

Recent modifications of MCM-22 and MOR zeolite in MTO reaction: a review

Muhamed Yusuf Shahul Hamid^{1,2*}, and Muhammad Hafizuddin Mohd Sofi¹

¹Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

²Centre of Hydrogen Energy, Institute of Future Energy, 81310 UTM Johor Bahru, Johor, Malaysia

Abstract. Since the discovery of the Methanol-to-Olefins (MTO) process as a sustainable and non-petroleum method for generating light olefins, there has been a growing interest in the utilization of acidic zeolite catalysts. In this review, we highlighted the application and modification of MCM-22 and MOR zeolite catalysts, shedding light on their distinctive properties and the ongoing endeavors to optimize their catalytic performance. Notably, the choice of catalyst and specific modifications significantly influence the outcomes of light olefin selectivity, propylene-to-ethylene (P/E) ratios, and catalytic lifetime. This research offers insights into the current status of research on MCM-22 and MOR zeolites and imparts a valuable understanding of the developments of both catalysts in this crucial catalytic field.

1 Introduction

Existing olefin production is highly dependent on fossil resources that are expended into energy-consuming processes, heavily contributing to the environmental problem [1,2]. Therefore, an innovative and non-traditional carbon-based feedstock will be needed to fulfill the world's need for fuels and chemicals, particularly olefins, which are one of the key components of many chemical industries. The methanol-to-olefins (MTO) reaction is one of the alternatives to turn low-value non-petroleum resources like biomass, natural gas, and coal into high-value petrochemical products [3].

Since its initial discovery, the MTO reaction has made use of a variety of zeolite materials (mostly acidic zeolites). Among the various zeolites that exhibit diverse morphologies and structures, SAPO-34 (CHA type) and ZSM-5 (MFI type) distinguish themselves as frequently employed as catalysts in MTO conversion [4,5]. SAPO-34 zeolite exhibits remarkable selectivity in the production of light olefins like ethylene and propylene due to its mild acidity and narrow openings of its pores. Nonetheless, the catalytic activity of SAPO-34 is restricted by its relatively short operational lifetime as it experiences rapid coke formation on its surfaces, requiring frequent regeneration to reestablish its catalytic activity [6,7]. In contrast, ZSM-5 possesses strong acidity and medium pore sizes and appears to exhibit greater resistance to catalyst deactivation compared to SAPO-34, but its selectivity for ethylene and propylene is slightly lower due to its strong acidity [8]. Nevertheless, as the disparity between worldwide demand and supply for light olefins continues to widen,

the selective production of light olefins from methanol is gaining increasing attention [9]. In addition, considering the fluctuating demand within the global olefin market, there is a strong desire to optimize selectivity in order to achieve a specific type of light olefin [10]. Thus, it is important to investigate new potential zeolite catalysts with high light olefin selectivity, different propylene-to-ethylene (P/E) ratios, and longer catalytic lifetimes such as MCM-22 and MOR.

To date, no review has been conducted on the utilization and modification of MCM-22 and MOR zeolite catalyst on MTO reaction. Thus, in this review, the potential and current modifications of MCM-22 and MOR were discussed. The discussion will revolve around the unique characteristics of the zeolite, along with the ongoing efforts to enhance its catalytic performance.

2 Application of MCM-22 zeolite in MTO reaction

According to S. Lawton et al., MCM-22 (MWW type) zeolite exhibits three distinct pore systems: the first pore system consists of large cylindrical supercages ($7.1\text{\AA} \times 7.1\text{\AA} \times 18.2\text{\AA}$) between layers, the second system comprises sinusoidal 10-member ring channels ($4.1 \times 5.1\text{\AA}$), and the final system is positioned at the external surface, which is covered with 12-member ring pockets ($7.1\text{\AA} \times 7.1\text{\AA} \times 7\text{\AA}$) [11]. With its unique pore system, MCM-22 zeolite has been utilized in a variety of catalytic reactions and is regarded as a potential

* Corresponding author: myusuf@utm.my

catalyst in the MTO reaction. To examine the influence of individual pore systems in MCM-22 on the MTO reaction, Min et al. conducted a comparison between the catalytic performance of MCM-22 and its delaminated material, which lacks the presence of large cylindrical supercages. They discovered that acid sites located in the external 12-member ring pockets had an adverse effect on both the selectivity and stability of the MTO process. Nevertheless, both the sinusoidal 10-member ring channels and the cage pore system are selective towards propylene formation, allowing for the achievement of a high propylene selectivity [12]. Wang et al. investigated the catalytic properties of MCM-22 zeolites in the methanol-to-hydrocarbons (MTH) conversion process. Their study revealed that the catalytic performance of MCM-22 was significantly influenced by the presence of external surface acid sites, and they found that lowering these acid sites through dealumination can improve the catalytic stability [13]. According to Lacarriere et al., acid sites within the supercages of MCM-22 experience rapid deactivation, while the acid sites situated on the external surface and inside the sinusoidal micropores primarily contribute to the MTH reaction [14]. Therefore, it was anticipated that MCM-22 would be an effective catalyst in the MTO reaction with high selectivity for propylene. Numerous attempts have been conducted to modify the acidic properties of MCM-22 in the MTO reaction, including modifying the Si/Al ratio by dealumination and incorporation of various metallic or non-metallic elements. These modifications are further discussed in this section.

2.1 Modifications of MCM-22

2.1.1 Silica-alumina (Si/Al) ratio

Since the acidity of this catalyst contributes significantly to the selectivity of light olefins, especially propylene, this trend was investigated by L. Zhang et al. in which HMCM-22 was synthesized with different Si/Al ratios ranging from 10.8 to 49.8 and dealumination of original sample using ammonium hexafluorosilicate (AHFS) [15]. Dealumination is a process that involves the extraction of aluminum from zeolite frameworks and is one of the effective methods for adjusting the acidity of zeolites. From this study, the removal of Al from the HMCM-22 framework that increases the Si/Al ratio will significantly reduce the weak and strong acid sites along with Brønsted and Lewis acid. The dealuminated HMCM-22 with the least Brønsted acid site shows an improvement in light olefin selectivity and the highest P/E ratio. However, in terms of catalytic lifetime, it appears to be dependent on the number of acid sites, particularly the Lewis acid sites, as an excessive or insufficient amount of Lewis acid does not contribute to enhancing the catalytic lifetime.

Following the successful dealuminated HMCM-22 using ammonium hexafluorosilicate (AHFS), L. Zhang et al. have done a study on different dealumination methods using nitric acid (HNO₃), oxalic acid (C₂H₂O₄) and AHFS solutions with varying

concentrations [16]. Compared with HNO₃ and C₂H₂O₄, the use of AHFS for dealumination proves to be a highly effective approach for MCM-22 zeolite. HNO₃ selectively removes framework aluminum, whereas C₂H₂O₄ eliminates both framework aluminum and extra-framework aluminum. Conversely, AHFS effectively targets the removal of extra-framework aluminum, leading to a concentration of Brønsted acid sites within the sinusoidal channels. Utilizing a 10 mmol/L AHFS solution for dealumination proves to be a successful approach in reducing the coke formation, resulting in outstanding stability with a 54-hour lifetime, as well as remarkable propylene and butylene selectivity of 71.8%.

2.1.2 Incorporation of metals/non-metals

Besides the dealumination method, a study on the effect of the incorporation of active metals has been done by García-Ruiz et al. [17]. It was reported that the incorporation of zinc (Zn) exerts significant effects on the morphology, structural characteristics, and acidic properties of MCM-22. It showed that the prepared catalyst comes with a smaller particle size and low acidity, which contributes to high selectivity towards light olefins. In addition, previous reports on the modification using non-metallic elements also have been done. Wang et al. utilized the impregnation of phosphorus to modify HMCM-22 for the MTH reaction. They discovered that by loading HMCM-22 with 3% phosphorus, a remarkable selectivity of approximately 40% towards propylene at 100% conversion of methanol could be achieved [18]. Unlike metal modification, the introduction of non-metallic phosphorus shows good preservation of the MWW framework structure in HMCM-22. The most noticeable change for this modification is a substantial reduction in the number of Brønsted acid sites within HMCM-22.

Following the achievement of using non-metallic elements, Chen et al., 2016 studied on regulating the aluminum framework and distribution of acidic sites in MCM-22 by Boron incorporation [19]. The findings indicate that by adjusting the boron content during synthesis, it is possible to regulate the distribution of framework aluminum and Brønsted acid sites within HMCM-22 across its three-pore system (sinusoidal channels, supercage windows, and external surface pockets). This is possible due to the competitive occupancy of different framework T sites by both boron and aluminum species. On the other hand, boron incorporation has a relatively minor impact on the morphology and the overall types and number of acid sites present in the material. By incorporating an appropriate amount of boron, it is feasible to strengthen the Brønsted acid sites within the sinusoidal channels rather than the surface pockets and supercages. However, a high boron content leads to a relocation of the acid sites back to the surface pockets and supercages. The strong Brønsted acid located at the surface pockets and supercages is prone to coke accumulation, leading to blockage of the pore, while the ones within the sinusoidal channels are essential in maintaining a stable reaction stage during a reaction. Thus, the proper

content of boron results in increased catalytic lifetime and greater catalytic performance of HMCM-22.

3 Application of MOR zeolite in MTO reaction

Mordenite (MOR) is commonly known as large-pore zeolite with unique properties of the structure as it possesses a 12-member ring main channel (0.7×0.65 nm) and 8-member ring small channel (0.57×0.26 nm) oriented along the *c*-axis and interconnected by 8-member ring side pockets (0.34×0.48 nm) [20,21]. In general, the catalytic properties of MOR are primarily determined by its framework's topologies and composition [22]. In addition to this structural characteristic, the properties of MOR as aluminosilicate zeolite can also be determined from the distribution of acid sites [23]. As a result, to improve the catalytic performance of MOR, researchers have been performing further studies aimed at achieving precise control over the synthesis of MOR.

To obtain light olefins as a major product in the MTO reaction, the subsequent reactions of the light olefins must be suppressed since they react with one another on the acid sites to form the undesired paraffins and aromatics. Thus, understanding the reaction mechanism is important to have a clear insight into the influence of acid strength on product distribution and catalytic lifetime. Based on the hydrocarbon pool mechanism, Hexamethylbenzene (HMB) serves as a reaction intermediate, which is situated in the zeolite cages and reacts with methanol to generate light olefins via side-chain alkylation and paring reactions [24]. However, the process of HMB formation necessitates an induction period for the creation of additional active species. Further condensation of HMB molecules to polyaromatic hydrocarbon (PAH) via alkylation ultimately results in catalyst deactivation [25].

3.1 Modifications of MOR

3.1.1 Silica-alumina (Si/Al) ratio

A study from Park et al., that used dealuminated MOR with vary Si/Al ratios (5, 12, 55, and 103) showed that all MOR catalysts produce high initial selectivity of olefins, mostly propylene as primary product regardless of their acid strength [26]. However, the MOR_{Si/Al=5}, which possesses the highest acid site strength, experiences rapid deactivation as the reaction time progresses. Conversely, the MOR_{Si/Al=103} catalyst, having the least acid strength, maintains its catalytic activity even after 240 minutes under identical operating conditions. From the in-situ FTIR and NMR results, MOR zeolites possessing a high strength of acid sites tend to generate PAH with numerous fused aromatic rings inside the pores, causing them to deactivate quickly. Since alkyl aromatics are usually produced within the MOR pores, the MOR zeolite with the least acid strength can facilitate a scattered distribution of alkyl aromatics within the pores, thereby inhibiting the formation of PAH. The reduced acid strength in MOR

zeolites contributes to their delayed deactivation, which enables them to maintain their catalytic activity and generate light olefins.

3.1.2 Pyridine modified

Another study by He et al. also focuses on the effect of acid site distribution on olefin selectivity and the activation of MOR zeolite during MTO reactions [27]. However, in this study, they take a different approach by regulating acid site density in the 12-member ring main channel of MOR using pyridine adsorption. The size of a pyridine molecule is approximately 0.58 nm, which makes it bigger than the 8-member ring side pockets but smaller than the 12-member ring main channels in MOR. Consequently, the absorption of pyridine molecules in MOR zeolites can be used to adjust the acid site density in the 12-member ring channels. Based on the reaction results, the methanol conversion on pyridine-modified MOR was decreased from 100% to 54%. This result may be due to a decrease in the ¹H MAS NMR signal of Brønsted acid sites located within 12-member ring channels of MOR zeolites, suggesting that the 12-member ring channels were fully filled and all the remaining Brønsted acid sites can be assigned to the 8-member ring side pocket. However, there is an improvement in light olefin selectivity, indicating that the acid sites in 12-member ring channels are more engaged in forming alkanes (C₃ aliphatic hydrocarbon as a major product) instead of olefin, whereas the acid sites within the 8-member ring side pockets predominantly produce olefins (C₃ olefin as a major product) rather than alkane. This explanation clearly demonstrated a slight difference from the previous studies from Park et al., that state the large 12-member ring pores facilitate the formation of alkyl aromatic intermediates with large alkyl substituents, leading to the production of C₄ and C₅ olefins while the 8-member ring small channel is selective towards light olefin (C₂ and C₃ olefins) in which similar with SAPO-34 ring type [26].

3.1.3 Incorporation of metals

Like other zeolite modifications, the common routes to adjust the zeolite acidity and structure are by incorporating metals. Currently, there is only one article that reports on the utilization of metal modification on MOR zeolite in MTO reaction. Shareh et al. prepared metal-impregnated dealuminated MOR (DMOR) using a variety of metals, including iron (Fe), lanthanum (La), and calcium (Ca) [28]. According to the study, the catalysts tested showed a reduction in acidity in a specific order, starting from DMOR and followed by Fe/DMOR, Ca/DMOR, and La/DMOR catalysts. Besides, the deposition of metal oxide onto the pores of MOR during the impregnation process reduced the average pore size of the metal-loaded catalysts, although it resulted in an increase in their surface area with the following order: La/DMOR > Ca/DMOR > Fe/DMOR > DMOR. This observation indicates that the type of metal impregnated on the zeolite support can

significantly affect its physicochemical properties. For the catalytic performance, the La/DMOR shows the highest yield of light olefins (especially propylene) after 7 h of time on stream. This clearly indicated that the catalyst's acidity affects propylene selectivity, with a lower acidity favored in promoting propylene formation and increasing the propylene/ethylene ratio. In addition, the presence of metal cations at the pore mouth of zeolites reduces pore size and dampens the formation of coke, which is a shape-selective reaction that depends on the zeolite's pore structure.

Table 1. Overall catalytic performance of distinctive zeolite catalyst.

Catalyst	LO selectivity (%)	P/E ratio	Stability (h)	Ref
MCM-22				
unmodified	42.5	6.8	48	[16]
(a)	47.2	10.2	46	
(b)	43.3	8.3	42	
(c)	44.6	9.2	48	
(d)	35.0	-	5	[17]
unmodified	40	2.0	40	[18]
(e)	50.0	2.7	40	
unmodified	46.2	4.6	52	[19]
(f)	49.4	5.7	102	
MOR				
(g)	39.9	0.5	1.7	[26]
(h)	68.8	0.7	1.7	
(i)	43.3	3.5	4	
(j)	42.3	5.3	4	
unmodified	19	0.1	0.7	[27]
(k)	60	0.9	2	
(l)	80	7.4	2	[28]
(o)	72	3.7	1.5	
(p)	79	3.6	2	
(q)	67	6.8	2	

Table 1 summarizes the complete catalytic performance results for each type of modified zeolite catalyst. Each label represented as (a) dealumination with AHFS, (b) dealumination with nitric acid (c) dealumination with oxalic acid, (d) Zn incorporation, (e) P incorporation, (f) Boron incorporation, (g) dealumination (Si/Al = 5), (h) dealumination (Si/Al = 12), (i) dealumination (Si/Al = 55), (j) dealumination (Si/Al = 103), (k) Pyridine MOR, (l) dealumination with HCL, (o) Fe incorporation, (p) Ca incorporation, and (q) La incorporation.

4 Conclusion

In conclusion, the modification of zeolite catalysts for the MTO reaction offers promising possibilities to improve their catalytic performance. The study focused

on two distinct zeolites: MCM-22 and MOR, and investigated various modification strategies to enhance their selectivity, P/E ratio, and catalytic lifetime. The modifications implemented have shown significant effects on the catalytic performance of these zeolite catalysts. Each modification technique has its advantages and limitations, impacting different aspects of the physicochemical properties of the zeolite catalyst in the MTO reaction. For instance, dealumination of MCM-22 zeolite effectively improves the selectivity of light olefins and the P/E ratio with only minor alterations to its lifetime. On the other hand, incorporating boron into the MCM-22 framework has a minimal impact on selectivity but enhances the overall catalytic lifetime. Further research and optimization are crucial to advancing the modified zeolite catalysts for the MTO reaction.

As authors, we are thankful for the financial support from Universiti Teknologi Malaysia for the Fundamental Research Grant (Grant No. 5F575).

References

1. M.R. Gogate, Methanol-to-olefins process technology: current status and future prospects. *Pet Sci Technol.* **37**, 559–565 (2019)
2. N. Nesterenko, J. Aguilhon, P. Bodart, D. Minoux, J.P. Dath, Methanol to Olefins: An Insight into Reaction Pathways and Products Formation. *Zeolites and Zeolite-like Materials.* 189–263 (2016)
3. A.K. Jamil, T. Nishitoba, M.H.M. Ahmed, Z.H. Yamani, T. Yokoi, O. Muraza, Stable Boron-Modified ZSM-22 Zeolite Catalyst for Selective Production of Propylene from Methanol. *Energy Fuels.* **33**, 12679–12684 (2019)
4. A.A. Ismail, R.M. Mohamed, O.A. Fouad, I.A. Ibrahim, Synthesis of nanosized ZSM-5 using different alumina sources. *Cryst Res Technol.* **41**, 145–149 (2006)
5. J. Li, Y. Wei, G. Liu, Y. Qi, P. Tian, B. Li, Y. He, Z. Liu, Comparative study of MTO conversion over SAPO-34, H-ZSM-5 and H-ZSM-22: Correlating catalytic performance and reaction mechanism to zeolite topology. *Catal Today.* 221–228 (2011)
6. D. Zapater, J. Lasobras, J. Soler, J. Herguido, M. Menéndez, MTO with SAPO-34 in a Fixed-Bed Reactor: Deactivation Profiles. *Ind Eng Chem Res.* **60**, 16162–16170 (2021)
7. D. Chen, K. Moljord, A. Holmen, A methanol to olefins review: Diffusion, coke formation and deactivation on SAPO type catalysts, *Microporous and Mesoporous Mater.* **164**, 239–250 (2012)
8. X. Jiang, X. Su, X. Bai, Y. Li, L. Yang, K. Zhang, Y. Zhang, Y. Liu, W. Wu, Conversion of methanol to light olefins over nanosized [Fe,Al]ZSM-5 zeolites: Influence of Fe

- incorporated into the framework on the acidity and catalytic performance. *Microporous and Mesoporous Mater.* **263**, 243–250 (2018).
9. R. Syah, A. Davarpanah, M. Elveny, A. Ghasemi, D. Ramdan, The economic evaluation of methanol and propylene production from natural gas at petrochemical industries in Iran. *Sustainability (Switzerland)*. **13** (2021)
 10. J. Zhong, J. Han, Y. Wei, Z. Liu, Catalysts and shape selective catalysis in the methanol-to-olefin (MTO) reaction. *J Catal.* **396**, 23–31 (2021)
 11. S.L. Lawton, M.E. Leonowicz, R.D. Partridge, P. Chu, M.K. Rubin, Twelve-ring pockets on the external surface of MCM-22 crystals. (1998)
 12. H.K. Min, M.B. Park, S.B. Hong, Methanol-to-olefin conversion over H-MCM-22 and H-ITQ-2 zeolites. *J Catal.* **271**, 186–194 (2010)
 13. P. Wang, L. Huang, J. Li, M. Dong, J. Wang, T. Tatsumi, W. Fan, Catalytic properties and deactivation behavior of H-MCM-22 in the conversion of methanol to hydrocarbons. *RSC Adv.* **5**, 28794–28802 (2015)
 14. A. Lacarriere, F. Luck, D. Świerczyński, F. Fajula, V. Hulea, Methanol to hydrocarbons over zeolites with MWW topology: Effect of zeolite texture and acidity. *Appl. Catal. A Gen.* **402**, 208–217 (2011)
 15. L. Zhang, H. Wang, G. Liu, K. Gao, J. Wu, Methanol-to-olefin conversion over H-MCM-22 catalyst. *J. Mol. Catal. A Chem.* **411**, 311–316 (2016)
 16. L. Zhang, H. Wang, G. Liu, K. Gao, J. Wu, Conversion of methanol to light olefins over H-MCM-22 dealuminated with different methods. *J. Chem Technol. Biotechnol.* **92**, 1353–1361 (2017)
 17. M. García-Ruiz, D.A. Solís-Casados, J. Aguilar-Pliego, C. Márquez-Álvarez, E. Sastre-de Andrés, D. Sanjurjo-Tartalo, R. Sáinz-Vaque, M. Grande-Casas, Synthesis of 10 and 12 Ring Zeolites (MCM-22, TNU-9 and MCM-68) Modified with Zn and Its Potential Application in the Reaction of Methanol to Light Aromatics and Olefins. *Top Catal.* **63**, 451–467 (2020)
 18. X. Wang, W. Dai, G. Wu, L. Li, N. Guan, M. Hunger, Phosphorus modified HMCM-22: Characterization and catalytic application in methanol-to-hydrocarbons conversion. *Microporous and Mesoporous Mater.* **151**, 99–106 (2012)
 19. J. Chen, T. Liang, J. Li, S. Wang, Z. Qin, P. Wang, L. Huang, W. Fan, J. Wang, Regulation of Framework Aluminum Siting and Acid Distribution in H-MCM-22 by Boron Incorporation and Its Effect on the Catalytic Performance in Methanol to Hydrocarbons. *ACS Catal.* **6**, 2299–2313 (2016).
 20. X. Wang, R. Li, C. Yu, Y. Liu, Study on the reconstruction in the crystallization process of mordenite. *Microporous and Mesoporous Mater.* **311**, (2021)
 21. M.G. Shelyapina, E.A. Krylova, A.S. Mazur, A.A. Tsyganenko, Y. V. Shergin, E.A. Satikova, V. Petranovskii, Active Sites in H-Mordenite Catalysts Probed by NMR and FTIR. *Catalysts*. **13**, 334 (2023)
 22. M. Cui, L. Wang, Y. Zhang, Y. Wang, C. Meng, Changes of medium-range structure in the course of crystallization of mordenite from diatomite. *Microporous and Mesoporous Mater.* **206**, 52–57 (2015)
 23. Z. Ma, J. Xie, J. Zhang, W. Zhang, Y. Zhou, J. Wang, Mordenite zeolite with ultrahigh SiO₂/Al₂O₃ ratio directly synthesized from ionic liquid-assisted dry-gel-conversion. *Microporous and Mesoporous Mater.* **224**, 17–25 (2016)
 24. W. Song, J.F. Haw, J.B. Nicholas, C.S. Heneghan, Methylbenzenes are the organic reaction centers for methanol-to-olefin catalysis on HSAPO-34. *J. Am. Chem. Soc.* **122**, 10726–10727 (2000)
 25. H.G. Kim, K.Y. Lee, H.G. Jang, Y.S. Song, G. Seo, Simulation of methanol-to-olefin reaction over SAPO-34 catalysts with different particle sizes: Formation of active sites and deactivation. *Korean J. Chem. Eng.* **27**, 1773–1779 (2010)
 26. J.W. Park, S.J. Kim, M. Seo, S.Y. Kim, Y. Sugi, G. Seo, Product selectivity and catalytic deactivation of MOR zeolites with different acid site densities in methanol-to-olefin (MTO) reactions. *Appl. Catal. A Gen.* **349**, 76–85 (2008)
 27. T. He, G. Hou, J. Li, X. Liu, S. Xu, X. Han, X. Bao, Highly selective methanol-to-olefin reaction on pyridine modified H-mordenite. *J. Energy Chem.* **26**, 354–358 (2017)
 28. F.B. Shareh, M. Kazemeini, M. Asadi, M. Fattahi, Metal promoted mordenite catalyst for methanol conversion into light olefins. *Pet. Sci. Technol.* **32**, 1349–1356 (2014)