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Conversion of Methanol to Olefin Over Zeolite Based Catalysts: A Review

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ABSTRACT

The increasing demand for olefins and continuous depletion of world oil reserves necessitated alternative routes to produce light olefins using non-petroleum feedstocks. Hence, MTO has attracted much attention; the conversion of methanol to olefin (MTO) has gained significant attention in the recent years due to potential in providing alternative routes for the production of valuable petrochemicals. Overall, this review offers a comprehensive analysis of conversion of methanol to olefins over zeolite-based catalysts. It provides valuable insight into current challenges and potential areas for future research, making it a useful resource for researchers, engineers and professionals working in the field of catalysis and petrochemical production.

Keywords: Methanol to olefin, Propylene, Zeolite, Catalysts

INTRODUCTION

Olefins belong to the class of unsaturated hydrocarbons consisting of a single double bond with a chemical formula of C_nH_{2n} (Liu et al. 2024)They are adjudged to be among the most important chemicals and raw materials in petrochemical industry (Meng, et al., 2018; Ahmed, et al., 2017). Economic growth coupled with skyrocketing demand for consumer products incited continual increase in worldwide olefin’s demand. Basically, light olefins (ethylene and propylene) are the most demanded, with global production in the range of 200 million tons per year (Pinilla-Herrero, et al., 2016). Ethylene is used in the manufacture of polyethylene, ethylene chloride and ethylene oxide. These products are very useful for plastic processing, construction, packaging and textile industries. Propylene on the other hand, is vital in the manufacture of polypropylene. It is a basic raw material for manufacture of several chemicals, plastics, and automotive components among others. Strikingly, the yearly production rate of propylene is around 100 x 106 tons, which still cannot satisfy the increasing global demand for propylene (Qi, et al., 2017; Lin, et al., 2009; Blay, et al., 2018).

Generally, olefins are produced via conventional thermal cracking of hydrocarbons such as ethane, propane and butane, liquefied petroleum gas, to liquid feedstocks such as light and heavy naphtha, gasoil and vacuum gas oils (Sadrameli, 2016). In addition, olefins are also produced through fluid catalytic cracking of petroleum fractions (passamonti et al. 2024). However, due to the rapid increase in the price of crude oil and the envisaged depletion of petroleum resources, alternative routes for production of light olefins from non-oil sources are desired (Dai, et al., 2011; Meng, et al., 2018). Interestingly, conversion of methanol to olefins (MTO) provides an alternative route for production of light olefins from a non-petroleum source (Yaripour, et al., 2015). The MTO reaction was first proposed by Mobil Corporation in 1977 (Tian, et al., 2015). Essentially, the reaction progresses in two stages. The first stage involves conversion methanol into equilibrium mixture of dimethyl ether (DME) and water. The second stage involve conversion of the equilibrium mixture into light olefins and other hydrocarbon products (Dai, et al., 2011; Deimund, 2015). The catalytic conversion of methanol to olefins have been investigated over numerous zeolite-based catalysts. The product composition and rate of deactivation are sturdily dependent on morphology since it governs the pore entrances and cage sizes (Khanmohammadi, et al., 2016). Zeolites such as SAPO-34, Beta and ZSM-5 zeolites are among the most explored due to their proven efficiency in selectively producing light olefin from methanol (Pinilla-Herrero, et al., 2016; Zhao, et al., 2018; Dai, et al., 2011). Nonetheless, there small micropores hinder molecular diffusion, which affect mass transport of reaction species within the catalyst. Consequently, large products are trapped inside the micropores which form poly condensed aromatic complex that triggers carbocation and lead to deactivation (Zhang, et al., 2016). More so, there high concentration of acid sites leads to propagation of secondary reactions such as aromatization and cyclization reactions.

Intrinsically, incorporation of metal oxides/heteroatoms or mesopores in zeolite materials has been reported to inhibit coke deposition by neutralizing concentration and strength of the acid sites (Park, et al., 2018; Yarulina et al., 2016). As a result, formation of undesired products such as aromatics are restricted, which in turn boots propylene selectivity during the MTO process (Ahmed, et al., 2017; Matam et al., 2018). Notably, introduction of seed material into template free synthesis batches has been reported to efficiently control topology and properties of the product zeolite. Also, development of modified zeolite catalyst with nano crystals can be achieved by seed induced technique in the presence of surfactant (Chen et al., 2017). More so, synthesis of ZSM-5 by template-free ZSM-11 seeds assisted technique, displayed outstanding performance in MTO reaction (Yu et al., 2013). Furthermore, ceramic foam and metal-fiber coated zeolites were fabricated by in-situ hydrothermal technique, which displayed excellent selectivity and stability in MTO as compared to the conventional zeolite catalysts (Jiao, et al., 2015; Wen, et al., 2015; Ding, et al., 2015). Zeolite-based catalysts have proven to be efficient in promoting this reaction, this paper aims to provide an overview of recent advancements and challenges faced in the conversion of methanol to olefins over zeolite-based catalysts. Furthermore, the review highlights the influence of catalyst properties, such as acidity, pore structure, topology, textural properties and crystal size on the selectivity and yield of olefin products. It explores the catalytic reaction pathways and the factors affecting the product distribution, including temperature, pressure and reactant concentration. Additionally, the challenges faced in optimizing the MTO reaction are addressed, including catalyst deactivation, coke formation and side reactions leading to undesired byproducts. Acidic zeolites remain the most applied catalyst in industrial MTO process. However, microporous nature of their framework and high strength and concentration of the acid sites lead to carbo-cation. At longer time on stream, these carbo-cation intermediates formed are readily adsorbed and form poly aromatic complexes, which lead to deactivation. This eventually shortens catalytic lifetime and reduces propylene selectivity. Hence, hindering catalysts deactivation and maximizing propylene selectivity remain a major challenge in MTO process. This review summarizes the progress in development and application zeolite-based materials for MTO.

Methanol to Olefin Process

The MTO process can potentially fill the gap for olefin demand. The process can serve as an alternative route for production of high-demand chemical commodities such as olefins. Interestingly, methanol can be obtainable from numerous feedstocks, and the process is operated at low reaction temperature (near 400°C) coupled with the high olefin yield (Varzaneh, et al., 2016). The MTO technology was discovered in the 1970s by the petrochemical giants Exxon-Mobil (Chang and Silvestri, 1977). The process converts methanol to hydrocarbons (Figure 1) over a zeolite containing active acid sites. In the Exxon-Mobil MTO process, ZSM-5 catalyst was used. The MTO process was later investigated by UOP/Hydro researchers, where SAPO-34 zeolite was the catalyst used. Conclusive investigations have been conducted over the years since the discovery of MTO, which paved way in understanding the reaction and catalyst design as well as leading to a significant improvement in the catalytic performance (Amghizar, et al., 2017).

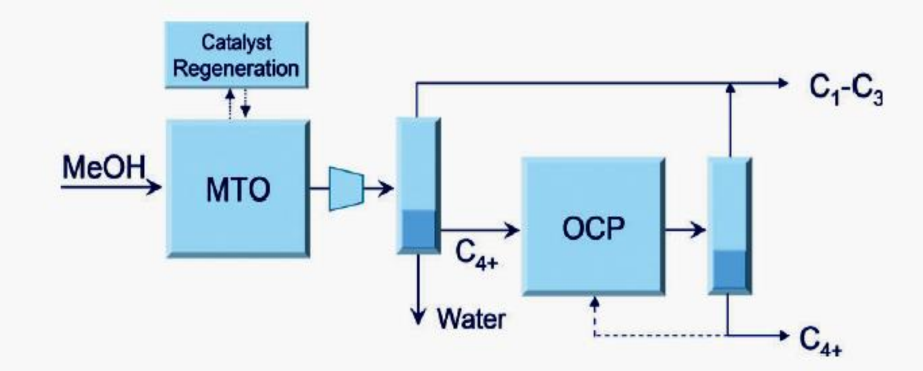


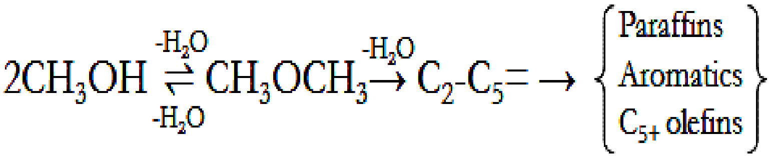
Figure 1: MTO fluidized-bed process (Olsbye et al., 2012)

Basically, the priority in MTO reaction is to maximize propylene selectivity. These is achieved via a number of strategies: (1) Reducing the Bronsted acidity of zeolite catalysts, so as inhibit occurrence of side reactions. The method consists of: altering zeolite Si/Al ratio, heteroatoms substitution and post-synthesis modifications. (2) Adjusting the zeolite porosity which improves molecular diffusion. This can be realized by either reducing particle size or incorporating additional mesoporous (3) Varying reaction conditions, for example co-feeding methanol with water, weight hourly space velocity or changing the reactor temperature, operating pressure, residence time, catalyst loading. (4) Changing the reactor configuration (Zhang et al., 2017; Li et al., 2019).

The technology of MTO is versatile, with catalyst properties and process conditions playing a greater role on the nature of products formed. Numerous products are formed in MTO reaction (Figure 2) through different reactions. The catalytic conversion of methanol progresses in two phases. Firstly, methanol is converted to an equilibrium mixture of dimethyl ether (DME), methanol and water. Then in the second phase, the equilibrium mixture is converted to olefins and other products (Olsbye, et al., 2015; Sadeghpour and Haghighi 2018).

The MTO reaction is initiated by the interaction of methanol with the acid sites. The equilibrium mixture of methanol and DME undergoes methylation reaction, thereby producing olefin species. The produced olefins are converted to alkenes, alkanes and aromatics through reactions such as methylation, cracking, hydrogen transfer among others. The MTO reaction proceeds via dual cycle mechanism over

ZSM-5 zeolite, which is the widely accepted route for olefins generation from methanol.



$$2CH_3OH \underset{-H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} C_2\text{-}C_5{=} \rightarrow \left\{\begin{array}{l}\text{Paraffins}\\ \text{Aromatics}\\ C_{5+}\ \text{olefins}\end{array}\right\}$$

Figure 2: Scheme of MTO reaction

The dual cycle represents a concession between two mechanistic cycles (olefinic and aromatic cycles) running in parallel (Figure 3). Both cycles can be grouped further into basic steps portrayed by six forms of reactions namely methylation and cracking of olefins, methylation and dealkylation of aromatics, hydrogen transfer and cyclization. The latter two reactions act as bridging step between the dual cycles (Ilias and Bhan, 2013). However, the consensus is that the generation of hydrocarbons is rationalized as a result of consecutive methylation and cracking reactions. All olefins formed except ethylene are adjudged to be produced from the olefinic cycle. Ethylene generation is related to the presence of lower methylbenzenes, signifying that ethylene is mostly a product of the aromatic cycle (Sadeghpour and Haghighi 2018; Bjorgen, et al., 2007).

Findings by Sun and co-workers further affirmed that both cycles are active for ethylene and propylene production, with the aromatic cycle yielding predominant ethylene and aromatic products. On the other hand, the olefin cycle, propagates propylene formation in relative to ethylene. These indicates that both cycles contribute to the product distribution, most ethylene will be generated via the aromatic cycle. Hence, the coexistence of both cycles naturally renders them as competing. In this vein, it can be concluded that the desired hydrocarbon range largely depend on either stimulating or suppressing of one cycle over the another (Sun, et al., 2010; Olsbye, et al., 2015).

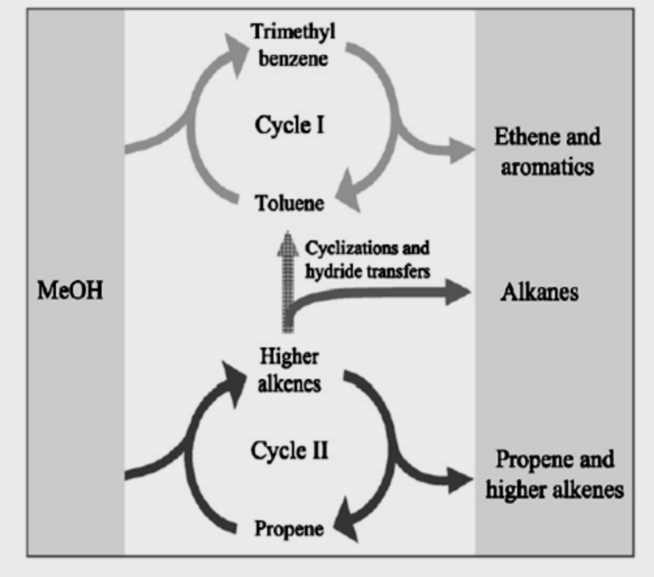


Figure 3: Dual cycle concept for MTO over ZSM-5 catalyst (Olsbye, et al., 2012)

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Catalysts for Methanol to Olefin Process

Catalysts are substances with ability to enhance rate of a reaction by lowering the activation energy of the reaction. Over the years, the increase in demand for products has been a driving force to the extraordinary progress in catalytic processes (Hambali et al 2019). One noteworthy stage in the development of catalysts occurred when Haber and Bosch established the process for the fixation of atmospheric nitrogen in the ammonia synthesis in the year 1909 (Fechete et al., 2012). The upsurge in industrial catalytic processes had prominent events of the history as a backdrop. For example, in the early 20th century, catalysts were developed mostly for the manufacture of synthetic fuels by inventive technologies such as FTS and FCC which were used as transport fuel during the second world war. However, towards the end of the 20th century, the incessant efforts were channelled on the petrochemical industry in other to cover the huge demands for petrochemical products such as polymers, fine chemicals among others (Fechete et al., 2012; Yaripour, et al., 2015). Currently, catalyst applications have gained momentum, due to the recent society apprehensions on the industry impacts on the environment. The priority for use of catalysts is to enhance selectivity and lessen process investments and operational costs.

Generally, catalysts can be categorized as homogeneous or heterogeneous, depending on the phase of the catalyst and the reactants. Intrinsically, MTO reaction is considered an acid catalyzed reaction. The reaction requires an acidic site to initiate the conversion process. Several types of zeolite with acidic sites have been widely used as catalyst in MTO reaction (Zhang, et al., 2016). Besides, the zeolites were used due to their high selectivity towards light olefins owing to the narrow pore diameter existing in the zeolite framework.

Zeolites as Methanol to Olefin Catalyst

Methanol is very sensitive to catalyst due to its high activity and could be catalyzed by acidic zeolites to produce hydrocarbons. The reactant molecule is small and simple, but the transformation process has been established to be very complicated with variety of products formed. Typically, the MTO reaction requires solid acid catalyst such as a zeolite as shown in Figure 4. The product distribution is strongly governed by the shape-selective effects of the diverse zeolite topologies, though the effect of Si/Al ratio, strength and density of acid sites have also been reported to be significant (Li et al., 2019). Small pore provided by zeolite catalysts, result to high selectivity towards ethylene and propylene during the methanol to olefin reaction (Liu and Liang, 1999). Hence, most investigations are channelled on the architecture of pore topology.

Zeolites are one of the subsets of molecular sieve family with an outstanding surface area and high acidity (Hambali et al. 2021). Molecular sieves were commonly used as MTO catalyst due to the existence of frameworks containing cages which allow small molecules such as methanol and linear alkenes to diffuse through the cages while hindering larger branched and aromatic species that may form (Ji, et al., 2016). Zeolites have a porous crystalline framework, composed of tetrahedral SiO_4 and AlO_4 with oxygen atom as the interconnecting bridge between tetrahedra (Vaughan, 1988). The secondary building units (SBU) are a polyhedral built from the geometric arrangements of tetrahedra. These SBUs are the component of composite building unit (CBU), as shown in Figure 5. These CBU of zeolite will create the uniform pore and channels in the zeolite after formed into framework, which provides the shape selective ability. Zeolite also requires extra framework cation, such as proton in order to balance the negative charge of the framework due to the substitution of several silica atoms with alumina atom. This property provides zeolite with ion-exchange capacity.

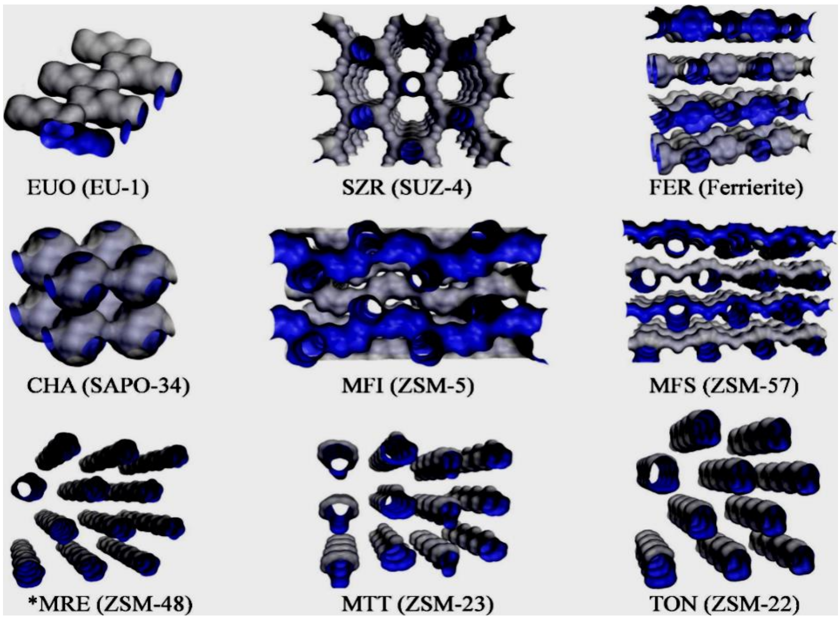

Figure 4: Examples of pore system zeolites used in MTO reaction. The blue color signifies interior of the pores (Teketel, et al., 2015)

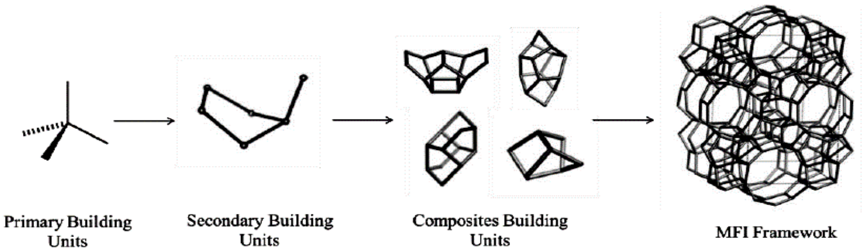

Figure 5: Zeolite framework building units (Vaughan, 1988)

Zeolites are classified into zeolites A and X which are termed as low silica zeolite and have Si/Al ratio of 1-1.5. Also, we have Zeolite Y and several natural zeolites which are referred as the intermediate silica zeolite with Si/Al ratio of 2-5. Then, the high silica zeolite with Si/Al ratio greater than 5. For example, Beta, SAPO-34, mordenite, ZSM-5 are high silica zeolites due to their Si/Al ratio of higher than 5. Decrease in alumina content led to both increase in thermal and acid stabilities (Meng, et al., 2009). The number of aluminum ions in the framework control the total acidity in zeolites (Corma, 1997).

Generally, ZSM-5, Beta and SAPO-34 are among the most explored catalysts in MTO reaction, due to their proven performance as displayed in Table 1 (Ahmed, et al., 2017; Zhao, et al., 2018). The dimension of the cages and channels determine the products formed inside the catalyst and those that can diffuse out from the cage. Hence, the framework topology of zeolite catalyst controls the product distribution of hydrocarbon formed from the reaction (Pinilla-Herrero, et al., 2016).

ZSM-5

ZSM-5 is a zeolite with MFI (Mordenite Framework Inverted) structure. ZSM-5 was first synthesized by Argauer and Landolt in 1978 and patented by Exxon-Mobil. ZSM-5 structure built from 10 membered rings of pentasil and crystallize in Pnma orthorhombic space group with lattice parameter constants of, a = 20.1, b = 19.9, and c = 13.4 Å. As shown in Figure 6, it incorporates two channel systems comprising of a straight channel (5.4 x 5.6 Å), which is parallel with y-axis, and a sinusoidal channel (5.5 x 5.1 Å) which is parallel with x-axis. In addition, it consist of a 10-membered ring with two distinct sets of intersecting channels and has found relevance in several industrial processes as a heterogeneous catalyst (Kokotailo, et al., 1978; Meng, et al., 2009). For example, in isomerization of light naphtha, alcohol to hydrocarbon and catalytic cracking reactions (Majhi, et al., 2015, Teh, et al., 2015; Setiabudi, et al., 2012).

Intrinsically, the total amount of acid sites in zeolite is directly proportionate to the number of aluminium species present, therefore as the content of aluminium atoms is amplified, the total acid sites eventually increase (Meng, et al., 2009; Ogura et al., 2001). ZSM-5 is fortified with strong acidity and medium channel dimensions and was reported to be more resistant towards deactivation compared to SAPO-34. Nevertheless, it has been extensively used in MTO reaction and the selectivity towards light olefins is reasonable, the propylene to ethylene (P/E) ratio, but there is still need for enhancement (Zhang, et al. 2016). The conventional ZSM-5 zeolite tends to suffer rapid deactivation, which is associated with deposition of coke species in the cage of catalyst. These demerits are attributed to its microporous nature, which pose a threat to application of ZSM-5 zeolites for industrial scale operations (Chen, et al., 2017).

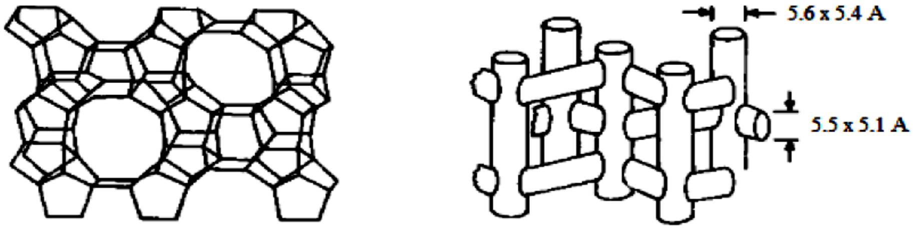

Figure 6: Channel systems in ZSM-5 (Kokotailo, et al., 1978)

SAPO-34

Molecular sieves of aluminophosphate (ALPO) were first discovered in 1982. The initial structure of SAPO type catalyst was from Al–O–P instead of Si–O–Al or Si–O–Si. However, because the molecular structure of ALPO is neutral, its tendency to act as a catalyst is weak and hence adding silicon to ALPO lead to the introduction of silico aluminophosphate (SAPO) molecules. Substitution of Si^{4+} with P^{5+} ions lead to the generation of acidic sites which marginally improves the catalytic activity. SAPO-34 has a shape of CHA (Chabazite) with pore size of 3.5–6 Å with an open oval octagonal shape (Sadrameli, 2016). SAPO-34 has also been explored in MTO process. It was reported to display high selectivity in formation of light olefin products due to its moderate acidity and small pore entrances, (Chargand, et al., 2014; Hwang, et al., 2016). However, despite being one of the suitable MTO catalyst, the microporous nature of SAPO-34 restricts diffusion of molecules within the pores. Also, the Chabazite-cage windows of SAPO-34 limit the diffusion of large branched aliphatic and aromatic hydrocarbons (Hwang, et al., 2016). These observations were reported to result in rapid deactivation by coke formation during the MTO process (Yang, et al., 2016). The deactivated catalyst needs

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to be regenerated frequently, which infers additional cost and a major setback for any industrial setup (Zhang, et al., 2016).

Other Zeolites

Besides ZSM-5 and SAPO-34 catalysts, continuous investigations to find other potential catalyst for MTO reaction are reported. Beta (BEA) zeolite with 3-dimensional 12-membered ring pore channels were tested in MTO reaction. The Beta zeolite is characterized as a large pore zeolite material with pore size of 0.66-0.68 nm (Liu et al. 2024). However, it was observed that the wide channel intersection of beta zeolite offers enough space for bulky intermediates (for example hexamethylbenzene) accumulation, which favour the formation of higher alkenes (Bjorgen and Kolboe, 2002). However, the propylene selectivity over beta zeolite is not much as compared to other zeolites, this is because the large pores facilitate higher olefins formation thereby leading to more C4+ hydrocarbons in the product distribution. Similarly, Beta zeolite catalyst yield a stable and good performance during MTO reaction, which was attributed to the tuned acidity of the parent Beta zeolite (Otomo, et al., 2016).

In addition, EU-1 zeolite represents one of the most promising one-dimensional (1D) channel zeolites and portrayed good performance in acid catalyzed processes. The structure of EU-1 contains 10 MR channel with size of 0.58-0.41 nm connected to a side pocket of 12 MR in the size of 0.68-0.58 nm. Similarly, low performance of EU-1 in MTO reaction was obtained. The generation of aromatics products was much, with higher ethylene selectivity and rapid catalyst deactivation observed (Enrico, et al., 2018). High silica EU-1 zeolite was also reported to yield high ethylene selectivity in MTO reaction (Si, et al., 2012). Generally, EU-1 catalyst seems to suffer from rapid deactivation during MTO reaction due their one-dimensional channel structure, which limit diffusion within the catalyst. Other than Beta and EU-1, numerous catalysts such as ZSM-11, ZSM-22, ZSM-23, ZSM-58, and mordenite displayed reasonable performance in MTO reaction (Li, et al., 2011; Wei, et al., 2014; Teketel, et al., 2015).

Deactivation of Zeolite in Methanol to Olefin

Zeolites used in conversion processes are progressively deactivated with time on stream, and hence must be regenerated to recover their catalytic activity. Basically, deactivation is understood to be triggered by formation of large and complex poly aromatic compounds. These compounds are formed on the surface and in the pore openings of the catalyst during MTO reaction (Olsbye, et al., 2015; Ilias and Bhan, 2013) These phenomena hinder the diffusion of both reactants and products into and out of the zeolite channels, thus rendering the catalyst inactive. Therefore, the major challenge in commercialization of MTO process still lies on improving catalytic lifetime.

Generally, the acid sites play a pivotal role in coke formation, via secondary reactions such as oligomerization, cyclization and aromatization. These reactions were reported to largely depend on the strength and density of acid sites. A comparative analysis by Tian et al. showed that varying acidity of CHA topology catalysts was advantageous to improving stability during MTO reaction (Tian, et al., 2015).

The optimization of the MTO process can be attained by changes in the operation conditions or in catalytic properties. Several techniques have been adapted to reduce rapid deactivation of zeolite catalysts by carbon deposition. The modification of zeolite acidity and porosity has been affirmed to remarkably improve properties of MTO catalyst. One of these methods include introduction of mesoporous into zeolite catalysts. Another technique to avert

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deactivation is modification of zeolite with certain quantity of promoters. These modifications amount to fast transport of the reactants to the active sites. Hence, each of these methods have different consequence on the acidity and catalytic activity (Wei et al., 2015; Zhang et al., 2014; Wang et al., 2016).

Addition of Promoters

Incorporation of promoter in zeolite framework reduce the amount of acid sites and hinder adsorption of hydrocarbon intermediates. These has been reported to consequently lead to improved MTO catalytic performance (Kim, et al., 2018). Mirza et al. investigated the influence of potassium species on SAPO-34 zeolite. The K^+ ion exchange of SAPO-34 catalyst, increased the pore volume, surface area and concentration of the weak acid sites. The modified K/SAPO-34 catalyst exhibited high stability and propylene selectivity (45 %) due to ability of coke thermal cracking to propylene (Mirza, et al., 2018).

Furthermore, tailoring the surface of zeolite with addition of magnesium metal contributed to slight increase in pore size due to the enforced location of Mg species inside the zeolite pores. The thus-modified catalyst displayed high propylene selectivity (37 %) and improved catalytic lifetime (Rostamizadeh and Taeb, 2015). In addition, the basic nature of Ca invoked redistribution of acidity within the ZSM-5 framework. The Ca promoter intensely increased propylene selectivity and prolong catalyst lifetime (Yarulina et al., 2016).

Table 1: Catalytic performance of zeolite in MTO reaction

Catalyst	Reaction Temperature (°C)	Propylene (%)	Stability (h)	References
K/SAPO-34	450	45	10	Mirza, et al., 2018
High silica ZSM-5	500	46	35	Liu et al., 2009
Ca/ZSM-5	500	53	60	Yarulina, et al., 2016
Micro-sized ZSM-5	450	41	25	Feng, et al., 2018
Hierarchical beta	330	20	13	Sun, et al., 2015
SAPO-34	500	32	9	Borodina, et al., 2017
Nano-sized ZSM-5	500	58	30	Kim et al., 2018
Micro-sized ZSM-5	500	58	30	Kim, et al., 2018
ZSM-5/SiC foam	470	46	60	Jiao, et al., 2019
ZSM-5	500	41	25	Dyballa et al. 2016
SAPO-34	400	37	10	Liu et al., 2021
Mg/ZSM-5	480	37	47	Rostamizadeh and Taeb, 2015
Nano-sized ZSM-5	400	29	42	Bleken et al. 2012
SAPO-34	450	40	8	Moradiyan et al., 2018

Mesoporous Zeolites

Zeolites with high mesoporosity have been reported to boost propylene selectivity and catalytic lifetime during conversion of methanol to olefins. Introducing mesopores to zeolite have been affirmed by several researches to improve molecular diffusion and catalytic activity.

Various approaches have been examined in order to generate interparticle mesopore in zeolites, especially macrotemplating, dealumination and desilication treatments. The macrotemplating techinique can be cataegorized into hard and soft templating. Hard-templating involves utilization of solid material to generate mesoporosity, example of these materials is polystyrene, carbon fiber, aerogel among others (Tao, et al., 2006). Soft-templating on the other hand involve usage of supramolecules such as polymer, and organosilane to introduce mesoporousity. The major phenomenon that contributes into generating mesopore are adsorption struggle and the colloidal interaction between the surfactant and surface directing agent during the zeolite development process (Li, et al., 2013).

Furthermore, dealumination and desilication by utilization of alkali or acid solution are used to generate mesopore in zeolites. Notably, the dealumination method, which is attainable by removal of aluminum from the zeolite framework as first reported by Barrer et al. in 1964. Dealumination technique encompasses application of chemical agents to remove aluminum from the framework, and hydrothermal dealumination. It entails hydrothermal treatment at temperature of 540 °C in a gas stream, by increasing water vapor partial pressure to achieve dealumination of zeolite (Qin, et al., 2015). Basically, for the hydrothermal treatment, the most adapted technique is the steaming process, which produces zeolite catalysts with high stability. The steaming process entails calcination of fresh catalyst in combination with acids over prolonged synthesis duration (higher than 10 h), and high temperature (400–800°C) (Zhang, et al., 2006).

Recently, Zhang et al. adopted steaming technique at optimum conditions (500^{o}C and 12h) to synthesize zeolite catalyst with improved activity in MTO reaction (Zhang et al., 2015). Also, dealuminated zeolite catalyst was synthesized with aid of ammonium surfactants. The result shows that deactivation due to coking effect largely depends on the BAS concentration. Zeolite with moderate acidity (BAS of 0.30 and LAS 0.20mmolg^{-1}) gave the highest propylene selectivity (37%) and less coke content (Wu, et al., 2014).

Astonishingly, passivated ZSM-5 catalysts were prepared by chemical dealumination technique, using tetraethyl-orthosilicate. The passivation was repeated for a second and third time to guarantee a complete surface coverage. The acidic properties and catalytic performance of the dealuminated catalysts is listed in Table 2. ZSM-5$_{NF}$ denotes the synthesised nano-zeolite, while ZSM-5$_{P1}$, ZSM-5$_{P2}$, ZSM-5$_{P3}$ represents once to thrice passivated samples respectively. The once passivated catalyst (ZSM-5$_{P1}$) had moderate acidity in relative to other catalysts and gave the highest propylene selectivity of 34% when compared with others (Losch, et al., 2016). More recently, modified zeolite was fabricated via surface dealumination. Consequently, improved light olefin selectivity (63.54%), propylene selectivity (40.79%), and catalyst lifetime (24 h) were observed (Feng et al., 2018). In all these findings, the underlining notion is focused on obtaining the appropriate acidity in zeolite catalyst to convert methanol to olefins with high selectivity and maintaining long time on stream by suppressing undesired products formation and coke formation.

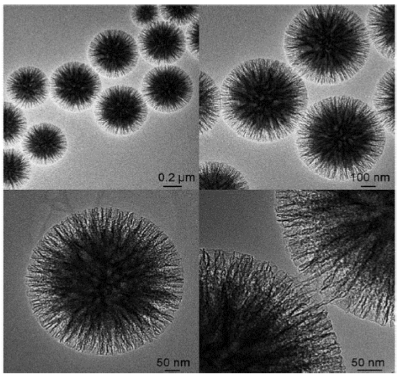

Figure 7: TEM images of KCC-1 (Polshettiwar et al., 2010)

Fibrous Material

The fibrous silica zeolite-based catalysts are rare and emerging mesostructured zeolite as shown in Figure 7 (Polshettiwar et al., 2010). As compared to other commercial zeolite materials, the fibrous silica zeolite-based catalyst has unique morphology with dendrimer like structure. This fibrous morphology with high porosity, surface area and moderate acidity tremendously affect the catalytic performance (Hambali et al., 2021). Furthermore, loading of appropriate metals on the fibrous silica zeolite catalyst enhance conversion of methanol into the desired light olefin products, due to expected good dispersion of metals on the high surface area support.

CONCLUSION

MTO is a promising route for production of olefins. Several efforts have been dedicated to modifying MTO catalyst. Approaches such as use of surfactants, dealumination, addition of promoters, introduction of seed materials, ceramic foam and metal-fiber coating, altering pore volume and Si/Al ratio among others were explored. To this end, various attempts to synthesize mesoporous zeolites have been explored. Incorporation of mesoporousity and promoters in zeolites seems the key to overcome these problems. Moreover, development of fibrous silica zeolite-based material, along with tunable acidity and high surface could potentially improve MTO process.

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