. Deactivation of methanol synthesis catalyst at lower temperature over catalyst Cu-Zn oxide. Deposition of Fe or Ni over HZSM-5 enhanced catalyst's activity, conversion and yield/selectivity.(Hutchings et al., 1990)

Methanol conversion over H-ZSM-5 has been studied in a microreactor using a mixture of ¹³C-methanol and propene (isopropanol). The products were analyzed with a GC instrument allowing an isotopic analysis of the emerging reaction product (Dahl et al., 1995).The addition of Ga₂O₃ to H-ZSM-5 enhances the

formation of aromatic hydrocarbons. This effect is obtained at temperatures 673 K, conversion up to 95%, and product selectivity enhanced up to 40-50% (Freeman et al., 2002)

MTH over H-SAPO-34 catalysts the product was obtained ethene, xylenes and trimethyl benzenes at temperatures 773 K, conversion up to 90%, and product selectivity enhanced up to 45% (Svelle et al., 2006). The phosphorus-modified ZSM-5/ZSM-11 intergrowth zeolites have been used for the catalytic conversion of MTH. Decrease of the Brønsted acid sites (proton donated capacity) and the acid strength of the catalysts in comparison with the parent ZSM-5/ZSM-11, which causes a dramatic improvement in the selectivity towards propylene at 673K (Li et al., 2010)

MTH over acidic zeolite HZSM-5 catalysts conversion of methanol/DME proceeds through a "hydrocarbon pool" mechanism. DME was reacted over H-ZSM-5, using propene and toluene as co-feeds to determine the effect of the hydrocarbon pool composition on product selectivity dominated by C₂-C₃ olefins (36%) and aromatics (45%) at T = 673 K, P= 1 bar, WHSV= 3 h⁻¹ ³³.

The catalytic, deactivation, and regeneration characteristics of large coffin-shaped H-ZSM-5 crystals were investigated during the MTH reaction in the fixed-bed reactor at 773K was given good conversion, selectivity and yield (Hofmann et al., 2013). An oxalic acid-treated ZnO/CuO/ HZSM-5 catalyst with High resistance to coke formation for the conversion of MTH at T=673 K, P=1atm, WHSV= 4 h⁻¹ deactivation behavior has been studied over HZSM-5, CuO/ HZSM-5, CuO/ ZnO/ HZSM-5 and oxalic acid treated ZnO/ CuO/ HZSM-5. Coke formed on strong acid sites in pore channels and the external surface of the catalyst and conversion 99%, yield of products 44% (Zaidi et al., 2014).

A series of MoO₃/H-ZSM-5 (Si/Al = 25) catalysts were prepared *via* calcination in the MTH reaction higher loading level of MoO₃ (7.5 wt% or higher) led to observable inner migration of the Mo species into the zeolite channels, with concomitant partial loss of the zeolite Brønsted acidity at T= 643K, P= 1 MPa, WHSV= 4.7 h⁻¹ the conversion 99%, selectivity 41%. The pore fabrication of Nano ZSM-5 zeolite crystals size 100 nm modified by internal desalination in NaOH solution so increased yield of liquid hydrocarbon for the conversion mesoporous introduced into nano ZSM-5 crystals. And external surface area increased the change pore structure by internal desalination high Al content increased the acidity of nano ZSM-5 ³⁶.

MTH over ZSM-5 was investigated with WHSV of 4 h⁻¹ at reaction temperature 683K. The product distribution result indicated that C₃-C₅+ and C₂-C₄ were the major products in the gaseous phase, and in the liquid phase xylenes, three methylbenzene and C₁₀ + aromatics with the highest activity (100%) (Lemraski et al., 2016)

Gd/HZSM-5 catalyst for conversion MTH , the effect of amounts of Gd loading on HZSM-5 catalyst due to its effect enhanced yield of hydrocarbons at T=673K, P= 1 bar and WHSV= 4.75 h⁻¹ (Kim et al., 2017). Conversion of methanol to hydrocarbons over zeolite ZSM-23(MTT) at T= 623K, P= 1 bar, WHSV= 2 h⁻¹ also given good hydrocarbons yield and selectivity (Molino et al., 2017)

MTH Process was probed over the H-SAPO-34 catalyst at T= 673K, P= 2 bar, WHSV= 6 h⁻¹. the conversion up to 95%, yield enhanced up to 67% (Chowdhury et al., 2018). A dual-templating synthesis strategy to hierarchical ZSM-5 zeolites as efficient catalysts for the MTH reaction. The zeolite materials were extensively characterized for their textural and acidic properties. Displayed similar performance in the MTH reaction as nanosheet ZSM-5. (Meng et al., 2018)

MTH processes over zeolites and zeotypes crystalline, microporous oxides widely deployed. Deposition and growth of highly unsaturated carbonaceous result in deactivation. Productive propagation reactions include olefin methylation, aromatic methylation, and aromatic dealkylation (Hwang et al., 2019)

MTH over a series of Zn/ZSM-5 zeolites at 673K, 0.1Mpa WHSV= 1-9 hr⁻¹ and product yield 50-60%. Methylbenzenes, as the intermediate product of the aromatic-based cycle. Lewis acid sites and Brønsted acid sites in the Ca modified zeolite material are indeed responsible for the inability to form surface-carbene species (Wang et al., 2019)

MTH process over zeolite ZSM-5 catalyst the conversion 97% at 573K, 1atm WHSV= 3 hr⁻¹, and product yield 39%. The dynamical behavior of methanol and DME in H-ZSM-5 catalysts Si/Al ratios (36 and 135) was probed using quasielastic neutron scattering method (Omojola et al., 2020)

Zeolite channel geometry–reactive intermediate relationships are studied in detail using anisotropic zeolite ZSM-5 crystals for the methanol-to-hydrocarbon (MTH) process, and advanced magic angle. homologation of alkanes, whereas the more extended straight zeolite channels, facilitate the aromatic cycle with a higher degree of alkylation of aromatics. (Fu et al., 2020)

MTH proceeds autocatalytically in H-ZSM-5 after an induction period where framework methoxy species are formed high methanol loadings and varying acid site densities using first-principles molecular dynamics simulations (Nastase et al., 2020)

MTH catalysis over ZSM-5 showing how inelastic neutron scattering spectroscopy can be used to identify species found in zeolite ZSM-5 used as a catalyst for conversion of MTH at 773K and 1 atm. Ultrasound-assisted rapid hydrothermal design of efficient nanostructured MFI-Type aluminosilicate ZSM-5 catalyst for methanol to propylene reaction at 773K and atmospheric pressure. The ZSM-5(UH-250) zeolite with a slower deactivation regime exhibited a constant level of methanol conversion (84%) and high propylene selectivity (78%) after 2100 min⁴⁷

MTH process at T=773K, P= 5 atm, WHSV = 2 h⁻¹ the conversion 95% yield enhanced up to 45% (Yin et al., 2021).MTO process was given propene over H-ZSM-5 zeolite at temperatures of 473, 573, and 673 K is studied over 6 hours, at these temperatures, propene undergoes acid protonation and subsequent oligomerization to form a pool of oligomers and cyclized oligomers, which subsequently react via the established 2-cycle hydrocarbon pool mechanism to give a mixture of aromatic and aliphatic products (Hawkins et al., 2021)

MTH process over zeolite have Brønsted acid sites and more Lewis acid sites the yields towards ethylene and propylene were respectively 8% and 6% (Nikolopoulos et al., 2021)

Three Zn-doped ZrO₂ catalysts prepared by co-precipitation catalysts, we combined ZrZnOX with two of the most performing zeolite/zeotype catalysts for the methanol-to-hydrocarbons over H-ZSM-5 and H-SAPO-34 and conversion 100% at T=773K, P=1atm and WHSV= 1-5 hr⁻¹ and product yield up to 69% (Ticali et al., 2021)

The conversion of methanol to DME over H-ZSM-5 is calculated as requiring higher activation energy than framework methoxylation, which indicates that a stepwise (indirect) mechanism, through a methoxy intermediate, is the most likely route to DME formation during the initiation of the MTH process (Nastase et al., 2021).

Methanol to gasoline

In the Mobil process, MTG was performed using an HZSM-5 catalyst at temperature 623-673 K, $P=1$ atm, $WHSV=5$ h⁻¹ and aromatics selectivity was 45% and gasoline yields 80%. Zeolite was synthesized by SiO₂/Al₂O₃ after removal of sodium and tetra propylammonium ions by ion exchange then ZSM-5 was obtained (Berg et al., 1981).

MTG in a fluidized bed reactor over zeolite catalyst it's a new route from coal or natural gas to high octane gasoline at $T=623$ K, $P=1-10$ bar, $WHSV=3$ hr⁻¹ and yield of hydrocarbon 67.7% (Keil et al., 1999).

Catalytic conversion of MTG over zeolite catalyst at $T=673$ K, $P=1$ atm, liquid space hour velocity (LHSV) = $1-9$ h⁻¹. The selectivity is a function of CuO/ZnO/HZSM-5 Concentration. Catalyst deactivation due to Coke deposition on catalytic surface. The addition of ZnO over CuO/HZSM-5 reduces the coke without affecting product yields. ZnO/HZSM-5 catalyst coke formation was reduced compared to CuO/HZSM-5 catalyst. ZnO/CuO/HZSM-5 enhanced the aromatics yield to 69% as compared to 66.9% over CuO/HZSM-5. The copper oxide loading over CuO/HZSM-5 (Si/Al=45) catalyst range 0-9 wt %. Improved selectivity of hydrocarbons 42.84% (Zaidi et al., 2008)

MTG over modified HZSM-5 catalyst at $T=673$ K, $P=1$ atm, $WHSV=4$ h⁻¹. Fluidized bed reactor used for MTG reaction when oxalic acid 0.5%, ZnO/7 wt%, CuO/ ZSM-5 by incipient wetness impregnation method used. Methanol conversion 100%, and yields of gasoline range hydrocarbon was 40%. (Zaidi et al., 2010)

Three different ZSM-5 zeolites (nano - ZSM-5, meso-ZSM-5, conventional- ZSM-5). ZSM-5 prepares a single completing procedure. Conventional ZSM-5 catalyst, nanocrystals, and mesoporous ZSM-5 catalyst showed high selectivity for light olefins and alkyl aromatics in the conversion of MTG (Rownaghi et al., 2011)

MTG process over ZSM-5/MCM-48 aluminosilicate composite material as a catalyst was used in the MTG reaction. Its high activity and stability, pore size distribution, and lowered pore surface acidity of the composite material (Di et al., 2013)

Production of gasoline range hydrocarbon from methanol on hierarchical ZSM-5 and Zn/ZSM-5 catalyst prepared with the soft second template. $T=634$ K, $P=1$ atm, $WHSV=1$ hr⁻¹. Zn/ ZSM-5 was made by wet impregnation method. Liquid hydrocarbon selectivity with ZSM-5 is 29.8%. but used Zn/ ZSM-5 selectivity enhanced up to 62.5%. (Wang et al., 2015)

Effect of ZSM-5 crystal size on its catalytic property conversion of MTG at $T=673$ K, $P=1$ MPa, $WHSV=4.74$ h⁻¹. Four-sized mono dispersed ZSM-5 crystal 70, 200, 400, and 650 nm were hydrothermally synthesized by changing H₂O/Si molar synthesis gel. Crystals size of 70 nm yields 30.8%. Increased ZSM-5 crystal size except for ZY5-650 give yields up to 41%, higher selectivity to aromatics 39.78 %. $T=663$ K approximating, $P=1$ atm (Shao et al., 2017).

CuO/NH₄-ZSM-5 catalyst was used in MTG the catalyst prepared by SONO chemistry methods at $T=673$ K, $P=1$ atm, $WHSV=5$ hr⁻¹. CuO loading on NH₄-ZSM-5 supports converting MTH. Fed 100% methanol and 7% catalyst CuO/NH₄-ZSM-5 was aromatic's selectivity 44% and olefin's selectivity 50.4% (Kianfar et al., 2018)

MTG catalysts based on Zn- and Pd-modified zeolites Zn/ZSM-5 and Pd/ZSM-5. Used Zn/ZSM-5 higher selectivity to liquid hydrocarbons (more than 84 wt%) with higher DME and methanol conversion over Pd/ZSM-5 (97.5wt%, respectively) ⁵³

Methanol to aromatics

The interplay between nanoscale reactivity and bulk performance of HZSM-5 catalysts during the MTA reaction was investigated. $T=623\text{K}$, $P=13\text{ bar}$, $\text{WHSV}=5\text{ h}^{-1}$. The effect of a mild hydrothermal treatment on activity, selectivity, and stability of zeolite HZSM-5. In MTA process, methanol conversion is 99%, aromatics selectivity 45% (Aramburo et al., 2013)

Coking kinetics and influence of reaction regeneration on acidity, activity, and deactivation of Zn/ZSM-5 catalyst during methanol aromatization. Methanol was converted into BTX yields 67.7%. Coking behavior catalytic activity of Zn/HZSM-5 to reaction regeneration cycle aromatic yield 80%. (Zhang et al., 2015)

Conversion of MTA OVER 0.5wt% Zn modified nano HZSM-5 zeolite catalyst at $T=723\text{K}$, $P=0.1\text{ MPa}$, and $\text{WHSV} 1-9\text{ h}^{-1}$. MTA over Zn/HZSM-5 the high BTX yields 67.7%. Wt of 0.5% Zn in Zn/HZ. Methanol conversion 100% highest aromatics yield 83% (Zhang et al., 2014)

Alkaline modification of ZSM-5 catalyst for methanol aromatization at $T=673\text{K}$, $P=1\text{ atm}$, $\text{WHSV}=3.2\text{ hr}^{-1}$. Alkaline treatment (0.2 and 0.3 mol/L NaOH) created mesoporous in the present zeolite. Alkaline treatment reduces the ZSM-5 (Si/Al=23.7) sites parent ZSM-5. Improved diffusion due to the presence of mesoporous treatment 0.4 mol/l NaOH produced better aromatics selectivity 43.2% (Wei et al., 2015)

When used Ga supported HZSM-5 with evolved meso and micropore sites by desilication HZSM-5 (Si/Al= 11.5) with varying alkalinities and impregnated with 1 wt % Ga for MTA. Aromatic selectivity 60.1 % at 773K treatment (NaOH= 0.05 M) of HZSM-5 (Lai et al., 2016)

Methanol aromatization over Cr-Zn modified HZSM-5 catalyst at $T=773\text{K}$, $P=0.1\text{ MPa}$, $\text{LHSV}=1.2\text{ hr}^{-1}$. HZSM-5 (HZ) zeolite co-modified with Zn and second promoter Zirconium, molybdenum, chromium, (Zr, Ce, Mo, and Cr) was synthesized in a fixed bed reactor. The influence of methanol conversion to BTX was enhanced (Liu et al., 2018)

Modification of HZSM-5 samples with sodium hydroxide and oxalic acid to provide the formation of the mesoporous structure of the zeolite Si/Al ratio at $T=673\text{K}$, $P=1\text{ atm}$, $\text{WHSV}=1\text{ h}^{-1}$. Zeolite active sites were modified with Co, Ni, Fe to decrease poly aromatic formation MTH. Formation of a mesopore structure with a mean diameter of 4-6 nm positive effect. Zeolite treatment with oxalic acid results decreasing of Si/Al ratio 0.76 to 0.41. The sample ZSM-5-Ni-0.001 M highest activity (Doluda et al., 2019)

MTA over HZSM-5 zeolite and two supported Co catalyst $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Co}/\text{SBA-15}$ at $T=623-663\text{K}$, $P=1\text{ atm}$, and $\text{WHSV}=4\text{ hr}^{-1}$ this enhanced the selectivity of long hydrocarbon ⁷³

Phosphorus modified ZSM-5 Zeolite synthesized by incipient wet impregnation at $T=663\text{K}$, $P=0.5\text{ Mpa}$, $\text{WHSV}=3.2\text{ 1/hr}$. Performance for MTA conversion evaluated. Introduction of phosphorus modification of the catalyst structure characteristics and properties. The reduction in external surface area and micropore volume, pore size, and decreases in the quantity and strength of acid sites. As a result, the P/ZSM-5 enhances selectivity for para-xylene. The selectivity of PX Increased from 23.8% to nearly 90 %. When P content 5 % selectivity of xylene in aromatics was enhanced from 41.3 % to 60.2 % PX yield could loading Zn over 5% P/HZSM-5 generates Zn-Lewis acid sites to enhance. (Niu et al., 2020)

MTA conversion process over HZSM-5 zeolite combined with unique zinc and phosphorus species, yields excellent selectivity (85%) towards aromatic at 673K, 1Mpa, and $\text{WHSV}=1-9\text{ h}^{-1}$ (Qiao et al., 2020)

The Zn-loaded zeolite ZSM-5 is an active and promising catalyst for the conversion of methanol to aromatics with a high yield. performance of shaped ZnZSM-5/alumina catalysts in this reaction at

industrially relevant pressures. This has been combined with extensive characterization to identify the active Zn species (Yarulina et al., 2021)

Catalytic conversion of MTA and hydrocarbons is regarded as a key alternative technology to oil processing. Although the inclusion of foreign metal species in H-ZSM-5 containing Brønsted acid site (BAS) is commonly found to enhance product yields, the nature of catalytically active sites and the rationalization for catalytic performance remain obscure. According to our DFT model, this could lead to the initial heterolytic cleavage of small molecules such as water and methanol by the pair with subsequent reactions to form products at high selectivity as that observed experimentally (Xia et al., 2021)

The incorporation of transition metal ions into acidic H-ZSM-5 by ion exchange can create catalytically active ion pairs within molecular distances in the internal cavity of the H-ZSM-5 structure with BAS. The internal surface anchored metal ion as unquenched Lewis acid site and O₂ from nearby BAS in proximity as an anchored base is established (Lin et al., 2021)

Effect of catalyst pore size and BET surface area

Alkane modification of ZSM-5 catalysts for methanol to aromatization the effect of alkaline concentration at 673K, 1 atm, and 3.2 h⁻¹. Effect of alkaline treatment on the physical property of ZSM-5 catalyst MTA conversion. Alkaline treatment (0.2 and 0.3 mol/L NaOH) created mesoporous in present zeolite on acidity. The presence of mesoporous gives the catalyst higher selectivity for aromatics lower deactivation rate. Alkaline treatment reduces the ZSM-5 (Si/Al = 23.7) sites. Due to 0.2 and 0.3 alkaline higher selectivity for BTX parent ZSM-5 Improved diffusion due to the presence of mesoporous treatment 0.4 mol/l NaOH produced better aromatics selectivity 43.2% (Wei et al., 2015)

MTH process a nano ZSM-5 zeolite crystal size 100 nm was modified by internal desilication in NaOH solution. Na-ZSM-5 was alkali treated 0.1 M NaOH with ZSM-5 then the external surface area increased from 72 to 115 m²/g by internal desilication due to its effect acidity also increased at 673 K and WHSV = 4.7 h⁻¹ and 1Mpa and catalyst lifetime and production of hydrocarbon enhanced factor of 2.5⁷⁷

MTH process over Ga/ZSM-5 at 673 K when Ga content changed from 0.25-1wt% then BET surface area also changed from 361-363 m²/g then effects the product distributions (Li et al., 2016). Methanol to gasoline process sample pore of HZM-5 treatment different TPAOH nHZ, T24, T48, T72 the BET surface area changed 345, 373, 377, 373 at p/p₀=0.99 then amount product increased from 40% to 80%⁷⁸

Effect of surface modification

Modification on HZSM-5 samples with NaOH and oxalic acid to provide the formation of the mesoporous structure of the zeolite and obtained optional Si/Al ratio at 673K, 1 atm, and 1 h⁻¹. Zeolite active sites were modified with Co, Ni, and Fe to decrease the polyaromatic formation of the MTH process. Mesopores structure with a mean diameter of 4-6 nm positive effect. Zeolite treatment with oxalic acid results in decreasing of Si/Al ratio 0.76 to 0.41 the sample ZSM-5-Ni-0.001 M highest activity⁷⁹

MTH process over ZSM-5 and its bulk sample with Si/Al ratio 30 were desilicated an amount of 3g of NaZSM-5 suspended in 150 ml NaOH solution (0.2 mol/L) at 388K for 0.5 h prepared modified zeolite catalyst with Si/Al ratio 20, enhanced the selectivity of the product (Meng et al., 2020)

MTH process we selected two pairs of samples when silicon to aluminum ratio changed from ZSM-25/M vs Z-27/M (Si/Al 25 and 27) at 643K and WHSV= 20 h⁻¹ to Z-38/M vs Z-45M (Si/Al of 38 and 45) also

reaction condition but the yield of hydrocarbon improved from 30% to 40%⁸¹. MTG process surface Si/Al ratios of HZSM-5 changed 8.2, 13.2, 10.4 then conversion enhanced up to 100% and product yield enhanced up to 28%⁷⁸

MTG process over H-ZSM-5 treatment with 0.20 M NaOH the total conversion increased 3.3 factor and selectivity increased 1.7 factor⁸². MTH over Ga/ZSM-5 when Si/Al ratios changed from 12.5, 12.8, 13.1, 14.2 changed BET surface area 451-418 m²/g at 723K the scale varies 10 h to 40 h²⁴. MTH process over ZSM-5 Si/Al ratios changed from 39, 44, 47, 50 then its effect the BET surface area 95-84 m²/g at p/p₀=0.97 at 773 K. It also affects on conversion and selectivity of the product⁴¹

Methanol aromatization over Cr-Zn modified HZSM-5 catalyst at temperature 773K, and pressure 0.1 MPa and WHSV= 1.2 h⁻¹. HZSM-5 (HZ) zeolite co-modified with Zn and second promoter (Zr, Ce, Mo, and Cr) was synthesized and aromatization of methanol over modified HZ in a fixed bed reactor. Influence of methanol conversion to yield of benzene, toluene, xylene (BTX). Over the Cr, Zn modification HZ (CrZn/HZ) higher than that ZrZn/HZ, CeZn/HZ, MOZn/HZn species exist in two forms of HZ zeolite. One ZnO particle and one ZnOH, improved yield of (BTX). Cr species external surface promoted the dispersion of ZnO increased the amount of ZnO improved the yield of BTX⁷²

Surface modification due to metal doping

MTH over ZSM-5 structure can modify the catalyst morphology surface area can be decreased in the presence of second metal. Ni-ZSM-5 contain Ni loading 3-4% doped on ZSM-5 and Me-ZSM-5 contain Me loading 1.1-1.9% doped into ZSM-5 then Si/Al ratios changed from 35, 31, and 30. Fe-ZSM-5 by chemical vapor deposition (CVD). Fe 0.2% wt loading on ZSM-5 at 823K its effect the product distribution increased^{83,84}

Transformation of MTG range hydrocarbon using HZSM-5 catalysts impregnated with copper oxide. Cu/HZSM-5 catalyst T = 673 K, P= 1 atm, WHSV= 4 h⁻¹ copper oxide loading over HZSM-5 (Si/Al = 45) catalyst range 0–9 wt %. A higher yield of gasoline range hydrocarbon (C₅-C₆) was obtained increased 5wt% CuO over HZSM-5. Lower coke deposition over HZSM-5 catalyst due to CuO impregnated on HZSM-5 catalyst then increased active sites for loading for MTO process. The optional loading 7 wt% HZSM-5 deactivation of HZSM-5 with increased CuO loading and coke deposition in the pores of the catalyst due to coverage active sites. Improved light alkane selectivity 18% hydrocarbon 42.84% (Zaidi et al., 2008)

MTH process over Ga/ZSM-5 gives better result compared to ZSM-5 it was found that Ga content outer regime of ZSM-5 is 2%, 2.5%. Ga/ZSM-5-0.25, Ga/ZSM-5-0.5, Ga/ZSM-5-1 these content effects the conversion of methanol increased 60%, 70%, 90% and affects the selectivity 20%, 40%, 60% at 673 K. Methanol to olefins process over P/ZSM-5 content of phosphorous doped over ZSM-5 1P-Z, 3P-Z, W5P-Z then affects the conversion 97%-100% and selectivity enhanced 10% to 44% at 723 K and WHSV = 1 h⁻¹ (Li et al., 2016; Vu et al., 2010)

MTH process Pd doped into ZSM-5 (MFI TPA 20). Pd content 0.44%, 0.28%, 0.37% add into ZSM-5 then effects the Si/Al ratio increased 20, 23, 37, 38 and effects its effect BET surface area at 4.5 bar and 673K then conversion increased up to 100% and yield of hydrocarbon increased up to 90% Ga modified nano-HZSM-5 zeolites content Ga applied methanol to aromatics process it strongly increased selectivity of product and decreased catalyst lifetime. Ga doped on HZSM-5 and loading 2% to 4%. Changed conversion from 70% to 100% and enhanced selectivity 20% to 40% at 723 K (Dai et al., 2018; Meng et al., 2020)

Catalytic conversion of MTG at T = 673 K, P = 1 atm, WHSV = 1-9 h⁻¹. When CuO and ZnO are doped into HZSM-5. Catalyst is mainly deactivation due to Coke. The addition of ZnO over CuO/HZSM-5 reduces the coke content without affecting product yield and selectivity. ZnO/HZSM-5 catalyst coke

formation was more reduced compared to a CuO/ HZSM-5 catalyst. ZnO/CuO/HZSM-5 also enhanced aromatics yield up to 69% (Zaidi et al., 2005)

Methanol to hydrocarbon process effects of zinc incorporation on hierarchical ZSM-11 catalyst the effects of two methods (direct synthesis and impregnation) of zinc incorporation on. Thus, the yield of propene and butene was enhanced through the direct synthesis method (2 % ZnZ11-C, 4 % ZnZ11-C), and the sample 4 % ZnZ11-C displayed a fast deactivation. (Xiaojing et al., 2015). MTG process over modified HZSM-5 catalysts at 673 K and 1 atm and 4 h⁻¹. Oxalic acid 0.5%, ZnO/7 wt%, doped into CuO/ZSM-5 by wet impregnation technique then its effect on conversion up to 99%, and selectivity of olefins up to 70 % and yields of hydrocarbon up to 40% (Zaidi et al., 2010)

Synthesis of modified catalyst and stabilization of CuO/NH₄-ZSM-5 for conversion MTG process. CuO/NH₄ZSM-5 (3, 5, 7, and 9 wt%) catalyst prepared by SONO chemistry methods. Copper oxide booster for NH₄-ZSM-5 catalyst properties at 673 K, 1 atm, and 5 h⁻¹. THE effect of CuO loading on NH₄-ZSM-5 support convert to MTG process analysis shows specific surface and volume of pores decreases. Fed 100% methanol and 7 wt% catalyst CuO/ NH₄-ZSM-5 better rate of aromatics enhanced up to 44% and olefins selectivity enhanced up to 50.4 %⁶³

Gd/HZSM-5 catalyst used for conversion of MTHs. Gd loading over ZSM-5 at 673 K, 1 bar, and 4.75 h⁻¹. 1wt% (1 GdHZ), 5 at % (5 Gd HZ).10 wt% (10 GdHZ) prepared incipient wet impregnation method. Gd modified HZSM-5 catalyst (GdHZ_IE) prepared ion exchange. Gd content catalyst uniformly dispersed into nano-sized particles thin films of Gd₂O₃ directly influenced crystallinity, surface area pore volume acid-base property reactivity of catalytic. GdHZ_IE catalyst possesses strong lewis acid sites then enhances higher selectivity³⁸

MTO reaction over ZSM-5 catalyst when Cr, Cu, Ga, La, Mg, Y, and Zn doped on 3D-printed ZSM-5 zeolite by direct addition of metal nitrate precursors into the 3D printing paste thus the metal doping procedure was integrated with the 3D printing fabrication. 10 wt% Mg exhibited the favorable effect on the light olefins production and showed ethylene and propylene selectivity of 24% and 33%, respectively with methanol conversion approaching 95% at 673 K¹⁷

Effect of process variables

Effect of temperature

MTOs process when temperature increased 623 K to 673 K then alkane content increased 43% to 80% over Ir/ZSM-5 catalyst surface at 40 min (Lou et al., 2017). Methanol to olefins process over H-SAPO-34 catalyst surface the temperature changed from 500 K to 773 K then olefins selectivity changed 5% to 45 %.⁸⁷

MTA process over Na/ZSM-5 catalyst surface then aromatic product selectivity changed from 8% to 38% at the WHSV = 1 h⁻¹ temperature changed from 553 K to 573 K then conversion of methanol 50% to 70% at 0.5 Mpa. (Adebajo et al., 2003; Cheng et al., 2019; Liu et al., 2020; Patel et al., 2020)

MTH process over Ni/ZSM-5 temperature enhanced 583 K to 833 K then hydrocarbon selectivity enhanced 30% to 38% the conversion changed 10-90%^{79,91,92}

Effect of pressure

MTO Selectivity of product vs conversion on HZSM-5 at 513 K effected by pressure increased from 1 to 5 bars then product distribution also enhanced. MTO process when pressure changed from 0.2-0.8 Mpa then the distribution of olefins 2.8% to 31% at WHSV 2 h⁻¹ and temperature 673 K. (Reviere et al., 2020).

MTA process when pressure changed from 0.2-1 MPa then reactant quantity adsorbed on HZSM-5 catalyst surface was 0-350 cm³/g the temperature varies 473 K to 873 K and methanol conversion changed up to

99% and selectivity changed up to 10 to 40%. MTA process when pressure changed from 10 bar to 20 bar then benzene selectivity changed up to 90 % .^{93,94}

MTHs process over ZSM-5 catalyst surface when temperature was increased to 623-673 K at 0.2 h⁻¹ due to this selectivity of hydrocarbons also effected ⁹¹. Methanol to hydrocarbons the temperature changed from 473 K to 1273 K at then selectivity changed of olefins 10 to 40% and for aromatics changed up to 90% at 1 bar ⁷²

Effect of WHSV-

MTH process the methanol conversion increased from 70% to 100% at 19.8 g_{cat}/h/mol at time stream 5 to 400 min⁻¹ due to this the yield of hexane increased from 30% to 45% at 5 KPa and 923 K. When GHSV changes from 1000 to 6000 h⁻¹ then conversion of methanol changed from 5-50% in methanol to hydrocarbon process at 723 K and time changed from 4 min to 36 min (Rubio et al., 2019; Ji et al., 2017; Williams et al., 1990).

MTH process over ZSM-5 when time scale changed from 10 h to 40 h then conversion changed 20% to 99% and selectivity changed for olefins from 10% to 40% and aromatics 5% to 50% at the WHSV = 6 h⁻¹ and temperature at 673 K. The conversion of methanol was shows 89% and selectivity of hydrocarbon changed from 10% to 80% time scale changed from 40 h to 160 h.

MTOs process over ZSM-5, the conversion enhanced 90% to 100% when time scale increased 2 to 24 h then it affects the selectivity of olefins 20% to 32% at 723 K and WHSV was 1.12 h⁻¹. When conversion enhanced 55% to 100% over HZSM-5 catalytic surface olefins selectivity enhanced on 5-78% at time stream varies on scale 10-100 h at 733 K, WHSV = 1 h⁻¹. Some olefins selectivity increased from 10-30% at 99% conversion of methanol and the time scale varies 50-250 min at the 873 K, and WHSV = 4 h⁻¹. MTH process at 723 K the time scale goes 100-600 min then conversion increased 60 to 100% over SAPO-34 catalyst the WHSV = 5 h⁻¹ (Ahmadpour et al., 2015; Saenluang et al., 2021.; Y. Wang et al., 2019)

MTOs process changed in time scale 5 h to 25 h then conversion also changed 10% to 95% over HZSM-5 catalyst surface at 723 K and selectivity changed 19% to 38% of hydrocarbons. Methanol to propylene process WHSV changed from 2.51 to 8.17 h⁻¹ at 673 K over Mn/ZSM-5 due to this selectivity enhanced from to 30% to 45%. MTOs process at WHSV changed 0.6-2.4 h⁻¹ then conversion was 100% and olefins was selectivity 90% and Olefin's yield changed from 10%-25% over Ag/ZSM-5 and time stream changed from 2 min to 12 min at 673 K and 1 atm (Hadi et al., 2014; Kedia et al., 2016; Maria et al., 2018; Missengue et al., 2018).

MTA process over ZSM-5 the conversion of methanol enhanced 43% to 80% then selectivity of BTX 44% on the time varies 20-100 min⁻¹ at 1 atm product yields go up to 99% at 723K. MTA over Fe/ZSM-5 the space velocity changed 1-9 h⁻¹ then product distribution changed from 30% to 61% of BTX. Zeolite ZSM-12 treated on 0.2M NaOH at 658 K for 60 min enhanced the catalytic activity 10-fold then selectivity 51% to 67% of aromatics while conversion 15% to 98% (Akyalcin et al., 2019; Imyen et al., 2020; Li et al., 2018; Missengue et al., 2018; Ndebele et al., 2018).

MTG process over SAPO-34 catalyst at 644 K, 1 atm and LHSV 1-10 h⁻¹ and product yield increased 10 to 50%. When catalyst run time changed 2 to 12 h the conversion up to 99% and product yield increased 10 to 50% (Gogate et al., 2019; Zaidi et al., 2004).

Table: Literature overview for Methanol conversion to Hydrocarbon.**2.1 Table: Literature overview for Methanol conversion to Hydrocarbon.**

S. N	Process	Reaction conditions	Catalyst	Conversion	Yield	Selectivity	Reference
1.	MTG	T = 673 K, P=1atm, WHSV= 4 h ⁻¹	CuO/ZSM-5	99.3%	69.33%	75%	(Kianfar et al., 2020)
2.	MTG	T=663K, P=1 atm, WHSV=4.75 h ⁻¹	ZSM-5/11 Zn-Cu-ZSM-5 Ga-Ag-ZSM-5/11	99% 99.5% 100%	28.2% 24.09% 24.88%	28.05% 24.4% 24.88%	(Juybar et al., 2019)
3.	MTA	T=673K, P=1 atm, WHSV =1 h ⁻¹	Zn/ZSM-5-38	100%	73.33%	73%	(Xi et al., 2019)
4.	MTA	T=673K, P= 1 MPa, WHSV =1 h ⁻¹	Na/ZSM-5	99%	56%	57%	(Long et al., 2014)
5.	MTA	T=653K, P=0.5 MPa, WHSV =3.2 h ⁻¹	HZSM-5 P/HZSM-5	99% 100%	40.59% 60.2%	41% 60.2 %	(Niu et al., 2020)
6.	MTA	T= 673K, P= 1 bar, WHSV =3.1 h ⁻¹	Ga ₂ O ₃ /	100%	18.2%	18.2%	(Freeman et al., 2001)

		1	HZSM-5				
7.	MTA	T=673K, P=1 atm, WHSV = 3 h ⁻¹	Gd/ZSM-5	99%	49.56%	50%	(Kim et al., 2017)
8.	MTA	T= 725K, P=0.1 MPa, LHSV =1.2 h ⁻¹	CrZn/HZSM-5	100%	70%	70%	(Liu et al., 2018)
9.	MTG	T=673K, P= 1 MPa, WHSV = 4.74 h ⁻¹	HZSM-5	98%	39%	39.78%	(Shao et al., 2017)
10.	MTG	T=683K, P= 1 MPa, WHSV =4 h ⁻¹	ZSM-5	99%	55%	52%	(Lemraski et al., 2016)
11.	MTA	T=773K, P=1 atm, WHSV = 5 h ⁻¹	Ga/ZSM-5	100%	60%	60%	(Lai et al., 2016)
12.	MTA	T=753K, P= 4 MPa, WHSV = 3 h ⁻¹	Fe/ZSM-5	90%	50%	56%	(Xu et al., 2020)
13.	MTA	T=823K, P=1 atm, WHSV = 2.2 h ⁻¹	Ga/ZSM-5	95%	73%	77%	(Wan et al., 2016)
14.	MTH	T= 623K, P= 1atm, WHSV = 5 h ⁻¹	HZSM-5	90%	54%	60%	(Bleken et al., 2013)

15.	MTA	T=750K, P=1atm, LHSV = 2 h ⁻¹	Zn/ZSM-5	98%	43.12%	44%	(Olsbye et al., 2012)
16.	MTA	T=673K, P=1 atm, WHSV =8 h ⁻¹	ZSM-5	100%	42%	42%	(Bjørngen et al., 2009)
			Zn/ZSM-5	100%	67%	67%	
17.	MTA	T=723K, P= 1 bar, WHSV =4 h ⁻¹	Ga/ZSM-5	85%	56.61%	66.6%	(Dai et al., 2018)
16.	MTA	T=723K, P=5bar, WHSV =8 h ⁻¹	Zn/ZSM-5	99%	60%	60.6%	(Conte et al., 2012)
19.	MTA	T=673K, P=1 atm, WHSV = 34 h ⁻¹	Zn/ZSM-5	100%	97.3%	97%	(Sudiyarmanto et al., 2016)
20.	MTA	T=634 K, P= 1atm, WHSV = 5.53 h ⁻¹	Ga ₂ O ₃ /ZSM-5	99%	39%	40%	(Wang et al., 2015)
21.	MTG	T= 673K, P= 1 atm, WHSV = 5 h ⁻¹	ZSM-5	99%	40%	40.80%	(Zaidi et al., 2008)
			ZnO/CuO/ HZSM-5	99.5%	41.58%	42.84%	
22.	MTA	T=673 K, P= 1 atm, LHSV = 10 h ⁻¹	ZSM-5	98%	25.48%	26%	(Zaidi et al., 2014)
			ZnO/CuO/ HZSM-5	99%	44%	45%	

			HZSM-5				
23.	MTA	T = 673 K, P = 1 atm, WHSV = 0.129 h ⁻¹	ZSM-5 CuO/ HZSM-5	99% 99.5%	37% 41%	38% 42.18%	(Zaidi et al., 2005)
24.	MTH	T=643K, P= 1 bar, WHSV =20 h ⁻¹	HZSM-5	99.5%	32%	30%	(Sazama et al., 2011)
25.	MTA	T=643K, P=2 atm, WHSV = 4 h ⁻¹	Ga/ZSM-5	100%	55%	55%	(M. Li et al., 2016)
26.	MTA	T=723K, P=0.1 MPa, WHSV =1 h ⁻¹	Zn/ZSM-5	100%	75%	75%	(Ni et al., 2021)
27.	MTA	T=663K, P= 5 MPa, WHSV =3.2 h ⁻¹	ZSM-5 P/HZSM-5	99% 99.5%	23% 89%	23.8% 90%	(Niu et al., 2020)
28.	MTA	T=573K, P=1 atm, WHSV = 4 h ⁻¹	HZSM-5 Co/SBA-15/ZSM-5	100% 100%	55% 85%	55% 85%	(Chotiwan et al., 2019)
29.	MTG	T=673K, P=1 MPa, WHSV = 4 h ⁻¹	CuO/NH ₄ -ZSM-5	99%	50%	51%	(Kianfar et al., 2018)
30.	MTA	T= 723 K, P= 1 bar, WHSV = 2 h ⁻¹	Zn/HZSM-5	100%	84%	84%	(Zhang et al., 2019)

31.	MTA	T=673K, P=2 bar, WHSV = 6 h ⁻¹	H-SAPO-34	98%	62%	64%	(Chowdhury et al., 2018)
32.	MTA	T=773K, P=5 atm, WHSV = 2 h ⁻¹	ZSM-5	99%	50%	52%	(Yarulina et al., 2021)
33.	MTA	T=663K, P= 1 MPa, WHSV =8 h ⁻¹	ZSM-5 Zn/ZSM-5	99% 99.5%	24% 24%	25% 25%	(N. Li et al., 2018)
34.	MTA	T= 690K, P=1 atm, WHSV = 1-9 h ⁻¹	ZSM-5	90%	52.20%	58%	(Hindman et al.,2017)
35.	MTA	T= 573K, P= 1 bar, WHSV = 1 h ⁻¹	Fe-Ni/ZSM-5	88%	28.60%	24.60%	(S. Cheng et al., 2017)
36.	MTA	T=673K, P= 1 atm, WHSV = 1 h ⁻¹	ZSM-5	99%	42.57%	43%	(Wei et al., 2015)
37.	MTH	T=673K, P= 1atm, WHSV = 1 h ⁻¹	SSZ-13	95%	66%	70%	(Santilli et al., 1985)
38.	MTA	T=673K, P= 0.5 MPa, WHSV = 1 h ⁻¹	ZSM-11	99%	26.73%	27%	(S. Wei et al., 2020)
39.	MTA	T= 723 K, P= 5 MPa, WHSV = 25	ZSM-48	64.9%	48.5%	62.8%	(J. Zhang et al., 2019)

		h^{-1}					
40.	MTH	T=733K, P= 1 atm, WHSV = 0.3 h^{-1}	B-ZSM-5	99%	84%	85%	(Xu et al.,2013)
41.	MTA	T=673K, P=1 atm, WHSV = 2.5 h^{-1}	HZSM-5	99.99%	54.17%	55%	(Ndebele et al., 2018)
42.	MTA	T=673K, P=1 atm, WHSV = 1.3 h^{-1}	ZSM-5	100%	20%	20%	(Maria et al., 2018)
43.	MTA	T=623K, P=1 atm, WHSV = 5.56 h^{-1}	HZSM-5	92%	59.80%	65%	(Aramburo et al., 2013)
44.	MTA	T=673K, P=1 atm, WHSV = 5 h^{-1}	Zn/HZSM-5	99%	67.70%	68%	(G. Zhang et al., 2015)
45.	MTA	T=673K, P=10 bar, WHSV = 5 h^{-1}	Fe-ZSM-5	100%	80%	80%	(Lin et al., 2021)
46.	MTA	T=673 K, P= 1MPa, WHSV= 0.15 h^{-1}	H-ZSM-5	100%	80%	80%	(Z. Chen et al., 2018)
47.	MTA	T=633K, P= 20 bar, WHSV = 1 h^{-1}	ZSM-5	100%	42%	42%	(Wei et al., 2015)

2.2 Table: Literature overview for methanol conversion to olefins.

S.N.	Process	Reaction conditions	Catalyst	Conversion	Yield	Selectivity	Reference
1.	Methanol to olefins	T=678K, P=1 MPa, WHSV = 4.74 h ⁻¹	ZSM-5	100%	30%	30%	(Shao et al.,2019)
2.	Methanol to olefins	T=673K, P= 5 bar, WHSV =2 h ⁻¹	Ru/ZSM-5	99%	37%	38%	(Conte et al., 2012)
3.	Methanol to olefins	T=723K, P= 1 bar, WHSV =1.2 h ⁻¹	ZSM-5	98%	36.86%	37%	(Missengue et al., 2018)
4.	Methanol to olefins	T=643K, P= 0.5 MPa, WHSV =4 h ⁻¹	ZSM-5 HSAPO-34	97% 98%	87.30% 83.30%	90% 85%	(Tian et al., 2015)
5.	Methanol to olefins	T=623K, P= 1 MPa, WHSV = 7 h ⁻¹	HZSM-5	85%	34.85%	41%	(Bjørngen et al., 2008)
6.	Methanol to olefins	T=673K, P=1 atm, WHSV = 0.35 h ⁻¹	Mg/ZSM-5	95%	44.65%	33%	(Li et al., 2019)
7.	Methanol to olefins	T=923K, P=1 atm, WHSV =3.83 h ⁻¹	Zn/ZSM-5	90%	51.7%	46.73%	(Cheng et al., 2019)

8.	Methanol to olefins	T=733K, P= 0.1MPa, WHSV = 1 h ⁻¹	B/ZSM-5	99.8%	84.83%	85%	(Öu et al., 2013)
9.	Methanol to olefins	T=673K, P= 1 MPa, WHSV =2 h ⁻¹	HZSM-5	99%	79.20%	80%	(Di et al., 2013)
10.	Methanol to olefins	T=573 K, P= 1 bar, WHSV =6 h ⁻¹	ZSM-11	99%	11%	12%	(Meng et al., 2015)
11.	Methanol to olefins	T=663K, P=1 atm, WHSV = 2.6 h ⁻¹	ZSM-5	99%	54%	55%	(Rownaghi et al., 2011)
12.	Methanol to olefins	T=673K, P= 1 MPa, WHSV = 6 h ⁻¹	ZSM-5 Nano-ZSM-5	100% 100%	70% 70%	70% 70%	(Wei et al., 2015)
13.	Methanol to olefins	T=733K, P=1 bar, WHSV =1 h ⁻¹	Zn/ZSM-5	100%	43.65%	43.65%	(Ahmadpour et al., 2015)
14.	Methanol to olefins	T=573K, P= 1 MPa, WHSV = 1 h ⁻¹	P/ZSM-5	100%	57%	57%	(Vu et al., 2010)
15.	Methanol to olefins	T=653K, P= 1 atm, WHSV = 2 h ⁻¹	HZSM-5	99%	28.21%	28.5%	(He et al., 2013)
16.	Methanol to olefins	T=643K, P= 0.1MPa, WHSV =1 h ⁻¹	H-ZSM-5	99%	39.60%	40%	(Palumbo et al., 2008)
17.	Methanol to olefins	T=723K, P=1 MPa, WHSV = 8 h ⁻¹	Ni/HZSM-5	96%	37%	39%	(Liu et al., 2018)

18.	Methanol to olefins	T=673K, P= 1 MPa, WHSV = 2 h ⁻¹	HZSM-5	99.5%	30.84%	31%	(Di et al., 2013)
19.	Methanol to olefins	T= 573K, P= 1 atm, WHSV = 4 h ⁻¹	HZSM-5	99%	39.60%	40%	(Sassi et al., 2002)
20.	Methanol to olefins	T=673K, P=1 atm, WHSV = 2 h ⁻¹	ZSM-5 ZnO/CuO/HZSM-5	94.2% 94.2%	23% 37%	25% 40%	(Zaidi et al., 2010)
21.	Methanol to olefins	T=673K, P= 1 MPa, WHSV = 9.4 h ⁻¹	ZSM-5	100%	35%	33%	(Qi et al., 2017)
22.	Methanol to olefins	T= 673K, P=1 atm, WHSV = 1 h ⁻¹	Na/ZSM-5	100%	43.2%	43.2%	(Wei et al., 2015)
23.	Methanol to olefins	T=673K, P=1 atm, WHSV = 7 h ⁻¹	CuO/NH ₄ -ZSM-5	99.99%	48.98%	48.99%	(Kianfar et al., 2018)
24.	Methanol to olefins	T=673K, P=1 atm, WHSV = 6 h ⁻¹	Zn/ZSM-11	100%	64%	64%	(Meng et al., 2018)
25.	methanol to olefins	T=623K, P=1 bar, LHSV = 2 h ⁻¹	Fe/HZSM-5	99%	31.68%	32%	(Doluda et al., 2019)

26.	Methanol to olefins	T=643K, P=1 atm, LHSV =1 h ⁻¹	HZSM-5	100%	18%	18%	(Gogate et al., 2019)
27.	Methanol to olefins	T=723K, P= 1 atm, WHSV = 4 h ⁻¹	Cu/ZSM-5	99%	49.50%	50%	(Kedia et al., 2016)
28.	Methanol to olefins	T=623K, P=1 bar, WHSV =2 h ⁻¹	ZSM-23	100%	58.20%	60%	(Molino et al., 2017)
29.	Methanol to olefins	T=673K, P=1 bar, WHSV = 7 h ⁻¹	ZSM-5	99%	69.50%	70%	(Olsbye et al., 2012)
30.	Methanol to olefins	T=673K, P= 1atm, WHSV = 2 h ⁻¹	ZSM-5	99%	41.58%	42%	(Grahn et al., 2020)
31.	Methanol to olefins	T=663K, P=1 bar, LHSV = 6 h ⁻¹	SAPO-34	96%	73.72%	76%	(Bare et al., 2007)
32.	Methanol to olefins	T=673K, P= 1atm, WHSV = 1-7 h ⁻¹	SAPO-34	97%	36.26%	38%	(Hunger et al., 2001)

33.	Methanol to olefins	T=623K, P= 5 bar, WHSV = 3 h ⁻¹	ZSM-5	100%	67.7%	67.7%	(Keil et al., 1999)
-----	---------------------	--	-------	------	-------	-------	---------------------



34.	Methanol to olefins	T=643K, P= 2 atm, LHSV = 2.4 h ⁻¹	ZSM-5	98%	59.78%	61%	(Maria et al., 2018)
35.	Methanol to olefins	T=773K, P= 1 atm, WHSV = 1 h ⁻¹	HZSM-5	97%	37.83%	39%	(Hou et al., 2021)
36.	Methanol to olefins	T=643K, P= 1atm, WHSV = 8 h ⁻¹	HZSM-5	95%	43.25%	45%	(Bjørngen et al., 2008)
37.	Methanol to olefins	T=750K, P= 1-9bar, WHSV = 1-20 h ⁻¹	HZSM-5	90%	15%	17%	(Li et al., 2019)
38.	Methanol to olefins	T=753K, P= 1atm, WHSV = 2h ⁻¹	ZSM-5	100%	42%	42%	(Wang et al., 2019)
39.	Methanol to olefins	T=723K, P= 1 atm, WHSV = 4 h ⁻¹	H-SAPO-34	99%	41%	42%	(Cnudde et al., 2020)
40.	Methanol to olefins	T= 753K, P= 1 atm, WHSV = 0.9 h ⁻¹	H-[B]-HZSM-5	99%	80%	80%	(Maryam et al., 2020)
41.	Methanol to olefins	T= 733K, P=1 atm, WHSV = 2 h ⁻¹	B/ZSM-5	99%	81.52%	85%	(Sadeghpour et al., 2021)
42.	Methanol to olefins	T= 673K, P= 1 atm, WHSV = 5 h ⁻¹	SAPO-34/ ZSM-5	99.5%	84.86%	85%	(Zhou et al.,

							2021)
43.	Methanol to olefins	T=723K, P= 1atm, WHSV = 4 h ⁻¹	SAPO-34	100%	80%	80%.	(Yang et al., 2019)
44.	Methanol to olefins	T=723K, P= 1 atm, WHSV = 11 h ⁻¹	ZSM-5	100%	80%	80%	(Weissenberger et al., 2020)
45.	Methanol to olefins	T=623K, P= 1atm, LHSV = 1 h ⁻¹	H-ZSM-5	100%	65%	65%	(Hawkins et al., 2021)
46.	Methanol to olefins	T=673K, P= 1 atm, WHSV = h ⁻¹	ZrO ₂ /HZSM-5	100%	68%	68%	(Ticali et al., 2021)
47.	Methanol to olefins	T=753K, P=1 bar, WHSV = 3 h ⁻¹	H-[B]-ZSM-5	90%	68.40%	76%	(Juybar et al., 2019)
48.	Methanol to olefins	T=823K, P= 1atm, WHSV = 8 h ⁻¹	H-ZSM-5	100%	16%	16%	(Nikolopoulos et al., 2021)

Conclusion-

Methanol can be synthesized from different sources such as coal, CO₂, biomass, natural gas, and municipal waste. Information about the methanol-to-hydrocarbon (MTH) process over ZSM-5, ZSM-11, SAPO-34, SAPO-17, and SAPO-18 catalyst has been discussed. Also, the methanol-to-olefins (MTO) process over ZSM-5 and methanol-to-aromatics (MTA) over ZSM-5 and ZSM-11 are discussed. Modification with metals enhances the catalyst acidity. It was observed that after modification, the catalytic performance is increased and showed better conversion, selectivity/yield towards the selective product. The effects of various parameters such as surface morphology, temperature, pressure, WHSV, etc., are discussed, which give a good understanding of the catalytic activity, selectivity, and stability in the MTH, methanol-to-gasoline (MTG), MTO, MTA process.

ACKNOWLEDGMENT-

I thankful to the Department of Chemical Engineering, Aligarh Muslim University Aligarh-India, to support research work

REFERENCES-

- Ahmadpour, J., & Taghizadeh, M. (2015). Catalytic conversion of methanol to propylene over high-silica mesoporous ZSM-5 zeolites prepared by different combinations of mesogenous templates. *Journal of Natural Gas Science and Engineering*, 23, 184–194. <https://doi.org/10.1016/j.jngse.2015.01.035>
- Adebajo, M.O., Long, M.A., 2003. The contribution of the methanol-to-aromatics reaction to benzene methylation over ZSM-5 catalysts. *Catalysis Communications* 4, 71–76. [https://doi.org/10.1016/S1566-7367\(02\)00259-5](https://doi.org/10.1016/S1566-7367(02)00259-5)
- Akyalcin, S., Akyalcin, L., Bjørgen, M., 2019. Optimization of desilication parameters of low-silica ZSM-12 by Taguchi method. *Microporous and Mesoporous Materials* 273, 256–264. <https://doi.org/10.1016/j.micromeso.2018.07.014>
- AlMohamadi, H., AlMohamadi, H., 2020. Production of gasoline from municipal solid waste via steam gasification, methanol synthesis, and Methanol-to-Gasoline technologies: A techno-economic assessment. *AIMS Energy* 2021 1:50 9, 50–67. <https://doi.org/10.3934/ENERGY.2021004>
- Aramburo, L. R., Teketel, S., Svelle, S., Bare, S. R., Arstad, B., Zandbergen, H. W., Olsbye, U., de Groot, F. M. F., & Weckhuysen, B. M. (2013). Interplay between nanoscale reactivity and bulk performance of H-ZSM-5 catalysts during the methanol-to-hydrocarbons reaction. *Journal of Catalysis*, 307, 185–193. <https://doi.org/10.1016/j.jcat.2013.07.009>
- Arora, S. S., Shi, Z., & Bhan, A. (2019). Mechanistic Basis for Effects of High-Pressure H₂ Cofeeds on Methanol-to-Hydrocarbons Catalysis over Zeolites. *ACS Catalysis*, 9(7), 6407–6414. https://doi.org/10.1021/ACSCATAL.9B00969/SUPPL_FILE/CS9B00969_SI_001.PDF
- Bare, S. R. (2007). Methanol to Olefins (MTO): Development of a Commercial Catalytic Process. In *researchgate.net*. <https://www.researchgate.net/file.PostFileLoader.html?id=59d390c4217e20a314618292&assetKey=AS%3A545368456216576%401507037380361>
- Benito, P. L., Gayubo, A. G., Aguayo, A. T., Castilla, M., & Bilbao, J. (1996). Concentration-Dependent Kinetic Model for Catalyst Deactivation in the MTG Process. *Industrial and Engineering Chemistry Research*, 35(1), 81–89. <https://doi.org/10.1021/IE950124Y>

- Behrens, M., Studt, F., Kasatkin, I., Kühl, S., Hävecker, M., Abild-Pedersen, F., Zander, S., Girgsdies, F., Kurr, P., Kniep, B. L., Tovar, M., Fischer, R. W., Nørskov, J. K., & Schlögl, R. (2012). The active site of methanol synthesis over Cu/ZnO/Al₂O₃ industrial catalysts. *Science (New York, N.Y.)*, 336(6083), 893–897. <https://doi.org/10.1126/SCIENCE.1219831>
- Beyraghi, S., Rostamizadeh, M., & Alizadeh, R. (1996). Dual-templated synthesis of Si-rich [B]-ZSM-5 for high selective light olefins production from methanol. *Polyolefins Journal*, 0. <https://doi.org/10.22063/poj.2021.2852.1176>
- Bjørngen, M., Joensen, F., Lillerud, K. P., Olsbye, U., & Svelle, S. (2009). Themechanisms of ethene and propene formation from methanol over high silica H-ZSM-5 and H-beta. *Catalysis Today*, 142(1–2), 90–97. <https://doi.org/10.1016/j.cattod.2009.01.015>
- Bjørngen, M., Joensen, F., Spangsborg Holm, M., Olsbye, U., Lillerud, K. P., & Svelle, S. (2008). Methanol to gasoline over zeolite H-ZSM-5: Improved catalyst performance by treatment with NaOH. *Applied Catalysis A: General*, 345(1), 43–50. <https://doi.org/10.1016/j.apcata.2008.04.020>
- Bleken, F. L., Barbera, K., Bonino, F., Olsbye, U., Lillerud, K. P., Bordiga, S., Beato, P., Janssens, T. V. W., & Svelle, S. (2013). Catalyst deactivation by coke formation in microporous and desilicated zeolite H-ZSM-5 during the conversion of methanol to hydrocarbons. *Journal of Catalysis*, 307, 62–73. <https://doi.org/10.1016/j.jcat.2013.07.004>
- Chang, C. D. (1980). A kinetic model for methanol conversion to hydrocarbons. *Chemical Engineering Science*, 35(3), 619–622. [https://doi.org/10.1016/0009-2509\(80\)80011-X](https://doi.org/10.1016/0009-2509(80)80011-X)
- Chang, C. D., & Silvestri, A. J. (1977). The conversion of methanol and other O- compounds to hydrocarbons over zeolite catalysts. *Journal of Catalysis*, 47(2), 249–259. [https://doi.org/10.1016/0021-9517\(77\)90172-5](https://doi.org/10.1016/0021-9517(77)90172-5)
- Chen, N. Y., & Reagan, W. J. (1979). Evidence of autocatalysis in methanol to hydrocarbon reactions over zeolite catalysts. *Journal of Catalysis*, 59(1), 123–129. [https://doi.org/10.1016/S0021-9517\(79\)80050-0](https://doi.org/10.1016/S0021-9517(79)80050-0)
- Chen, Z., Ni, Y., Zhi, Y., Wen, F., Zhou, Z., Wei, Y., Zhu, W., & Liu, Z. (2018). Coupling of Methanol and Carbon Monoxide over H-ZSM-5 to Form Aromatics. *Angewandte Chemie - International Edition*, 57(38), 12549–12553. <https://doi.org/10.1002/anie.201807814>
- Cheng, Q. T., Shen, B. X., Sun, H., Zhao, J. G., & Liu, J. C. (2019). Methanol promoted naphtha catalytic pyrolysis to light olefins on Zn-modified high-silicon HZSM-5 zeolite catalysts. *RSC Advances*, 9(36), 20818–20828. <https://doi.org/10.1039/c9ra02793a>
- Cheng, S., Wei, L., Julson, J., Muthukumarappan, K., & Kharel, P. R. (2017). Upgrading pyrolysis bio-oil to hydrocarbon enriched biofuel over bifunctional Fe-Ni/HZSM-5 catalyst in supercritical methanol. *Fuel Processing Technology*, 167, 117–126. <https://doi.org/10.1016/j.fuproc.2017.06.032>
- Choe, J., Choe, C., Kim, T., Pak, Y., Han, C., & Yun, H. (2021). Novel kinetic modelling of methanol-to-gasoline (MTG) reaction on HZSM-5 catalyst: Product distribution. *Journal of the Indian Chemical Society*, 98(2), 100003. <https://doi.org/10.1016/J.JICS.2021.100003>
- Chotiwan, S., Somwongsa, P., Lao-Ubol, S., Lao-Auyporn, P., Attanatho, L., Laosombut, T., & Larpiattaworn, S. (2019). Two-step catalytic hydrogenation of methanol to hydrocarbons conversion. *Materials Today: Proceedings*, 17, 1362–1369. <https://doi.org/10.1016/j.matpr.2019.06.156>
- Chowdhury, A. D., Paioni, A. L., Houben, K., Whiting, G. T., Baldus, M., & Weckhuysen, B. M. (2018). Bridging the Gap between the Direct and Hydrocarbon Pool Mechanisms of the

- Methanol- to- Hydrocarbons Process. *Angewandte Chemie*, 130(27), 8227–8231.
<https://doi.org/10.1002/ange.201803279>
- Chun, S. W., & Montagna, A. A. (1973). *United States Patent Office* 288 ACD NUMBER REDUCTION OF HYDROCARBON FRACTIONS USING A SOLID CATALYST AND METHANOEL.
- Conte, M., Lopez-Sanchez, J. A., He, Q., Morgan, D. J., Ryabenkova, Y., Bartley, J. K., Carley, A. F., Taylor, S. H., Kiely, C. J., Khalid, K., & Hutchings, G. J. (2012). Modified zeolite ZSM-5 for the methanol to aromatics reaction. *Catalysis Science and Technology*, 2(1), 105–112.
<https://doi.org/10.1039/c1cy00299f>
- Cnudde, P., Demuynck, R., Vandenbrande, S., Waroquier, M., Sastre, G., & Speybroeck, V. van. (2020). Light Olefin Diffusion during the MTO Process on H-SAPO-34: A Complex Interplay of Molecular Factors. *Journal of the American Chemical Society*, 142(13), 6007–6017.
<https://doi.org/10.1021/JACS.9B10249>
- Dai, W., Yang, L., Wang, C., Wang, X., Wu, G., Guan, N., Obenaus, U., Hunger, M., & Li, L. (2018). Effect of *n*-Butanol Cofeeding on the Methanol to Aromatics Conversion over Ga-Modified Nano H-ZSM-5 and Its Mechanistic Interpretation. <https://doi.org/10.1021/acscatal.7b03457>
- Dang, S., Yang, H., Gao, P., Wang, H., Li, X., Wei, W., & Sun, Y. (2019). A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation. *Catalysis Today*, 330, 61–75. <https://doi.org/10.1016/J.CATTOD.2018.04.021>
- Di, Z., Yang, C., Jiao, X., Li, J., Wu, J., & Zhang, D. (2013). A ZSM-5/MCM-48 based catalyst for methanol to gasoline conversion. *Fuel*, 104, 878–881.
<https://doi.org/10.1016/j.fuel.2012.09.079>
- Dahl, I.M., Kolboe, S., 1996. On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34: 2. Isotopic Labeling Studies of the Co-reaction of Propene and Methanol. *Journal of Catalysis* 161, 304–309. <https://doi.org/10.1006/JCAT.1996.0188>
- Dessau, R.M., 1986. On the H-ZSM-5 catalyzed formation of ethylene from methanol or higher olefins. *Journal of Catalysis* 99, 111–116. [https://doi.org/10.1016/0021-9517\(86\)90204-6](https://doi.org/10.1016/0021-9517(86)90204-6)
- Doluda, V. Y., Matveeva, V. G., Lakina, N. v., Sulman, E. M., Sulman, M. G., & Brovko, R. v. (2019). Modified zeolites in methanol to hydrocarbons transformation. *Chemical Engineering Transactions*, 74, 499–504. <https://doi.org/10.3303/CET1974084>
- Djeugoue, M. A., Prakash, A. M., & Kevan, L. (2000). Catalytic study of methanol- to-olefins conversion in four small-pore silicoaluminophosphate molecular sieves: Influence of the structural type, nickel incorporation, nickel location, and nickel concentration. *Journal of Physical Chemistry B*, 104(27), 6452–6461.
<https://doi.org/10.1021/JP000504J>
- Ehsan Kianfar, Mahmoud Salimi, & Behnam Koohestani. (2020). Methanol to Gasoline Conversion over CuO / ZSM-5 Catalyst Synthesized and Influence of Water on Conversion. *Fine Chemical Engineering*, 74–81. <https://doi.org/10.37256/fce.122020499>
- Freeman, D., Wells, R. P. K., & Hutchings, G. J. (2001). Methanol to hydrocarbons: Enhanced aromatic formation using a composite Ga₂O₃-H-ZSM-5 catalyst. *Chemical Communications*, 1(18), 1754–1755.
<https://doi.org/10.1039/b104844a>
- Gogate, M. R. (2019). Methanol-to-olefins process technology: current status and future prospects. In *Petroleum Science and Technology* (Vol. 37, Issue 5, pp. 559–565). Taylor and

Francis Inc.

<https://doi.org/10.1080/10916466.2018.1555589>

- Grahn, M., Faisal, A., Öhrman, O. G. W., Zhou, M., Signorile, M., Crocellà, V., Nabavi, M. S., & Hedlund, J. (2020). Small ZSM-5 crystals with low defect density as an effective catalyst for conversion of methanol to hydrocarbons. *Catalysis Today*, 345, 136–146. <https://doi.org/10.1016/j.cattod.2019.09.023>
- Hawkins, A. P., Zachariou, A., Parker, S. F., Collier, P., Howe, R. F., & Lennon, D. (2021). Studies of propene conversion over H-ZSM-5 demonstrate the importance of propene as an intermediate in methanol-to-hydrocarbons chemistry. *Catalysis Science and Technology*, 11(8), 2924–2938. <https://doi.org/10.1039/d1cy00048a>
- He, Y., Liu, M., Dai, C., Xu, S., Wei, Y., Liu, Z., & Guo, X. (2013). Modification of nanocrystalline HZSM-5 zeolite with tetrapropylammonium hydroxide and its catalytic performance in methanol to gasoline reaction. *CuihuaXuebao/Chinese Journal of Catalysis*, 34(6), 1148–1158. [https://doi.org/10.1016/S1872-2067\(12\)60579-8](https://doi.org/10.1016/S1872-2067(12)60579-8)
- Hindman, M. (n.d.). *Advances in the Conversion of Methanol to Gasoline*.
- Hou, Y., Li, X., Sun, M., Li, C., Bakhtiar, S. ul H., Lei, K., Yu, S., Wang, Z., Hu, Z., Chen, L., & Su, B. L. (2021). The effect of hierarchical single-crystal ZSM-5 zeolites with different Si/Al ratios on its pore structure and catalytic performance. *Frontiers of Chemical Science and Engineering*, 15(2), 269–278. <https://doi.org/10.1007/s11705-020-1948-3>
- Hunger, M., Seiler, M., & Buchholz, A. (2001). In situ MAS NMR spectroscopic investigation of the conversion of methanol to olefins on silicoaluminophosphates SAPO-34 and SAPO-18 under continuous flow conditions. *Catalysis Letters*, 74(1–2), 61–68. <https://doi.org/10.1023/A:1016687014695>
- Hwang, A., & Bhan, A. (2019). Deactivation of Zeolites and Zeotypes in Methanol- to-Hydrocarbons Catalysis: Mechanisms and Circumvention. *Accounts of Chemical Research*. <https://doi.org/10.1021/acs.accounts.9b00204>
- Jiang, X., Nie, X., Guo, X., Song, C., & Chen, J. G. (2020). Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chemical Reviews* 120(15), 7984–8034. <https://doi.org/10.1021/ACS.CHEMREV.9B00723>
- J.P. Berg, van den. (1981). *The conversion of methanol to gasoline on zeolite H-ZSM-5 : a mechanistic study*. <https://doi.org/10.6100/IR30334>
- Jadhav, S. G., Vaidya, P. D., Bhanage, B. M., & Joshi, J. B. (2014). Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies. *Chemical Engineering Research and Design*, 92(11), 2557–2567. <https://doi.org/10.1016/J.CHERD.2014.03.005>
- Juybar, M., Khorrami, K., & Bagheri Garmarudi, A. (2039). Conversion of methanol to aromatics over ZSM-5/11 intergrowth Zeolites and bimetallic Zn-Cu-ZSM- 5/11 and Ga-Ag-ZSM-5/11 catalysts prepared with direct synthesis method. *Journal of Chemical Sciences*. <https://doi.org/10.1007/s12039-019-1684-8S>
- Kedia, A. O., & Zaidi, H. A. (2016). CONVERSION OF METHANOL TO HYDROCARBONS OVER METAL MODIFIED ZSM-5 CATALYST. *International Journal of Advanced Research*, 4(10), 917–923. <https://doi.org/10.21474/ijar01/1877>
- Keil, F. J. (1999). Methanol-to-hydrocarbons: Process technology. *Microporous and Mesoporous Materials*, 29(1–2), 49–66. [https://doi.org/10.1016/S1387-1811\(98\)00320-5](https://doi.org/10.1016/S1387-1811(98)00320-5)

- Kuld, S., Thorhauge, M., Falsig, H., Elkjær, C. F., Helveg, S., Chorkendorff, I., & Sehested, J. (2016). Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science*, 352(6288), 969–974. https://doi.org/10.1126/SCIENCE.AAF0718/SUPPL_FILE/KULD-SM.PDF
- Kianfar, E., Salimi, M., Pirouzfard, V., & Koohestani, B. (2018). Synthesis of modified catalyst and stabilization of CuO/NH₄-ZSM-5 for conversion of methanol to gasoline. *International Journal of Applied Ceramic Technology*, 15(3), 734–741. <https://doi.org/10.1111/ijac.12830>
- Kim, S., Kim, Y. T., Zhang, C., Kwak, G., & Jun, K. W. (2017). Effect of Reaction Conditions on the Catalytic Dehydration of Methanol to Dimethyl Ether Over a K-modified HZSM-5 Catalyst. *Catalysis Letters*, 147(3), 792–801. <https://doi.org/10.1007/s10562-017-1981-0>
- Kokotailo, G. T., Lawton, S. L., Olson, D. H., & Meier, W. M. (1978). Structure of synthetic zeolite ZSM-5. *Nature*, 272(5652), 437–438. <https://doi.org/10.1038/272437a0>
- Lai, P. C., Chen, C. H., Hsu, H. Y., Lee, C. H., & Lin, Y. C. (2016). Methanol aromatization over Ga-doped desilicated HZSM-5. *RSC Advances*, 6(71), 67361–67371. <https://doi.org/10.1039/c6ra16052b>
- Lemraski, A. S., Behbahani, R. M., Ghavipour, M., & Hashemi Shahraki, B. (2016). Study on product distribution and catalytic performance of ZSM-5 in methanol conversion to gasoline-range hydrocarbons (MTHC). *Petroleum Science and Technology*, 34(15), 1323–1328. <https://doi.org/10.1080/10916466.2016.1200081>
- Li, M., Zhou, Y., Oduro, I. N., & Fang, Y. (2016). Comparative study on the catalytic conversion of methanol and propanal over Ga/ZSM-5. *Fuel*, 168, 68–75. <https://doi.org/10.1016/j.fuel.2015.11.076>
- Li, N., Meng, C., & Liu, D. (2018). Deactivation kinetics with activity coefficient of the methanol to aromatics process over modified ZSM-5. *Fuel*, 233, 283–290. <https://doi.org/10.1016/j.fuel.2018.06.044>
- Li, X., Rezaei, F., & Rownaghi, A. A. (2019). Methanol-to-olefin conversion on 3D-printed ZSM-5 monolith catalysts: Effects of metal doping, mesoporosity and acid strength. *Microporous and Mesoporous Materials*, 276, 1–12. <https://doi.org/10.1016/j.micromeso.2018.09.016>
- Lin, W. C., Wu, S., Li, G., Ho, P. L., Ye, Y., Zhao, P., Day, S., Tang, C., Chen, W., Zheng, A., Lo, B. T. W., & Edman Tsang, S. C. (2021). Cooperative catalytically active sites for methanol activation by single metal ion-doped H-ZSM-5. *Chemical Science*, 12(1), 210–219. <https://doi.org/10.1039/d0sc04058d>
- Liu, B., Lu, S., Liu, E., Hu, X., & Fan, J. (2018). Methanol aromatization over CrZn-modified HZSM-5 catalysts. *Korean Journal of Chemical Engineering*, 35(4), 867–874. <https://doi.org/10.1007/s11814-017-0345-1>
- Long, H., Jin, F., Xiong, G., & Wang, X. (2014). Effect of lanthanum and phosphorus on the aromatization activity of Zn/ZSM-5 in FCC gasoline upgrading. *Microporous and Mesoporous Materials*, 198, 29–34. <https://doi.org/10.1016/j.micromeso.2014.07.016>
- Maria, G. (2018). *From Residual Biomass and Inferior Quality Coal to the Synthesis of Methanol and then to Hydrocarbons and Gasoline – A Romanian Project of High Success*.
- Meng, L., Zhu, X., Wannapakdee, W., Pestman, R., Goesten, M. G., Gao, L., van Hoof, A. J. F., & Hensen, E. J. M. (2018). A dual-templating synthesis strategy to hierarchical ZSM-5 zeolites as efficient catalysts for the methanol-to-hydrocarbons reaction. *Journal of Catalysis*, 361, 135–142. <https://doi.org/10.1016/j.jcat.2018.02.032>

- Meng, X., Chen, C., Liu, J., Zhang, Q., Li, C., & Cui, Q. (2016). Effects of zinc incorporation on hierarchical ZSM-11 catalyst for methanol conversion. *Applied Petrochemical Research*, 6(1), 41–47. <https://doi.org/10.1007/s13203-015-0120-3>
- Missengue, R. N. M., Losch, P., Musyoka, N. M., Louis, B., Pale, P., & Petrik, L. F. (2018). Conversion of South African coal fly ash into high-purity ZSM-5 zeolite without additional source of silica or alumina and its application as a methanol-to-olefins catalyst. *Catalysts*, 8(4). <https://doi.org/10.3390/catal8040124>
- Molino, A., Łukaszuk, K. A., Rojo-Gama, D., Lillerud, K. P., Olsbye, U., Bordiga, S., Svelle, S., & Beato, P. (2017). Conversion of methanol to hydrocarbons over zeolite ZSM-23 (MTT): Exceptional effects of particle size on catalyst lifetime. *Chemical Communications*, 53(51), 6816–6819. <https://doi.org/10.1039/c6cc10118f>
- Ndebele, M. S., & Isa, Y. M. (2018). Comparative performance of ZSM-5 and activated carbon supports in alcohol conversion over Fe, Zn and Ni based catalysts. In *International Journal of Applied Engineering Research* (Vol. 13). <http://www.ripublication.com>
- Ni, Y., Zhu, W., & Liu, Z. (2021). Formaldehyde intermediate participating in the conversion of methanol to aromatics over zinc modified H-ZSM-5. *Journal of Energy Chemistry*, 54, 174–178. <https://doi.org/10.1016/j.jechem.2020.05.063>
- Nikolopoulos, N., Geitenbeek, R. G., Whiting, G. T., & Weckhuysen, B. M. (2021). Unravelling the effect of impurities on the methanol-to-olefins process in waste-derived zeolites ZSM-5. *Journal of Catalysis*, 396, 136–147. <https://doi.org/10.1016/j.jcat.2021.02.015>
- Niu, X., Wang, K., Bai, Y., Du, Y. E., Chen, Y., Dong, M., & Fan, W. (2020). Selective formation of para-xylene by methanol aromatization over phosphorous modified ZSM-5 zeolites. *Catalysts*, 10(5). <https://doi.org/10.3390/catal10050484>
- Olsbye, U., Svelle, S., Bjrgen, M., Beato, P., Janssens, T. V. W., Joensen, F., Bordiga, S., & Lillerud, K. P. (2012). Conversion of methanol to hydrocarbons: How zeolite cavity and pore size controls product selectivity. In *Angewandte Chemie - International Edition* (Vol. 51, Issue 24, pp. 5810–5831). John Wiley & Sons, Ltd. <https://doi.org/10.1002/anie.201103657>
- Olson, D. H., Haag, W. O., & Lago, R. M. (1980). Chemical and physical properties of the ZSM-5 substitutional series. *Journal of Catalysis*, 61(2), 390–396. [https://doi.org/10.1016/0021-9517\(80\)90386-3](https://doi.org/10.1016/0021-9517(80)90386-3)
- Ōu, A., Ma, H., Zhang, H., & Fang, D. (2013). Effect of boron on ZSM-5 catalyst for methanol to propylene conversion. *Polish Journal of Chemical Technology*, 15(4), 95–101. <https://doi.org/10.2478/pjct-2013-0075>
- Palumbo, L., Bonino, F., Beato, P., Bjrgen, M., Zecchina, A., & Bordiga, S. (2008). Conversion of methanol to hydrocarbons: Spectroscopic characterization of carbonaceous species formed over H-ZSM-5. *Journal of Physical Chemistry C*, 112(26), 9710–9716. <https://doi.org/10.1021/jp800762v>
- Pearson, D. E., & Primary Examiner-Herbert Dalsimer, L. (1975). *HYDROCARBONS FROM METHANOL AND PHOSPHORUS PENTOXIDE PROCESS FOR PREPARING " " " Attorney, Agent, or Firm-Kane, Sullivan and Kurucz [57]*.
- Pinilla-Herrero, I., Borfecchia, E., Cordero-Lanzac, T., Mentzel, U. v., Joensen, F., Lomachenko, K. A., Bordiga, S., Olsbye, U., Beato, P., & Svelle, S. (2021). Finding the active species: The

conversion of methanol to aromatics over Zn- ZSM-5/alumina shaped catalysts. *Journal of Catalysis*, 394, 416–428. <https://doi.org/10.1016/j.jcat.2020.10.024>

Pinto, A. (1980). *Methanol synthesis process*.

Qi, R., Fu, T., Wan, W., & Li, Z. (2017). Pore fabrication of nano-ZSM-5 zeolite by internal desilication and its influence on the methanol to hydrocarbon reaction. *Fuel Processing Technology*, 155, 191, 199. <https://doi.org/10.1016/j.fuproc.2016.05.046>

Rownaghi, A. A., & Hedlund, J. (2011). Methanol to gasoline-range hydrocarbons: Influence of nanocrystal size and mesoporosity on catalytic performance and product distribution of ZSM-5. *Industrial and Engineering Chemistry Research*, 50(21), 11872–11878. <https://doi.org/10.1021/ie201549j>

Ruiz Esquiús, J., Bahruji, H., Bowker, M., & Hutchings, G. J. (2021). Identification of C₂–C₅ products from CO₂ hydrogenation over PdZn/TiO₂–ZSM-5 hybrid catalysts. *Faraday Discussions*. <https://doi.org/10.1039/d0fd00135j>

Sadeghpour, P., Haghghi, M., & Ebrahimi, A. (2021). Ultrasound-assisted rapid hydrothermal design of efficient nanostructured MFI-Type aluminosilicate catalyst for methanol to propylene reaction. *Ultrasonics Sonochemistry*, 72, 105416. <https://doi.org/10.1016/j.ultsonch.2020.105416>

Santilli, D. S., & Zones, S. I. (1985). *Selective conversion of methanol to low molecular weight olefins over high silica SSZ-13 zeolite*.

Sassi, A., Wildman, M. A., & Haw, J. F. (2002). Reactions of butylbenzene isomers on zeolite Hbeta: Methanol-to-olefins hydrocarbon pool chemistry and secondary reactions of olefins. *Journal of Physical Chemistry B*, 106(34), 8768–8773. <https://doi.org/10.1021/jp020811k>

Sedran, U., Mahay, A., & de Lasa, H. I. (1990). Modelling methanol conversion to hydrocarbons: Alternative kinetic models. *The Chemical Engineering Journal*, 45(1), 33–42. [https://doi.org/10.1016/0300-9467\(90\)80023-6](https://doi.org/10.1016/0300-9467(90)80023-6)

Sazama, P., Wichterlova, B., Dedecek, J., Tvaruzkova, Z., Musilova, Z., Palumbo, L., Sklenak, S., & Gonsiorova, O. (2011). FTIR and ²⁷Al MAS NMR analysis of the effect of framework Al- and Si-defects in micro- and micro-mesoporous H-ZSM-5 on conversion of methanol to hydrocarbons. *Microporous and Mesoporous Materials*, 143(1), 87–96. <https://doi.org/10.1016/j.micromeso.2011.02.013>

Schipper, P. H., & Krambeck, F. J. (1986). A reactor design simulation with reversible and irreversible catalyst deactivation. *Chemical Engineering Science*, 41(4), 1013–1019. [https://doi.org/10.1016/0009-2509\(86\)87187-1](https://doi.org/10.1016/0009-2509(86)87187-1)

Shao, J., Fu, T. J., Chang, J. W., Wan, W. L., Qi, R. Y., & Li, Z. (2017). Effect of ZSM-5 crystal size on its catalytic properties for conversion of methanol to gasoline. *Ranliao Huaxue Xuebao / Journal of Fuel Chemistry and Technology*, 45(1), 75–83. [https://doi.org/10.1016/s1872-5813\(17\)30009-9](https://doi.org/10.1016/s1872-5813(17)30009-9)

Sudiyarmanto, S., Kristiani, A., Luthfiana, N., Andreas, A., & Abimanyu, H. (2016). Catalytic conversion of ethanol to aromatic compounds using metal/zeolite catalysts. *AIP Conference Proceedings*, 1755(1), 80007. <https://doi.org/10.1063/1.4958515>

Tian, P., Wei, Y., Ye, M., & Liu, Z. (2015). Methanol to olefins (MTO): From fundamentals to commercialization. In *ACS Catalysis* (Vol. 5, Issue 3, pp. 1922–1938). American Chemical Society. <https://doi.org/10.1021/acscatal.5b00007>

- Ticali, P., Salusso, D., Ahmad, R., Ahoba-Sam, C., Ramirez, A., Shterk, G., Lomachenko, K. A., Borfecchia, E., Morandi, S., Cavallo, L., Gascon, J., Bordiga, S., & Olsbye, U. (2021). CO₂hydrogenation to methanol and hydrocarbons over bifunctional Zn-doped ZrO₂/zeolite catalysts. *Catalysis Science and Technology*, 11(4), 1249–1268. <https://doi.org/10.1039/d0cy01550d>
- Tuo, J., Fan, S., Gao, X., Zhao, T.-S., Lv, J., Li, H., Yang, N., Cheng, S., & Zhao, T. (2021). *One-pot synthesis of [Mn,H]ZSM-5 and the role of Mn in methanol-to-propylene reaction The Key R & D plan (East-West Cooperation) of Ningxia and the First-rate Discipline Construction Project of Ningxia View project One-pot synthesis of [Mn,H]ZSM-5 and the role of Mn in methanol-to-propylene reaction*. <https://doi.org/10.1016/j.fuel.2021.121995>
- van Vu, D., Hirota, Y., Nishiyama, N., Egashira, Y., & Ueyama, K. (2010). High propylene selectivity in methanol-to-olefin reaction over H-ZSM-5 catalyst treated with phosphoric acid. *Journal of the Japan Petroleum Institute*, 53(4), 232–238. <https://doi.org/10.1627/jpi.53.232>
- Vora, B. v., Marker, T. L., Barger, P. T., Nilsen, H. R., Kvisle, S., & Fuglerud, T. (1997). Economic route for natural gas conversion to ethylene and propylene. *Studies in Surface Science and Catalysis*, 107, 87–98. [https://doi.org/10.1016/S0167-2991\(97\)80321-7](https://doi.org/10.1016/S0167-2991(97)80321-7)
- Wan, H., & Chitta, P. (2016). Catalytic conversion of propane to BTX over Ga, Zn, Mo, and Re impregnated ZSM-5 catalysts. *Journal of Analytical and Applied Pyrolysis*, 121, 369–375. <https://doi.org/10.1016/j.jaap.2016.08.018>
- Wang, X., Gao, X., Dong, M., Zhao, H., & Huang, W. (2015). Production of gasoline range hydrocarbons from methanol on hierarchical ZSM-5 and Zn/ZSM-5 catalyst prepared with soft second template. *Journal of Energy Chemistry*, 24(4), 490–496. <https://doi.org/10.1016/j.jechem.2015.06.009>
- Wang, L., Qi, J., Jiao, H., An, L., Guan, C., Yong, X., Jin, Z., Zhang, A., & Liu, D. (2019). The guiding role of pre-coking on the coke deposition over ZSM-5 in methanol to propylene. *Royal Society Open Science*, 6(9). <https://doi.org/10.1098/RSOS.190218>
- Wei, S., Xu, Y., Jin, Z., & Zhu, X. (2020). Co-conversion of methanol and n-hexane into aromatics using intergrown ZSM-5/ZSM-11 as a catalyst. *Frontiers of Chemical Science and Engineering*, 14(5), 783–792. <https://doi.org/10.1007/s11705-019-1868-2>
- Wei, Z., Xia, T., Liu, M., Cao, Q., Xu, Y., Zhu, K., & Zhu, X. (2015a). Alkaline modification of ZSM-5 catalysts for methanol aromatization: The effect of the alkaline concentration. *Frontiers of Chemical Science and Engineering*, 9(4), 450–460. <https://doi.org/10.1007/s11705-015-1542-2>
- Wei, Z., Xia, T., Liu, M., Cao, Q., Xu, Y., Zhu, K., & Zhu, X. (2015b). Alkaline modification of ZSM-5 catalysts for methanol aromatization: The effect of the alkaline concentration. *Frontiers of Chemical Science and Engineering*, 9(4), 450–460. <https://doi.org/10.1007/s11705-015-1542-2>
- Weissenberger, T., Machoke, A. G. F., Bauer, J., Dotzel, R., Casci, J. L., Hartmann, M., & Schwieger, W. (2020). Hierarchical ZSM-5 Catalysts: The Effect of Different Intracrystalline Pore Dimensions on Catalyst Deactivation Behaviour in the MTO Reaction. *ChemCatChem*, 12(9), 2461–2468. <https://doi.org/10.1002/cctc.201902362>
- Weitkamp, J. (2000). Zeolites and catalysis. *Solid State Ionics*, 131(1–2), 175–188. [https://doi.org/10.1016/S0167-2738\(00\)00632-9](https://doi.org/10.1016/S0167-2738(00)00632-9)
- Xi, Z., Zhou, B., Jiang, B., Wang, J., Liao, Z., Huang, Z., & Yang, Y. (2019). Efficient conversion of methane to aromatics in the presence of methanol at low temperature. *Molecular Catalysis*, 475, 110493.

<https://doi.org/10.1016/j.mcat.2019.110493>

Xu, Y., Wang, J., Ma, G., Bai, J., Du, Y., & Ding, M. (2020). Direct synthesis of aromatics from syngas over Mo-modified Fe/HZSM-5 bifunctional catalyst. *Applied Catalysis A: General*, 598, 117589.

<https://doi.org/10.1016/j.apcata.2020.117589>

Xu, X., Liu, Y., Zhang, F., Di, W., & Zhang, Y. (2017). Clean coal technologies in China based on methanol platform. *Catalysis Today*, 298, 61–68.
<https://doi.org/10.1016/J.CATTOD.2017.05.070>

Yarulina, I. ; Chowdhury, A., Dutta, ;, Meirer, F. ;, Weckhuysen, B. M. ;, & Gascon, J. (n.d.). *Recent trends and fundamental insights in the methanol-to- hydrocarbons process* Item Type Article. <https://doi.org/10.1038/s41929-018- 0078-5>

Yang, M., Fan, D., Wei, Y., Tian, P., & Liu, Z. (2019). Recent Progress in Methanol- to-Olefins (MTO) Catalysts. *Advanced Materials (Deerfield Beach, Fla.)*, 31(50).
<https://doi.org/10.1002/ADMA.201902181>

Zaidi, H. A., & Kishore Pant, K. (2010). Combined experimental and kinetic modeling studies for the conversion of gasoline range hydrocarbons from methanol over modified HZSM-5 catalyst. *Korean J. Chem. Eng*, 27(5), 1404–1411. <https://doi.org/10.1007/s11814-010-0232-5>

Zaidi, H. A., & Pant, K. K. (2005). Transformation of methanol to gasoline range hydrocarbons using HZSM-5 catalysts impregnated with copper oxide. *Korean Journal of Chemical Engineering*, 22(3), 353–357. <https://doi.org/10.1007/BF02719410>

Zaidi, H. A., & Pant, K. K. (2008). Activity of oxalic acid treated ZnO/CuO/HZSM-5 catalyst for the transformation of methanol to gasoline range hydrocarbons. *Industrial and Engineering Chemistry Research*, 47(9), 2970–2975. <https://doi.org/10.1021/ie071339y>

Zaidi, H. A., & Pant, K. K. (2014). An oxalic-acid-treated ZnO/CuO/ HZSM-5 catalyst with high resistance to coke formation for the conversion of methanol to hydrocarbons. *International Journal of Green Energy*, 11(4), 376–388. <https://doi.org/10.1080/15435075.2013.772054>

Zhang, G. Q., Bai, T., Chen, T. F., Fan, W. T., & Zhang, X. (2014). Conversion of methanol to light aromatics on Zn-modified nano-HZSM-5 zeolite catalysts. *Industrial and Engineering Chemistry Research*, 53(39), 14932–14940. <https://doi.org/10.1021/ie5021156>

Zhang, G., Zhang, X., Bai, T., Chen, T., & Fan, W. (2015). Coking kinetics and influence of reaction-regeneration on acidity, activity and deactivation of Zn/HZSM-5 catalyst during methanol aromatization. *Journal of Energy Chemistry*, 24(1), 108–118. [https://doi.org/10.1016/S2095-4956\(15\)60291-1](https://doi.org/10.1016/S2095-4956(15)60291-1)

Zhang, J., Huang, Z., Xu, L., Zhang, X., Zhang, X., Yuan, Y., & Xu, L. (2019). Verifying the olefin formation mechanism of the methanol-to-hydrocarbons reaction over H-ZSM-48. *Catalysis Science and Technology*, 9(9), 2132–2143. <https://doi.org/10.1039/c8cy02621a>

Zheng, Y., Li, X., & Dutta, P. K. (2012). Exploitation of Unique Properties of Zeolites in the Development of Gas Sensors. *Sensors 2012, Vol. 12, Pages 5170-5194*, 12(4), 5170–5194. <https://doi.org/10.3390/S120405170>

Zhou, J., Gao, M., Zhang, J., Liu, W., Zhang, T., Li, H., Xu, Z., Ye, M., & Liu, Z. (2021). Directed transforming of coke to active intermediates in methanol-to- olefins catalyst to boost light olefins selectivity. *Nature Communications*, 12(1), 1–11. <https://doi.org/10.1038/s41467-020-20193-1>