

ABSTRACT

Title of Dissertation: THE UPGRADING OF METHANE TO AROMATICS OVER TRANSITION METAL LOADED HIERARCHICAL ZEOLITES

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With the boom of shale gas production, the conversion of methane to higher hydrocarbons (MTH) promises a great future as the substituent for hydrocarbon production from crude oil based processes. Among various MTH processes, direct methane aromatization (DMA) is promising since it can achieve one-step methane valorization to aromatics. The molybdenum/zeolite (Mo/MFI or Mo/MWW) has been the most active catalyst for the DMA reaction, which, however, is impeded from industrial practice due to the rapid deactivation by coke deposition. To address this challenge, in this work, transition metal loaded hierarchical 2 dimensional (2D) lamellar MFI and MWW zeolites have been studied as catalysts for the DMA reaction. The effects of micro- and mesoporosity, external and internal Brønsted acid sites, as well as particle size of 2D lamellar zeolites on the DMA reaction have been investigated.

Firstly, the spatial distribution of Brønsted acid sites in 2D lamellar MFI and MWW zeolites has been quantified by a combination of organic base titration and methanol dehydration reaction. The unit-cell thick 2D zeolites after Mo loading showed mitigation on deactivation, increase in activity, and comparable aromatics selectivity to the Mo loaded 3D zeolite analogues. A detailed analysis of the DMA reaction over Mo/hierarchical MFI zeolites with variable micro- and mesoporosity (equivalent to variation in particle sizes) showed a balance between dual porosity was essential to modulate the distribution of active sites (Mo and Brønsted acid sites) in the catalysts as well as the consequent reaction and transport events to optimize performance in the DMA reaction.

External Brønsted acid sites have been proposed to be the cause of coke deposition on Mo/zeolite catalysts. Deactivation of the external acid sites have been practiced to improve the catalyst performances in the DMA reaction in this work. Atomic layer deposition (ALD) of silica species was conducted on the external surface of 2D lamellar MFI and MWW zeolites to deactivate the external acid sites in Mo/2D lamellar zeolites for the DMA reaction. Another strategy to deactivate external acid sites in Mo/zeolite catalysts was the overgrowth of 2D lamellar silicalite-1 on the microporous zeolites. The as-prepared catalysts showed higher methane conversion and aromatics formation as well as higher selectivity to naphthalene and coke in comparison with Mo loaded microporous analogues.

THE UPGRADING OF METHANE TO AROMATICS OVER TRANSITION
METAL LOADED HIERARCHICAL ZEOLITES

by

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Dedication

I would like to take this opportunity to dedicate this dissertation to my beloved mother and father. They have tried their best and scarified a lot to let me achieve my potential. I was born and raised in a small, beautiful riverside town in China, which, however, has limited resources for a kid to be well educated, not to mention to stand out and realize his or her dream. When I was 11, my parents brought me to the capital city of my home province and it was this move that opened a new door to me. Afterwards, I was always on the move, from the provincial capital to the national capital, and finally came to US to pursue a PhD degree with a hope to receive a highly advanced education, see a bigger world and taste a totally different culture. Throughout the entire course, my parents are always willing to support me with all they have without a hesitation. It is hard to imagine that I have been US for five and half years. Indeed, I had my up and down during this period but never thought of giving up. Now I am very proud to be the first one in my entire family to carry a Dr. before the surname. I hope my parents will be proud of their son and more importantly, be proud of themselves for their endless love and selfless sacrifice.

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I would like to thank my advisor, Prof. Dongxia Liu, for her help and support through my whole PhD study. She is always full of passion in the research and eager to take immediate action, which set a model for me not only in the PhD study but also in the future career. She has an impressive insight to establish a logic and convincing story from a series of data, and a wonderful skill to deliver it to the readers, which I deeply admire and learned a lot from. It was not easy to go through the transition from an undergraduate to a graduate student and I really appreciate her time spent with me during that period. I will keep working hard and hope I do not let her down now and in the future.

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I always like to collaborate with others to combine our techniques and facilities to push the research forward. Therefore, I would like to thank Zheng Lu from Prof. Yu Lei's group at University of Alabama, Lu Liu and Scott Holdren from Prof. Michael Zachariah's group as well as Junkai Hu and Luning Wang from Prof. Bryan Eichhorn's group.

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Chapter 1: Introduction

1.1. Methane from the boom of shale gas production

One of the great challenges in heterogeneous catalysis is the conversion of methane, an abundant hydrocarbon source on earth, to useful chemicals and fuels. Because of the boom of shale gas, which mainly consists of methane, conversion of methane to hydrocarbons (MTH) has received intensive global research efforts since the beginning of this century. Shale gas is the natural gas trapped in the sedimentary rocks termed shale rocks and has been placed in the heart of energy discussion since the beginning of the century due to its ubiquitous abundance and relatively low production cost, as demonstrated in Figure 1.1 [1, 2]. Compared to other common sedimentary rocks such as sandstone and limestone, shale rocks have an insufficient permeability to allow a significant out-flow of natural gas to a wellbore, which in turn requires a large number of wells to assess one section of shale layers [1]. Therefore, shale gas has long been regarded as an impractical or expensive source of natural gas since its discovery in 1821.

Two important techniques, horizontal drilling and hydraulic cracking, were developed to make the production of shale gas practical and profitable, as illustrated in Figure 1.2. Horizontal drilling, as its name indicates, consists of a 90-degree turn of a drilling pipe into the rocks, allowing for contact with a large area of shale layers, thus avoiding the need for a large number of vertical wells. Hydraulic cracking fractures the shale rocks to release the trapped natural gas and allows the gas to flow out of the wells by pressurizing tons of water and other fluids through the pipeline into the shale layers.

When the hydraulic pressure is released, a proppant consisting of sand and other chemicals is immediately pumped into the openings to keep the fractures open. The combination of horizontal drilling and hydraulic cracking has achieved a massive success in the commercialization of the shale gas production, increasing the percentage of shale gas in the US total production of natural gas from only 1% in 2000 to more than 30% in 2013, the largest share among all of the sources. The dramatic increase of natural gas production has significantly lowered the price of natural gas [4], which provides an unprecedented opportunity for the MTH process to be economically competitive with the crude oil-based hydrocarbon production, particularly in the era of an increasing demand for high quality distillates [5].

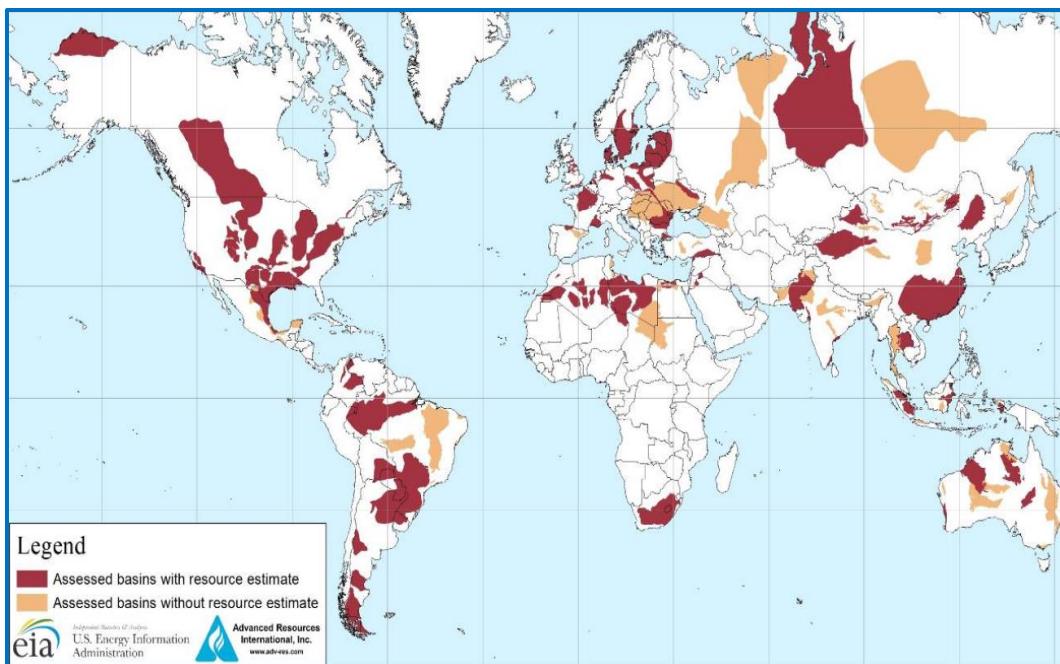


Figure 1.1. Map of basins with assessed shale gas and shale oil formations, as of May 2013. (Image from U.S. Energy Information Administration with title ‘Technically Recoverable Shale Oil and Shale Gas Resources: An Assessment of 137 Shale Formations in 41 Countries Outside the United States’ as published in 2013.)

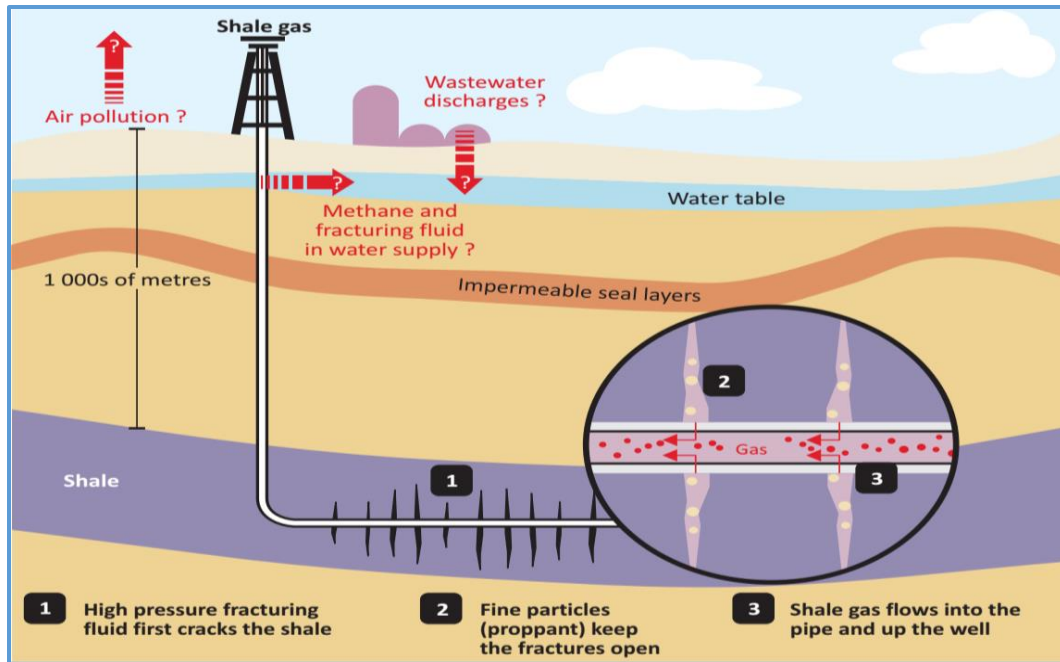


Figure 1.2. Scheme of horizontal drilling and hydraulic cracking in the production of shale gas. (Ref. [3])

1.2. Overview of major MTH techniques

Several MTH techniques have been developed, with the major techniques being indirect conversion consisting of methane reforming to syngas (H_2/CO) followed by conversion of syngas to fuels and chemicals [6-9], and direct conversion, such as oxidative coupling of methane (OCM) [10-12] and non-oxidative direct methane aromatization (DMA) [13-16].

At present, methane reforming is the only commercial MTH technique in the industry. The syngas from methane reforming can be converted into chemicals by a variety of synthetic routes, among which the Fischer-Tropsch process is the most commonly employed technique, as shown in Figure 1.3(A). Several methane reforming processes have been developed, including (1) steam methane reforming (SMR), (2) partial oxidation (POX), (3) auto thermal reforming, (ATR), (4) dry methane reforming

(DMR), (5) combined methane reforming (CMR), (6) methane reforming with membranes and (7) tri-reforming of methane (TMR) [17, 18]. The major difference between these methods lies in the composition of syngas, i.e. the H_2/CO ratios, as shown in Figure 1.3(B), which can be used as the criteria to select the proper reforming process for a specific application of syngas [18]. Among these reforming processes, the first three, i.e. SMR, POX and ATR, have been well developed and widely employed in the industry while the rest are developed as innovations to reduce greenhouse gas, minimize the energy cost or fine tune the product yields [18].

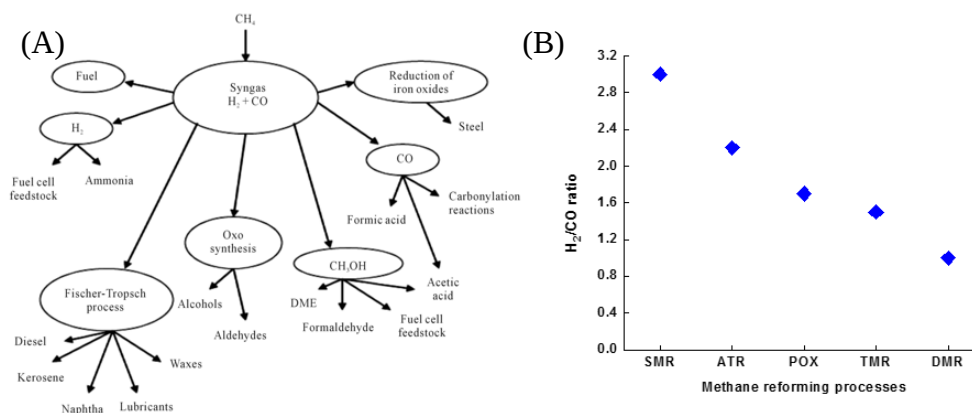
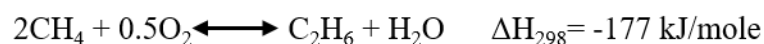


Figure 1.3. Synthetic routes of syngas produced from methane reforming (A) and the H_2/CO ratios in various methane reforming processes (B).

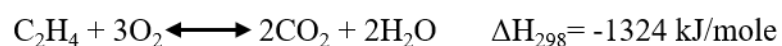
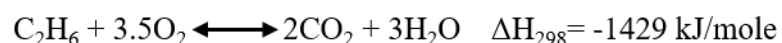
The methane reforming process and the subsequent conversion of syngas to fuels and chemicals include many energy intensive intermediate steps and require harsh conditions, like high temperature and high pressure. For example, SMR, the most widely commercialized reforming process, is practiced at the temperature of 1073-1173 K and the pressure of 30 bar. In order to develop a cost-effective approach, it is not surprising that intensive research efforts have been attempted to find a direct conversion of methane operated at mild conditions. The challenge of the direct methane

conversion lies in the high energy barrier of methane activation that requires ~440 kJ/mole to break down the first C-H bond in the methane tetrahedral structure [19, 20]. To address this challenging issue, OCM was first developed in the 1980s to obtain direct methane conversion with the assistance of reactive oxygen to break down the extremely stable C-H bond. The primary product from OCM is ethylene, the world's largest commodity chemical with >137 million metric tons of global usage in 2013 alone [21]. In the commonly accepted OCM mechanism, methane is partially oxidized to ethane and subsequently to ethylene as shown in Scheme 1.1.

OCM reactions



Undesired side reactions



Scheme 1.1. Catalytic routes in the OCM reactions.

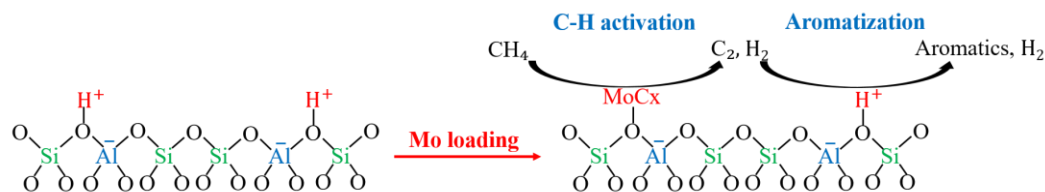
The catalysts used in the OCM reaction are mainly oxide catalysts, which can be pure or modified oxides of transition metals and the mixed or promoted oxides of group IA and IIA metals [21, 22]. The best catalytic performance ever reported can reach 81% selectivity for C₂, including ethylene and ethane, at 20% methane conversion [21, 22]. However, the over-oxidation of ethane and ethylene to CO₂ and CO, which are far more thermodynamically stable than C₂ as illustrated in the Scheme 1.1, prevents a high selectivity to C₂ at a high conversion of methane. In addition,

methane to CO_x is highly exothermic reaction, and the dissipation of heat generated from the over-oxidation is a formidable engineering problem. In view of this, researchers started to study MTH reactions under non-oxidative conditions. In the early 1990s, Wang et al. discovered that methane could be directly converted into benzene with a selectivity close to 100% with a conversion of 7~8% in the absence of oxygen. Since then, the DMA reaction, converting methane to aromatics and ethylene in one step, has attracted a continuous, intensive research attention, particularly in the golden era of shale gas production since 2000. The mechanism, common catalysts and major achievements in the DMA reaction will be reviewed in the following sections.

1.3. Review of recent progress in the DMA reaction

In 1993, Wang et al. first reported the direct methane conversion to aromatics, primarily benzene, over Mo-loaded MFI zeolite (Mo/MFI) catalyst at 973 K and ambient pressure, which immediately attracted intensive research interests [13]. Since then, a variety of transition metals and zeolites have been combined to form transition metal loaded zeolite catalysts for the DMA reaction in order to further improve the catalytic performance and understand the reaction mechanism. A bifunctional reaction mechanism has been well established in literature [15, 16, 23-27], as illustrated in Scheme 1.2. In this mechanism, with the most widely studied Mo/MFI catalyst as an example, Brønsted acid sites function as the anchoring sites to stabilize the MoO_x species in the zeolites. During the initial contact with methane at high temperatures, 973 K for example, MoO_x species are reduced to Mo₂C [23, 25-27] or MoC_xO_y [24] species that can activate methane into CH₃· radicals. Immediately upon the formation of methyl radicals, their dimerization leads to formation of C₂ intermediates, such as

ethylene and ethane, which go through the cyclization and aromatization over Brønsted acid sites to produce benzene and other aromatics.



Scheme 1.2. The DMA reaction over Mo loaded MFI zeolite

Zeolites are three-dimensional (3D) crystalline aluminosilicates with well-defined angstrom-size micropores and strong acidity, which are widely used as heterogeneous acid catalysts in petrochemical and fine chemical syntheses [28-32]. In the zeolite framework, a tetrahedral coordinated four-valent Si atom is replaced by a three-valent Al atom to form a Si-O-Al tetrahedral structure, which creates an imbalanced negative charge centered at the Al atom. The acidity of zeolites originates from the attachment of a proton to the oxygen atom bridging Si and Al atoms in order to balance the negative charge, forming Si-O(H)-Al acid sites, as shown in the Scheme 1.2. The unique feature of zeolite in catalysis compared to other solid acid sites lies in the pore size of the micropores in zeolite, which is on the order of molecule size, and thus renders zeolites excellent shape selectivity in catalytic reactions. Zeolites can exist in the nature, which, however, is not useful in industrial practices due to their non-uniform structure and unknown impurities. Hence, synthetic zeolites have been developed for practical applications, and, to date, there are more than 200 types of synthetic zeolites with different structure of porous channels. Faujasite (FAU), shown in Figure 1.4(A), is the most widely employed zeolite in industry, primarily for fluid catalytic cracking in petrochemical processes [15]. Mordenite Framework Inverted

(MFI) (or ZSM-5) zeolite, shown in Figure 1.4(B), is another commonly used zeolite in the synthesis of ethylbenzene, isomerization of xylenes and disproportionation of toluene [15].

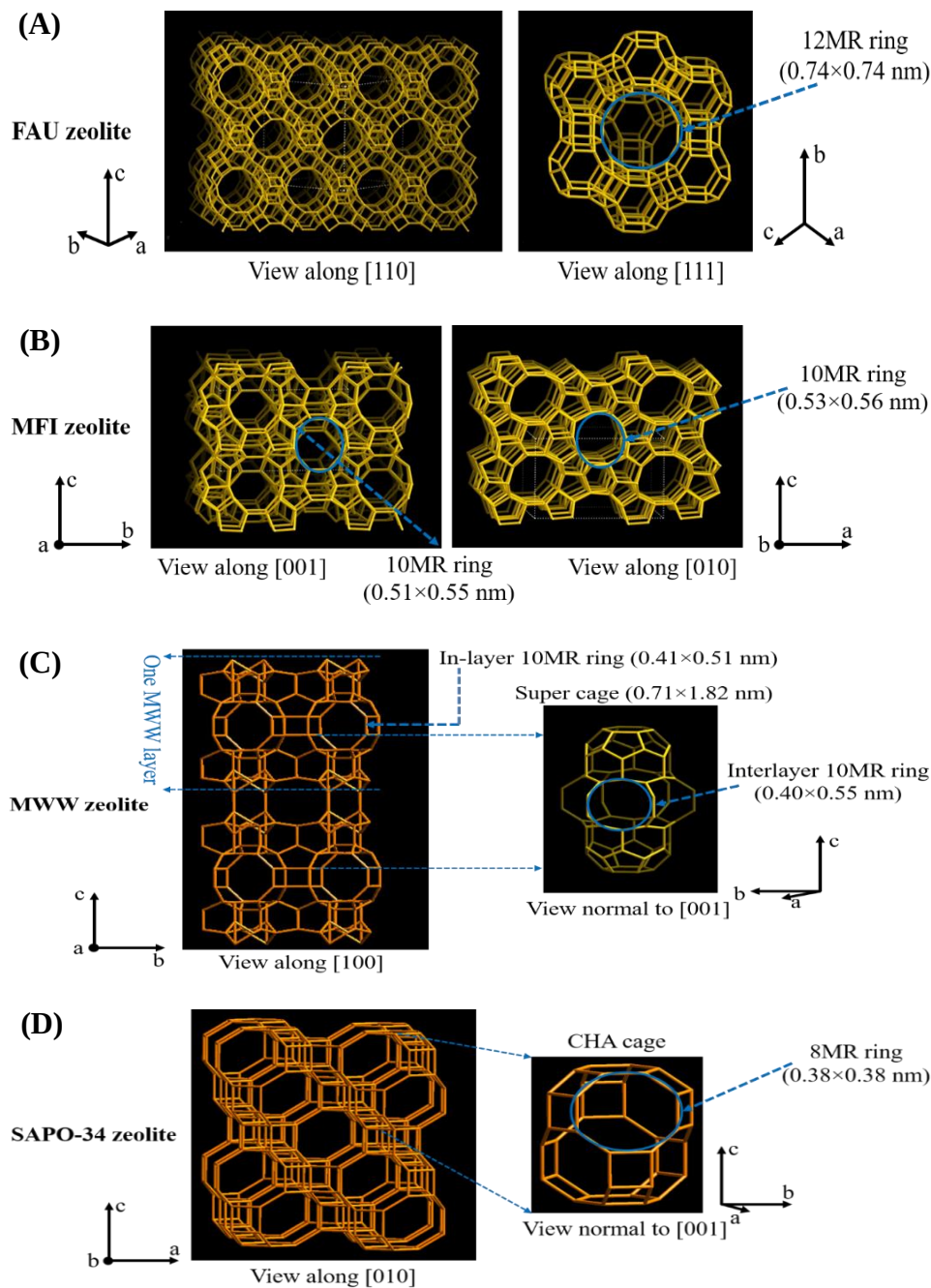


Figure 1.4. Structure schemes of FAU zeolite (A), MFI zeolite (B), MWW zeolite (C) and SAPO-34 zeolite (D). (Images from International Zeolite Association)

In the DMA reaction, a variety of zeolites have been investigated, including MFI [13, 26, 33-47], MWW [39, 45, 48-53], BEA [54], ZSM-8 [55], ZSM-11 [55], MCM-41 [55], SAPO-34[55], MOR [41], FAU [41, 56] and FSM-16 [41], MCM-49 [57, 58], TNU-9 [59, 60]. So far, the Mo/MFI catalyst has shown the best catalytic performance in terms of methane conversion and selectivity to desired aromatics, enabling it to be the most widely studied catalyst for the DMA reaction. Compared to Mo/MFI, the Mo-loaded MWW (Mo/MWW) zeolite catalyst showed similar catalytic performance. The high activity and selectivity of Mo/MFI and Mo/MWW can be attributed to the shape selectivity of their 10-member ring (MR) microporous channels. MFI zeolite has two intersecting 10-member ring porous channels, one with a pore size of 0.53×0.56 nm along the b-axis direction and the other with a pore size of 0.51×0.56 nm along the a-axis direction (Figure 1.4(B)) [61, 62], which are close to the kinetic diameter of benzene (~ 0.5 nm) [16, 63]. MWW zeolite consists of two types of 10 MR channels, one with a pore size of 0.41×0.51 nm as the aperture of the supercage and the other one with a pore size of 0.40×0.55 nm inside the MWW layer (Figure 1.4(C)) [61, 62]. The similarity between micropore size in MFI (or MWW zeolite) and the kinetic diameter of the benzene ring facilitates the formation of benzene while restricting the formation of polycondensed aromatics, sources of coke, leading to the high activity and better stability of Mo/MFI and Mo/MWW catalysts in the DMA reaction. On the contrary, SAPO-34 zeolite is comprised of 8 MR micropores with a pore size of 0.38×0.38 nm (Figure 1.4(D)), which limit the formation of benzene due to steric confinement, resulting in poor selectivity in the DMA reaction. On the other side of the spectrum, the 12 MR micropores in FAU zeolite have a pore size of $0.74 \times$

0.74 nm (Figure 1.4(A)), which is much larger than the diameter of benzene and thus promotes the accumulation of heavy aromatics, leading to poor catalytic activity in the DMA reaction.

So far, Mo, Re, W, Fe, Zn, Cu, Mn, Ni, Cr, V and Ga have been tested as the other key component in the bifunctional transition metal/zeolite catalyst in the DMA reaction, among which the Mo shows the best catalytic performance, followed by Re and W[14, 15, 64]. Instead of using only one type of transition metal, a second type of transition metal has been added as the promoter [15]. For example, the addition of Pt [65] or Cu[66] led to the increase of activity and selectivity of the Mo/MFI catalyst in the DMA reaction, which can be attributed to the lower carbonization rate due to the presence of the second metal.

Additionally, in 2014, Bao's group discovered a new type of catalyst with 0.5% Fe embedded in the framework of silica to form a Fe@SiO₂ catalyst that showed 48% conversion of methane at 1363 K with 50% selectivity for ethylene, 25% selectivity for benzene and 25% selectivity for naphthalene under a methane space velocity of 21400 gcat⁻¹ hour⁻¹ [67]. The operating temperature of Fe@SiO₂ is more than 1223 K, which is much higher than the commonly employed temperature of transition metal/zeolite catalysts (950-973 K) in the DMA reaction.

1.4. Challenges with the DMA reaction

Despite high activity and selectivity, both Mo/MFI and Mo/MWW catalysts suffer from a rapid deactivation within a few hours during the DMA reaction, which prevents them from industrial practice. The commonly accepted mechanism of the deactivation is the fast accumulation of coke on the active sites, which can block the

channels of zeolites and lower the accessibility of active sites. The nature of the carbonaceous deposits has been intensively studied by a variety of methods and mostly over Mo/MFI catalysts [34, 52, 53, 68-70]. Three types of coke have been identified in the spent Mo/MFI catalyst, i.e. coke associated with Brønsted acid sites consisting of dense polyaromatics, coke deposited on the Mo active sites such as Mo₂C and coke deposited on the external surface consisting of pre-graphite structures. Among them, the coke associated with the Brønsted acid sites has been demonstrated as the most harmful for the DMA reaction. In order to overcome the rapid deactivation as well as to promote the activity of catalysts in the MDA reaction, several approaches have been proposed, which are reviewed in detail in the following paragraphs.

1.4.1. Introduction of mesoporosity into microporous zeolites

As discussed above, the success of zeolites in the DMA reaction is mainly attributed to the encapsulation of acid sites within the well-defined, angstrom-size microporous channels that enable excellent shape selectivity towards benzene [28-30]. The relatively small size of micropores, on the other hand, renders low catalyst utilization due to limited access to the acid sites and the slow mass transport in zeolites where the processing of bulky molecules is concerned [62, 71-73]. In the DMA reaction, the slow mass transport of bulky aromatic products will facilitate the polyaromatization reaction, resulting in the accumulation of polyaromatic coke and thus causing the rapid deactivation of catalysts. Recently, hierarchical zeolites with both mesoporosity (2-50 nm in pore size) and microporosity (< 2 nm in pore size) have been tested in the DMA reaction to address this challenging issue associated with conventional microporous zeolites [35, 36, 59, 74, 75]. The mesoporosity in hierarchical zeolites is capable of

enhancing the mass transport and facilitating the accessibility of active sites while the microporosity can retain the shape selectivity to desired products.

Several methods have been studied to introduce mesopores into zeolites, such as hard carbon template assisted hydrothermal synthesis [35, 36] and alkali treatment [74, 75]. The DMA reaction test results over Mo-loaded hierarchical meso-/microporous MFI zeolites prepared by these methods consistently showed that the introduction of mesoporosity significantly improved catalyst stability by alleviating the mass transport limitation and functioning as a coke trap to increase the tolerance to coke. In addition, compared to Mo-loaded microporous zeolites, Mo-loaded meso-/microporous zeolites showed higher conversion of methane and higher yields of aromatics without sacrificing the benzene selectivity. Despite these positive preliminary results, there is a lack of systematic study on the effect of mesoporosity on the catalytic performance of Mo-loaded meso-/microporous zeolite catalysts in the DMA reaction.

1.4.2. Deactivation of external acid sites

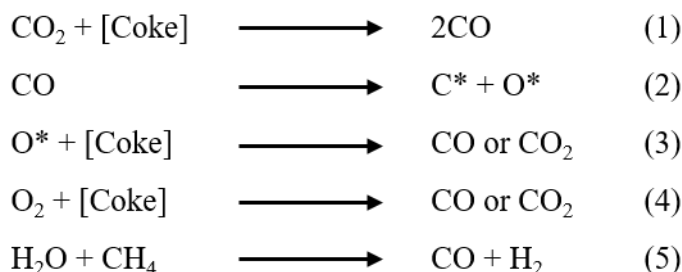
Although the acid sites on the external surface of zeolites allow for easy accessibility of reactant and better mass transport compared to those deep inside the micropores, the lack of shape selectivity due to the absence of steric confinement on the external surface leads to a heavy accumulation of carbonaceous species on the external acid sites, causing rapid deactivation of the catalyst in the DMA reaction. In order to overcome the deactivation, two different methods have been proposed to deactivate the external acid sites. The first method was to deposit silica species via chemical liquid deposition (CLD) [76, 77] or chemical vapor deposition (CVD) [38]

onto the external surface of MFI zeolite to cover and deactivate the external acid sites. Since the kinetic diameters of the silica precursors were much larger than the micropore size of MFI zeolite, they were unable to penetrate the micropores, leaving the acid sites in micropores intact after the silanation treatment. The other method was to coat a silicalite-1 (Al-free form MFI) shell on the MFI surface to form a core-shell MFI@silicalite-1 structure in which the external acid sites were fully covered and deactivated by the silicalite-1 shell [78]. The DMA reaction test results confirmed that both methods led to an increase of catalyst stability.

1.4.3. Addition of co-feed to methane

In the DMA reaction, a variety of co-feeds, such as CO₂, CO, O₂, H₂, and H₂O, have been added into the methane in order to mitigate the catalyst deactivation, primarily over the Mo/MFI catalysts [49, 79-88]. Scheme 1.3 illustrates the mechanism of these co-feeds against the deactivation. CO₂ is capable of oxidizing surface coke, CH_x (x=1-4), to CO and H₂ (reaction (1) in Scheme 1.3) to restore the activity of catalysts. In the DMA reaction, CO can be dissociated to form active carbon and oxygen species (reaction (2) in Scheme 1.3). The formed active oxygen species can oxidize coke to CO or CO₂ (equation (3) in Scheme 1.3), while the formed active carbon can participate in the DMA reaction [84, 85, 88]. Similarly, the addition of O₂ can remove coke via oxidization (reaction (4) in Scheme 1.3), which, however, needs to be performed with caution since the Mo₂C active sites can also be oxidized to inactive MoO_x species [89, 90]. The addition of H₂ can inhibit the formation of dense polyaromatic coke from dehydrogenation reaction as well as remove the surface coke via hydrogenation [80, 83, 91, 92]. In contrast, the mechanism of water addition against

coke formation follows an indirect approach by reacting with methane to form H₂ and CO (reaction (5) in Scheme 1.3) [93]. Furthermore, in order to save gas or avoid over-oxidization, periodical pulses of O₂ or H₂ instead of continuous addition have also been carried out to remove coke and restore the catalyst activity [34, 91].



Scheme 1.3. The mechanisms of coke removal with the addition of CO₂ (1), CO (2, 3), O₂ (4) and H₂O (5).

1.4.4. Reactor design

The design of the reactor is another important approach to overcoming fast deactivation of catalysts and improving their catalytic performance in the DMA reaction. For example, the DMA reaction can be coupled with an OCM reaction by using a two-layer reactor with SrO–La₂O₃/CaO as the OCM catalyst in the top layer and the Mo-loaded MCM-49 zeolite catalyst (Mo/MCM-49) as the DMA catalyst in the bottom layer, which led to a significant improvement of catalyst stability compared to the sole Mo/MCM-49 catalyst [58]. This enhancement of catalyst stability was attributed to the in-situ formation of CO₂ and H₂O from the OCM reaction in the top layer, which efficiently removed the coke formed from the DMA reaction in the bottom layer. Similarly, the DMA reaction can be coupled with the methane dry reforming reaction by using a two-layer reactor with Mo/Al₂O₃ as the methane reforming catalyst in the top layer and the Mo/MCM-49 catalyst in the bottom layer [57]. The in-situ

formation of H₂ and CO from the methane dry reforming reaction significantly lowered the coke accumulation in the DMA reaction and consequently mitigated the deactivation rate of the Mo/MCM-49 catalyst.

Besides the coupling of reactions, another strategy is to use an oxygen-permeable membrane to let oxygen flow diffuse from the sweep side to the reaction side to oxidize the coke formed in the DMA reaction. For example, a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2} (BSCF) perovskite membrane has been used as an oxygen-permeable membrane to provide a continuous flow of O₂ to lower the coke formation over the Mo/MFI catalyst in the DMA reaction [94]. Electrochemical membranes, such as a BaZrO₃-based membrane, has also been studied in alleviating the deactivation of Mo/MFI catalyst in the DMA reaction. In this type of membrane, O₂ ions are electrically driven into the reaction side to remove the coke and enhance the stability of catalyst [95].

1.5. Layout of this dissertation

As discussed in the Section 1.4.1, the introduction of mesoporosity into the microporous zeolites via demetalization or the hard template method led to a higher methane conversion and a better stability in the DMA reaction compared to their microporous counterparts. This improvement can be ascribed to the enhanced mass transport, the easy accessibility of active sites and the high tolerance for coke accumulation in the synthesized meso-/microporous zeolites. In addition to the demetalization and hard template methods, another approach to creating mesopores is to slice 3D zeolites into nearly unit-cell thick (~2-3 nm) 2D structures [96-103]. 2D lamellar zeolite is an innovative type of meso-/microporous zeolite in the hierarchical

zeolite family [98, 99, 101, 102, 104-106] in which the acid sites are exposed directly on the external surface or caged within a single-micropore distance from the surface.

In recent years, a variety of synthesis strategies have been carried out to produce 2D lamellar zeolites, such as exfoliation [34] or pillaring of layered zeolites [35-37] and growth of zeolites in templates [38-41], and, as a result, 15 lamellar zeolites have been synthesized [98, 99, 104, 106, 107]. The extremely thin slices of crystals in these zeolites provide high external surface areas, exposing most of their acid sites for catalytic reactions, which eliminates the need for diffusion of reactants to the internal acid sites inside the micropores. Among them, lamellar MFI zeolite and lamellar MWW zeolite deserve more attention since microporous MFI and MWW zeolites are among the most active zeolite supports for the DMA reaction.

Although they possess the desired mesoporosity, the application of 2D lamellar zeolites in the DMA reaction has not yet been studied. Hence, in the present research, we aim to study: (1) the unique spatial distribution of acid sites in 2D lamellar zeolites (2) the catalytic performance of Mo-loaded 2D lamellar zeolites in the DMA reaction (3) the effect of surface modification on the catalytic behaviors of 2D lamellar zeolites (4) the overgrowth of lamellar MFI nanosheets on the surface of microporous zeolites and its consequence on the catalytic behaviors of the resultant zeolite composites in the DMA reaction.

The spatial distribution of acid sites in zeolites is essential to their catalytic performance in acid catalyzed reactions. It has been reported that differentiation and quantification of external acid sites on the zeolite surface and internal acid sites inside the micropores can be obtained via titrations of bulky base molecules that can solely

access external acid sites, including 2,6-di-tert-butylpyridine (DTBP) [29, 47, 62, 108-115], 1,3,5-trimethylpyridine (collidine) [116-118], triphenylphosphine (TPP) [119, 120] and trimethylphosphine (TMP) [121]. Recently, a third type of acid sites located on the entrance of micropores, pore mouth acid sites, was reported to show a distinct catalytic selectivity compared to external acid sites and internal acid sites. For example, the etherification of β -citronellene with ethanol was reported to only occur on the pore mouth acid sites in the BEA zeolite, while the undesired isomerization of β -citronellene was catalyzed by the acid sites inside the micropores [122]. As the length of the micropore domains shrinks to close-to-single unit cell thickness, 2D lamellar zeolites expose more pore openings and consequently comprise more pore mouth acid sites accessible for reactants compared to conventional bulk zeolites. Despite the synthesis and catalysis over 2D lamellar zeolites, the identification of pore mouth acid sites in 2D zeolites and their catalytic behaviors have not been studied in the literature. Hence, in the first part of this dissertation (Chapter 2), we aim to differentiate and quantify the spatial distribution of acid sites on the external surface, at the pore openings and deep inside the micropores via a combination of base titrations. The base titration molecules were selected to have different kinetic diameters and basic strengths, enabling them to access acid sites at different locations in 2D zeolites. Furthermore, the catalytic behaviors of these three types of acid sites were rigorously evaluated in the shape-selectivity sensitive, diffusion-constrained benzyl alcohol alkylation with mesitylene reaction.

After the identification and quantification of acid site distribution, in Chapter 3, we explored the effect of mesoporosity on the activity, selectivity and stability of Mo-

loaded 2D lamellar zeolite catalysts in the DMA reaction. We compared the catalytic performances of Mo-loaded lamellar MFI zeolite and lamellar MWW zeolite catalysts in the DMA reaction to those of Mo-loaded conventional microporous MFI zeolite and microporous MWW zeolite catalysts. The results showed that mesoporosity led to a significant improvement in the activity and stability of the Mo-loaded 2D lamellar zeolite catalysts in the DMA reaction, especially in the initial stage.

Inspired by the positive effect of mesoporosity demonstrated in the second part, in Chapter 4, we systematically and rigorously studied the effect of mesoporosity on the textural properties, active site distribution and the catalytic performance (activity, selectivity and stability) of Mo-loaded 2D lamellar MFI zeolites in the DMA reaction. The lamellar 2D MFI zeolites were synthesized based on a dual template method reported in our previous work [123], and their mesoporosity was tailored by simply tuning the ratio of two templates, i.e. $C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}(Br)_2$ (C_{22-6-6}) and tetrapropylammonium hydroxide (TPAOH). Results showed that a balance between mesoporosity and microporosity was essential to obtain desired textural properties and active site distribution as well as to optimize the catalytic performance of Mo-loaded 2D lamellar MFI zeolite catalysts in the DMA reaction.

As demonstrated in Chapter 2, 3 and 4, 2D lamellar structure provides a large amount of external acid sites, leading to an enhanced accessibility of acid sites, which, however, is accompanied with an inferior selectivity to desired products due to the lack of a shape selective environment compared to those enclosed in the micropores. For example, in the DMA reaction, external acid sites were reported to favor the accumulation of coke and thus became one of the main causes of fast catalyst

deactivation. To circumvent this disadvantage, CVD [76, 77] and CLD [38] have been carried out to deposit silica species on the zeolite surface to deactivate external acid sites. However, both CVD and CLD are likely to deposit excessive amounts of silica species, resulting in blockage of the pore openings and narrowing of the porous channels, due to the lack of precise control of the deposition process. Compared to CVD and CLD, the state-of-art atomic layer deposition (ALD) technique is capable of achieving a far more precise control of the deposition sites at the atomic level. Hence, in Chapter 5, we proposed to deactivate the external sites of 2D lamellar zeolites, i.e. pillared MFI (PMFI) and pillared MWW (PMWW) zeolites, via ALD of silica (ALD-Si) or alumina species (ALD-Al) onto the surface of these pillared zeolites and study the consequent effect on their catalytic behaviors. Furthermore, the kinetic diameters of precursors for ALD-Si (tris(dimethylamino)silane, TDMAS) and ALD-Al (trimethylaluminium, TMA) are larger than those of micropores in both PMFI and PMWW zeolites, which prevent their access from the micropores and thus only allow them to access and deactivate the external acid sites. The catalytic performance of ALD modified PMFI and PMWW zeolites were rigorously evaluated in the ethanol dehydration reaction, alkylation and etherification of benzyl alcohol in mesitylene, and the shape-selectivity sensitive DMA reaction.

Lastly, in Chapter 6, we provided another effective method to deactivate the external acid sites on the widely employed microporous MFI and BEA zeolites via overgrowth of inactive lamellar silicalite-1 nanosheets onto their surfaces. Silicalite-1, as an Al-free form of MFI zeolite, has been reported to be the proper material to deactivate the external acid sites in zeolites [78, 124-126]. For example, silicalite-1 was

coated on the MFI zeolite to form an MFI@silicalite-1 core-shell structure to mitigate the accumulation of coke in the methanol to olefin reaction [126] or to enhance the selectivity to the desired p-xylene in toluene methylation with methyl bromide [125]. However, the silicalite-1 shell is likely to fully wrap the zeolite core and consequentially cause the blockage of pore openings and aggravate the diffusion limitation. Herein, by taking advantage of the facilitated mass transport of the 2D lamellar structure, we aim to overcome the drawback of the conventional core-shell structure by growing lamellar silicalite-1 nanosheets on the microporous MFI and BEA zeolites to form lamellar silicalite-1/MFI and lamellar silicalite-1/BEA zeolite composites. This zeolite composite structure can deactivate the external acid sites and simultaneously retain the facile mass transport. The catalytic performance of these zeolite composites was examined in the DMA reaction.

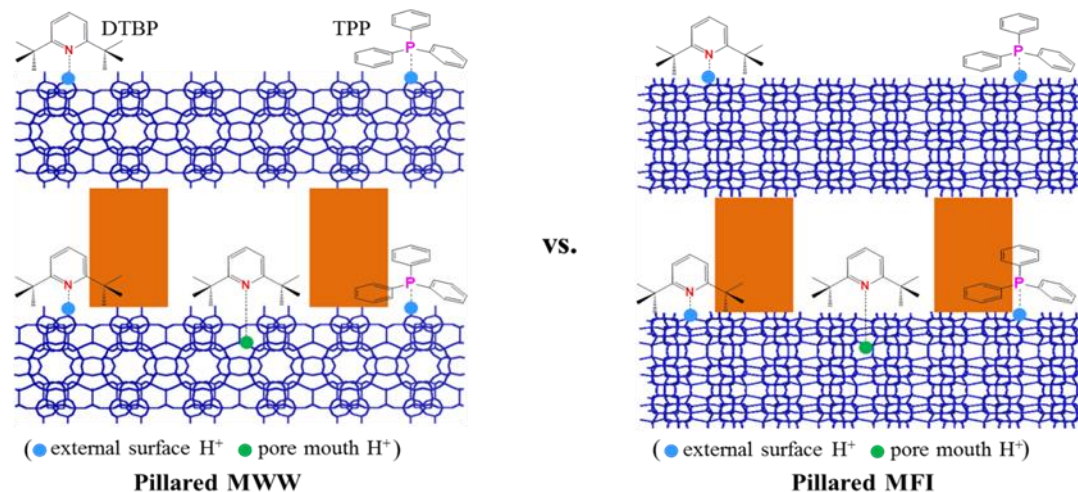
Chapter 2: Quantification of External Surface and Pore Mouth Acid Sites in Unit-Cell Thick Pillared MFI and Pillared MWW Zeolites

2.1. Introduction

Recently, a third type of acid sites located at the micropore openings of zeolites, i.e. pore mouth acid sites, was reported to show distinct catalytic selectivity compared to those located on the external surface (external surface acid sites) and deep inside the micropores of zeolites (internal acid sites) [116, 122, 127, 128]. In the reactions involving with bulky molecules unable to penetrate the micropores or in the situation of micropore blockage, pore mouth acid sites may become the major active sites [122]. Compared to bulky zeolites, the 2D lamellar zeolites expose a much higher fraction of pore openings to the reactants and thus contain a much larger amount of pore mouth acid sites. However, despite the synthesis and catalytic tests of the unit-cell thick 2D zeolite catalysts, the differentiation and quantification of acid sites that sit on the external surface or at the pore mouth regions of 2D zeolites, however, have not been explored in literature.

In the present work, we report the identification and quantification of acid sites on external surface or at pore mouth of 2D pillared MFI (PMFI) and pillared MWW (PMWW) zeolites. We implemented a combined dimethyl ether (DME) titration and methanol dehydration in the presence of 2,6-di-tert-butylpyridine (DTBP) or triphenylphosphine (TPP) base titrant, respectively, to quantify the fractions of acid sites on external surface, at pore mouth regions and in micropores of PMFI and PMWW

zeolites, as shown in Scheme 2.1. The same measurements were also carried out on PMFI and PMWW zeolites after their external surface acid sites were selectively passivated by the atomic layer deposition (ALD) of silica-species to further confirm the quantifications on fractions of external surface and pore mouth acid sites in these zeolites.



Scheme 2.1. Titrations with DTBP and TPP over PMWW and PMFI zeolites to identify and quantify external surface and pore mouth acid sites.

DME has a kinetic diameter of 0.47 nm [129], which can access all the active acid sites in PMFI and PMWW zeolites. The difference in number of acid sites in zeolites before and after their external surface acid sites passivated by silica-species reflects the concentration of external surface acid sites. DTBP molecule is sterically bulky with a diameter of 0.79 nm [110] and has a strong base strength which can titrate acid sites on the external surface and at the pore mouth regions but cannot access those in the micropores of PMFI and PMWW zeolites [108, 115, 130]. Compared to DTBP, the TPP molecule is sterically bulkier with a diameter of 0.94 nm [120] but has a weaker base strength [131, 132]. It can solely access the acid sites on the external surface [119]. The decrease in methanol dehydration rate in the presence of DTBP or TPP titrant

reflects the fractions of external surface and/or pore mouth acid sites in PMFI and PMWW zeolites. Additionally, the catalytic behavior of the external surface and pore mouth acid sites was evaluated by alkylation of benzyl alcohol in mesitylene with cumulative DTBP or TPP addition. The non-linear correlation between the decrease in alkylation rate and added DTBP or TPP quantity suggests that individual external surface or pore mouth acid site performed differently in the studied catalytic reaction.

2.2. Experiments

2.2.1. Materials preparation

PMFI was prepared by pillaring of a multilamellar MFI precursor following the method reported by Na et al. [133]. The multilamellar MFI precursor was synthesized using the method reported by Ryoo and co-workers [102]. PMWW zeolite was derived from the precursor, MCM-22(P). The hydrothermal synthesis of MCM-22(P) was carried out by using the method described by Corma et al. [134]. The MCM-22(P) was swollen according to the method developed by Maheshwari et al. [135], followed by pillaring of the swollen material using the procedure reported by Barth et al. [136] to make PMWW zeolite. The as-synthesized PMFI and PMWW zeolites were ion-exchanged three times using 1 M aqueous ammonium nitrate (NH_4NO_3) (weight ratio of zeolite to NH_4NO_3 solution = 1:10) at 353 K for 12 h, and subsequently, collected by centrifugation and washed with deionized (DI) water three times, and dried at 343 K overnight. All zeolite samples in their NH_4^+ -form were treated in dry air (100 mL min^{-1} , Airgas) by increasing the temperature from ambient temperature to 823 K at 0.03 K s^{-1} and holding at 823 K for 4 h to thermally decompose NH_4^+ to NH_3 and H^+ .

The ALD of silica species (ALD-Si) on PMFI and PMWW zeolites was performed as our previous report [46]. A viscous flow benchtop reactor (Gemstar-6, Arradiance) was used to carry out this experiment. N₂ (Airgas, 99.999% purity) was used as a carrier gas (50 mL min⁻¹) and further purified by a Supelco gas purifier (Sigma-Aldrich) before entering the reactor. 0.5 g of zeolite was uniformly spread onto a stainless steel tray with a mesh on top of it. The mesh prevented the spill of the sample and allowed access to the Si-precursor vapor in the ALD process. The ALD-Si was carried out by alternative exposure of zeolite sample to tris(dimethylamino)silane (TDMAS, Sigma-Aldrich, 99.999%) and ozone at 573 K for 15 s, followed by N₂ purge for 200 s after each exposure. The resultant zeolite samples from ALD-Si modifications of PMFI and PMWW were denoted as Si-PMFI and Si-PMWW, respectively.

2.2.2. Quantification and differentiation of acid sites in PMFI and PMWW zeolites

2.2.2.1. Total number of acid sites determined by DME titration

The total number of Brønsted acid sites in the PMFI and PMWW zeolite was measured via the DME titration. The Brønsted acid sites in zeolite participate in the reaction of DME with H⁺ in two-to-one manner to form surface methyl groups, $\text{CH}_3\text{OCH}_3 + 2[\text{SiO}(\text{H})\text{Al}] = 2[\text{SiO}(\text{CH}_3)\text{Al}] + \text{H}_2\text{O}$. The titration experiment was carried out in a tubular packed-bed quartz reactor (10 mm inner diameter) under atmospheric pressure. The temperature of the reactor was held at 423 K by a resistively heated furnace (National Electric Furnace FA120 type). Catalyst temperature was measured using a K-type thermocouple touching the bottom of a well on the external surface of the quartz reactor. A mixture of DME, Ar and He (7.5% DME, 22.5% Ar, 70% He, Airgas) flowed (50 cm³ s⁻¹) through a sample loop (0.250 mL) and pulsed over

zeolite samples in a He carrier stream ($50 \text{ cm}^3 \text{ s}^{-1}$; 99.99%, Airgas) at 2 min intervals. Only Ar ($m/z = 40$) was detected in reactor effluent from initial pulses of DME over the zeolite samples. DME ($m/z = 45$) was only detected in the reactor effluent after all H^+ sites had been replaced with CH_3 groups. Thus, the number of H^+ sites was determined from the number of disappeared DME in the effluent. Details on the DME titration experimental setup and reaction conditions were described in our previous publications [45, 47]. The same setup was used for the following methanol dehydration reactions in the presence of organic bases.

2.2.2.2. External surface and pore mouth acid sites determined by methanol dehydration in presence of organic base

To distinguish and quantify external surface, pore mouth and internal acid sites in PMFI and PMWW zeolites as well as Si-PMFI and Si-PMWW samples, methanol (CH_3OH) dehydration in the presence of DTBP or TPP was measured at 433 K. Typically, the liquid mixture of methanol (Fisher Scientific, 99.9%) and organic base (either DTBP (Alfa Aesar, 98% purity) or TPP (Alfa Aesar, 99+% purity)) was introduced into a flowing He stream heated at 348 K using a syringe pump (NE 1000, New Era Pump System Inc.). The reactor effluent was sent via heated transfer lines (at $\sim 373 \text{ K}$) to a mass spectrometer (MS, Ametek Proline). The methanol dehydration rate was reflected by the signal of dimethyl ether ($m/z=45$) in MS spectra. The loss in methanol dehydration rate with DTBP or TPP addition reflects the accessibility of acid sites to DTBP or TPP molecules in PMFI and PMWW zeolites. The fraction of Brønsted acid sites on external surface ($f_{\text{ext},\text{H}^+}$) of zeolites was determined by the degree of loss in CH_3OH dehydration rate in the presence of TPP titrants. The sum of

fractions of external surface and pore mouth acid sites ($f_{\text{sum},\text{H}^+}$) was indicated by the degree of loss in CH_3OH dehydration rate in the presence of DTBP molecules. The fractions of pore mouth acid sites (f_{pm,H^+}) can be calculated by $f_{\text{pm},\text{H}^+} = f_{\text{sum},\text{H}^+} - f_{\text{ext},\text{H}^+}$. Together with the total number of acid sites quantified by the DME titration above, the number of external surface and pore mouth acid sites can then be evaluated by mutilation of $N_{\text{tot},\text{H}^+}$ with the corresponding fractions of acid sites in each location.

2.2.3. Conversion of benzyl alcohol in mesitylene in the presence of DTBP or TPP titrant

The liquid phase catalytic conversion of benzyl alcohol in mesitylene in the presence of organic bases was carried out in a three-necked round-bottom flask (100 mL) under atmospheric pressure and magnetic stirring, as reported in our previous work [45]. In a typical experiment, a desired amount of DTBP or TPP and 15 mL of mesitylene were added to the zeolite catalyst, which was maintained for 2.5 h at the required reaction temperature and stirring conditions. Afterwards, 0.25 mL of benzyl alcohol was added to above mixture. The moment of addition of benzyl alcohol was taken as the initial reaction time. Liquid samples were withdrawn at regular time intervals and analyzed by the gas chromatograph (Agilent 7890 A GC) equipped with a methyl-siloxane capillary column (HP-1, 50.0 m $\times$ 320 μm $\times$ 0.52 μm) connected to a flame ionization detector. In the measurement, 1 μL liquid sample was injected into the GC inlet at temperature of 523 K with a split ratio of 50. The oven program was as follows: holding at 323 K for 5 mins, ramping to 473 K at a rate of 20 K min^{-1} , holding at 473 K for 7 mins and then cooling down to 323 K within ~ 5 min. The N_2 carrier gas

flow rate in the column was set at 2.4 mL min⁻¹. The temperature of FID detector was 573 K. A H₂ flow rate of 30 mL min⁻¹, air flow rate of 400 mL min⁻¹, and N₂ make-up flow rate of 22.8 mL min⁻¹ was used in the FID detector.

2.3. Results and discussion

2.3.1. Topological properties of 2D PMFI and PMWW zeolites

Figure 2.1 shows the topological structures of PMFI and PMWW zeolites, viewed along the b- and c-axis direction, respectively. The PMFI zeolite (Figure 2.1(A)) consists of ~1.5 unit-cell (~3.2 nm) [137] thick microporous MFI layer and the inorganic silica pillars (~ 2.8 nm in height) between two zeolite nanosheet layers. The microporous MFI layer contains two interconnected 10-membered ring (MR) channel systems: one is straight running along the b-axis direction (0.53 × 0.56 nm) and the other one is zigzag running parallel to the a-axis direction (0.51 × 0.55 nm). The PMFI contains mesopores created by the pillars sitting between MFI layers, parallel to the zigzag channels and perpendicular to the straight channels within the layers. Figure 2.1(B) shows the schematic structure of PMWW zeolite. Similarly, PMWW zeolite contains inorganic silica pillars with height of ~1.8 nm and unit-cell thick (~2.5 nm) microporous MWW layers [137]. Different from the microporous portion of PMFI structure, the microporous layer of PMWW contains two independent pore systems. One system is defined by sinusoidal 10-MR channels with dimensions of 0.41 × 0.51 nm and the other system consists of hourglass shaped pores (half of the supercages with dimensions of 0.71 × 0.71 × 1.81 nm in MWW) delimited by 6-MR channels. The mesopores in PMWW was created by pillaring the MWW layers by SiO₂, which

directly talks to the hourglass shaped 12-MR pores in the microporous zeolite layers. The comparable dimensions on thickness of microporous layers and height of mesoporous galleries in either PMFI or PMWW zeolites suggest that a comparable number of acid sites stay on the external surface or at the pore mouth regions to that encapsulated in the micropores. The morphologies and textural properties of PMFI and PMWW zeolites have been studied by scanning and transmission electron microscopy and Ar adsorption-desorption measurements, respectively, which have been reported in our previous work [46].

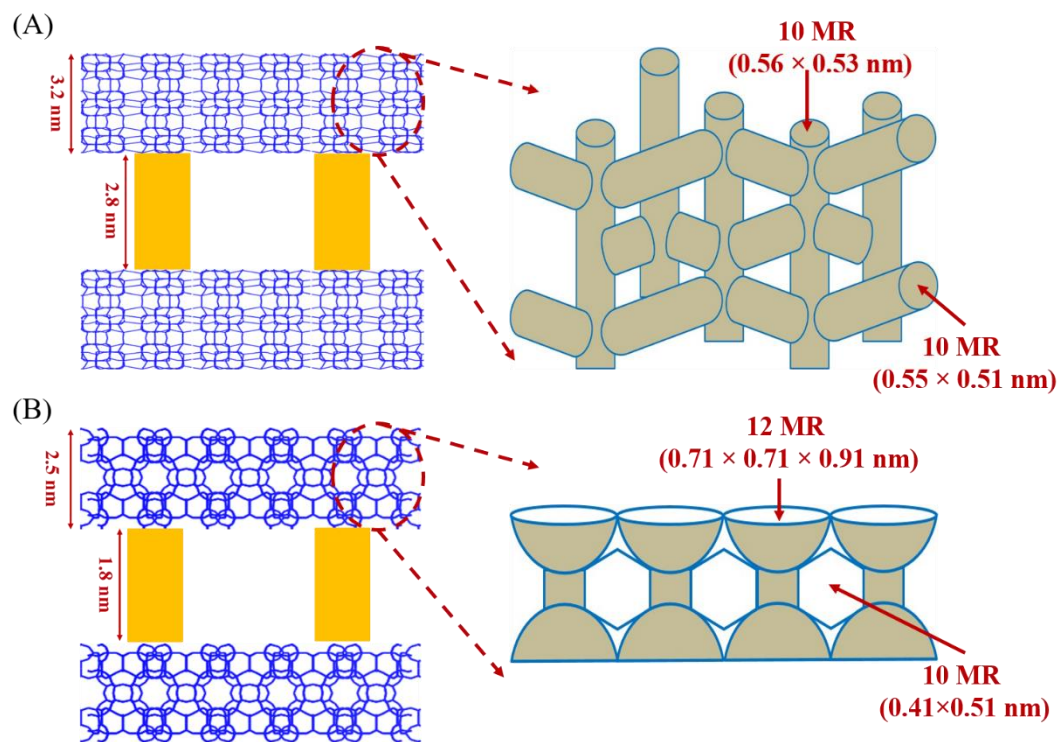


Figure 2.1. Schematic pictures showing the topological structure of PMFI (A) and PMWW (B) zeolites.

2.3.2. Structures of organic titrant molecules

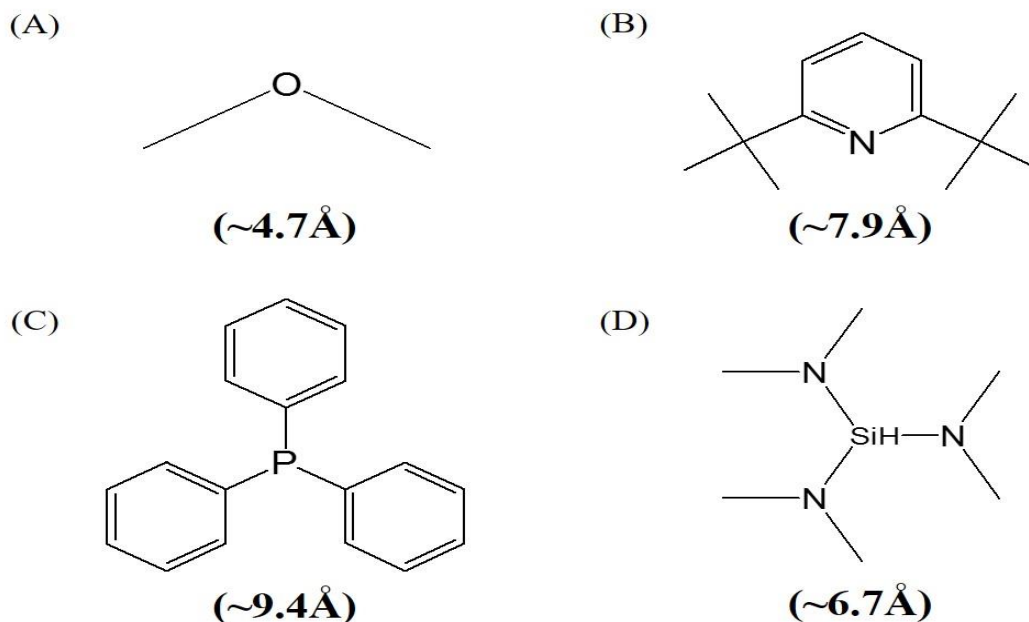


Figure 2.2. Molecular structure and kinetic diameter of DME (A), DTBP (B), TPP (C) and TDMAS (D) molecules.

To identify the number of external surface and pore mouth acid sites in PMFI and PMWW zeolites, organic base molecules, DME, DTBP and TPP, respectively, were employed in the titration experiments. Figure 2.2 (A)-(C) shows the molecular structures and kinetic diameters of these three organic base molecules. As shown in Figure 2.2(A), DME has a kinetic diameter of 0.47 nm [129], which is relatively small and thus is expected to access to the acid sites on external surface, at pore mouth regions and in micropores of PMFI and PMWW zeolites. On the contrary, DTBP (Figure 2.2(B)) has a kinetic diameter of 0.79 nm and a strong base strength, which can titrate acid sites both on the external surface and at the pore mouth regions but cannot access those in the micropores of PMFI and PMWW zeolites. Compared to DTBP, the TPP molecule (Figure 2.2(C)) is sterically bulkier with a diameter at 0.94 nm, but has a

weaker base strength[120]. It is expected to solely access the acid sites on the external surface. The passivation of external surface of PMFI and PMWW zeolites were done by ALD with TDMAS precursor (Figure 2.2(D)). The large size of TDMAS (~0.67 nm, determined with Avogadro software) has prevented its accessibility from the micropores of PMFI and PMWW zeolites, as indicated in our previous study [46].

2.3.3. Quantification of external surface and pore mouth acid sites

2.3.3.1. Fractions of external surface acid sites determined by DME titration

In DME titration experiments, the number of Brønsted acid sites (H^+) was determined directly by their chemical reaction with DME to form methyl groups via sequential pulses of DME to replace H^+ sites with CH_3 groups. Figure 2.3 shows that the titration profiles of PMFI, PMWW, Si-PMFI and Si-PMWW, respectively. DME and CH_3OH were undetectable in the reactor effluent during the initial pulses on the zeolite samples, consistent with the fast and irreversible nature of this methylation reaction [138, 139]. DME was detected in the effluent only after all protons were replaced by CH_3 groups, while CH_3OH was never detected in the effluent stream under the tested conditions, consistent with the work reported previously [138-140].

Table 2.1 summarizes the total number of acid sites (N_{tot, H^+}) in PMFI, PMWW, Si-PMFI and Si-PMWW zeolites, respectively, which are calculated from the DME titration profiles shown in Figure 2.3. The PMFI and PMWW zeolites contain 185 and 330 $\mu mol H^+ g^{-1}$, respectively. The Si-PMFI and Si-PMWW zeolites, however, consist of 126 and 239 $\mu mol H^+ g^{-1}$ acid sites, respectively, which are smaller by 59 and 91 $\mu mol H^+ g^{-1}$, respectively, than their parent pillared zeolites. The decrease in the number of acid sites in Si-PMFI and Si-PMWW zeolites was caused by the coverage

of external surface acid sites in PMFI and PMWW zeolites by SiO₂ species from the ALD modifications.

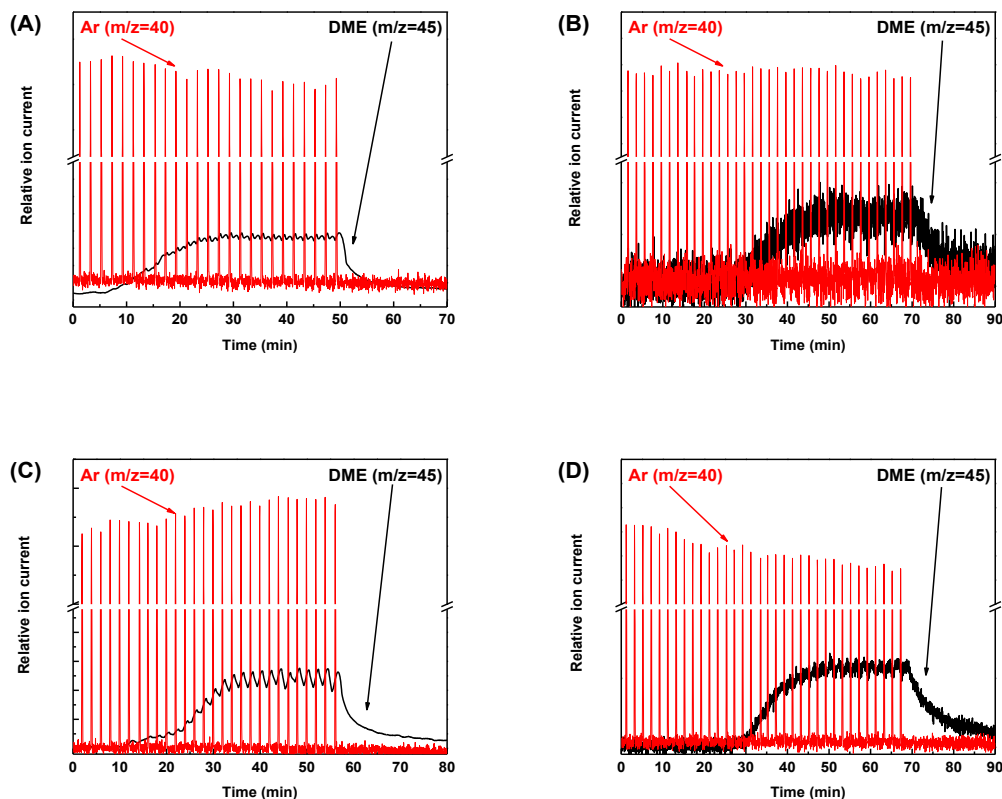


Figure 2.3. Mass spectra signals of DME ($m/z=45$, thick black line) and Ar ($m/z = 40$, thin red line) during DME/Ar pulses on PMFI (A), PMWW (B), Si-PMFI (C) and Si-PMWW (D), respectively (measured at 423 K).

Table 2.1. Fractions of external surface acid sites ($f_{\text{ext},\text{H}^+}$) in PMFI and PMWW zeolites, respectively, determined by DME titration before and after ALD of SiO₂ species.

Zeolite	Si/Al ratio	$N_{\text{tot},\text{H}^+}^a$	$N_{\text{ext},\text{H}^+}^{(1)b}$	$f_{\text{ext},\text{H}^+}^{(1)c}$
		$(\mu\text{mol H}^+ \text{ g}^{-1})$		(%)
PMFI	56	185	59	32
Si-PMFI	57	126	-	-
PMWW	32	330	91	28
Si-PMWW	33	239	-	-

^a Total amount of Brønsted acid sites measured by DME titration; ^b Calculated by subtracting the total amount of acid sites in ALD-treated zeolite from that in its parent zeolite; ^c Fraction of external surface acid sites, calculated by $f_{\text{ext},\text{H}^+}^{(1)} = N_{\text{ext},\text{H}^+}^{(1)} / N_{\text{tot},\text{H}^+}$. (1) stands for the method (1) used for determination of $f_{\text{ext},\text{H}^+}$.

As indicated in Figure 2.2(D), the molecular size of the SiO₂ precursor, TDMAS, is 0.67 nm, which can diffuse freely in the mesopores of both PMFI and PMWW zeolites to reach acid sites on external surface of zeolites, given the size of mesopores in PMFI (~2.8 nm) and PMWW (~1.8 nm) zeolites. However, the steric constraint of the bulky TDMAS prevents its access to acid sites in micropores of PMFI and PMWW zeolites. Therefore, the external surface acid sites is expected to be deactivated upon ALD passivation of PMFI and PMWW zeolites. The elemental compositions (represented by Si/Al ratios) of PMFI and PMWW zeolites and their derivatives after ALD modification were measured by inductively coupled plasma optical emission spectrometry in our previous study [46], which is repeatedly shown in Table 2.1 (column 2) for comparison purpose. For both PMFI and PMWW zeolites, the ALD modification resulted in a very slight increase in Si/Al ratios. The weight gains of PMFI and PMWW zeolites due to ALD of SiO₂-species are calculated to be 1.7 wt% and 3.8 wt%, respectively, in Si-PMFI and Si-PMWW zeolites. The mismatch between the slight weight gain for both PMFI and PMWW zeolites and the significant drop in total amount of acid sites in both Si-PMFI and Si-PMWW zeolites indicates that the decrease of total acid sites was mainly resulted from the passivation of external surface acid sites via ALD treatment instead of the dilution effect. Therefore, the comparative analyses of DME titrations of acid sites over PMFI and PMWW zeolites before and after ALD treatment, respectively, is a feasible approach to quantify the fractions of external surface acid sites. As calculated in Table 2.1, the fractions of external surface acid sites in PMFI and PMWW zeolites are 32% and 28%, respectively.

2.3.3.2. Fractions of external surface and pore mouth acid sites determined by methanol dehydration in presence of DTBP or TPP titrant, respectively

To investigate further on the distributions of acid sites on the external surface or at the pore mouth regions of PMFI and PMWW zeolites, a series of titration experiments with TPP or DTBP organic base were conducted during methanol dehydration reactions. Figure 2.4 shows methanol dehydration rates as a function of cumulative DTBP (Figure 2.4(A)) or TPP (Figure 2.4(B)) titrant addition on the pillared zeolites, respectively. Titration with DTBP or TPP over all zeolites initially resulted in a sharp decrease in methanol dehydration rates. At saturation of DTBP or TPP titrants, methanol dehydration maintained different residual rates over the PMFI and PMWW zeolites, suggesting that the bulky DTBP or TPP molecules have limited and different accessibility to Brønsted acid sites in PMFI and PMWW zeolites [29, 108, 119, 130, 141]. For the same zeolite, apparently, the residual methanol dehydration rate was higher upon TPP saturation than that of DTBP saturation, suggesting that TPP has less accessibility to acid sites in both PMFI and PMWW zeolites.

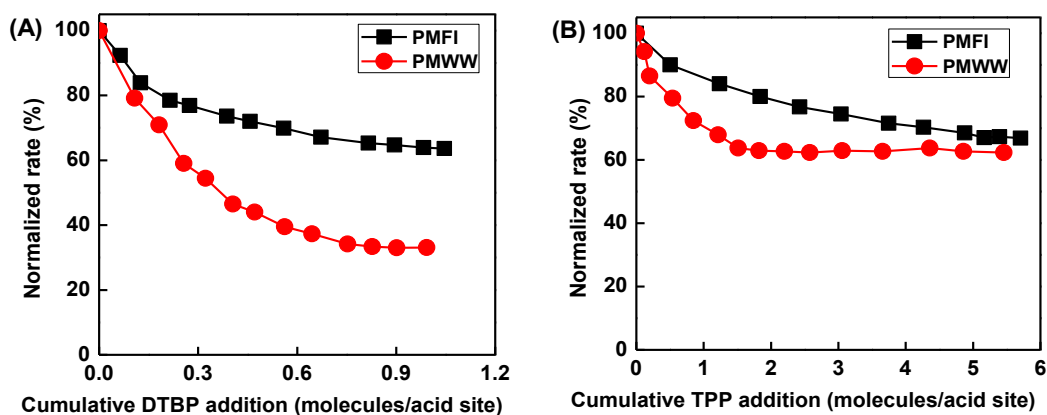


Figure 2.4. DTBP (A) and TPP (B) base titration of acid sites on PMFI and PMWW zeolites during methanol dehydration reaction.

DTBP base molecules can only titrate Brønsted acid sites because the steric hindrance around its N-atom prevents its coordination to Lewis acid sites [108, 138, 142]. Additionally, its bulkiness and strong base strength determine that DTBP is not capable of accessing acid sites in micropores of PMWW and PMFI zeolites, but can coordinate with acid sites at pore mouth regions and on external surface [108, 113, 143]. Compared to DTBP, TPP is sterically bulkier and has a weaker base strength [131, 132] and can solely access the acid sites on the external surface. Both DTBP and TPP have been reported to coordinate with the Brønsted acid sites in zeolites at 1:1 ratio [108, 113, 115, 119, 144]. Therefore, the degree in loss of methanol dehydration rate upon DTBP saturation reflected the fractions of the sum of acid sites on the external surface and at pore mouth regions ($f_{\text{sum}, \text{H}^+}$). The degree in loss of methanol dehydration rate upon TPP saturation indicated the fraction of external surface acid sites ($f_{\text{ext}, \text{H}^+}$). The fraction of acid sites at pore mouth regions, $f_{\text{pm}, \text{H}^+}$, can be evaluated by the calculation, $f_{\text{pm}, \text{H}^+} = f_{\text{sum}, \text{H}^+} - f_{\text{ext}, \text{H}^+}$.

Table 2.2 lists the fractions of external surface and pore mouth acid sites in both PMFI and PMWW zeolites. The sum of fractions of external surface and pore mouth acid sites are 37% and 67%, respectively, in PMFI and PMWW zeolites. The fractions of external surface acid sites are 32% and 37%, respectively. The fraction of external surface acid sites of PMFI zeolite is consistent with the number determined from the DME titration of acid sites in PMFI before and after ALD treatment. The fraction of external surface acid sites of PMWW zeolite, however, is slightly higher than that measured from the DME titration of acid sites in PMWW before and after ALD treatment. The differences in mechanisms of both quantification methods as well as the

differences in sizes and configurations of TDMAS and TPP probe molecules could contribute to the different fractions of external surface acid sites in PMWW zeolite. Hence, the fractions of pore mouth acid sites in PMFI and PMWW zeolites can be calculated to be 5% and 30%, respectively. Eventually, the fractions of internal acid sites, $f_{\text{int}, \text{H}^+}$, are calculated to be 63% and 33%, respectively, in PMFI and PMWW zeolites (Table 2.2).

Table 2.2. Fractions of external surface ($f_{\text{ext}, \text{H}^+}$) and pore mouth acid sites ($f_{\text{pm}, \text{H}^+}$) in PMFI and PMWW zeolites determined by DTBP and TPP titrations in methanol dehydration reaction.

Zeolite	$f_{\text{sum}, \text{H}^+}^a$ (%)	$f_{\text{ext}, \text{H}^+}^{(2)b}$ (%)	$f_{\text{pm}, \text{H}^+}^{(2)c}$ (%)	$f_{\text{int}, \text{H}^+}^d$ (%)
PMFI	37	32	5	63
PMWW	67	37	30	33

^a Sum of fractions of external surface and pore mouth acid sites determined by DTBP titration during methanol dehydration reaction; ^b Fraction of external surface acid sites determined by TPP titration during methanol dehydration reaction; ^c Fraction of pore mouth acid sites calculated by $f_{\text{pm}, \text{H}^+}^{(2)} = f_{\text{sum}, \text{H}^+} - f_{\text{ext}, \text{H}^+}^{(2)}$. (2) stands for method (2) used for determination of fractions of external surface and pore mouth acid sites; ^d Fraction of internal acid sites calculated by $f_{\text{int}, \text{H}^+} = 1 - f_{\text{sum}, \text{H}^+}$.

2.3.3.3. Fractions of pore mouth acid sites determined by methanol dehydration over Si-PMFI and Si-PMWW in presence of DTBP titrant

It has been reported that silylation of zeolites with tetraethyl orthosilicate (TEOS) preferentially deactivates acid sites on the external surface or at the pore mouth regions [112, 145]. As discussed in Section 2.3.3.1, passivation of external surface acid sites of PMFI and PMWW zeolites was achieved by ALD with TDMAS precursor. Our previous report [46] also indicates that the mesoporosity of Si-PMFI and Si-PMWW decreased significantly from that of PMFI and PMWW zeolites but the microporosity remained almost intact. All these results suggest that acid sites at pore mouth regions and in micropores of Si-PMFI and Si-PMWW zeolites are active in reactions. By taking

the advantage of Si-PMFI and Si-PMWW zeolites, the fractions of pore mouth acid sites in both zeolites can be quantified via methanol dehydration reaction in the presence of DTBP titrant.

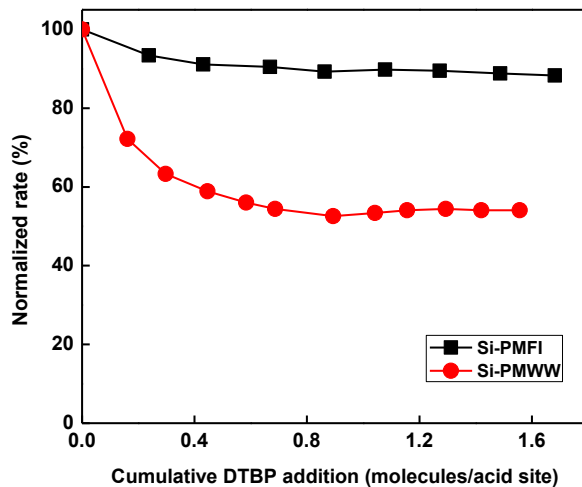


Figure 2.5. DTBP base titration of acid sites on Si-PMFI and Si-PMWW zeolites during methanol dehydration reaction.

As shown in Figure 2.5, methanol dehydration rates decreased monotonically with cumulative addition of DTBP. The degrees in loss of methanol dehydration rate upon DTBP saturation were 12% and 45%, respectively, for Si-PMFI and Si-PMWW zeolites (Table 2.3). Since the external surface acid sites were passivated by SiO_2 species in Si-PMFI and Si-PMWW zeolites, the degrees in loss of methanol dehydration rates reflect only the fractions of pore mouth acid sites. Given the total amount of acid sites shown in Table 2.1, the amount of pore mouth acid sites in Si-PMFI and Si-PMWW zeolites can be calculated to be $15 \mu\text{mol H}^+ \text{g}^{-1}$ and $108 \mu\text{mol H}^+ \text{g}^{-1}$, respectively. Because the pore mouth acid sites remained intact in the ALD treatment, the amount of pore mouth acid sites in PMFI and PMWW zeolites equals to

that of Si-PMFI and Si-PMWW zeolites, namely $15 \mu\text{mol H}^+ \text{g}^{-1}$ and $108 \mu\text{mol H}^+ \text{g}^{-1}$, respectively. Therefore, the fractions of pore mouth acid sites ($f_{\text{pm}, \text{H}^+}^{(3)}$) in PMFI and PMWW zeolites can be calculated by $f_{\text{pm}, \text{H}^+}^{(3)} = N_{\text{pm}, \text{H}^+} / N_{\text{tot}, \text{H}^+}$, which equal to 8% and 32%, respectively.

Table 2.3. Fractions of pore mouth acid sites ($f_{\text{pm}, \text{H}^+}$) in PMFI and PMWW zeolites determined by DTBP titration of Si-PMFI and Si-MWW zeolites in methanol dehydration reaction.

Zeolite	$f_{\text{pm}, \text{H}^+}^a$ (%)	$N_{\text{pm}, \text{H}^+}^b$ ($\mu\text{mol H}^+ \text{g}^{-1}$)	Zeolite	$N_{\text{pm}, \text{H}^+}^c$ ($\mu\text{mol H}^+ \text{g}^{-1}$)	$f_{\text{pm}, \text{H}^+}^{(3)d}$ (%)	$f_{\text{pm}, \text{H}^+}^e$ (%)	$f_{\text{ext}, \text{H}^+}^f$ (%)
Si-PMFI	12	15	PMFI	15	8	6	32
Si-PMWW	45	108	PMWW	108	32	31	33

^a Determined by degree of the loss in methanol dehydration rate in presence of DTBP titrant; ^b Calculated by $N_{\text{pm}, \text{H}^+} = f_{\text{pm}, \text{H}^+}(\text{Si-PMFI or Si-PMWW}) \times N_{\text{tot}, \text{H}^+}(\text{Si-PMFI or Si-PMWW})$; ^c $N_{\text{pm}, \text{H}^+}$ of PMFI and PMWW equal to $N_{\text{pm}, \text{H}^+}$ of Si-PMFI and Si-PMWW, respectively; ^d Calculated by $f_{\text{pm}, \text{H}^+}^{(3)} = N_{\text{pm}, \text{H}^+} / N_{\text{tot}, \text{H}^+}(\text{PMFI or PMWW in Table 2.1})$. (3) stands for method (3) used for determination of $f_{\text{pm}, \text{H}^+}$; ^e $f_{\text{pm}, \text{H}^+} = (f_{\text{pm}, \text{H}^+}^{(2)} + f_{\text{pm}, \text{H}^+}^{(3)})/2$; ^f $f_{\text{ext}, \text{H}^+} = (f_{\text{ext}, \text{H}^+}^{(1)} + f_{\text{ext}, \text{H}^+}^{(2)})/2$.

Up to now, we have conducted three different approaches to quantify the fractions of external surface and pore mouth acid sites in PMFI and PMWW zeolites. The first method, DME titration of acid sites in PMFI and PMWW zeolites before and after ALD treatment, directly calculated the fractions of external surface acid sites to be 32% and 28%, respectively. The third method, methanol dehydration with cumulative poisoning of acid sites by DTBP over Si-PMFI and Si-PMWW zeolites showed that the fractions of pore mouth acid sites are 8% and 32%, respectively. The second method by methanol dehydration over PMFI and PMWW zeolites with cumulative addition of DTBP or TPP differentiated and quantified the fractions of acid sites on the external surface and at pore mouth regions. Overall, the fractions of external surface or pore mouth acid sites were both identified twice by these three different approaches. If we take average of these measurement results, PMFI has 32% external

surface, 6% pore mouth and 62% internal acid sites. Similarly, PMWW has 33% external surface, 31% pore mouth and 36% internal acid sites, as shown in Table 2.3.

2.3.4. Catalytic behavior of acid sites on external surface and at pore mouth regions

In order to study the role of acid sites within different local environments, i.e. external surface and pore mouth regions, in the catalytic reaction, the liquid phase parallel catalytic conversion of benzyl alcohol in mesitylene (etherification to dibenzyl ether and alkylation to 1,3,5-trimethyl-2-benzylbenzene) was used as the probe reaction. The apparent rate constant of the alkylation reaction was evaluated at 348 K, with less than 10% conversion of benzyl alcohol, under rigorous agitation, and in excess amount of mesitylene (molar ratio of mesitylene to benzyl alcohol = 45:1) to eliminate the effect of catalyst deactivation and external surface mass transfer limitation, and reaction that converts dibenzyl ether to 1,3,5-trimethyl-2-benzylbenzene [71, 101]. Figure 2.6 shows the representative GC chromatographs of the benzyl alcohol reaction in mesitylene solvent in the absence and presence of zeolite catalyst, respectively. After 5 h reaction in the absence of zeolite catalyst, the peak areas of both mesitylene and benzyl alcohol (Figure 2.6(B)) were almost identical to their values at the beginning of reaction (Figure 2.6(A)). In contrast, the addition of zeolite catalyst (PMWW) enabled a significant decrease in benzyl alcohol peak area and an emergence of the product peaks: dibenzyl ether and 1,3,5-trimethyl-2-benzylbenzene (Figure 2.6(C)). The GC chromatographs clearly show the almost zero conversion of benzyl alcohol in the absence of zeolite catalyst and the formation of the products when the catalyst is added into the liquid mixture at the investigated reaction

condition. It has been reported that alkylation occurs only on the external surface and pore mouth acid sites of PMFI and PMWW zeolites due to the bulkiness of mesitylene compared to 10-MR micropores [71, 101]. Since the primary focus of the present study is to evaluate the catalytic behaviors of external surface and pore mouth acid sites, only the alkylation results were discussed in the present study. In addition, in order to understand the catalytic behavior of the individual external surface and pore mouth acid sites, the external surface and pore mouth acid sites of PMFI and PMWW zeolites were purposely and progressively poisoned by addition of DTBP or TPP base titrants in the alkylation reaction.

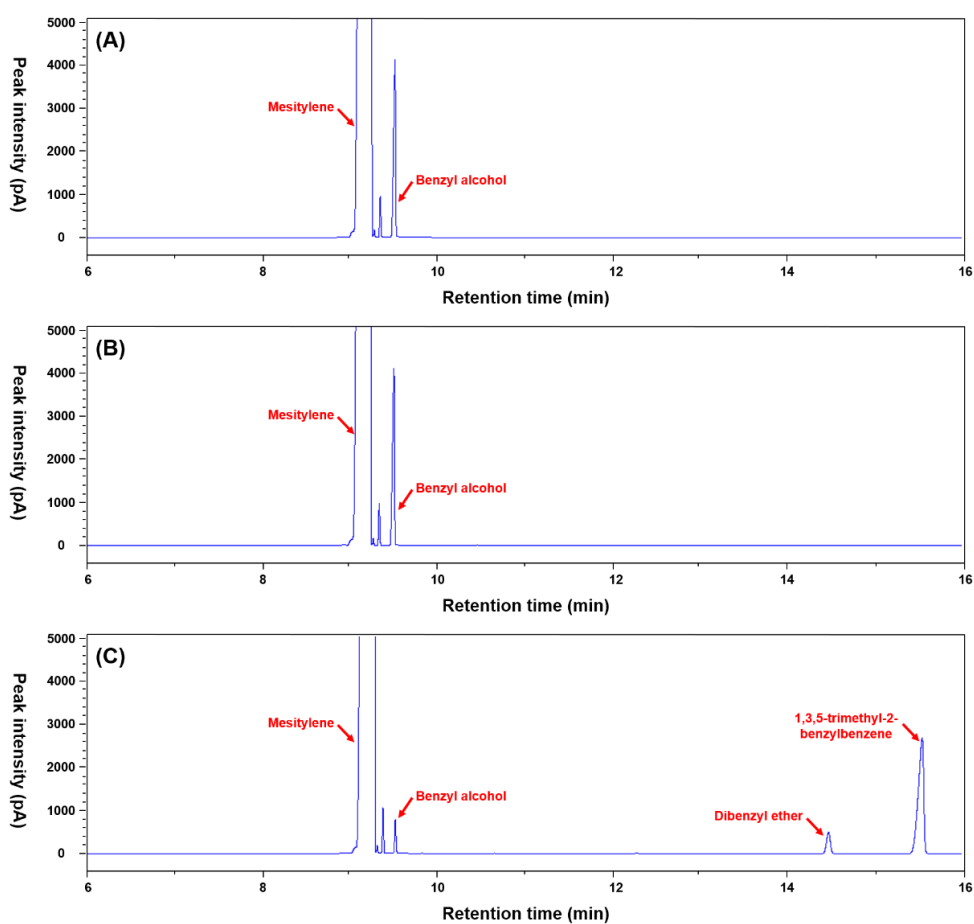
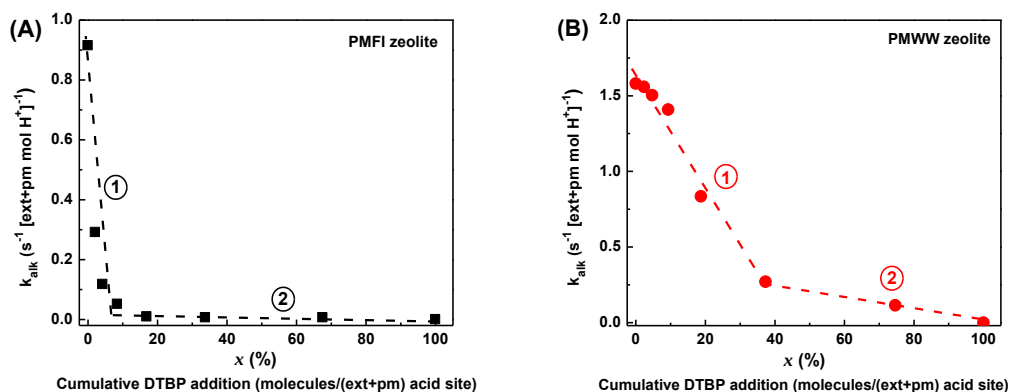


Figure 2.6. GC chromatographs of benzyl alcohol reaction in mesitylene solvent at the beginning of reaction (A), after 5 h reaction in the absence of zeolite catalyst (B) and after 5 h reaction in the presence of PMWW zeolite catalyst (C).

By applying pseudo-first order reaction model on the reaction data, the alkylation rate constant, k_{alk} , can be readily analyzed. The model for the alkylation reaction is: $\ln \frac{C_A^0}{C_A} = k_{\text{alk}} (N_{\text{ext}, \text{H}^+} + N_{\text{pm}, \text{H}^+}) (1 - x\%) (1 + \alpha) t$, where C_A^0 is the initial benzyl alcohol concentration in solution (mol L^{-1}), C_A is benzyl alcohol concentration in solution (mol L^{-1}), $N_{\text{ext}, \text{H}^+}$ (mol H^+) and $N_{\text{pm}, \text{H}^+}$ (mol H^+) are the moles of external surface and pore mouth acid sites, respectively, of the catalyst present in the batch reactor (Table 2.2), x (%) is the percentage of external surface and pore mouth acid sites that were poisoned by base titrant, α is the product selectivity ($\alpha = 2C_E/C_C$, C_E and C_C are the concentrations of dibenzyl ether and 1,3,5-trimethyl-2-benzylbenzene in solution (mol L^{-1}), respectively), and t is the reaction time (s), respectively.

Figure 2.7 demonstrates that the alkylation rate constant per acid site (external surface and pore mouth acid sites, i.e., ext + pm acid sites) with continuous addition of DTBP or TPP to progressively poison portions of these external surface and/or pore mouth acid sites. For the reaction over PMFI zeolite, a prompt drop in alkylation activity (>90%) per acid site with a small fraction of external surface and pore mouth acid sites (~10%) poisoned by DTBP and then the slow drop (only ~10%) in activity with ~90% of external surface and pore mouth acid sites poisoned by DTBP imply that some external surface and pore mouth acid sites are very active while others are insignificant in enabling the alkylation reaction (Figure 2.7(A)). This result suggests that the individual external surface or pore mouth acid site in PMFI performs differently in alkylation reaction. Different from PMFI zeolite, the alkylation reaction rate constant per ext+pm acid site in PMWW drops slowly upon cumulative DTBP addition into the

reaction mixture. As shown in Figure 2.7(B), the k_{alk} ($\text{s}^{-1} [\text{ext+pm mol H}^+]^{-1}$) of PMWW drops by $\sim 85\%$ when $\sim 40\%$ of external surface and pore mouth acid sites were poisoned by DTBP. The further addition of DTBP to poison the ext+pm acid sites from 40% to 100% caused $\sim 15\%$ decrease in the alkylation rate constant. The significant difference in k_{alk} decrease when different portions of acid sites in PMFI or PMWW zeolite were poisoned by DTBP might result from different acid strengths of these acid sites, as evidenced by the fact that the basic DTBP prefers to poison highly active acid sites [115]. The different acid strengths of these acid sites may be correlated to their locations, as quantified in this study. Apparently, PMFI and PMWW zeolites have different pore topologies, as discussed in section 2.3.1, and as consequences, the alkylation on both zeolites have different responses when the external surface and pore mouth acid sites were progressively deactivated by DTBP titrant. It should be noted that the alkylation reaction disappeared when 100% external surface and pore mouth acid sites were occupied by DTBP titrants, which reflects that the alkylation reaction solely occurred on the external surface and pore mouth acid sites of PMFI and PMWW zeolites.



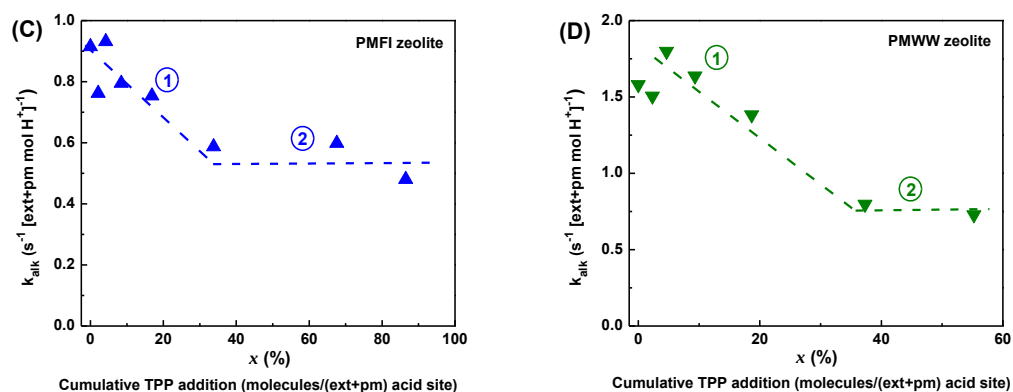


Figure 2.7. Alkylation rate constant per external surface and pore mouth acid site with cumulative addition of DTBP on PMFI (A) and PMWW (B) or with cumulative addition of TPP on PMFI (C) and PMWW (D) in the alkylation of mesitylene with benzyl alcohol. (x (%)) represents the percentage of active external surface and pore mouth acid sites poisoned by DTBP or TPP). (① and ② show two distinct segments in each plot, indicating two different catalytic behavior of external surface and/or pore mouth acid sites upon cumulative poisoning in alkylation reaction)

Figure 2.7 (C) and (D) show the changes in alkylation rate constant of PMFI and PMWW zeolites when the external surface acid sites were progressively poisoned by cumulative addition of TPP titrants into the reaction mixture. For PMFI zeolite, the initial addition of TPP (~40% of external surface and pore mouth acid sites) led to ~40% decrease in k_{alk} (s⁻¹ [ext+pm mol H⁺]⁻¹), as illustrated in Figure 2.7(C). The further addition of TPP into the reactant solution, however, did not influence the catalytic capability of individual acid site. Similarly, the changes in catalytic behavior of individual external surface or pore mouth acid sites in PMWW zeolite upon TPP progressively poisoning (Figure 2.7(D)) follow the trend of PMFI zeolite, in which a significant catalytic activity remained upon TPP saturation. Since the bulky configuration and less basicity of TPP led to the sole poisoning of acid sites on the external surface, the remaining activity could be assigned to the contribution from pore mouth acid sites in both PMFI and PMWW zeolites. The initial decrease followed by

a plateau in k_{alk} (s^{-1} [ext+pm mol H^+] $^{-1}$) in both Figure 2.7 (C) and (D) demonstrates that external surface and pore mouth acid sites have different reaction rate constants in the alkylation reaction.

2.4. Conclusion of Chapter 2

The quantification of acid sites on external surface and at pore mouth regions in PMFI and PMWW zeolites was conducted via three approaches: DME titration of acid sites before and after the external surface of zeolites passivated by SiO_2 -species, methanol dehydration over PMFI and PMWW with cumulative addition of TPP or DTBP titrants, and methanol dehydration over Si-PMFI and Si-PMWW with cumulative addition of DTBP titrants, respectively. The fractions of external surface or pore mouth acid sites identified by these methods consistently show that PMFI and PMWW have 32% and 33% external surface acid sites, and 6% and 31% pore mouth acid sites, respectively. The catalytic behavior of individual external surface or pore mouth acid site was evaluated by alkylation of benzyl alcohol in mesitylene with cumulative addition of DTBP or TPP titrants. The rapid decrease with small fraction of acid sites poisoned and then a slow decrease with the remaining acid sites poisoned in the alkylation rate constant per external surface and pore mouth acid site in both PMFI and PMWW zeolites suggest that the individual acid site performs significantly different in the catalytic reaction. Additionally, the cumulative poisoning experiment with TPP titrants suggests that external surface and pore mouth acid sites have different rate constants in the alkylation reaction, reflected by the residual activity of both PMFI and PMWW zeolites after the external surface acid sites were fully poisoned by TPP titrants.

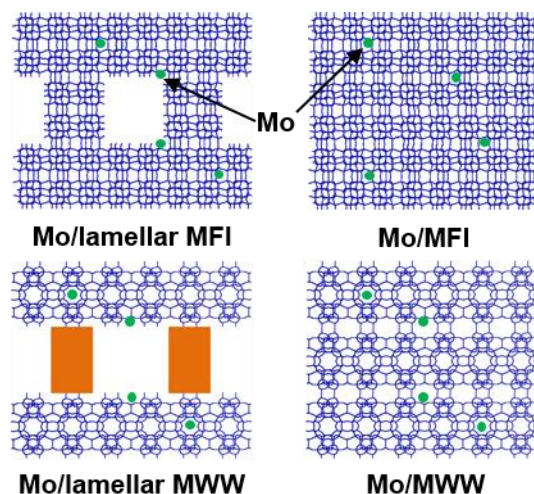
Chapter 3: Textural and Catalytic Properties of Mo Loaded Hierarchical Meso-/microporous Lamellar MFI and MWW Zeolites for Direct Methane Conversion

3.1. Introduction

As discussed in Chapter 1, compared to other methane conversion techniques, the DMA reaction is more selective and cost effective due to its unique capability in forming aromatics and hydrogen while circumventing the intermediate energy intensive steps [11,15]. So far, Mo/MFI and Mo/MWW are the most active catalysts in the DMA reaction but still suffer rapid deactivation due to fast accumulation of coke. It has been reported that the presence of mesopores in MFI zeolites could lead to higher accessibility of active sites, better accommodation of aromatics and faster diffusion of products and thus improve stability and performance of the Mo/MFI catalyst in the DMA reaction [35, 36, 146, 147]. In the present study, we firstly studied the catalytic performances of lamellar MWW and lamellar MFI zeolites, which comprise both mesoporosity and microporosity, in the DMA reaction as shown in Schemes 3.1. Lamellar MWW, derived from a layered precursor, MWW(P), is the first pillared zeolite material with microporous layers and mesoporous interlayer spaces [135, 136, 148, 149]. For synthesis of lamellar MWW, layers of MWW(P) are expanded by use of a surfactant, and then intercalated by silica species which convert into inorganic pillars upon condensation and hold the layers apart creating interlayer mesopores [135, 136]. Lamellar MFI zeolite was obtained from multilamellar MFI [133] that was created through coherent assembly of the zeolite layer and the structure directing agent,

a diquatarnary ammonium surfactant with relatively long hydrocarbon chains. The lamellar MFI zeolite was obtained as a stacking of MFI nanosheets that contained a large number of three-dimensional crystal intergrowths [102]. The intergrown crystals could act as a 'pillar' supporting each other, preventing complete collapse of the mesoporous structure upon calcination. Therefore, lamellar MFI retains the interlamellar spaces upon removal of the surfactant by calcination.

For comparison purpose, conventional microporous MFI with crystal size of 0.2 μm and 1.4 μm and MWW samples with equivalent Mo loading and Si/Al ratio were studied under the same conditions. For simplicity in nomenclature, conventional microporous MFI with particle size 0.2 μm and 1.4 μm were designated as MFI-0.2 and MFI-1.4, respectively. The crystal sizes were named after the MFI crystal thickness along *a*-axis direction.



Schemes 3.1. Mo-loaded lamellar MFI, MFI, lamellar MWW and MWW zeolite catalysts for the DMA reaction.

3.2. Experiments

3.2.1. Synthesis of MFI and MWW Zeolites

A multilamellar MFI was synthesized using the method reported by Ryoo and co-workers [102]. Calcination in flowing air was conducted at 823 K for 6 hours to produce lamellar MFI with mesoporosity retained by MFI nanosheet “pillars” due to the large number of three-dimensional crystal intergrowths. The conventional MFI with different crystallite sizes (1.4 μm and 0.2 μm , respectively) were synthesized following reported procedures in references [150] and [151], respectively. MWW and lamellar MWW were derived from the same precursor, MWW(P). The hydrothermal synthesis of MWW(P) was carried out by using the method described by Corma et al. [134]. One portion of the crystalline product MWW(P) was dried and calcined to produce MWW. The other portion of MWW(P) was swollen according to the method developed by Maheshwari et al. [135], followed by pillaring of the swollen materials using the procedure reported by Barth et al. [136]. The resulting solid was treated using the same conditions as those for MWW to produce lamellar MWW. The as-synthesized MFI and MWW zeolites were ion-exchanged three times using 1 M aqueous ammonium nitrate (NH_4NO_3) (weight ratio of zeolite to NH_4NO_3 solution = 1:10) at 353 K for 12 h, and subsequently, collected by vacuum filtration, washed with deionized water three times, and dried at 343 K overnight. All zeolite samples in their NH_4^+ -form were treated in dry air (100 mL min^{-1} , ultrapure, Airgas) by increasing the temperature from ambient temperature to 823 K at 1.45 K min^{-1} and holding for 4 h to thermally decompose NH_4^+ to NH_3 and H^+ . The Si/Al ratio of each zeolite sample was tentatively controlled around 30 by modulating the amount of Si and Al precursors during the zeolite preparation.

3.2.2. Synthesis of Mo loaded MFI and MWW catalysts

The 4.7 wt% Mo loaded zeolite catalysts were prepared by the wetness impregnation method. Typically, 0.046 g of ammonium molybdenum tetrahydrate (Sigma-Aldrich, 99% purity) was dissolved in 0.25 g deionized water at room temperature to form an ammonium molybdenum solution, which was then added to 0.5 g zeolite catalyst drop by drop under rigorous stirring. The as-prepared Mo loaded zeolite catalysts were dried at 393 K overnight, followed by heating at 1 K min⁻¹ under flowing air (100 mL min⁻¹) to 823 K and kept at this temperature for 4 h to decompose the ammonium molybdenum to MoO_x species. After cooling the sample to room temperature, the resultant Mo/zeolite catalysts were pelleted, crushed, and sieved to retain the particle sizes between 180 and 425 μm (40-80 mesh). All the DMA reaction tests were carried out over the as-obtained 4.7 wt% Mo/zeolite samples.

3.2.3. Characterization of catalysts

Scanning electron microscope (SEM) was employed for direct visualization of crystal morphologies of meso-/microporous lamellar and microporous zeolite catalysts. SEM images were collected on a JEOL 6500 SEM without crushing or a metal coating of the samples. Powder X-ray diffraction (XRD) patterns were collected on a Bruker AXS D5005 diffractometer using Cu-Kα radiation. Data were collected with a step size of 0.04° and a step time of 3 s. Nitrogen adsorption/desorption measurements were carried out at 77 K on an Autosorb-iQ analyzer (Quantachrome Instruments). Prior to the measurement, samples were evacuated overnight at 523 K and 1 mmHg. Si, Al, and Mo and trace metal contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, University of Minnesota). X-ray photon

spectroscopy (XPS) was measured over a Kratos AXIS 165 spectrometer equipped with 165 mm radius hemispherical analyzer and eight channeltron detection system coupled with Monochromatic Al radiation (1486.6 eV). Thermo gravity analysis (TGA) (TA Instrument, SDT Q600) was conducted to identify and quantify the coke formed on each catalyst after the DMA reaction.

The number of Brønsted acid sites in pristine zeolites and Mo/zeolite samples was determined by chemical titration using dimethyl ether (DME) by following a reported procedure [139, 140]. Typically, the DME titration experiment was carried out in a tubular packed-bed quartz reactor (10 mm inner diameter) under atmospheric pressure. The catalyst samples (~ 0.05 g) were supported on a coarse quartz disk inside the reactor and were treated in He (50 mL min^{-1} , ultrapure, Airgas) at 773 K (1 K min^{-1}) for 3 h prior to cooling in He flow to the reaction temperature of 423 K. A mixture of DME/Ar/He (50 mL min^{-1} ; 24.8% DME, 25.2% Ar and 50% He; Airgas) was introduced by He during each pulse with 120 s intervals. The effluent, physisorbed DME and water formed upon dehydration reactions, were subsequently removed by He (50 mL min^{-1}) for 2.5-3.5 h. A gas chromatography (Agilent 7890A) was used to record the titration curves of DME, and the number of Brønsted acid sites was calculated on the basis of these curves using a DME/H⁺ ratio of 0.5.

3.2.4. Catalytic DMA reactions

The catalytic conversion of methane was carried out in a fixed bed reactor (11 mm in inner diameter, 8 mm in height). Catalyst samples (~ 0.30 g) were treated in He (50 mL min^{-1} , ultrapure, Airgas) at 773 K (1 K min^{-1}) for 4 h prior to heating in He flow to the reaction temperature. After pretreatment, the temperature was increased to

983 K in 0.5 h and air (ultrapure, Airgas) was introduced to the catalysts for 0.25 h. The DMA reaction test was carried out under ambient pressure. Methane was introduced into the catalyst at a flow rate of 7.9 mL min^{-1} (at normal temperature and pressure, NTP, condition) and Ar (2.1 mL min^{-1} at NPT condition, Airgas) as internal standard. The transfer lines (stainless steel tubes) were maintained at temperatures greater than 473 K by resistive heating to prevent product condensation. A gas chromatography (Agilent 7890A) equipped with a methylsiloxane capillary column (HP-1, $50.0 \text{ m} \times 320 \text{ }\mu\text{m} \times 0.52 \text{ }\mu\text{m}$) connected to a flame ionization detector and a packed column detector (SUPELCO HAYESEPP R 80/100 mesh packed column, 10 ft) connected to a thermal conductivity detector was used to quantify the reactants and products.

3.3. Results and discussion

3.3.1. Textural properties of catalysts

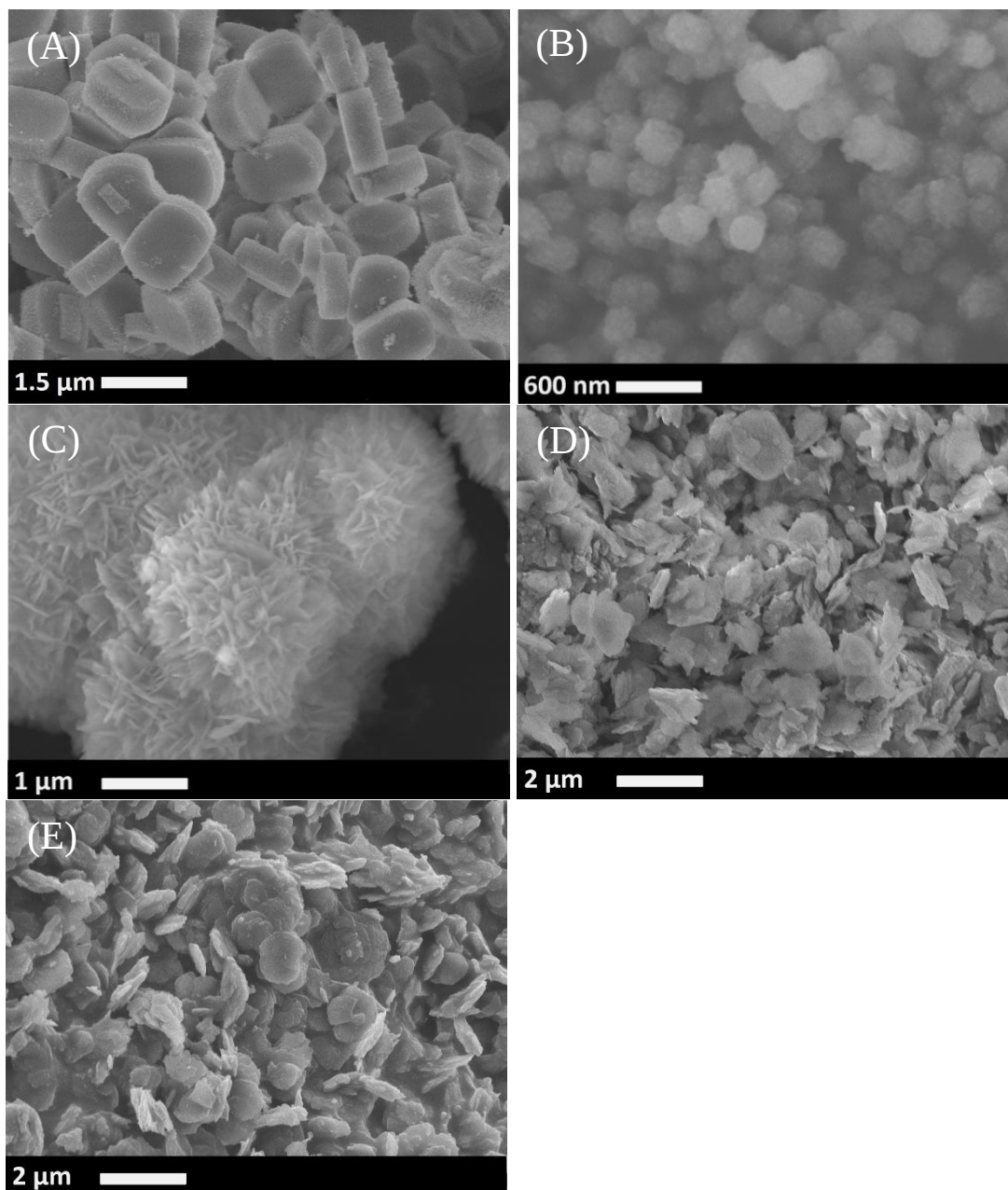
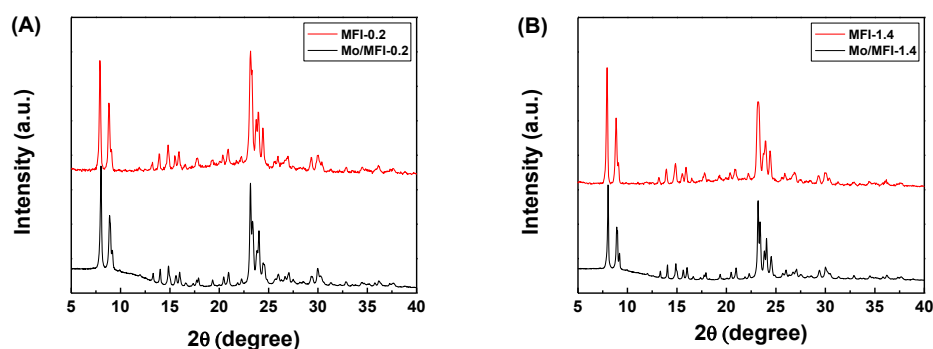


Figure 3.1. SEM images of (A) MFI-1.4, (B) MFI-0.2, (C) lamellar MFI, (D) MWW, and (E) lamellar MWW, showing the crystallite morphology of each zeolite catalyst.

Figure 3.1 shows the SEM images of zeolite samples that are used for preparation of Mo/zeolite catalysts in the DMA reaction. The conventional microporous MFI zeolites with crystallite sizes of 1.4 μm and 0.2 μm are shown in Figure 3.1(A)-(B). Both conventional microporous MFI zeolites have uniform crystallite sizes. The lamellar MFI in Figure 3.1(C) is comprised of aggregated platelet-like particles with thickness around 40-80 nm, similar to that reported by Ryoo's group [102, 133]. The synthesized MWW zeolites crystallize as thin rounded flakes, which are 500-1000 nm in diameter and 50-100 nm in thickness, as shown in Figure 3.1(D). Lamellar MWW, derived from the same precursor as MWW, resembles the disc-like crystal morphology of MWW, as evidenced by comparing the morphology of lamellar MWW in Figure 3.1(E) to that of MWW in Figure 3.1(D). The XRD patterns of MWW and lamellar MWW shown in Figure 3.2 confirmed that the samples are highly crystalline and all peaks observed correspond to those of the MWW material reported by Tsapatsis et al. [135]. The XRD patterns of conventional MFI and lamellar MFI samples confirmed that they are highly crystallized materials, similar to the XRD patterns reported in our previous publication [62].



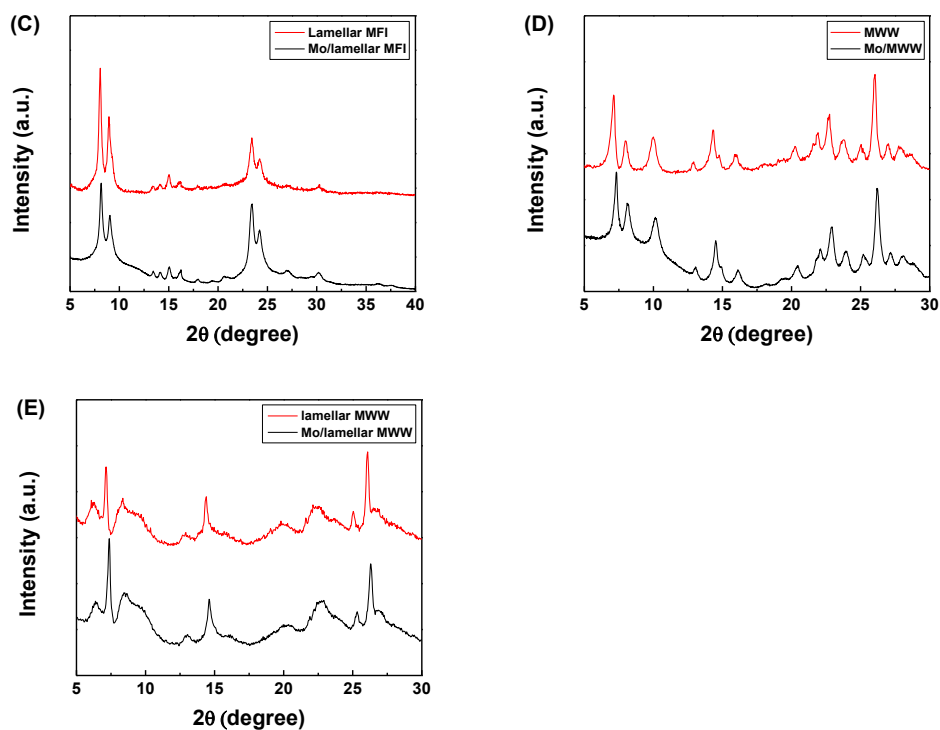


Figure 3.2. XRD patterns of MFI-1.4 and Mo/MFI-1.4 (A), MFI-0.2 and Mo/MFI-0.2 (B), lamellar MFI and Mo/lamellar MFI (C), MWW and Mo/MWW (D), lamellar MWW and Mo/lamellar MWW (E) catalyst samples.

3.3.2. N_2 isotherm analysis

N_2 adsorption/desorption isotherms were used to reveal the porosity differences between meso-/microporous and microporous zeolite catalysts before and after loading Mo species. Figure 3.3(A) shows the N_2 adsorption/desorption isotherms of MFI type zeolites. At the low relative pressures ($p/p_0 < 0.6$), conventional MFI zeolites (MFI-1.4 and MFI-0.2) have similar isotherms, which indicates that they both have similar microporous structures. However, the increase of adsorption volume in lamellar MFI, compared to conventional MFI zeolites, up to relative pressures of $p/p_0 \sim 0.6$, indicates the presence of large mesopores in lamellar MFI. A comparison of the NLDFT pore size distributions of these three MFI zeolite samples on the basis of N_2 adsorption

branch is shown in Figure 3.4(A). Lamellar MFI has broad pore size distributions with a maximum at ~ 6.8 nm, while other two microporous MFI zeolites have narrow pore size distributions with a small peak at ~ 3 nm. Figure 3.3(B) shows clearly the differences between the isotherms of MWW and lamellar MWW. At a relative pressure $p/p_0 \sim 0.1$, the majority of the sorption capacity for MWW is already used because of the large driving force to adsorb in the zeolite micropores [148]. For lamellar MWW, an increase in the adsorption volume up to relative pressures of $p/p_0 \sim 0.4$ indicates capillary condensation in the mesopores, which is the evidence for the presence of a significant mesopore volume. The NLDFT pore size distribution, shown in Figure 3.4(B), clearly shows that lamellar MWW has mesopores (~ 2.7 nm) when compared to the MWW catalyst sample with no obvious mesopores.

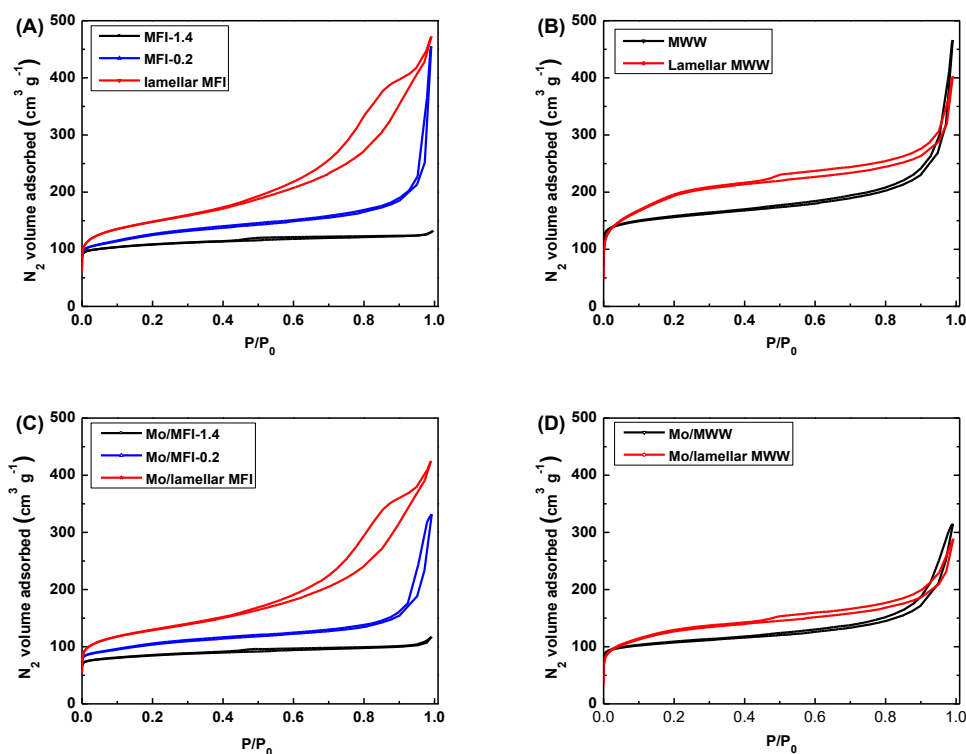


Figure 3.3. N₂ isotherms of (A) MFI zeolites, (B) MWW zeolites, (C) 4.7 wt% Mo loaded MFI catalysts, and (D) 4.7 wt% Mo loaded MWW catalysts.

The N₂ isotherms of 4.7 wt% Mo loaded MFI and MWW zeolite catalysts are shown in Figure 3.3(C)-(D), respectively. At the measured relative pressure range, Mo loaded MFI-type zeolites have similar trend on isotherms to those of MFI zeolites, but the sorption capacity of Mo/MFI-1.4, Mo/MFI-0.2, and Mo/lamellar MFI decreases by a factor of ~25%, ~20%, and 16% in comparison with N₂ isotherms of the corresponding pristine zeolite catalysts in Figure 3.3(A). Table 3.1 shows that the surface area, micropore volume, and cumulative pore volume of Mo loaded MFI zeolites are apparently lower than those of corresponding MFI zeolites. The NLDFT pore size distributions of Mo loaded MFI zeolites, shown in Figure 3.4(C), indicate the pore size distribution of Mo/lamellar MFI centers ~6.3 nm, slightly lower than that of lamellar MFI. The decrease in pore sizes and sorption capacity of Mo loaded zeolites indicates Mo exists in both micropore and mesopores of the lamellar MFI zeolites. Figure 3.3(D) shows Mo/MWW and Mo/lamellar MWW have similar trend on N₂ isotherms to those of MWW and lamellar MWW zeolites, but the sorption capacity for Mo loaded MWW and lamellar MWW at relative pressure of $p/p_0 \sim 0.1$ is decreased by ~30%. For Mo/lamellar MWW, the degree of increase in the adsorption volume up to relative pressures of $p/p_0 \sim 0.3$ is slightly lower than that of lamellar MWW, indicating the presence of slightly smaller mesopore volume. The NLDFT pore size distribution in Figure 3.4(D) illustrates that Mo/lamellar MWW has relatively smaller mesopores when compared to the lamellar MWW catalyst sample with mesopores of ~2.5 nm. The N₂ isotherm data indicate the Mo species present in both micro- and mesopores of the lamellar MWW zeolite.

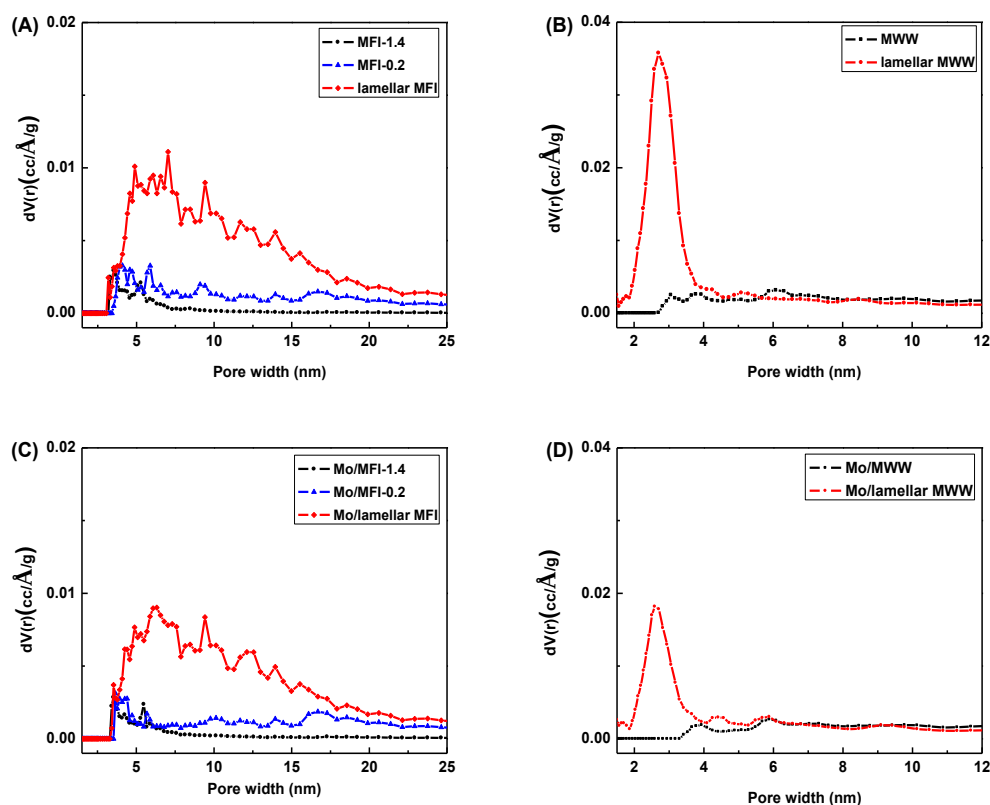


Figure 3.4. NLDFT pore size distribution of (A) MFI zeolites, (B) MWW zeolites, (C) 4.7 wt% Mo loaded MFI catalysts, and (D) 4.7 wt% Mo loaded MWW catalysts.

Table 3.1. Porosity and structural characterization of MWW and MFI zeolite catalysts before/after Mo loading.

Catalyst	Zeolite				Mo loaded zeolite		
	Crystal size (μm)	S_{BET}^a (m ² g ⁻¹)	V_{micro}^b (cm ³ g ⁻¹)	V_{total}^c (cm ³ g ⁻¹)	S_{BET}^a (m ² g ⁻¹)	V_{micro}^b (cm ³ g ⁻¹)	V_{total}^c (cm ³ g ⁻¹)
MFI-1.4	1.4	250	0.14	0.21	199	0.11	0.18
MFI-0.2	0.2	310	0.14	0.48	257	0.11	0.44
lamellar MFI	0.0034	402	0.10	0.68	355	0.09	0.61
MWW	0.1	375	0.18	0.55	260	0.12	0.43
lamellar MWW	0.0025	481	0.23	0.56	316	0.14	0.38

^a Determined from multi-point BET analysis; ^b Micropore volume determined by t-plot method; ^c Cumulative pore volume determined using NLDFT method;

3.3.3. XPS analysis

XPS analysis of the chemical states and near surface concentrations of Mo species in 4.7 wt% Mo loaded zeolite catalysts are shown in Figure 3.5. All the Mo loaded zeolite samples were activated at 823 K for 4 h before the XPS measurement. The binding energies of Mo(3d) for all the Mo loaded samples (Figure 3.5(A)) were in doublet centering at ~ 232.9 and ~ 236.2 eV, which indicate Mo species in the form of Mo^{6+} , in consistence with previous reports [44, 75]. The presence of mesopores in the lamellar MFI and lamellar MWW does not affect the chemical states of the Mo species since the peak positions are almost the same between Mo loaded microporous zeolite and Mo loaded meso-/microporous zeolite catalysts. Figure 3.5(B) shows the near-surface Si/Mo ratios in 1.4 μm , 0.2 μm , and lamellar MFI are 13, 14, and 32, showing the near surface Mo concentration decreased with decreasing MFI zeolite crystallite sizes. A similar trend was observed on Mo near surface concentration of MWW and lamellar MWW zeolites, illustrated by 28 and 34 of Si/Mo ratios on MWW and lamellar MWW, respectively. The ICP-OES analysis showed that the Si/Mo ratios of the zeolites were around 27, as listed in Table 3.2. The higher concentration of Mo on the zeolite surface suggests that the majority of Mo species stayed on the external surface of zeolite supports because they had difficulty in diffusing into the micropores of large zeolite crystals. This result is consistent with the previous reports that both ammonium molybdenum tetrahydrate and MoO_3 precursors were too large to penetrate the MFI and MWW channels during the impregnation process or during calcinations at temperatures below 873 K [152-154]. However, the smaller crystallite sizes or

mesopores in meso-/microporous lamellar MFI and MWW zeolites facilitate the diffusion of Mo precursors into zeolite channels.

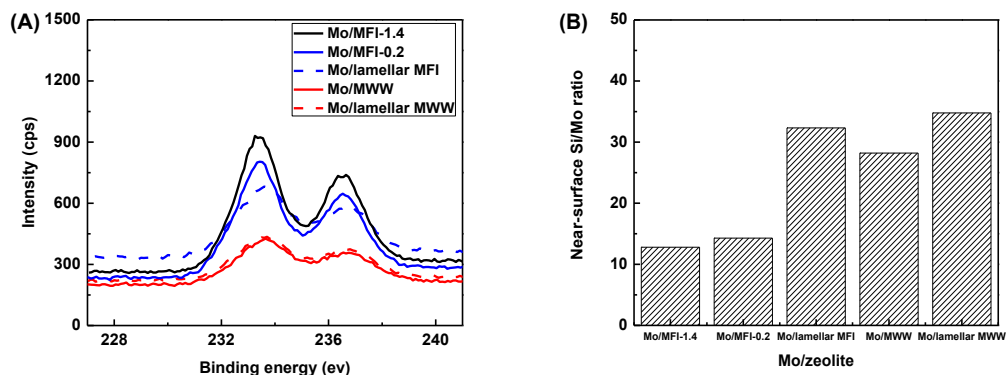


Figure 3.5. Chemical state (A) and near surface Mo concentration (B) of 4.7 wt% Mo/zeolite catalysts, measured by ex-situ XPS.

3.3.4. Free Brønsted acid sites measured by DME titration

It is generally accepted that Mo species diffused into the zeolite channels interact with Brønsted acid sites inside in different anchoring modes, which are responsible for the catalytic methane aromatization reactions [40, 153, 155, 156]. Although a discrepancy on the anchoring modes of Mo-Brønsted acid sites has been existed in the literature, the number of free Brønsted acid sites generally decreases with increasing amount of Mo loading. In order to understand the effect of lamellar zeolite structures on the Mo-Brønsted acid site interactions and their consequences on the catalytic activity and the coke formation in the DMA reaction, the number of free Brønsted acid sites after the Mo loading was quantified by the DME titration method. Table 3.2 lists the acidity of the zeolite and Mo/zeolite catalysts measured by both elemental analysis and DME titrations after 983 K activation treatment for 0.5 h. It should be mentioned that elemental analysis gives the total number of Al sites, while DME titrations indicate the number of active Brønsted acid sites assuming that the

active Brønsted acid sites participate in reactions of DME with H^+ to form surface methyl groups, $CH_3OCH_3 + 2[SiO(H)Al] = 2[SiO(CH_3)Al] + H_2O$ [139, 140]. The Si/Al ratios of pristine MFI zeolite samples measured by elemental analysis were around 30, similar to those of determined via DME titration experiments. The consistence on Si/Al ratios determined by two different methods implies that the concentration of Brønsted acid sites is nearly identical to the concentration of Al in the MFI zeolite samples. The MWW and lamellar MWW have higher Si/Al ratios determined from DME titrations than those determined from elemental analysis, which may suggest that there is a considerable amount of nonframework Al in the synthesized MWW and lamellar MWW zeolite samples [45]. The number of free Brønsted acid sites in Mo-loaded zeolite catalysts was also determined from DME titrations. The Si/Al ratios of Mo/zeolite samples determined from DME titrations increased with decreasing zeolite crystallite sizes from MFI-1.4 to lamellar MFI and from MWW to lamellar MWW, as shown in Table 3.2. During the impregnation and calcination processes, a portion of Mo species may migrate into zeolitic channels and anchor on Brønsted acid sites, leading to a decrease in the population of these free Brønsted acid sites [152, 153]. This result indicates that the interactions between Mo and Brønsted acid sites are influenced by the meso-/microporous lamellar zeolite structures [39, 55]. MFI and MWW zeolites have been the most favorable support structures in the DMA reaction, showing that their unique 10MR channels, whose size is close to the benzene molecule kinetic diameter, favor the synthesis of aromatic molecules but prevent accumulation of polycondensed aromatic substances [43, 157, 158]. Studies of the DMA reaction on MFI zeolites with different particle sizes show that the zeolite crystal

size has a significant effect on the activity and selectivity of Mo/ZSM5 catalysts [35, 159]. Mo species located predominately on the external surface of zeolite when the crystal size is small, while diffusion of aromatic products out of zeolite channels from large zeolite was restrained [160, 161]. The inclusion of mesopores in zeolite facilitates the mass transports, especially for the aromatic products molecules [35, 36, 146]. The increasing mesoporosity in lamellar zeolites by decreasing the crystallite size to unit-cell thickness increases dispersion of Mo species, and thus enhances the number of interacting Mo-Brønsted acid nanoclusters in the catalysts and decreases the number of free Brønsted acid sites. The MoO_x species within zeolite channels are precursors of the active sites (molybdenum carbide, MoC_x) required for the DMA reactions, which are formed upon the reduction and carburization of dispersed Mo species in the initial stage of the reaction, as discussed below [23, 26, 27, 39, 52, 162].

Table 3.2. Number of active sites (Brønsted acid sites and Mo species) determined by elemental analysis (ICP-OES), DME titration, and XPS analysis methods.

Catalyst	Zeolite		Mo loaded zeolite		
	Si/Al ^a	Si/Al ^b	Si/Mo ^a	Si/Mo ^c	Si/Al ^b
MFI-1.4	30	32	25	13	95
MFI-0.2	32	33	27	14	129
lamellar MFI	30	31	28	32	152
MWW	30	58	26	28	99
lamellar MWW	32	62	25	34	162

^a Calculated from elemental analysis; ^b Measured from DME titration; ^c Near surface Si/Mo ratio determined from XPS analysis.

3.3.5. Catalytic DMA reactions

The methane conversion with time-on-stream (TOS) at 983 K and 1600 mL (g_{cat}⁻¹) h⁻¹ space velocity is shown in Figure 3.6. For all the investigated catalyst systems, the methane conversion sharply increased in the initial period of the reaction (i.e.,

induction period) and reached a maximum after about 1 h. Afterwards, the methane conversions decreased with TOS. The methane conversion-TOS trend over all the investigated catalysts is similar to that observed in literature [15, 44, 52, 68, 159]. The conversion during the initial induction reaction stage (~ 1.0 h) is due to the rapid buildup of carbonaceous deposits on the dispersed Mo species to form MoC_x sites that convert methane into ethane and ethylene, which then react to form $\text{C}_6\text{-C}_{10}$ aromatics on Brønsted acid sites via rapid oligomerization, cracking, and cyclization reactions [27]. Based on the pretreatment with pure air prior the DMA reaction, MoC_x species were probably in the form of hexagonally close packed (hcp) structure in our experiments. The induction time of Mo/lamellar MFI and Mo/lamellar MWW is slightly longer than the microporous Mo/MFI and Mo/MWW zeolites. The increase in induction time with increasing zeolite mesoporosity and external surface areas is ascribed to the higher degree dispersion of Mo species in lamellar MFI and lamellar MWW zeolites, which is consistent with that indirectly inferred from the N_2 isotherm measurement, XPS analysis, and DME titrations of Brønsted acidity discussed above.

After the reaction induction period, the methane conversion over Mo/MFI and Mo/MWW zeolites (Figure 3.6) followed a sequence of Mo/lamellar MFI > Mo/MFI-0.2 > Mo/MFI-1.4, and Mo/lamellar MWW > Mo/MWW, respectively. Under the investigated reaction conditions, the thermodynamic equilibrium conversion of methane is $\sim 11\%$ [163, 164]. The initial conversion methane in the present study is close to the equilibrium conversion. Despite their high initial activity, the Mo/lamellar MFI and Mo/lamellar MWW samples deactivated at faster rates compared to the Mo loaded microporous zeolite catalysts. As shown in Figure 3.6(A), the methane

conversion over Mo/lamellar MFI was close to that obtained from Mo/MFI-0.2 and Mo/MFI-1.4 after TOS of 6 h. The conversion over Mo/lamellar MWW, shown in Figure 3.6(B), approached to that of Mo/MWW with TOS up to 10 h. It may be reasonable to consider that the higher initial activity of Mo/lamellar MFI and Mo/lamellar MWW catalysts results from their higher number of MoC_x-Brønsted acid nanoclusters in comparison with that of Mo loaded microporous MFI and MWW catalysts. The active sites (MoC_x-Brønsted acid) in mesopores and external surfaces of Mo/lamellar MFI and Mo/lamellar MWW enable formation of large aromatic products that could promote coke formation to accelerate catalyst deactivation [27]. On the contrary, the Mo loaded microporous zeolite catalysts have MoC_x-Brønsted acid nanoclusters mainly located in the zeolite microchannels, which displayed lower initial activity for methane activation and better stability due to the shape selectivity effect of zeolite microchannels.

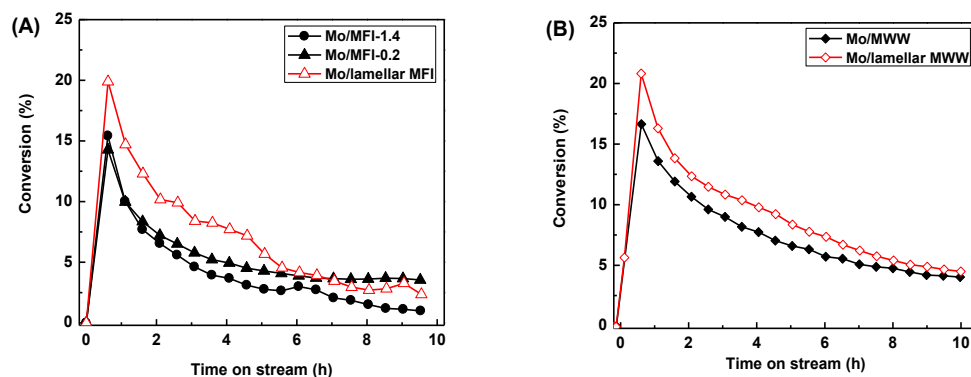


Figure 3.6. Methane conversion with TOS over 4.7 wt% Mo-loaded MFI type (A) and MWW type (B) catalysts at 983 K, atmospheric pressure, and space velocity of 1600 mL gcat⁻¹ h⁻¹.

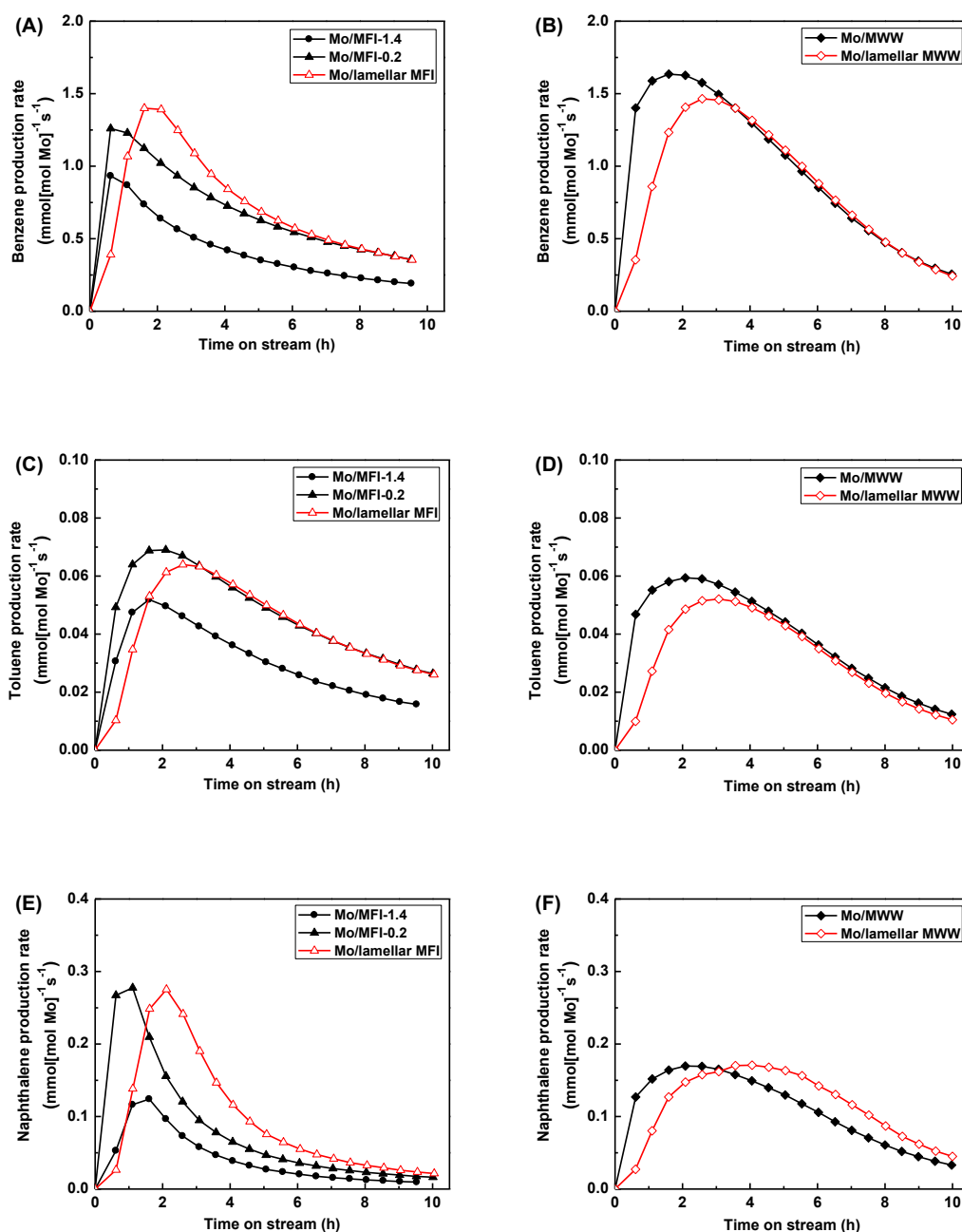


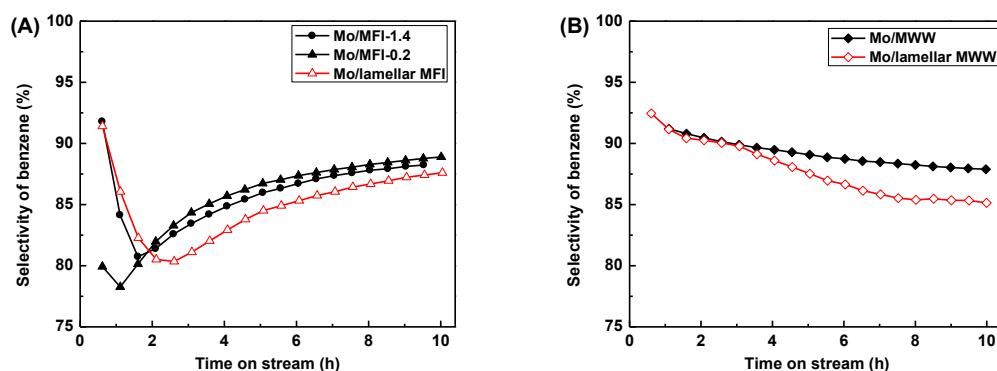
Figure 3.7. Formation of benzene(A)-(B), toluene (C)-(D) and naphthalene (E)-(F) with TOS over 4.7 wt% Mo/MFI (A), (C) and (E) and 4.7 wt% Mo/MWW (B), (D) and (F) catalysts.

The trend of production rates of benzene, toluene, and naphthalene versus TOS in the DMA reaction were similar to that of methane conversions. As shown in Figure

3.7, the aromatic production rate sharply increased in the initial TOS, and then monotonously declined with TOS in the later reaction stages. The increasing zeolite crystallite sizes reduced the production rates of these aromatic products. As discussed above, the higher aromatic formation rates over Mo loaded lamellar zeolite catalysts might be due to their higher number of MoC_x active sites associated to the Brønsted acid sites compared to that of Mo loaded microporous zeolites. The facilitated mass transport as a consequence of mesopores in these lamellar catalysts would also favor the formation of aromatic products.

The selectivities to the main aromatic products, i.e., benzene, toluene, and naphthalene, over the Mo loaded microporous and meso-/microporous MFI and MWW zeolites are shown in Figure 3.8. The data were calculated on the basis of main aromatic products without accounting for coke, smaller hydrocarbon, and other heavy aromatic molecules. The trend of selectivity-TOS is different between the Mo loaded MFI-type and MWW-type zeolite catalysts. In the case of Mo/MFI catalysts, shown in Figure 3.8(A), benzene selectivity initially increased and tended to reach a plateau at TOS of 10 h (85-90% selectivity). The toluene selectivity was relatively stable over all the investigated catalysts, initially increasing with TOS and reaching a plateau value of 6% after TOS > 5 h. The naphthalene selectivity gradually declined with TOS after the induction period. The inclusion of mesopores in the Mo/MFI catalyst systems does not obviously change the trend of product selectivity-TOS in the DMA reaction. The comparison of product selectivity among Mo/MFI-0.2, Mo/MFI-1.4, and Mo/lamellar MFI, however, shows that Mo/lamellar MFI catalyst slightly favored naphthalene production, while Mo/MFI-0.2 and Mo/MFI-1.4 favored benzene formation. For

Mo/MWW and Mo/lamellar MWW zeolite catalysts, the benzene selectivity monotonically decreased with TOS, while toluene and naphthalene selectivity monotonically increased with TOS (Figure 3.8(B)). Similar to that of Mo/lamellar MFI, Mo/lamellar MWW also favors the naphthalene formation in comparison with Mo/MWW catalysts. It is commonly recognized that naphthalene is predominantly formed on the active sites near the external surface of the Mo/MFI catalysts [36, 38, 76]. Taking into account that Mo/lamellar MFI and Mo/lamellar MWW zeolites have larger external surface areas than the Mo loaded microporous MFI and MWW catalysts, the higher naphthalene selectivity might be due to the contribution of the active sites on the external surface and in the mesopores of the catalysts. Besides, the interconnection between micropores and mesopores decreases path length for naphthalene diffusion to the exterior of crystallites, which contributes to the high formation rate of naphthalene.



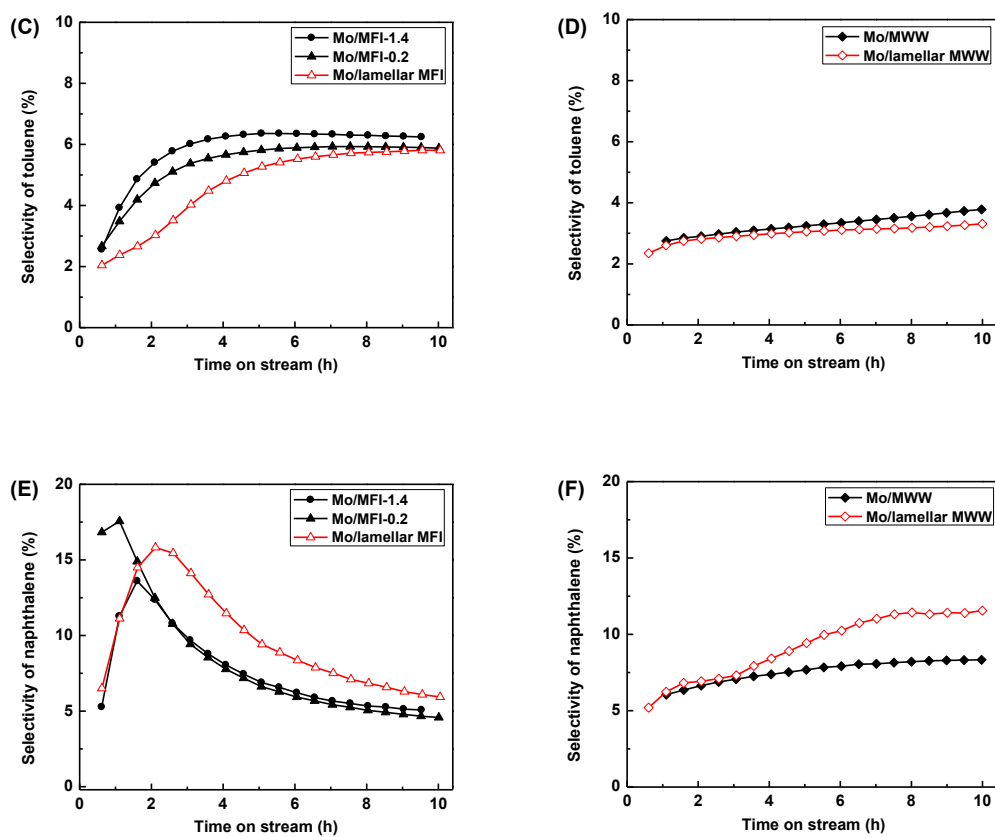


Figure 3.8. Evolution with time-on-stream of the selectivities to the aromatic products (benzene (A)-(B), toluene (C)-(D) and naphthalene (E)-(F) formed in the DMA reaction over Mo loaded MFI and MWW catalysts.

3.3.6. Coke formation over Mo/zeolite catalysts

The amount and nature of the coke formed on Mo/MFI and Mo/MWW catalysts after TOS of 20 h under DMA reaction conditions were studied by TGA analysis. The TGA curves, shown in Figure 3.9(A)-(B), reveal a substantial weight loss in the temperature range of 690–870 K that corresponds to the burning-off of the coke deposits. The weight loss in this temperature range is 14.9 %, 6.8 %, and 5.2 % for Mo/lamellar MFI, Mo/MFI-0.2, and Mo/MFI-1.4, and 19.6 %, 15.6% for Mo/lamellar MWW and Mo/MWW, respectively. The higher weight loss in Mo loaded meso-

/microporous lamellar MFI and MWW zeolite catalysts reflects a higher amount of coke in these catalysts. Weight loss at 300 K - 690 K was mainly related to evaporation of physisorbed and chemisorbed water. The small increase in weight observed below 690 K is attributed to the oxidation of MoC_x species [36, 147].

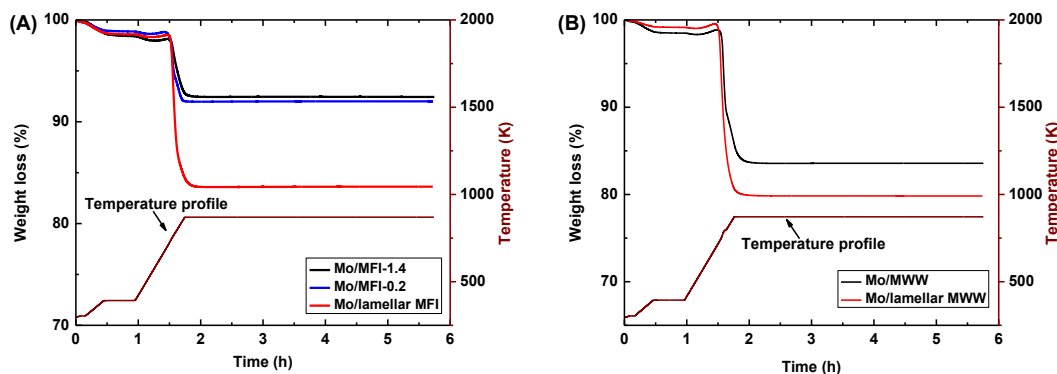


Figure 3.9. TGA analysis of coke formed on Mo loaded MFI (A) and MWW (B) catalysts after being used for 20 h in the DMA reaction.

It has been reported that the coke deposits on the Mo species and zeolite Brønsted acid sites in the DMA reaction [36, 52, 165]. The coke on the zeolite Brønsted acid sites is mainly responsible for the gradual catalyst deactivation [52, 68, 69, 165, 166]. The coke may cover the Brønsted acid sites and therefore gradually lead to the blockage of the zeolite channels, thus making the active sites inaccessible for the reactant and reaction intermediates. Mo/lamellar MFI and Mo/lamellar MWW have lower degree of available Brønsted acid sites and therefore the lower amount of more deactivating coke formed in the DMA reaction. Their deactivation rates in the beginning of the DMA reaction and coke amount formed after TOS of 20 h, however, are higher than those of microporous Mo/MFI and Mo/MWW zeolites, as shown in Figure 3.6 and Figure 3.9, respectively. In order to explain this apparent contradiction,

we hypothesize that not only the number of available Brønsted acid sites but also the environment of active sites as a result of structure/porosity of zeolites plays important roles in the DMA reaction. A fraction of active sites in lamellar MFI and lamellar MWW zeolites are circumscribed by mesoporous environment, which is responsible for higher reaction rate in the beginning of the reaction. The formed aromatic products can be adsorbed and condensed on the active sites from the mesoporous environment to form coke which are responsible for the rapid deactivation in the initial reaction and higher amount of coke formation. After coke formed in mesopores, the active sites in micropores of the Mo/lamellar MFI and Mo/lamellar MWW are responsible for catalytic activity over a long term run, with performance similar to those of their microporous analogues.

3.4. Conclusion of Chapter 3

The Mo/lamellar MFI and Mo/lamellar MWW catalysts (4.7 wt% Mo, Si/Al = 30) were prepared and their textural and acidity properties were systematically investigated. In comparison with Mo/MFI and Mo/MWW catalysts, the Mo loaded lamellar zeolites have higher surface area, lower number of free Brønsted acid sites, and lower number of near surface Mo species. The presence of mesopores in lamellar zeolites facilitated the diffusion of MoO_x species in zeolites to form large number of MoC_x-Brønsted acid site species upon the DMA reactions, which are active sites for the DMA reactions. The catalytic performance of Mo/lamellar MFI and Mo/lamellar MWW in the DMA reaction was examined, showing that methane conversion, aromatic production, and coke formation were higher than those of Mo loaded microporous MFI and MWW catalysts in the initial stage of the reaction. The presence of mesopores in

zeolites leads to easier access to the active sites for reactants and faster diffusion of products, thus improving the formation of aromatic products. On the other hand, the mesopores result in formation of polycondensed aromatic substances that block the accessibility to active sites via mesopores. For the long term run, the Mo/lamellar MFI and Mo/lamellar MWW showed similar behaviors to those of Mo/MFI and Mo/MWW catalysts. This indicates that active sites in the catalysts can be accessed through microspores of the lamellar zeolites.

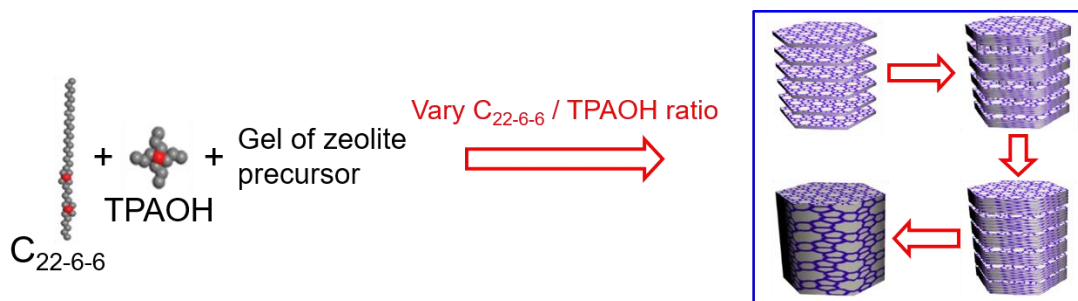
Chapter 4: Spatial Distribution and Catalytic Performance of Metal-Acid Sites in Mo/MFI Catalysts with Tunable Meso-/microporous Lamellar Zeolite Structures

4.1. Introduction

Recently, the interdependence between the porosity, acidity, and catalytic performance in the DMA reaction of hierarchical zeolites prepared by demetallization method has been evaluated [72, 167-170]. However, for 2D lamellar zeolites, a novel type of hierarchical zeolites, a comparative systematic analysis of the effectiveness of the mesoporosity has not been explored. Given the significant positive effect of 2D lamellar structure on the performance of catalysts in the DMA reaction shown in Chapter 3, herein, we systematically and rigorously studied the catalytic behaviors of Mo-loaded 2D lamellar MFI zeolites on four key fronts, i.e. the balance between mesoporosity and microporosity, spatial distribution of active sites, aromatics yields and coke formation.

In this study, we synthesized lamellar MFI zeolites with tunable ratio of mesoporosity/microporosity via a dual template method developed previously in our group. In this dual template synthesis approach, C₂₂₋₆₋₆ is responsible for the creation of interlayer mesopores between the 2D lamellar MFI layers, while TPAOH, a common template for bulky MFI zeolite, is responsible for growth of the microporous structure. Hence, the meso-/microporosity balance can be readily tailored by simply tuning the ratio of C₂₂₋₆₋₆/TPAOH, as shown in Scheme 4.1. The implications of the concomitant tunable meso- and microporosity on the physicochemical, acidic and catalytic

properties of the lamellar MFI zeolites were investigated in this study. Mo-loaded lamellar MFI zeolite catalysts (Mo/lamellar MFI) were employed as the catalysts to explore the spatial distribution and catalytic performances of metal and acid active sites in these lamellar zeolite catalysts in the DMA reaction. The interplay between the shape selective environment of micropores and facilitated mass transport in mesopores in the Mo/lamellar MFI zeolite should reveal the relationships among the textural properties, the distribution of active sites (metal and Brønsted acid sites), and the catalytic performances (stability, selectivity, and coke formation) of meso-/microporous hierarchical lamellar zeolites.



Scheme 4.1. Hypothetical dual template synthesis of lamellar MFI with tunable mesoporosity and microporosity.

4.2. Experiments

4.2.1. Catalyst preparation

4.2.1.1. Dual template synthesis of lamellar MFI zeolite catalysts

The lamellar MFI with tunable meso-/microporosity was synthesized using the method reported our previous work [123]. The typical synthesis recipe was as follows: $30\text{Na}_2\text{O}/1\text{Al}_2\text{O}_3/100\text{SiO}_2/10\text{C}_{22-6-6}/x\text{TPAOH}/4000\text{H}_2\text{O}/18\text{H}_2\text{SO}_4$, where x equals to 2, 5, 8, 12, and 36, respectively. The as-obtained lamellar zeolite samples were named after the usage of C_{22-6-6} and TPAOH during synthesis, which are MFI-10/2, MFI-10/5,

MFI-10/8, MFI-10/12 and MFI-10/36, respectively. For comparison, a multi-lamellar MFI was synthesized by using the method reported by Ryoo and co-workers [102], which was the same as dual template synthesis of MFI zeolites except that TPAOH was not added. The as-synthesized multi-lamellar sample was designated as MFI-10/0. All zeolite samples were calcined in dry air (1.67 mL s^{-1}) by increasing the temperature from ambient temperature to 873 K at 0.024 K s^{-1} and holding for 6 h. The as-obtained lamellar MFI zeolites were ion-exchanged three times using 1 M NH_4NO_3 solution at 353 K for 12 h, and subsequently washed with deionized (DI) water three times, and dried at 343 K overnight. After ion-exchange, the sample was treated in dry air (1.67 mL s^{-1}) by increasing the temperature from ambient temperature to 823 K at 0.024 K s^{-1} and holding at this temperature for 4 h to thermally decompose NH_4^+ to NH_3 and H^+ .

4.2.1.2. Synthesis of Mo/lamellar MFI catalysts

The wetness impregnation method was used to prepare the Mo/lamellar MFI catalyst. Typically, 0.022 g of ammonium molybdenum tetrahydrate (Sigma-Aldrich, 99% purity) was dissolved in 0.5 g DI water at room temperature to form an ammonium molybdenum solution, which was then added dropwise to 1 g of zeolite catalyst. The as-prepared Mo/lamellar MFI catalyst was dried at 393 K overnight, followed by a two-stage calcination procedure reported by Iglesia's group [153]. During the first stage, the sample was heated from room temperature to 623 K at 0.017 K s^{-1} in flowing air (1.67 mL s^{-1}) and soaked at this temperature for 16 h. During the subsequent stage, the sample was heated to 973 K at 0.017 K s^{-1} and soaked at this temperature for 10 h. The resultant Mo/lamellar MFI catalyst was pelletized, crushed, and sieved to retain the particle sizes between 180 and $425 \text{ }\mu\text{m}$ (40-80 mesh) for subsequent experiments. The

Mo loaded lamellar zeolite samples were named Mo-MFI-10/0, Mo-MFI-10/2, Mo-MFI-10/5, Mo-MFI-10/8, Mo-MFI-10/12, and Mo-MFI-10/36, respectively.

4.2.2. Catalyst characterization

4.2.2.1. Structural and textural property determination

The morphologies of the catalysts were observed using scanning electron microscopy (SEM, Hitachi SU-70). The crystalline phases were examined by the powder X-Ray diffraction (XRD), collected using a Bruker D8 Advance Lynx Powder Diffractometer (LynxEye PSD detector, sealed tube, Cu K α radiation with Ni β -filter). Argon (Ar) and nitrogen (N₂) adsorption-desorption isotherms were measured at 87 K and 77 K, respectively, using an Autosorb-iQ analyzer (Quantachrome Instruments) to characterize the porosity, pore sizes, and surface areas of the catalysts. Prior to the measurement, all the samples were evacuated overnight at 623 K and 1 mm Hg.

4.2.2.2. Composition and acidity determination

Si, Al and Mo contents of the lamellar MFI and Mo loaded lamellar MFI zeolites were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 4300 DV instrument, Perkin-Elmer). The surface Si, Al, and Mo concentrations were quantified using a X-ray photon spectrometer (Kratos AXIS 165) equipped with 165 mm radius hemispherical analyzer and eight channeltron detection system coupled with Monochromatic Al radiation (1486.6 eV). The number of free Brønsted acid sites in the catalyst samples were measured via dimethyl ether (DME) titration experiments given that the Brønsted acid sites participate in reactions of DME with H⁺ to form surface methyl groups, $\text{CH}_3\text{OCH}_3 + 2[\text{SiO}(\text{H})\text{Al}] = 2[\text{SiO}(\text{CH}_3)\text{Al}] + \text{H}_2\text{O}$ [139, 140]. The experiments were carried out in a tubular packed-bed quartz reactor

(10 mm inner diameter) under atmospheric pressure. The temperature of the reactor was held constant by a resistively heated furnace (National Electric Furnace FA120 type) where the temperature was controlled by a Watlow Controller (96 series). Catalyst temperatures were measured using a K-type thermocouple touching the bottom of a well on the external surface of the quartz reactor. Details on the DME titration experimental setup and reaction conditions were described in our previous publication [62].

The acidity of acid sites in lamellar MFI and Mo/lamellar MFI catalysts was determined by ammonia (NH_3) temperature programmed desorption (TPD) with a mass spectrometer (MS, Ametek Proline) using the set-up described in DME chemical titrations. Prior to measurement, 0.1 g of catalyst sample was activated by heating in a He (0.5 mL s^{-1} , ultrapure grade, Airgas) flow at 873 K for 4 h. After cooling to 393 K, NH_3 adsorption was carried out. Physically adsorbed NH_3 was removed by purging with a He flow (0.5 mL s^{-1}) at 393 K for 2 h. The NH_3 -TPD of the samples was carried out by increasing the temperature linearly from 393 to 983 K with a heating rate of 0.25 K s^{-1} .

4.2.2.3. External free acid site determination

To study the location of Brønsted acid sites in mesopores or the external surfaces of lamellar MFI, which was defined as the external acid sites, methanol (CH_3OH) dehydration reactions to dimethyl ether in the presence of 2,6-di-tert butylpyridine (DTBP) organic base molecules were measured at differential conversions (<2%) at 433 K using the reactor setup described in Section 4.2.2.2. A liquid mixture of methanol (Fisher Scientific, 99.9%) and DTBP (Alfa, 98% purity) was introduced into a flowing He stream using a syringe pump (NE 1000, New Era

Pump System Inc.). The reactor effluent was sent via heated transfer lines to mass spectrometer (MS, Ametek Proline). The dehydration rate was measured as titrant was continuously added until it reached a plateau indicating that acid sites accessible to the titrant became saturated with the organic base. The loss in dehydration rate after saturation by the titrant given by the difference between the initial and the residual rates was used to calculate the number of active sites accessed by the organic base titrant. The number of the external free Brønsted acid sites in Mo/lamellar MFI catalysts was measured by the DME titration experiment in the presence of DTBP organic base using the setup described above.

4.2.3. Catalytic DMA reactions

4.2.3.1. Experimental setup for the DMA reaction

The catalytic conversion of methane was carried out in a quartz reactor described in Session 4.2.2.2. Mo/lamellar MFI catalysts (~ 0.30 g) were treated in Ar (0.167 mL s^{-1} , research grade, Airgas) at 773 K (0.0167 K s^{-1}) for 4 h. After pretreatment, the temperature was increased to 950 K , and the DMA reaction was carried out at this temperature under ambient pressure. Methane was introduced into the catalyst at a flow rate of 0.132 mL s^{-1} (at normal temperature and pressure, NTP, condition) and Ar (0.035 mL s^{-1} at NPT condition, Airgas) as internal standard. The transfer lines were maintained at temperatures greater than 473 K by resistive heating to prevent product condensation. The reaction was analyzed using a gas chromatograph (Agilent 7890 A GC) equipped with a methyl-siloxane capillary column (HP-1, $50.0 \text{ m} \times 320 \text{ }\mu\text{m} \times 0.52 \text{ }\mu\text{m}$) connected to a flame ionization detector and a packed

column (SUPELCO HAYESEP R 80/100 mesh packed column, 12 ft) connected to a thermal conductivity detector.

4.2.3.2. Coke analysis in the DMA reaction

Thermo-gravity analysis (TGA, TA Instrument, SDT Q600) and Ar isotherm measurement were conducted to quantify the amount of coke formed and to identify the location of coke formation in the catalysts after the DMA reaction for time on stream (TOS) of 10 h. In the TGA analysis, the temperature was increased to 1073 K under flowing air (1 mL s^{-1}) at a ramp rate of 0.167 K s^{-1} to quantify the total amount of coke formed in the DMA reaction. Ar adsorption measurement conducted at 87 K was used to determine the micropore volume of the catalysts to interpret the coke formation location. The internal coke (defined for coke formed in the zeolite micropores) was calculated from the decrease in the micropore volume of the spent catalysts, as compared with the Mo/lamellar samples. The amount of external coke (coke formed on the external surface or mesopores in the lamellar zeolites) was calculated by subtracting the internal coke content from the total coke content. This analysis is based on the assumption that the remaining micropore volume is fully accessible to Ar molecules in the spent catalyst samples, as reported by Ryoo et al., [171]. The internal coke content was calculated with the assumption that the coke density was 1.22 g mL^{-1} , as described in reference [171].

4.3. Results and discussion

4.3.1. Structural and textural properties of catalysts

4.3.1.1. Morphologies of lamellar MFI and Mo/lamellar MFI catalysts

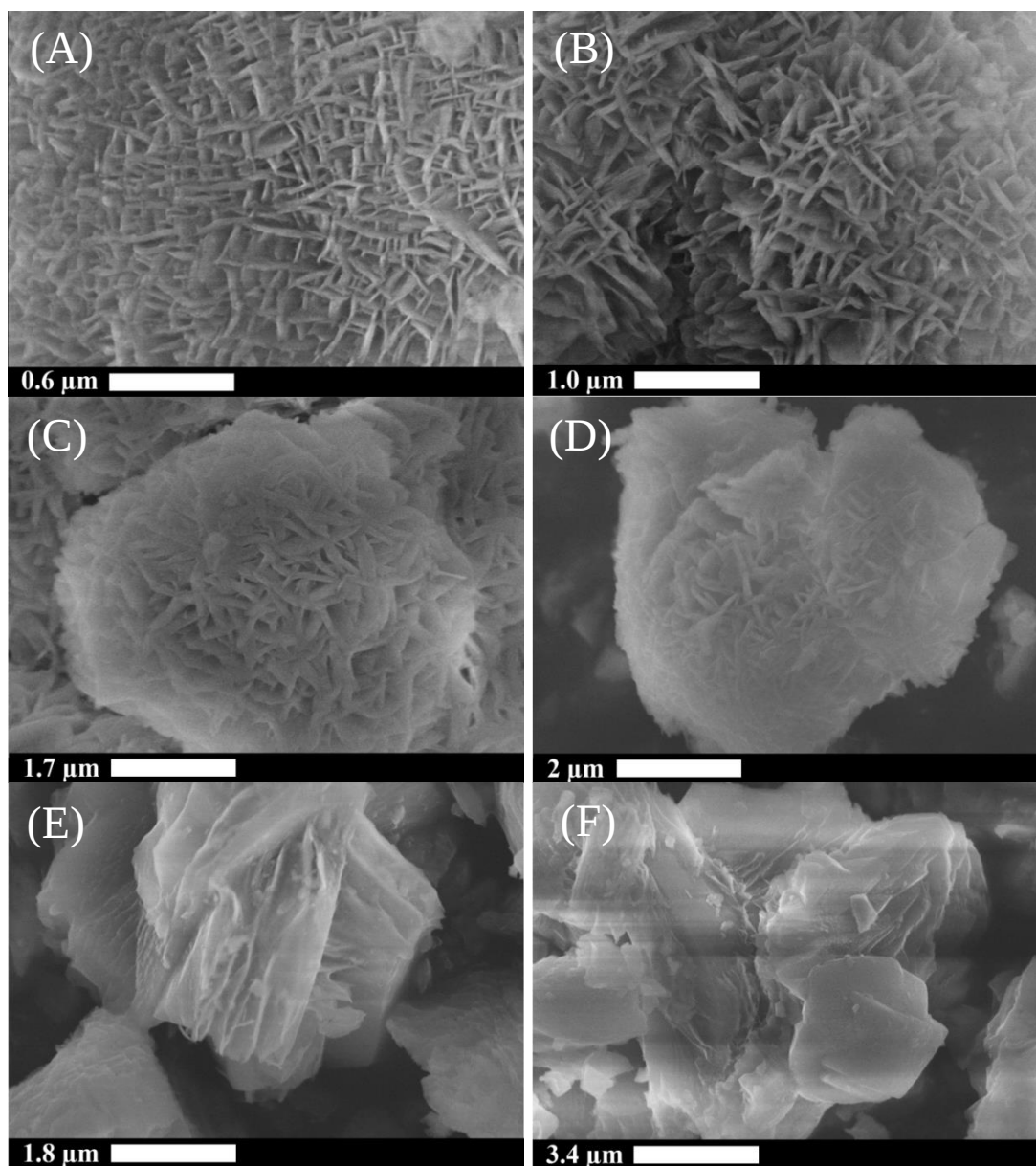


Figure 4.1. SEM images showing morphologies of lamellar MFI zeolites: (A) MFI-10/0, (B) MFI-10/2, (C) MFI-10/5, (D) Mo-10/8, (E) MFI-10/12, and (F) MFI-10/36.

Figure 4.1 shows the SEM images of meso-/microporous lamellar MFI zeolites. The MFI-10/0 sample, shown in Figure 4.1(A), is comprised of intertwined nanosheet-like particles with randomly organized structure, similar to multilamellar MFI reported by Na et al., [102]. With addition of small quantity of TPAOH to the synthetic recipe, as shown by MFI-10/2 in Figure 4.1(B), the crystal morphology is similar to that of

MFI-10/0, but the MFI nanosheets become thicker. A continual increase of TPAOH concentration in the synthesis increases the thickness of the MFI nanosheets, as shown by MFI-10/5, MFI-10/8, and MFI-10/12 in Figure 4.1(C)-(E), respectively. The further increase of TPAOH concentration in the synthesis (MFI-10/36) results in dense bulk zeolite particles, as illustrated in Figure 4.1(F). Figure 4.2 shows the XRD patterns of the synthesized lamellar MFI zeolite samples after template removal by calcination. All the samples have the characteristic signature reflections of crystalline MFI diffraction patterns, resembling the characteristic of a crystalline MFI reported by Ryoo and coworkers [102] and our previous study [123].

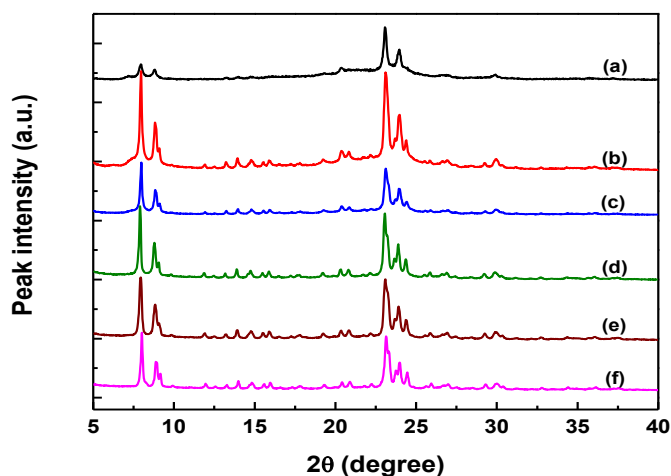
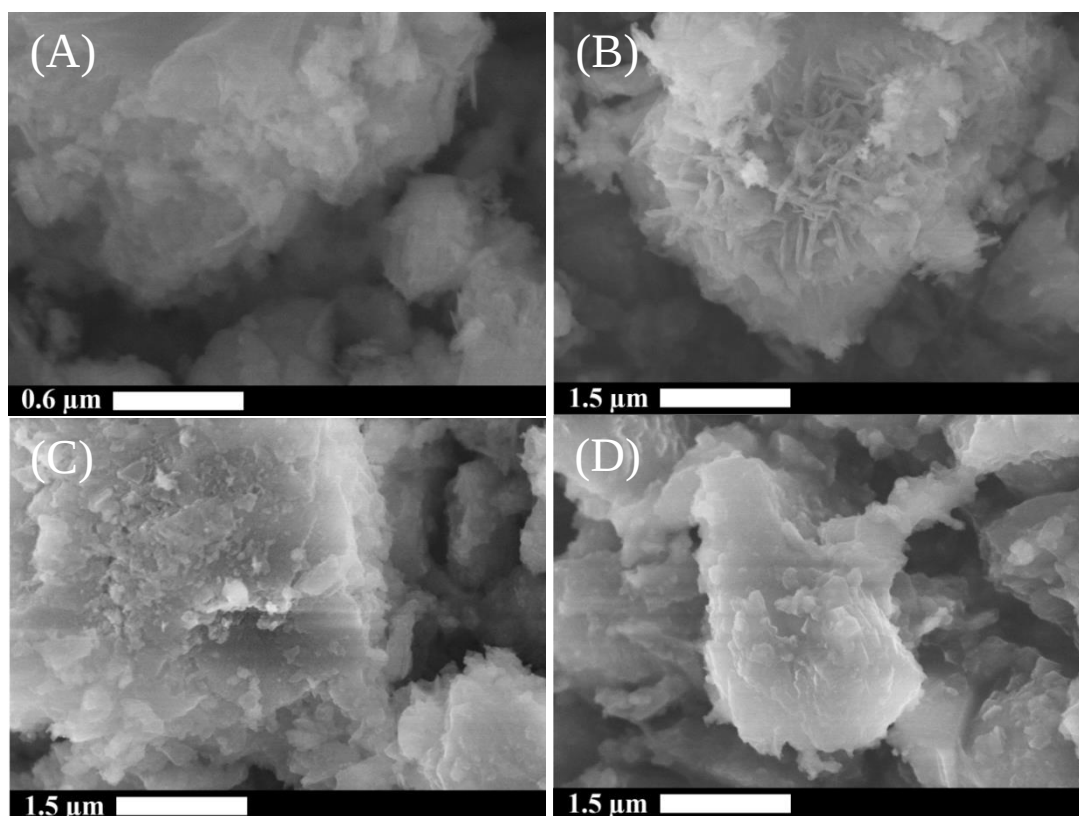


Figure 4.2. XRD patterns of MFI-10/0 (a), MFI-10/2 (b), MFI-10/5 (c), MFI-10/8 (d), MFI-10/12 (e) and MFI-10/36 (f).

The morphologies of Mo loaded lamellar MFI catalysts after the two-stage calcination treatment are shown by SEM images in Figure 4.3. Apparently, the high temperature calcination led to collapse of the ordered lamellar structure in the Mo/lamellar MFI zeolite catalysts. Additionally, the particles in each sample broke into

relatively small pieces. The residual lamellar structure can be observed slightly in Mo-MFI-10/0 and Mo-MFI-10/2 samples (Figure 3(A)-(B)). Mo-MFI-10/5, Mo-MFI-10/8, and Mo-MFI-10/12 (Figure 4.3(C)-(E)), respectively, all turned into dense irregular particles compared to MFI-10/5, MFI-10/8, and MFI-10/12. Mo-MFI-10/36 (Figure 4.3(F)) has the largest particle size among the investigated Mo/lamellar MFI catalysts. The XRD data in Figure 4.4 show that all the Mo/lamellar MFI samples resemble the diffraction patterns of lamellar MFI samples shown in Figure 4.2, indicating that no new crystalline phase was formed in the Mo loading and calcination processes during the preparation of Mo/lamellar MFI catalysts.



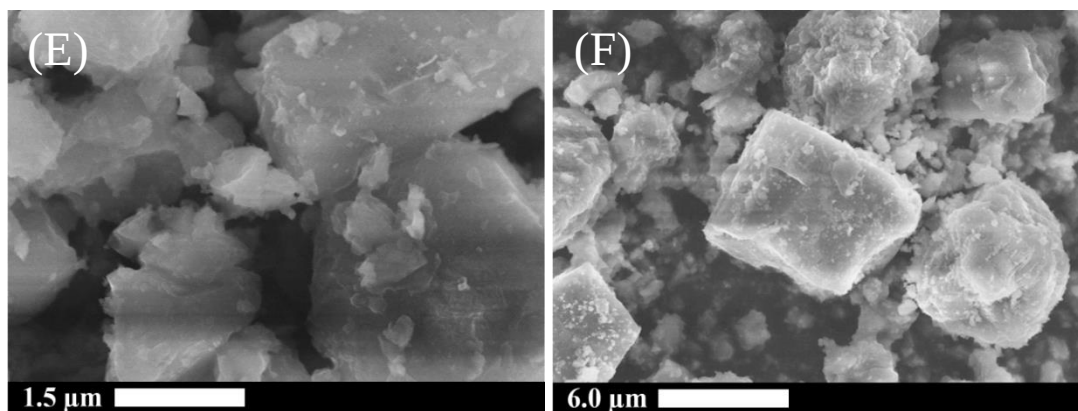


Figure 4.3. SEM images showing morphologies of Mo loaded lamellar MFI catalysts: (A) Mo-MFI-10/0, (B) Mo-MFI-10/2, (C) Mo-MFI-10/5, (D) Mo-MFI-10/8, (E) Mo-MFI-10/12, and (F) Mo-MFI-10/36.

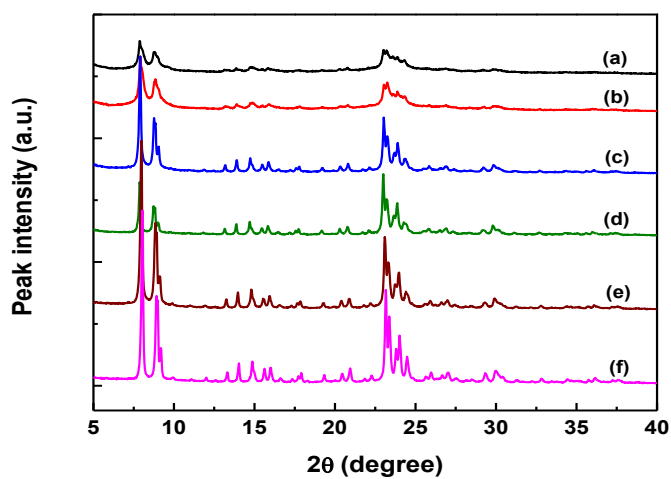


Figure 4.4. XRD patterns of Mo-MFI-10/0 (a), Mo-MFI-10/2 (b), Mo-MFI-10/5 (c), Mo-MFI-10/8 (d), Mo-MFI-10/12 (e) and Mo-MFI-10/36 (f).

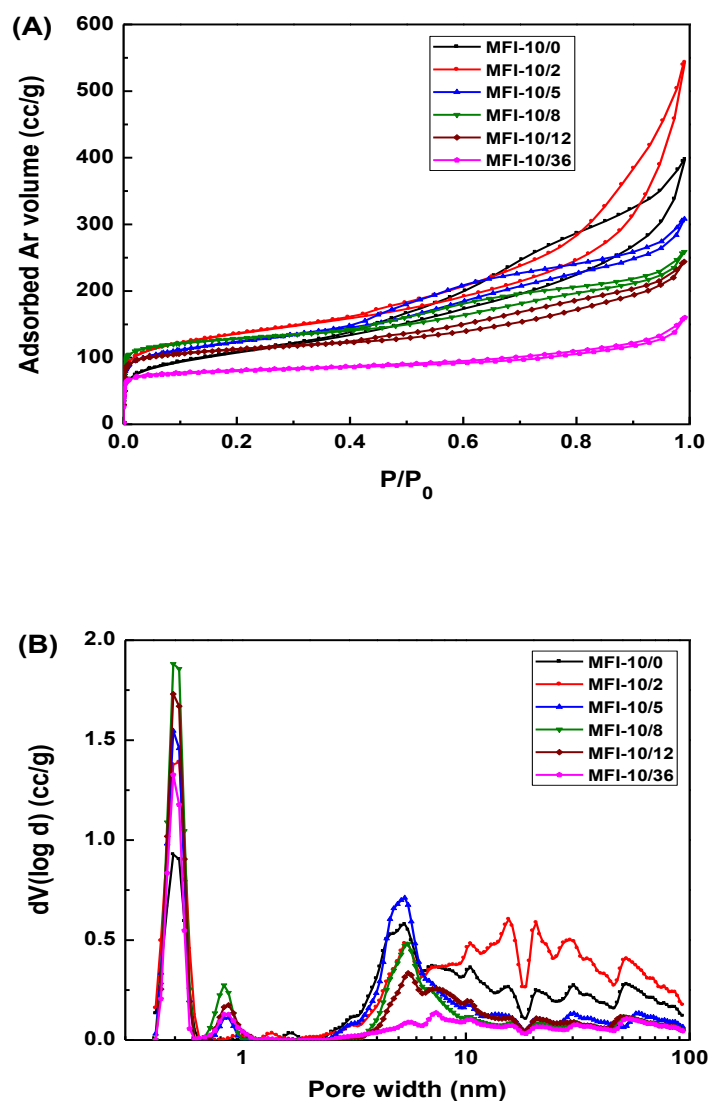


Figure 4.5. Ar adsorption-desorption isotherm (A) and NLDFT pore size distribution determined from adsorption branch of Ar isotherm (B) of lamellar MFI zeolites.

4.3.1.2. Textural properties of lamellar MFI and Mo/lamellar MFI catalysts

Ar isotherms in Figure 4.5 reveal the meso-/microporosity features of the lamellar MFI zeolites synthesized by the dual template method. At the low relative pressures ($p/p_0 < 0.45$), the lamellar MFI samples have similar Ar uptake as shown in Figure 4.5(A), which indicates that they have similar microporosity. In the high relative

pressure region ($p/p_0 = 0.45-1.0$), an increase in the adsorption volume and the presence of hysteresis loops in all the lamellar MFI samples indicate capillary condensation in the mesopores. A detailed examination on the Ar uptake in this relative pressure region shows a trend of MFI-10/0 $\sim$ MFI-10/2 $>$ MFI-10/5 $\sim$ MFI-10/8 $\sim$ MFI-10/12 $>$ MFI-10/36, reflecting a decrease in the mesoporosity with an increase of TPAOH quantity used in the dual template synthesis of lamellar MFI zeolites. The NLDFT pore size distributions, derived from adsorption branches of Ar isotherms, of the lamellar MFI samples in Figure 4.5(B) further underscore the changes of the mesoporosity across these lamellar MFI samples. MFI-10/0 and MFI-10/2 have broad pore sizes: micropore size of 0.55 nm, mesopore sizes centered at 5.5 nm, and macropores ranging up to 100 nm. MFI-10/5, MFI-10/8, and MFI-10/12 contain micropore of 0.55 nm and mesopores around 5.9 nm. For MFI-10/36 samples, both meso- and macroporosity, however, disappear in comparison to the samples synthesized with less amount of TPAOH. The small peak below 1 nm might be due to the reminiscence of a phase transition in the Ar adsorption, which has been previously reported for certain MFI zeolite samples [172-175]. The trend of porosity distribution across the lamellar MFI samples indicates that a systematic modulation on the textural properties of the zeolite structures can be realized.

Figure 4.6 shows Ar adsorption-desorption isotherms and the NLDFT pore size distributions of Mo loaded lamellar MFI catalysts. In comparison with lamellar MFI samples, Mo/lamellar MFI catalysts have lower surface areas and meso-/microporosity. The Ar uptake in the Mo/lamellar sample (Figure 4.6(A)) is less than that of the parent

lamellar MFI zeolite. In addition, the hysteresis loop in each sample becomes narrower compared to that of lamellar MFI in Figure 4.5(A).

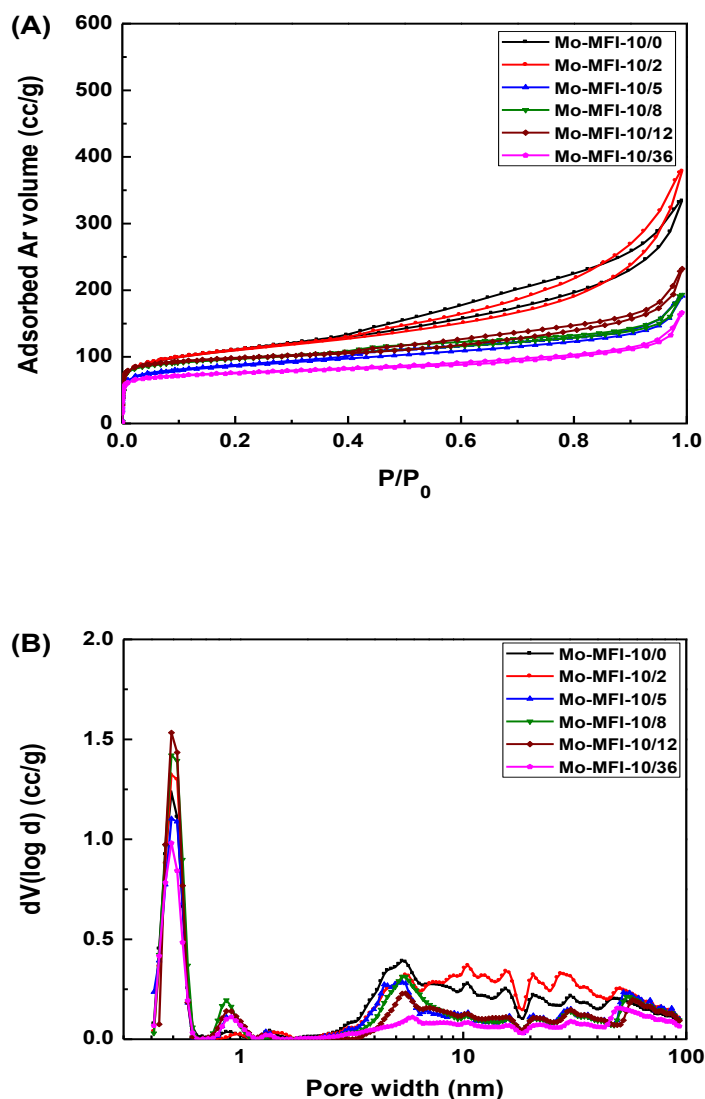


Figure 4.6. Ar adsorption-desorption isotherm (A) and NLDFT pore size distribution determined from adsorption branch of Ar isotherm (B) of Mo/lamellar MFI catalysts.

The pore size distribution (Figure 4.6(B)) shows that meso-/micropores in all Mo/lamellar MFI catalysts and macropores in Mo-MFI-10/0 and Mo-MFI-10/2 decreased in different degrees with loading of Mo species into the lamellar MFI

structures. It should be noted that the meso-/microporous textural features and the trend of pore size distributions across all the samples remain in the Mo loaded lamellar MFI catalysts.

Table 4.1. Textual properties of lamellar MFI catalysts derived from N₂ isotherms.

Catalyst	S_{BET}^a	S_{ext}^b	S_{micro}^b	V_{total}^c	V_{meso}^d	V_{micro}^b
	$(\text{m}^2 \text{ g}^{-1})$			$(\text{cm}^3 \text{ g}^{-1})$		
MFI-10/0	459	213	246	0.43	0.31	0.11
MFI-10/2	462	236	226	0.53	0.42	0.10
MFI-10/5	439	180	259	0.34	0.22	0.12
MFI-10/8	448	155	293	0.32	0.19	0.13
MFI-10/12	444	138	306	0.33	0.19	0.14
MFI-10/36	388	71	306	0.25	0.10	0.15

^a Calculated from multi-point BET method; ^b Calculated from *t*-plot method; ^c Calculated from the adsorption isotherm at $p/p_0=0.95$; ^d $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

Table 4.2. Textual properties of Mo/lamellar MFI catalysts derived from N₂ isotherms.

Catalyst	S_{BET}^a	S_{ext}^b	S_{micro}^b	V_{total}^c	V_{meso}^d	V_{micro}^b
	$(\text{m}^2 \text{ g}^{-1})$			$(\text{cm}^3 \text{ g}^{-1})$		
Mo-MFI-10/0	362	194	168	0.34	0.26	0.08
Mo-MFI-10/2	371	165	206	0.38	0.28	0.10
Mo-MFI-10/5	385	171	214	0.30	0.20	0.10
Mo-MFI-10/8	378	141	237	0.28	0.17	0.11
Mo-MFI-10/12	387	135	252	0.29	0.18	0.12
Mo-MFI-10/36	350	66	285	0.23	0.10	0.13

^a Calculated from multi-point BET method; ^b Calculated from *t*-plot method; ^c Calculated from the adsorption isotherm at $p/p_0=0.95$; ^d $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

To quantify the trend of the meso-/microporosity modulation with the molar ratios of the dual templates in the synthesis, the hierarchy factor as being the product of the relative micropore volume and the relative mesopore surface area, $(V_{\text{micro}}/V_{\text{pore}}) \times (S_{\text{meso}}/S_{\text{BET}})$, defined by Pérez-Ramírez [167], was considered. The hierarchy factor was derived from N₂ isotherms whereby the contribution of micropore volume to the total pore volume and the contribution of mesopore surface area to the total surface area of the sample are weighed. Table 4.1 and Table 4.2 summarize the textural

properties of lamellar MFI and Mo/lamellar MFI catalysts, respectively. The hierarchy factor across all the lamellar MFI zeolites has a volcano-type dependence on the $C_{22-6}/TPAOH$ ratios in the synthesis, as shown in Figure 4.7(A). The hierarchy factors of MFI-10/5, MFI-10/8, and MFI-10/12 are higher than those of the MFI-10/0 and MFI-10/2 zeolites since the relative increase of microporosity is higher than the relative decrease of mesoporosity in these zeolites. The hierarchy factor of MFI-10/36 is lower than those of MFI-10/5, MFI-10/8, and MFI-10/12 because of the extensive decrease in mesopores coupled with the preserved micropore volume. Figure 4.7(B) shows the hierarchy factors of the Mo/lamellar MFI samples, showing similar volcano-type dependence to that shown in Figure 4.7(A). The systematic tailoring of TPAOH concentration in the dual template synthesis of MFI zeolites leads to tunable meso-/microporosity in the resultant Mo/lamellar MFI catalysts.

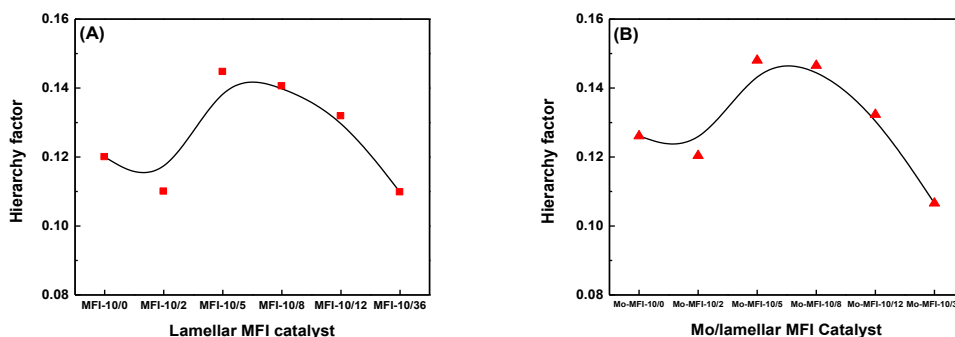


Figure 4.7. Hierarchy factor, described as the product $(V_{\text{micro}}/V_{\text{total}}) \times (S_{\text{ext}}/S_{\text{BET}})$, of lamellar MFI (A) and Mo/lamellar MFI (B) catalysts.

4.3.2. Active sites of lamellar MFI and Mo/lamellar MFI catalysts

4.3.2.1. ICP-OES and XPS analyses

The Si, Al, and Mo contents of the lamellar MFI and Mo/lamellar MFI catalysts were quantified by ICP-OES and XPS analyses. Table 4.3 shows that the Si/Al and

Si/Mo ratios of all the samples are ~30 and ~100, respectively, consistent with the element concentrations added in the preparation of these samples. The near-surface Mo concentrations in Mo/lamellar MFI catalysts, described by the Si/Mo ratios from XPS analysis, are 131, 191, 77, 64, 61 and 23, for Mo-MFI-10/0, Mo-MFI-10/2, Mo-MFI-10/5, Mo-MFI-10/8, Mo-MFI-10/12, and Mo-MFI-10/36, respectively, showing that the surface Mo concentration increases with increasing TPAOH content in the dual template synthesis of lamellar MFI zeolites. The external surface areas decrease and the particle sizes increase from Mo-MFI-10/0 to Mo-MFI-10/36, suggesting that Mo species had difficulty in diffusing into the microporous channels of large MFI zeolite crystals [45, 159]. In contrast, the smaller crystallite sizes of mesopores in meso-/microporous lamellar MFI zeolites facilitate the diffusion of Mo precursors into zeolite channels. The presence of mesopores in the lamellar MFI does not affect the chemical states of the Mo species since the peak positions shown in Figure 4.8 are almost the same in all the Mo/lamellar MFI catalysts.

Table 4.3. Composition and acidity of the lamellar MFI catalysts before and after Mo loading.

Catalyst	Before Mo loading					After Mo loading			
	Si/Al ^a	Si/Al ^b	Si/H ⁺ ^c	Si/Al ^d	f _{ext, H⁺} (%) ^e	Si/H ⁺ ^c	Si/Mo ^a	Si/Mo ^b	f _{ext, H⁺} (%) ^f
MFI-10/0	32	27	33	31	12	140	126	131	10
MFI-10/2	32	33	33	33	14	105	124	191	12
MFI-10/5	31	46	29	35	10	76	96	77	12
MFI-10/8	33	34	28	32	9	66	103	64	7
MFI-10/12	32	56	32	40	8	55	101	61	10
MFI-10/36	26	38	21	28	5	42	98	23	1

^a Measured by ICP-OES; ^b Measured by XPS; ^c Determined by DME titration (refer to Table 4.4 for the number of free Brønsted acid sites in each sample); ^d Average Si/Al ratio, calculated from $\text{Si/Al}^d = (\text{Si/Al}^a + \text{Si/Al}^b + \text{Si/H}^{+c})/3$, under the assumption that the number of H⁺ sites determined by DME titration equals to that of framework Al in zeolite; ^e Determined by DTBP titration during methanol dehydration reaction; ^f Determined by DME titration with and without the presence of DTBP.

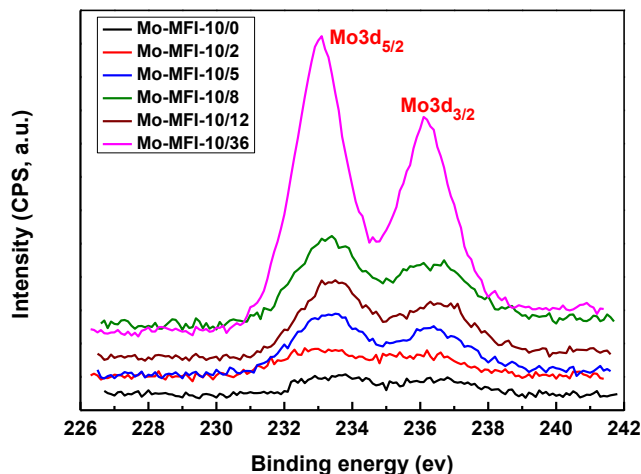


Figure 4.8. Chemical state of Mo species in Mo-lamellar MFI zeolite measured by ex-situ XPS.

4.3.2.2. Brønsted acid sites measured by DME titration

In order to understand the effect of lamellar zeolite structures on the Mo-Brønsted acid sites interactions and their consequences on the catalytic activity and the catalyst stability in the DMA reaction, the number of free Brønsted acid sites (represented by Si/H^+ ratio) before and after Mo loading into the lamellar zeolites was quantified by the DME titration measurement. The Si/H^+ ratios of lamellar MFI zeolite samples were around 30 (Table 4.3), similar to Si/Al ratios determined *via* ICP-OES analysis, showing that the Al mainly stayed in zeolite framework. The Si/H^+ ratios of Mo/lamellar MFI catalysts, however, increased with decreasing TPAOH quantity in the lamellar zeolite synthesis, as shown in Table 4.3. During the impregnation and calcination processes, a portion of molybdenum species migrated into zeolitic channels and anchored on Brønsted acid sites, leading to a decrease in the population of the free Brønsted acid sites. This result indicates that the interactions between Mo and Brønsted

acid sites are influenced by the distribution of Brønsted acid sites as a consequence of tunable meso-/microporous lamellar structures of MFI zeolite. The increasing mesoporosity in zeolites increases the dispersion of Mo species, and thus enhances the number of interacting Mo-Brønsted acid nanoclusters in the catalysts.

4.3.2.3. Spatial distribution of active sites in catalysts

To investigate further the surroundings of Brønsted acid and Mo sites in the meso-/microporous lamellar MFI zeolites, the fraction of external free acid sites in each lamellar MFI and Mo/lamellar MFI was quantified. The methanol reaction in the presence of DTBP organic base was conducted to quantify the fraction of external free acid sites in lamellar MFI samples. The cumulative DTBP addition resulted in a linear decrease in methanol rates for zeolite catalysts, consistent with stoichiometric titration of the active acid sites along the catalyst bed. The loss in methanol reaction rates reflects the degree of accessibility of bulky DTBP molecules to Brønsted acid sites in lamellar MFI zeolites, and hence, the number of active sites accessible from the external surface and/or mesoporous environment and the fraction of external acid sites ($f_{\text{ext}}, \text{H}^+$) can be calculated. Table 4.3 indicates that 12%, 14%, 10%, 9%, 8% and 5% of Brønsted acid sites exist in MFI-10/0, MFI-10/2, MFI-10/5, MFI-10/8, MFI-10/12 and MFI-10/36 samples, respectively. The base titration results confirm that MFI-10/0 and MFI-10/2 have comparable number of external Brønsted acid sites to access large molecules. MFI-10/5, MFI-10/8, and MFI-10/12 have lower number of external Brønsted acid sites than MFI-10/0 and MFI-10/2, but higher than that of MFI-10/36.

Table 4.4. Acidity of lamellar MFI and Mo-lamellar MFI catalysts.

Catalyst	No. of acid sites before Mo loading (10^{-4} mol g $^{-1}$)			No. of acid sites after Mo loading (10^{-4} mol g $^{-1}$)		
	$C_{\text{total}, \text{H}^+}^a$	$C_{\text{int}, \text{H}^+}^c$	$C_{\text{ext}, \text{H}^+}^d$	$C'_{\text{total}, \text{H}^+}^e$	$C'_{\text{int}, \text{H}^+}^f$	$C'_{\text{ext}, \text{H}^+}^g$
MFI-10/0	0.49	0.43	0.058	0.15	0.14	0.015
MFI-10/2	0.49	0.42	0.070	0.13	0.12	0.016
MFI-10/5	0.56	0.50	0.057	0.19	0.17	0.024
MFI-10/8	0.57	0.52	0.051	0.19	0.18	0.014
MFI-10/12	0.51	0.46	0.041	0.19	0.17	0.018
MFI-10/36	0.76	0.72	0.040	0.39	0.39	0.004

^a Calculated from the average Si/Al ratio obtained from ICP-OES, DME titration and XPS measurement, respectively; ^b Determined by DTBP titration during methanol dehydration reaction; ^c Calculated by $C_{\text{int}, \text{H}^+} = C_{\text{total}, \text{H}^+} \times (1 - f_{\text{ext}, \text{H}^+})$; ^d Calculated by $C_{\text{ext}, \text{H}^+} = C_{\text{total}, \text{H}^+} \times f_{\text{ext}, \text{H}^+}$; ^e Determined by DME titration; ^f Determined by DME titration in the presence of DTBP; ^g Calculated by $C'_{\text{ext}, \text{H}^+} = C'_{\text{total}, \text{H}^+} - C'_{\text{int}, \text{H}^+}$; ^h Calculated by $f'_{\text{ext}, \text{H}^+}(\%) = (C'_{\text{total}, \text{H}^+} - C'_{\text{int}, \text{H}^+}) / C'_{\text{total}, \text{H}^+}$.

The fraction of external free acid site in Mo/lamellar MFI catalysts were determined by DME titration experiment in the presence of DTBP organic base molecules. The saturation of the acid sites with DTBP base before DME titration only allowed DME to react with acid sites located in microporous environment. The difference between the number of acid sites measured and the one quantified by the DME titration in the absence of DTBP (Table 4.4) is the number of the external free acid sites in Mo/lamellar MFI catalysts. Table 4.3 lists the fractions of free Brønsted acid sites accessible to DTBP ($f_{\text{ext}, \text{H}^+}$) are 10%, 12%, 12%, 7%, 10% and 1%, respectively, from Mo-MFI-10/0 to Mo-MFI-10/36 catalysts. In comparison to the fractions of external Brønsted acid sites in lamellar MFI zeolites, a very slight decrease in the fractions of acid sites accessible to DTBP molecules was observed in most of the Mo loaded lamellar MFI catalysts. This result suggests that the interactions of external Brønsted acid sites with the Mo species were not highly dependent on the textural properties of the lamellar zeolite catalysts.

The co-existence of Mo and Brønsted acid sites in the catalysts is required to activate the DMA reaction [51, 80, 147, 159]. To quantify the distribution of the Mo and free Brønsted acid active sites on the external surface and mesopores of the Mo/lamellar MFI catalysts, the product of the relative external Mo species and the relative external free Brønsted acid sites ($(f_{\text{ext, Mo}} \times (f_{\text{ext, H}^+}))$) was considered. The concentration of Mo in the bulk zeolite ($C_{\text{bulk, Mo}}$) and on the external surface/mesopores ($C_{\text{ext, Mo}}$) of the zeolite as well as the relative external/mesoporous surface areas of the catalysts ($S_{\text{ext}}/S_{\text{BET}}$) analyzed from N_2 isotherms were used to calculate for the relative external Mo species ($f_{\text{ext, Mo}} = (C_{\text{ext, Mo}} \times S_{\text{ext}})/(C_{\text{bulk, Mo}} \times S_{\text{BET}})$) on the catalysts. The details in assessment of $f_{\text{ext, Mo}}$ for each catalyst were listed in Table 4.5. A linear increase in $f_{\text{ext, Mo}}$ is observed from Mo-MFI-10/0 to Mo-MFI-10/36 catalysts, indicating that the number of external Mo species increases with decreasing mesoporosity in the catalysts, in contrast to the increasing trend in Brønsted acid sites across the same catalysts. The intersection of the two opposite trendlines in $f_{\text{ext, Mo}}$ and $f_{\text{ext, H}^+}$ versus the Mo/lamellar MFI catalysts, respectively, determines the maximum chances for presence of both Mo and H^+ species on the external surface and mesopores of the catalysts. The consideration for the contribution of external surface and mesopores of lamellar MFI zeolites on the active sites locations in Mo/lamellar zeolite is represented by the product of $(f_{\text{ext, Mo}} \times (f_{\text{ext, H}^+}))$. Figure 4.9 shows the product of $(f_{\text{ext, Mo}} \times (f_{\text{ext, H}^+}))$ as a function of the dual template ratios in the synthesis of lamellar MFI zeolites. The Mo- H^+ sites coexisted on the external surface increase with TPAOH concentration in the synthesis from Mo-MFI-10/0 to Mo-MFI-10/2, reach a maximum at Mo-MFI-10/5, Mo-MFI-10/8, and Mo-MFI-10/12, and then decrease with a further

increase in TPAOH in the synthesis (Mo-MFI-10/36). Given the total amount of Mo and Brønsted acid sites are comparable in all the studied Mo/lamellar MFI catalysts, the Mo and Brønsted acid active sites coexisted in the internal micropores of the catalysts are expected to exhibit an opposite trend to that of the external Mo-H⁺ active sites. The volcano-type trend for the distribution of Mo and Brønsted acid sites suggests the spatial distribution of the active sites can be systematically tailored by the controlled synthesis of the meso-/microporous zeolite catalysts. The slight changes in the fractions of external free acid sites before and after Mo loading into the zeolite samples suggest that Mo stays as large clusters on the external surface of the lamellar MFI with large crystallite sizes.

Table 4.5. Mo concentration in the Mo/lamellar MFI catalysts.

Catalyst	Mo Concentration (10 ⁻⁴ mol g ⁻¹)		Surface area (m ² g ⁻¹)		f _{ext, Mo} ^e (%)
	C _{total, Mo} ^a	C _{ext, Mo} ^b	S _{total} ^c	S _{ext} ^d	
MFI-10/0	0.13	0.12	362	194	49
MFI-10/2	0.13	0.09	371	165	31
MFI-10/5	0.17	0.21	385	171	55
MFI-10/8	0.16	0.25	378	141	58
MFI-10/12	0.16	0.27	387	135	59
MFI-10/36	0.16	0.70	350	66	83

^a Calculated from ICP-OES with an assumption of constant Si concentration; ^b Calculated from XPS with an assumption of constant and evenly distributed Si concentration; ^c Calculated from multi-point BET method; ^d Calculated from t-plot method; ^e Calculated from $f_{\text{ext, Mo}} (\%)^e = (C_{\text{ext, Mo}}^b \times S_{\text{ext}}^d) / (C_{\text{total, Mo}}^a \times S_{\text{total}}^c) \times 100\%$.

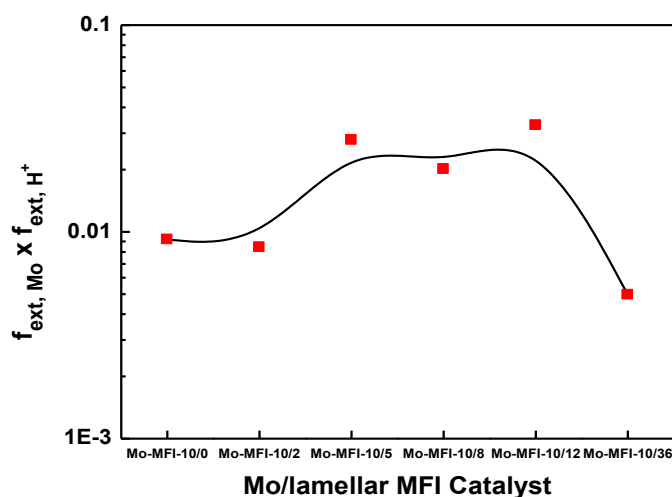


Figure 4.9. Acid and Mo active sites distribution, described as the product ($f_{\text{ext, Mo}}$) $\times$ ($f_{\text{ext, H}^+}$), of Mo/lanellar MFI catalysts.

4.3.2.4. Acidity differences between lamellar MFI and Mo/lanellar MFI catalysts

Figure 4.10(A)-(B) shows the NH_3 desorption peaks of lamellar MFI and Mo/lanellar MFI catalysts, which can be deconvoluted into three peaks centered at ~ 540 K, ~ 620 K and ~ 740 K, corresponding to physisorbed NH_3 , NH_3 adsorbed onto Lewis acid sites and Brønsted acid sites, respectively [38, 152, 176]. Detailed information on deconvolution of the NH_3 -TPD peaks can be found in our previous work [47]. The intensity of desorption peak at ~ 740 K in Figure 4.10(B) is significantly reduced in comparison to NH_3 -TPD of lamellar MFI (Figure 4.10(A)). This change might reflect the Mo species are associated with the Brønsted acid sites in the lamellar zeolite catalysts, which form active Mo-acid site species for the DMA catalytic reaction.

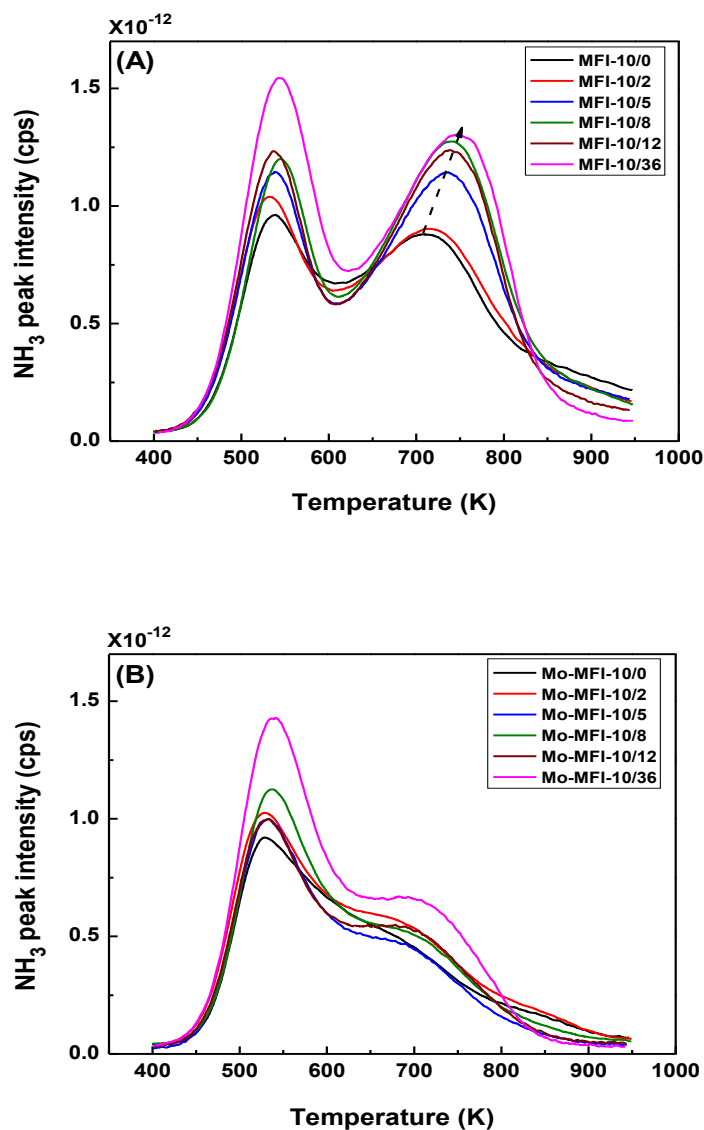


Figure 4.10. NH₃-TPD curves of lamellar MFI (A) and Mo/lamellar MFI (B) catalysts.

4.3.3. Catalytic performance of Mo/lamellar catalysts in the DMA reaction

4.3.3.1. Product formation rate and selectivity.

Benzene, toluene and naphthalene are the major products in the DMA reaction. Figure 4.11(A)-(C) shows the formation rates of these three compounds as a function of the time on stream. For all the investigated Mo/lamellar catalysts, the product

formation rates sharply increased in the initial period of the reaction (i.e., induction period). Afterwards, the product formation rate monotonically decreased with TOS. The overall trend of aromatic production rate versus TOS over all the investigated catalysts is similar to that observed in literature [15, 44]. After the reaction induction period (for example, TOS between 2 h and 4 h), the benzene (Figure 4.10(A)) and toluene (Figure 4.10(B)) formation rates over Mo/lamellar MFI catalysts followed a sequence of Mo-MFI-10/2 ~ Mo-MFI-10/0 > Mo-MFI-10/5 ~ Mo-MFI-10/8 ~ Mo-MFI-10/12 > Mo-MFI-10/36. The trend in naphthalene formation rate (Figure 4.11(C)) was similar to that of benzene or toluene formation, except that Mo-MFI-10/36 had a comparable rate to that of Mo-MFI-10/2 and Mo-MFI-10/0 catalysts. After TOS of ~5 h, the benzene and toluene product formation rates over Mo/lamellar MFI catalysts followed a sequence of Mo-MFI-10/5 ~ Mo-MFI-10/8 ~ Mo-MFI-10/12 > Mo-MFI-10/2 > Mo-MFI-10/0 ~ Mo-MFI-10/36. The naphthalene production rate showed a linear increase from Mo-MFI-10/0 to Mo-MFI-10/36 after the reaction rate reaches a more or less plateau. The changes in the trends of product formation versus TOS over the Mo/lamellar MFI catalysts indicate that Mo-MFI-10/0 and Mo-MFI-10/2 had a fast deactivation rate than other catalysts. It is commonly recognized that heavy compounds are predominantly formed on the active sites near the external surface of the Mo-MFI catalysts. The high number of external active sites in Mo-MFI-10/0 and Mo-MFI-10/2 catalysts might contribute to the formation of coke on their external surface or mesopores, and the consequent fast deactivation rates, compared to Mo loaded MFI-10/5, MFI-10/8, MFI-10/12, and MFI-10/36 catalysts. It is worth noting that production rate of benzene and toluene aromatic products at longer TOS (> 4 h) followed a volcano

trend with increasing textural properties and thus the TPAOH concentration in the dual template synthesis.

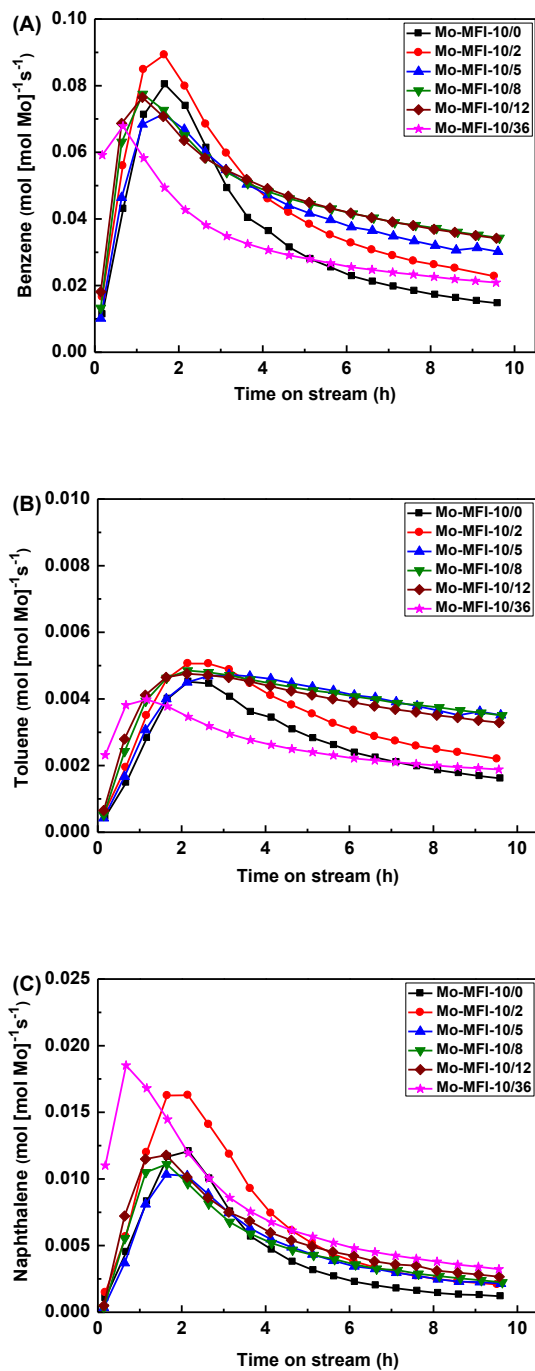


Figure 4.11. Production rates of benzene (A), toluene (B) and naphthalene (C), respectively, over the Mo/lamellar MFI catalysts.

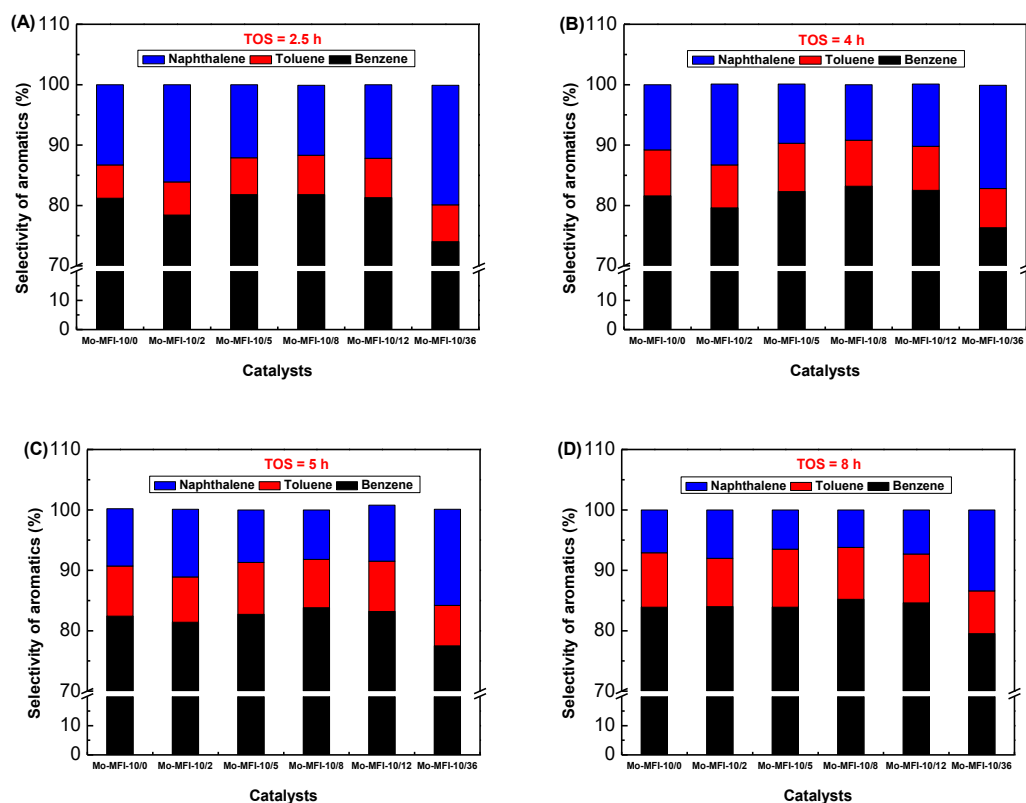


Figure 4.12. Selectivity of aromatic products at TOS of 2.5 h (A), 4 h (B), 5 h (C) and 8 h (D), respectively, in the DMA reaction over Mo/lamellar MFI catalysts.

The selectivity to the main aromatic products, i.e., benzene, toluene, and naphthalene, over the Mo-lamellar MFI catalysts are different with TOS of the DMA reaction. Figure 4.12(A)-(D) shows the product selectivity at TOS of 2.5 h, 4 h, 5 h, and 8 h, respectively. The data were calculated on the basis of main aromatic products without accounting for coke, smaller hydrocarbon, and other heavy aromatic molecules. The selectivity to benzene and toluene increased with TOS for each catalyst, while selectivity to naphthalene exhibited an opposite trend, as shown in Figure 4.12. At each TOS, the benzene selectivity slightly increased and then decreased when the catalyst was tuned from Mo-MFI-10/0 and Mo-MFI-10/2 to Mo-MFI-10/5, Mo-MFI-10/8, and Mo-MFI-10/12, and then to Mo-MFI-10/36. The toluene selectivity was relatively

stable across all the investigated catalysts at the same TOS of the DMA reaction. The naphthalene selectivity gradually declined with increasing TPAOH in the synthesis (from Mo-MFI-10/0 and Mo-MFI-10/2 to Mo-MFI-10/5, Mo-MFI-10/8, and Mo-MFI-10/12), and then increased with a further increase in TPAOH content (Mo-MFI-10/36), exhibiting an opposite trend to that of benzene selectivity at each TOS of the reactions. The comparison of product selectivity among Mo loaded lamellar MFI shows that Mo-MFI-10/5, Mo-MFI-10/8, and Mo-MFI-10/12 slightly favored benzene and disfavored naphthalene productions, in contrast to Mo-MFI-10/0, Mo-MFI-10/2, and Mo-MFI-10/36, respectively.

The micropore size of MFI is close to the dynamic diameter of benzene, which has been understood to be responsible for the activation methane to form aromatic products. It is commonly recognized that naphthalene is predominantly formed on the active sites near the external surface of the Mo-MFI catalysts. Taking into account that Mo-MFI-10/0 and Mo-MFI-10/2 catalysts have larger external surface areas than those of Mo loaded MFI-10/5, MFI-10/8, and MFI-10/12 catalysts, the higher naphthalene selectivity might be due to the contribution of the active sites on the external surface and in the mesopores of the catalysts. Besides, the interconnection between micropores and mesopores decreases the path length for naphthalene diffusion to the exterior of crystallites, which contributes to the high formation rate of naphthalene. A further increase in the microporosity or decrease in mesoporosity led to the decrease in benzene formation, as shown in the selectivities of Mo-MFI-10/36 catalyst. The mass transport limitations as a consequence of increasing crystallite sizes in Mo-MFI-10/36 catalyst would also favor the formation of naphthalene aromatic products. Previously Cui et al.,

[159] also reported that production rate showed a volcano trend with gradually increased external surface area caused by decrease of crystal size.

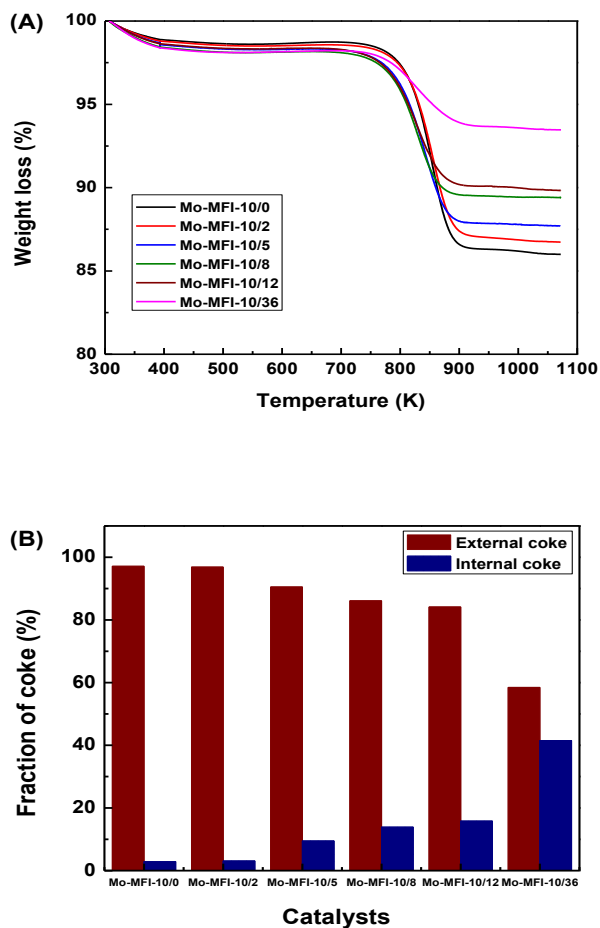


Figure 4.13. TGA curves of coke formed in Mo/lamellar MFI catalysts (A) and distribution of coke in mesopore or external surface (external coke) and micropores (internal coke) of the catalysts (B) after TOS of 10 h in the DMA reaction.

4.3.3.2. Coke deposition

Coke deposits on the Mo species and zeolite Brønsted acid sites in the DMA reaction result in the catalyst deactivation. To investigate the influence of the coke deposition in the meso-/microporous lamellar zeolite catalysts and its influences on the catalytic performances, the amount and location of coke formed on Mo/lamellar MFI

catalysts after TOS of 10 h under the DMA reaction conditions were studied by TGA analysis.

The TGA curves, shown in Figure 4.13(A), reveal a substantial weight loss in the temperature range of 690–870 K that corresponds to the burning-off of the coke deposits. The weight loss in this temperature range is 12.8%, 11.8%, 10.3%, 8.8%, 8.5% and 4.7% for Mo-MFI-10/0, Mo-MFI-10/2, Mo-MFI-10/5, Mo-MFI-10/8, Mo-MFI-10/12, and Mo-MFI-10/36, respectively. Weight loss at 300 K - 690 K was contributed by evaporation of physisorbed and chemisorbed water. The small increase in weight observed below 690 K is attributed to the oxidation of MoC_x species. The coke deposition in these catalysts increases with increasing mesopore volume or external surface area of the catalysts, reflecting that mesopores function as a coke reservoir in the DMA reaction.

To quantify the location of coke formed in the Mo/lamellar MFI catalysts and to understand the correlations between the coke formation and the active sites distribution, and hence the structures of the meso-/microporous lamellar catalyst, the spent Mo/lamellar MFI catalysts after TOS of 10 h were further analyzed by Ar adsorption-desorption isotherms. Table 4.6 summarizes the BET surface area, micropore surface area, external surface area, micropore volume and total pore volume of the spent catalysts. In comparison with the Mo/lamellar MFI catalysts, both surface areas and pore volumes decreased, caused by the deposition of coke in the DMA reaction. The amount of internal coke in the zeolite micropores was determined from the decrease in the micropore volume, as compared with a Mo/lamellar MFI sample.

Table 4.6. Textual properties of the spent Mo/lamellar MFI catalysts after the DMA reaction.

Catalyst	S_{total}^a	S_{ext}^b	S_{micro}^b	V_{total}^c	V_{meso}^d	V_{micro}^b
	$(\text{m}^2 \text{ g}^{-1})$			$(\text{cm}^3 \text{ g}^{-1})$		
Mo-MFI-10/0	272	135	137	0.23	0.17	0.06
Mo-MFI-10/2	286	135	151	0.28	0.22	0.06
Mo-MFI-10/5	260	114	147	0.19	0.13	0.06
Mo-MFI-10/8	289	96	193	0.19	0.11	0.08
Mo-MFI-	266	81	185	0.18	0.10	0.08
Mo-MFI-	194	74	120	0.14	0.09	0.05

^a Calculated from multi-point BET method; ^b Calculated from t-plot method; ^c Calculated from the adsorption branch at $P/P_0=0.95$; ^d $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

Figure 4.13(B) shows the fractions of coke deposited in micropores and external surface/mesopores of the catalysts, respectively. The coke in micropores over the total amount of the coke in Mo-MFI-10/0 is 2.9 % while it increases gradually with the decrease of mesoporosity, reaching 41.5 % for Mo-MFI-10/36. Considering that the zeolite micropore is the major place for aromatization to take place, the large amount of coke on external surface or in mesopores of Mo-MFI-10/0 and Mo-MFI-10/2 might block the entrance of the reactant into or product out of the active sites in the micropores, and thus cause the fast catalyst deactivation. In contrast to Mo-MFI-10/0 and Mo-MFI-10/2 samples, Mo-MFI-10/36 catalyst has higher amount of internal coke that block the active sites for the reaction to take place. For the Mo-MFI-10/5, Mo-MFI-10/8, Mo-MFI-10/12 catalysts, the coke deposited on external surface or in mesopores and in internal micropores formed a good balance, and thus, these three catalysts show the better catalytic performance compared to other catalysts.

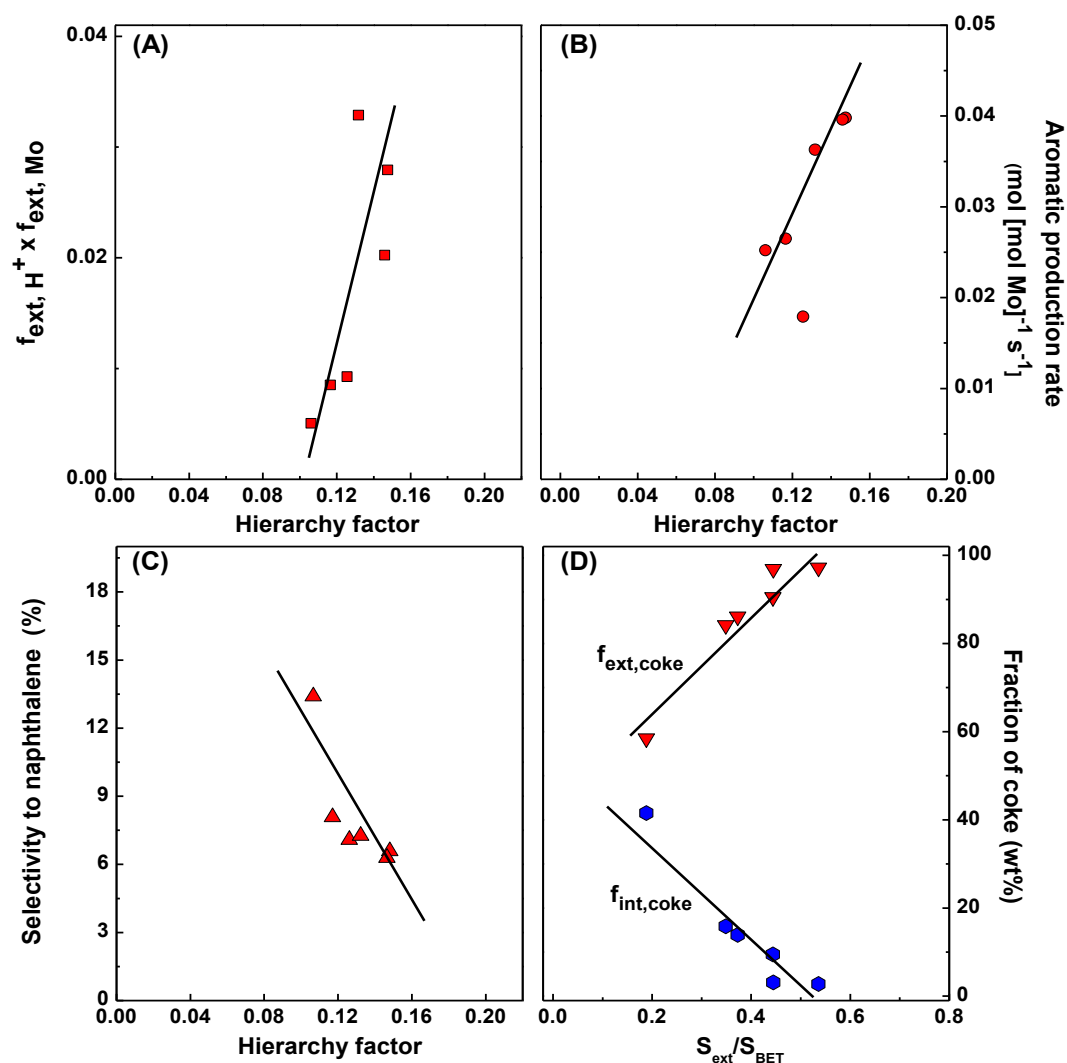


Figure 4.14. Interdependence between active site distribution, catalytic performance, and textural properties (described as the product $(V_{\text{micro}}/V_{\text{total}}) \times (S_{\text{ext}}/S_{\text{BET}})$) of the Mo/lamellar MFI catalysts. (A) Active site distribution, described as the product $(f_{\text{ext, Mo}} \times f_{\text{ext, H}^+})$, versus hierarchical factor; (B) Aromatic product formation rate at TOS 10 h versus hierarchical factor; (C) Selectivity to naphthalene at TOS of 10 h versus hierarchical factor; and (D) Coke distribution ($f_{\text{ext, coke}}$ and $f_{\text{int, coke}}$) versus relative external surface area of the catalysts.

4.3.4. Synthesis-structure-performance correlations

On the basis of the textural properties, spatial distribution of acid and metal active sites, and catalytic performances of the Mo/lamellar MFI catalysts in the DMA reaction, correlations between the dual template synthesis, structural and textural

properties, and functions of the meso-/microporous lamellar catalysts can be reasonably developed. A volcano-type trend in Figure 4.7(B) and Figure 4.9 has shown the dependence of the morphology and spatial distribution of the active sites, respectively, on the dual templates ratios in the hydrothermal synthesis. The spatial distribution of the active sites ($(f_{\text{ext, Mo}} \times f_{\text{ext, H}^+})$) is apparently influenced by the morphological features, determined by the hierarchy factor ($(V_{\text{micro}}/V_{\text{total}}) \times (S_{\text{ext}}/S_{\text{BET}})$), of the Mo/lamellar MFI catalysts, and therefore, a correlation between these two parameters may exist. Figure 4.14(A) shows a linear dependence of the $(f_{\text{ext, Mo}} \times f_{\text{ext, H}^+})$ on the morphological hierarchy factor of the Mo/lamellar MFI catalysts. The systematic tailoring of TPAOH concentration in the dual template synthesis of lamellar MFI zeolites leads to tunable textural parameters and consequently the distribution of active sites in the catalysts.

The implications of the tunable textural properties (or hierarchy factors) on the DMA reaction were analyzed to interpret the aromatics production rates and internal/external coke formation. Figure 4.14(B) shows a linear relation between the aromatics production and the hierarchy factor. The selectivity to naphthalene product versus the hierarchy factor of the catalysts is shown in Figure 4.14(C), illustrating a linear relationship, too. The coke formation does not follow a linear correlation with the hierarchy factor of the Mo/lamellar MFI catalysts. The fractions of internal and external coke, however, have linear-type dependence with the relative external surface area of the catalysts (Figure 4.14(D)). The increase in mesoporosity of the catalysts results in concomitantly increase in external coke and decrease in internal coke. The performance of the hierarchical meso-/microporous zeolites is better than the purely

microporous or mesoporous zeolites. The benefits of improved transport as the consequence of presence of mesopores and the catalytic selectivity due to the micropores in the catalyst samples are, therefore, both influential on the catalytic performance. The two linear lines in Figure 4.14(D) incline to intersect at some point, at which the catalysts seem to have the balanced meso-/microporosity to enable the optimized reaction and transport events for the DMA reaction. The experimental evidence proves the interdependent correlations between the catalyst synthesis, structural and compositional properties, and the catalytic performances. The study demonstrates that maximization of the hierarchy factor is crucial for attaining optimal catalytic performance of meso-/microporous lamellar zeolites in mass transport limited catalytic reactions.

4.4. Conclusion of Chapter 4

Implications of the tunable meso-/microporosity on the spatial distribution and catalytic performance of metal-acid sites in molybdenum/lamellar zeolite (Mo/lamellar MFI) catalysts have been studied using organic chemical titration, x-ray photoelectron spectroscopy and the DMA reaction. The meso-/microporous lamellar MFI zeolite with tunable meso-/microporosity was prepared by a dual template synthesis strategy by adding a secondary template (tetrapropylammonium hydroxide, TPAOH) to lamellar MFI synthesis using a diquatery ammonium template. The implications of the tunable meso-/microporosity on the spatial distribution and catalytic performance of active sites in Mo/lamellar MFI catalysts was investigated. Volcano-type dependence between the hierarchy factor, distribution of Brønsted acid and Mo sites, and aromatics production rate with the dual template ratios in the hydrothermal synthesis suggest that

the textural and composition properties and thus the catalytic performance of the catalysts can be optimized by the designed zeolite synthesis. The internal and external coke formed on the catalysts in the DMA reaction linearly depended on the relative external surface area of the lamellar MFI zeolites. A balance between the meso- and microporosity in lamellar MFI can be achieved by the dual template synthesis approach to optimize the catalyst performance. For the first time, a designed synthesis and description of the two dimensional meso-/microporous zeolite catalysts with tunable textural and catalytic properties for the DMA reaction was studied. Optimization of the contributions of the meso- and micropores in hierarchical zeolites to the catalytic reactions can be achieved by the one-step simple and versatile dual template synthesis method.

Chapter 5: Tuning External Surface of Unit-Cell Thick Pillared MFI and MWW Zeolites by Atomic Layer Deposition and Its Consequences on Acid-Catalyzed Reactions

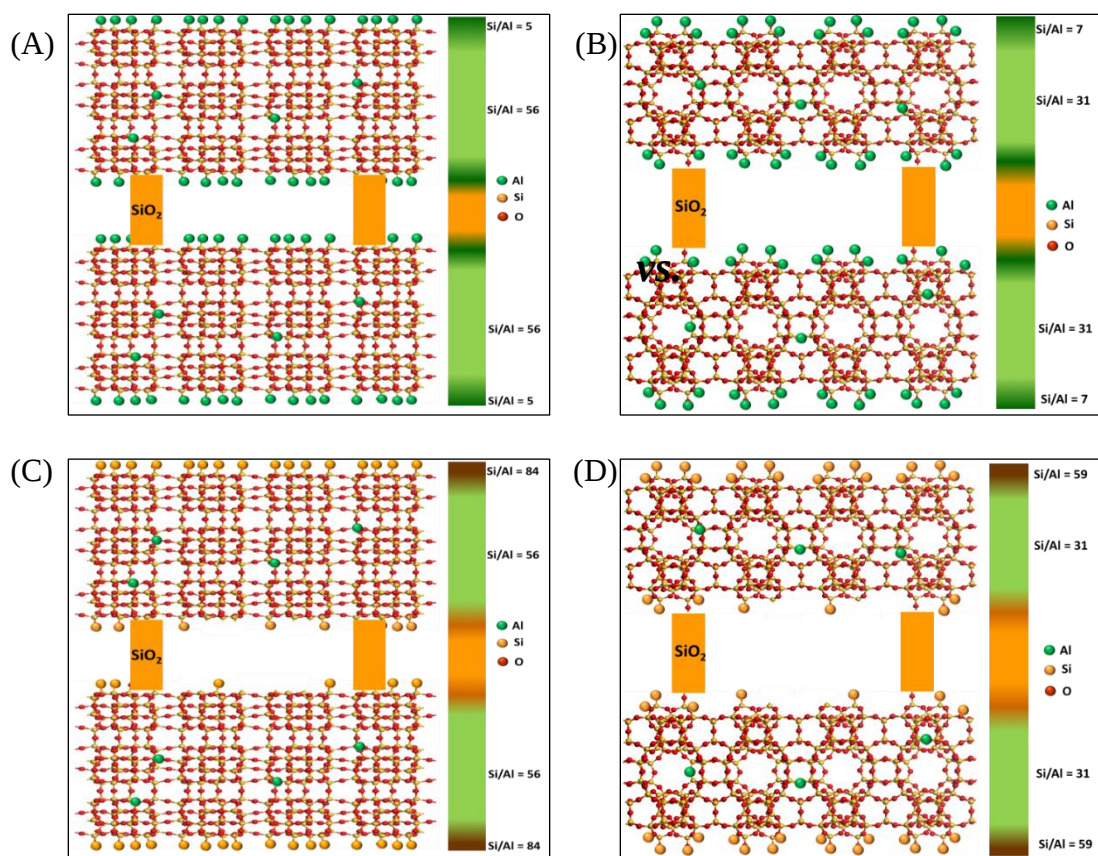
5.1. Introduction

Compared to bulky zeolites, 2D lamellar zeolites provide a much higher external surface area and thus a larger amount of external acid sites, which have a lower shape selectivity than those inside the micropores due to the absence of steric confinement. This lack of shape selectivity has been suggested to be one of the main causes of fast accumulation of coke, resulting in rapid deactivation of catalysts in the DMA reaction. Despite the intensive study of the catalytic performance of 2D lamellar zeolites, the modification of external surface properties of 2D zeolites and its consequent effect on the catalytic behaviors have not yet been studied.

Atomic layer deposition (ALD) has emerged as an attractive method for atomic level design and synthesis of catalytic materials [177-179]. It involves a synthesis process using alternating, self-limiting reactions between gaseous precursors and solid surface to deposit materials in an atomic layer-by-layer fashion. The self-limiting character of the reactions makes it possible to achieve uniform deposits on high-surface-area porous solid materials. ALD has been used to control the porosity and surface properties of mesoporous catalytic materials [180-183] in order to synthesize zeolite materials [184] as well as to load metal or metal oxide onto zeolite materials [185-187]. Application of ALD to microporous zeolites is a new area and is presumably more complicated compared to aforementioned applications because of the subtle

differences in diameters between the ALD precursors and the zeolite pore apertures. Previous attempt to conduct ALD of aluminum (ALD-Al) into silicalite-1 zeolite was not successful [188]. It was ascribed to the small pore size of silicalite-1, which is too narrow to adsorb trimethylaluminium (TMA) precursor molecules used in ALD-Al process.

In this study, we aim to employ the ALD technique to tune the surface properties of unit-cell thick 2D zeolites, i.e. PMWW and PMFI zeolites, in order to tailor their catalytic properties, as shown in Scheme 5.1. ALD of silicon (Al-Si) and ALD-Al were conducted to tune the porosity and surface acidity of PMWW and PMFI zeolites. The physicochemical and acidic properties of the resultant ALD-modified 2D zeolites were investigated using a variety of characterization techniques. The catalytic properties were explored by the ethanol dehydration reaction, alkylation and etherification of benzyl alcohol in mesitylene, and the DMA reaction. Ethanol dehydration reaction was used to probe intrinsic catalytic consequences of Brønsted acid sites in ALD-modified 2D zeolite catalysts. Alkylation and etherification of benzyl alcohol in mesitylene were used to evaluate the catalytic activity and selectivity of external acid sites in these catalysts. The DMA reaction was carried out to evaluate the overall performance of the catalysts when the external acid sites were passivated by ALD-Si modifications.



Scheme 5.1. Composition and acidity tuned spatially by ALD-Al on PMFI (A) and PMWW (B) zeolites and by ALD-Si on PMFI (C) and PMWW (D) zeolites.

5.2. Experiments

5.2.1. Preparation of zeolite catalysts

5.2.1.1. Synthesis of PMWW and PMFI Zeolites

PMWW zeolite was derived from the precursor, MCM-22(P). The hydrothermal synthesis of MCM-22(P) was carried out by using the method described by Corma et al. [134] The MCM-22(P) was swollen according to the method developed by Maheshwari et al. [135], followed by pillaring of the swollen material using the procedure reported by Barth et al. [136] to make PMWW zeolite. PMFI was made by following the method reported by Na et al. [133] using a multilamellar MFI precursor.

The multilamellar MFI was synthesized using the method reported by Ryoo and co-workers [102]. The as-synthesized PMFI and PMWW zeolites were ion-exchanged three times using 1 M aqueous ammonium nitrate (NH_4NO_3) (weight ratio of zeolite to NH_4NO_3 solution = 1:10) at 353 K for 12 h, and subsequently, collected by vacuum filtration, washed with deionized (DI) water three times, and dried at 343 K overnight. All zeolite samples in their NH_4^+ -form were treated in dry air (100 mL min^{-1} , Airgas) by increasing the temperature from ambient temperature to 823 K at 0.03 K s^{-1} and holding for 4 h to thermally decompose NH_4^+ to NH_3 and H^+ .

5.2.1.2. ALD modification of PMWW and PMFI zeolites

The ALD-Si and ALD-Al were performed in a viscous flow benchtop reactor (Gemstar-6, Arradiance). N_2 (Airgas, 99.999% purity) was used as a carrier gas (50 mL min^{-1}) and further purified by a Supelco gas purifier (Sigma-Aldrich) before entering the reactor. 0.5 g of zeolite (PMWW or PMFI) was uniformly spread onto a stainless steel tray with a mesh on top of it. The mesh prevented the spill of the sample and allowed access to the Si- or Al- precursor vapor in the ALD process. The ALD-Si was carried out by alternative exposure of zeolite sample to tris(dimethylamino)silane (TDMAS, Sigma-Aldrich, 99.999%) and ozone at 573 K for 15 s, followed by N_2 purge for 200 s after each exposure. The ALD-Al was conducted by exposing the zeolite sample to TMA (Sigma-Aldrich, 97%) for 15 s, purging with N_2 for 100 s, exposing the sample to DI water for 22.5 s, and purging with N_2 for 100 s again. The zeolite sample temperature was kept at 473 K in the ALD-Al preparation process. One ALD cycle was used for either Si or Al modification of PMWW and PMFI zeolites, unless specially specified in the paper. The resultant zeolite samples from ALD-Si and ALD-

Al modifications were denoted as Si-PMWW and Si-PMFI, or Al-PMWW and Al-PMFI, respectively.

5.2.1.3. Preparation of Mo/zeolite catalysts for the DMA reaction

The wetness impregnation method was used to prepare the 2 wt% molybdenum/zeolite (Mo/zeolite) catalysts for the DMA reaction. Typically, 0.0378 g of ammonium molybdenum tetrahydrate (99% purity, Sigma-Aldrich) was dissolved in 0.5 g DI water at room temperature to form a solution, which was then added dropwise to 1 g of Si-PMFI zeolite sample. The as-prepared Mo/Si-PMFI catalyst was dried at 393 K overnight, followed by a two-stage calcination procedure reported in our previous work [45, 47]. In the first stage, the sample was heated from room temperature to 623 K at 0.017 K s^{-1} in flowing air (100 mL min^{-1}) and soaked at this temperature for 16 h. For the subsequent stage, the sample was heated to 973 K at 0.017 K s^{-1} and soaked at this temperature for 10 h. The resultant Mo/zeolite catalyst was pelletized, crushed, and sieved to retain the particle sizes between 180 and 425 μm (40–80 mesh) for the subsequent DMA reaction.

5.2.2. Characterization of zeolite catalysts

5.2.2.1. Textural property and composition analysis

The morphologies of the 2D PMWW and PMFI zeolite samples, before and after ALD treatments, respectively, were observed using scanning electron microscopy (SEM, Hitachi SU-70). N_2 adsorption-desorption isotherms were measured at 77 K with an Autosorb-iQ analyzer (Quantachrome Instruments) to characterize the textural properties of the zeolite samples. Prior to the measurement, all the zeolites were evacuated overnight at 623 K and 1 mm Hg. Elemental compositions of the samples

were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 7000). ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were used to examine the bonding environment of Al sites in the zeolite catalysts. The NMR spectra were recorded at 130.34 MHz using 4 mm rotors at 14 kHz spinning speed, a dwell time of 0.5 μs , a selective $\pi/18$ pulse of 0.3 μs and a recycle delay of 0.1 s. An aqueous solution of aluminum sulfate (0.1 M) was used as the external reference (0 ppm). The surface Si and Al concentrations were quantified using a X-ray photon spectrometer (Kratos AXIS 165) equipped with 165 mm radius hemispherical analyzer and eight channeltron detection system coupled with monochromatic Al radiation (1486.6 eV).

5.2.2.2. Acidity determination

The Fourier transform infrared (FTIR) spectra of adsorbed pyridine were used to determine the type and concentration of Brønsted and Lewis acid sites in the catalysts. The spectra were recorded using a spectrophotometer (Equinox 55, Bruker) equipped with a Spectra-Tech Collector II diffuse reflectance accessory and a Praying Mantis high temperature reaction chamber (Harrick). Prior to the measurement, the zeolite sample was dried at 823 K under He flow (50 mL min $^{-1}$) for 1 h. After cooling the sample to 393 K, adsorption of pyridine was performed by flowing a mixed pyridine and He gas stream through the catalyst. Following adsorption, the sample was heated to 523 K under a flowing He to desorb the physisorbed pyridine, cooled to the temperature of 393 K, and then FTIR spectra were recorded in the range of 4000–400 cm $^{-1}$ with 128 scans at an effective resolution of 2 cm $^{-1}$.

The number of free Brønsted acid sites in the catalyst samples were measured via dimethyl ether (DME) titration experiments given that the Brønsted acid sites participate in reactions of DME with H^+ to form surface methyl groups, $CH_3OCH_3 + 2[SiO(H)Al] = 2[SiO(CH_3)Al] + H_2O$ [139, 140]. The experiments were carried out in a tubular packed-bed quartz reactor (10 mm inner diameter) under atmospheric pressure. The temperature of the reactor was held constant by a resistively heated furnace (National Electric Furnace FA120 type) where the temperature was controlled by a Watlow Controller (96 series). Catalyst temperatures were measured using a K-type thermocouple touching the bottom of a well on the external surface of the quartz reactor. Details on the DME titration experimental setup and reaction conditions were described in our previous publications [45, 47]. The same setup was used for the following organic base titration and gas-phase catalytic reaction studies.

5.2.2.3. External free acid site determination

To study the spatial distribution of external Brønsted acid sites (*i.e.*, acid sites stay nearby micropore mouth or on the external surface of 2D zeolite samples, which was defined as the external acid sites), methanol (CH_3OH) dehydration to DME in the presence of 2,6-di-tert butylpyridine (DTBP) organic base was measured at differential conversions (<2%) at 433 K. Liquid mixture of methanol (Fisher Scientific, 99.9%) and DTBP (Alfa, 98% purity) was introduced into a flowing He stream using a syringe pump (NE 1000, New Era Pump System Inc.). The reactor effluent was sent via heated transfer lines to a mass spectrometer (MS, Ametek Proline). The methanol dehydration rate was measured as DTBP titrant was continuously added until it reached a plateau. The loss in methanol reaction rate reflects the degree of accessibility of bulky DTBP

molecules to Brønsted acid sites in zeolites, and hence, the number of active sites accessible from the external surface of pillared zeolites was determined. The fraction of external acid sites, $f_{\text{ext, H}^+}$, was calculated as the ratio of the external acid sites to the acid sites quantified by the DME titration. Details on method for external acid site determination can be referred to our previous work [47].

5.2.3. Acid-catalyzed reactions over ALD-modified 2D zeolite catalysts

5.2.3.1. Ethanol dehydration reaction

Ethanol dehydration was used as the probe reaction to determine the intrinsic activity of Brønsted acid sites in the zeolite catalysts. Typically 0.05 g catalyst was pre-treated in He flow (30 mL min⁻¹, UHP grade, Airgas) at 823 K for 3 h (0.03 K s⁻¹) prior to cooling down to reaction temperature in He flow. Steady-state ethanol reaction with differential conversion (<2%) was carried out under atmospheric pressure and in a reaction temperature range of 393-423 K. Liquid ethanol was injected by the syringe pump and vaporized at 353 K into a He carrier flow (48 mL min⁻¹) with Ar (2 mL min⁻¹) as inner standard. The transfer line was heated over 353 K by resistively heating tape to avoid the condensation of ethanol. The unreacted ethanol, diethyl ether (DEE, reaction product) and Ar were recorded to calculate the reaction rate by a gas chromatograph (Agilent 7890 A GC) equipped with a methyl-siloxane capillary column (HP-1, 50.0 m × 320 μm × 0.52 μm) connected to a flame ionization detector (FID) and a packed column (ShinCarbon ST Columns, 80/100 mesh, 6 feet) connected to a thermal conductivity detector (TCD).

5.2.3.2. Catalytic conversion of Benzyl alcohol in Mesitylene

The liquid phase catalytic conversion of benzyl alcohol in mesitylene was carried out in a three-necked round-bottom flask (100 mL) under atmospheric pressure and magnetic stirring, as reported in our previous work [123]. In a typical experiment, 15 mL of mesitylene was added to the desired amount of zeolite catalyst, which was maintained for 0.5 h at the required reaction temperature and stirring conditions and then 0.25 mL of benzyl alcohol was added. The moment of addition of benzyl alcohol was taken as the initial reaction time. Liquid samples were withdrawn at regular time intervals and analyzed by the gas chromatograph described above.

5.2.3.3. Catalytic performance in the DMA reaction

The DMA reaction was conducted by heating 2 wt% Mo/Si-PMFI catalyst (~ 0.30 g) from ambient temperature in He flow (30 mL min^{-1}) to 950 K at ramp rate 0.167 K s^{-1} under atmospheric pressure. After temperature of catalysts reached 950 K, the DMA reaction was carried out by introducing methane into the catalyst at a flow rate of 8.0 mL min^{-1} and Ar of 2.0 mL min^{-1} as internal standard. The transfer lines were maintained at temperatures greater than 473 K by resistive heating to prevent product condensation. The effluents from the reaction were analyzed using the gas chromatograph described above.

5.3. Results and discussion

5.3.1. Textural properties of ALD-modified pillared zeolite catalysts

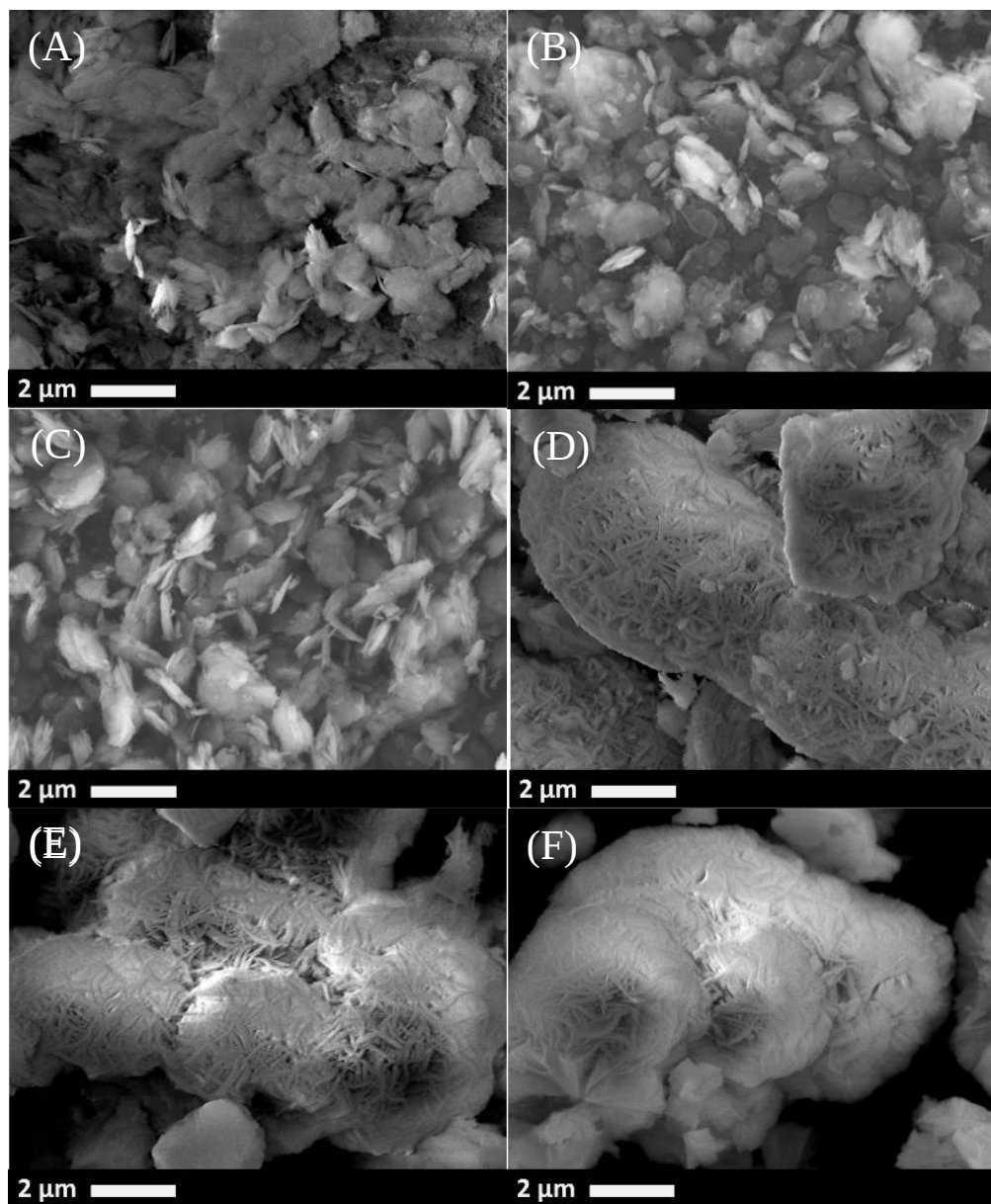


Figure 5.1. SEM images of PMWW (A), Si-PMWW (B), Al-PMWW (C), PMFI (D), Si-PMFI (E) and Al-PMFI (F), showing the morphology of unit-cell thick 2D pillared zeolites before and after ALD modifications.

SEM observation was conducted for direct visualization of zeolite morphologies before and after ALD-Si or ALD-Al onto the pillared 2D zeolite samples.

The PMWW sample (Figure 5.1(A)) contains flake-like particles with length of 0.5-1 μm and thickness of 50-100 nm. Si-PMWW and Al-PMWW samples resemble the flake-like morphology of PMWW zeolite, as evidenced in Figure 5.1(B) and (C), respectively. The similarity in morphologies of these three samples indicates that one cycle of ALD-Si or ALD-Al did not considerably alter the morphologies of 2D PMWW zeolite. The PMFI (Figure 5.1(D)) is comprised of intertwined platelet-like particles with widely distributed sizes, similar to pillared MFI reported by Na et al. [102]. Figure 5.1(E) and (F) show that Si-PMFI and Al-PMFI have similar morphologies to that of PMFI, further confirming that no obvious morphology alteration occurred on the PMFI sample in the one cycle ALD process.

N_2 adsorption-desorption isotherms and pore size distributions extracted from adsorption branch of isotherms were used to reveal the textural property changes in PMWW and PMFI zeolites after ALD-Si or ALD-Al modifications. Figure 5.2(A) shows that the PMWW, Si-PMWW and Al-PMWW samples have slightly different sorption behavior up to a relative pressure $p/p_0 \sim 0.05$ and distinct sorption capacities when p/p_0 is higher than 0.1. The majority of the sorption results from zeolite micropores when the relative pressure is below $p/p_0 \sim 0.05$ [148], indicating that ALD treatment only mildly altered the micropore volume of the PMWW zeolite (Figure 5.2(B)). The N_2 uptake at higher relative pressures is ascribed to capillary condensation in mesopores of pillared zeolite materials [148]. The sequential decrease in sorption capacity from PMWW, Si-PMWW to Al-PMWW suggests ALD treatment significantly decreased the mesopore volume of PMWW zeolite, and ALD-Al caused more obvious reduction in mesopore volume than that of ALD-Si. The mesoporosity

change indicates that ALD-Al process deposited more materials than ALD-Si on the PMWW zeolite. The reduction in mesopore volume is also evidenced by the non-local density functional theory (NLDFT) pore size distributions of these three materials in Figure 5.2(C). It should be noted that the average mesopore sizes of PMWW, Si-PMWW and Al-PMWW are similar. The present analysis demonstrates that ALD modification of PMWW decreased the mesopore volume while keeping the mesopore size almost intact.

Figure 5.2(D)-(F) show the N₂ adsorption-desorption isotherms of PMFI, Si-PMFI and Al-PMFI, and their corresponding pore size distributions. Similar to the textural property changes in PMWW-type zeolites, PMFI, Si-PMFI and Al-PMFI have similar sorption capacity at relatively low pressures ($p/p_0 < 0.1$), which suggests that they all have similar microporosity (Figure 5.2(E)). The mesopore volume, indicated by sorption capacity at higher relative pressures ($p/p_0 = 0.1-0.5$), follows the order of Al-PMFI < Si-PMFI < PMFI (Figure 5.2(F)). Different from PMWW-type zeolite, the ALD treatment of PMFI zeolite led to constant micropore volume, reduction in mesopore volume and decrease in mesopore size. As shown in Figure 5.2(F), the average mesopore size shifted from 3.5 nm, 3.3 nm to 3.0 nm from PMFI, Si-PMFI to Al-PMFI zeolites.

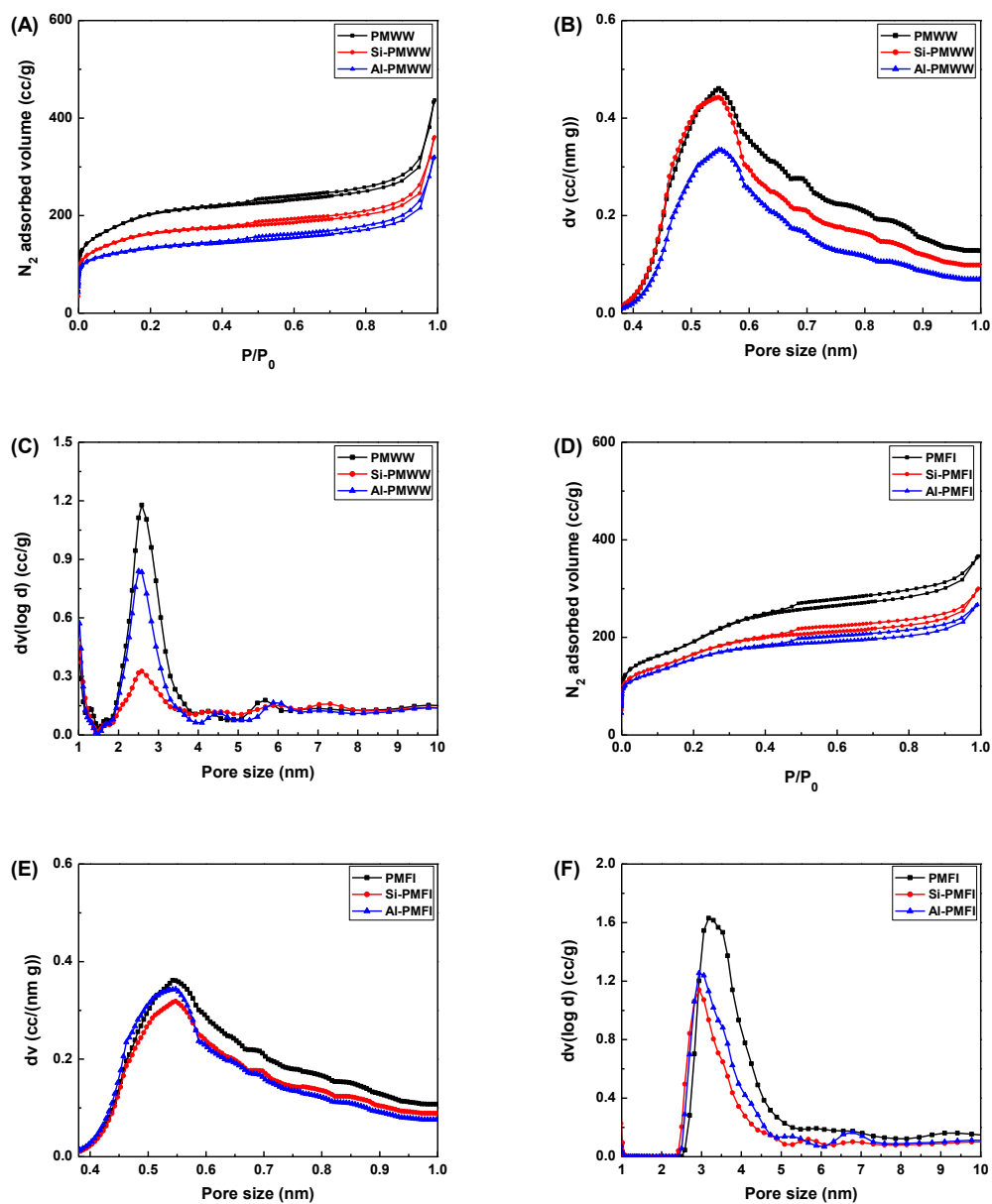


Figure 5.2. N₂ adsorption-desorption isotherm (A and D), Horváth-Kawazoe (HK) micropore size distribution (B and E) and NLDT mesopore size distribution (C and F) of PMWW and PMFI zeolites before and after ALD modifications.

PMWW is a silica pillared layered 2D zeolite material, derived from the precursor MCM-22 (P) [189, 190]. The PMWW structure possesses independent micropore and mesopore systems within the layers and between the layers, respectively. Within the layers, PMWW contains 2D sinusoidal 10 MR channels (diameters 0.41 nm

×0.51 nm) running parallel to the layer's basal plane. Perpendicular to the layers, PMWW contains hourglass shaped pores with 12 MR openings (with dimensions of 0.71 × 0.91 nm) at the entrance and 6 MR channels at the central constrictions [61, 191]. PMFI zeolite is also a silica pillared 2D zeolite material, consisting of two interconnected 10 MR pore systems within each layer: one is a straight channel running along the *b*-axis direction (0.53 × 0.56 nm); and the other is a zigzag channel running parallel to the *a*-axis (0.51 × 0.55 nm). The PMFI contains mesopores created by the silica pillars running between layers, parallel to the zigzag channels and perpendicular to the straight channel within the layers [62, 133]. The almost intact micropore volume in PMFI after ALD modifications is consistent with previous report that ALD-Al of silicalite-1 using TMA precursor was unsuccessful due to the small 10-MR pore aperture [188]. The slight decrease in micropore volume in PMWW after ALD treatment was caused by deposition of Si- or Al-species in the 12-MR cups in the MWW zeolitic layer, similar to ALD of FAU zeolite that has 12-MR micropores [188, 192]. The higher mesopore volume loss upon ALD-Al compared to ALD-Si resulted from the smaller molecular size of Al-species precursor (TMA) compared to Si-species precursor (TDMAS), since the former has less diffusion limitation when marched on the zeolite nanosheets in the ALD process. The persistence and decrease in average mesopore sizes in PMWW and PMFI, respectively, in ALD processes might be relevant to the different micro- and mesopore topologies and the consequent different dynamic behaviors of Al- or Si-precursor molecules in the zeolites during diffusion and deposition processes.

Table 5.1. Composition and acidity of PMWW and PMFI zeolites after ALD modifications.

Zeolites	Si/Al ^a	Si/Al ^b	$N_{\text{total,H}^+}^c$ (10 ⁻⁴ mol H ⁺ g ⁻¹)	$f_{\text{ext,H}^+}^d$ (%)	$N_{\text{ext,H}^+}^e$ (10 ⁻⁴ mol H ⁺ g ⁻¹)
PMWW	31	50	3.3	67	2.2
Si-PMWW	33	59	2.4	45	1.1
Al-PMWW	7	7	3.7	35	1.3
PMFI	56	68	1.9	36	0.7
Si-PMFI	57	84	1.3	25	0.3
Al-PMFI	6	5	4.2	22	0.9

^a Measured by ICP-OES; ^b Measured by XPS; ^c Concentration of Brønsted acid sites in entire catalyst particles, determined by DME titration, error with in ± 1 -6%; ^d Determined by DTBP titration during methanol dehydration reaction; ^e Concentration of external Brønsted acid sites ($N_{\text{ext,H}^+} = N_{\text{total,H}^+} \times f_{\text{ext,H}^+}$).

5.3.2. Composition of ALD-modified pillared zeolite catalysts

The compositions of PMWW and PMFI zeolites and their derivatives after ALD modifications were measured by ICP-OES analysis, and the results (represented by Si/Al ratios) are shown in Table 5.1. For both PMWW and PMFI zeolites, the ALD-Al resulted in a decrease in Si/Al ratios, while ALD-Si caused an opposite trend in changes of Si/Al ratios. The amount of Si- or Al-species deposited on the PMWW and PMFI zeolite samples can be calculated from the changes in their Si/Al ratios after ALD processes. The calculation indicates that ALD-Si led to 1.7 wt% and 3.8 wt% weight gains in Si-PMFI and Si-PMWW, respectively. The ALD-Al process, however, led to 11.0 wt% and 9.8 wt% weight increases in PMFI and PMWW, respectively, much higher than those in ALD-Si process. The TDMAS precursor used in ALD-Si is bulkier than TMA precursor in ALD-Al, which mainly contributes to the differences in zeolite weight gains in both ALD processes, since the former has more severe steric hindrances when diffusing through the mesopores of pillared zeolites. The difference in topological structures of PMFI and PMWW zeolites also affects deposition of Si-

species in ALD-Si process, as evidenced by > 2 times higher amount of Si-species deposited on Si-PMWW than Si-PMFI.

The surface compositions of PMWW and PMFI zeolites before and after ALD treatments were evaluated by XPS analysis. The Si/Al ratio, calculated from atomic percentages quantified by XPS signals, increased from 50 to 59, and decreased to 7 for PMWW, Si-PMWW and Al-PMWW zeolites in sequence. Similar changes in Si/Al ratio were observed for PMFI (Si/Al = 68), Si-PMFI (Si/Al = 84) and Al-PMFI (Si/Al = 5) zeolite samples (Table 5.1). If we make an assumption that the entire zeolite particle has the same composition as that of the external surface determined by XPS in Table 5.1, the Si- or Al-species deposited on the exterior of PMWW and PMFI zeolite particles can be estimated. From such analysis, the weight increases on the exterior of the Si-PMFI, Si-PMWW, Al-PMFI and Al-PMWW particles are estimated to be 18.8 wt%, 15.0 wt%, 13.4 wt% and 9.3 wt%, respectively. The significant higher weight gains on the exterior than that of the entire zeolite particles in ALD-Si process indicate that Si-species mainly resides on the geometrical surfaces of the PMWFI and PMWW zeolite samples. The weight gains on the exterior and the entire particles in the ALD-Al process, however, are similar, suggesting that Al-species distributes uniformly on geometrical surfaces of zeolite particles and in mesopore (i.e., external surface of unit-cell thick zeolite nanosheets) of the Al-PMFI and Al-PMWW samples. The mesopore gallery between two unit-cell thick zeolitic nanosheets, parallel to the width of PMWW flakes and PMFI platelets, might be big enough to allow TMA to transport through but resist TDMAS diffusion, and as a result, led to more Si-species deposited on the exterior of the zeolite particles. This analysis suggests that the spatial composition

(exterior – mesopore (or external surface) - micropore) of 2D pillared zeolites is different, which is easily realized and tailored by the ALD of Si- or Al-precursor molecules with variant sizes.

5.3.3. Acidity of ALD-modified pillared zeolite catalysts

To determine the number of active Brønsted acid sites ($N_{\text{total, H}^+}$) in Si-PMFI, Al-PMFI, Si-PMWW and Al-PMWW samples, DME titrations, with reactions of DME with Brønsted acid sites (H^+) to form surface methyl groups, $\text{CH}_3\text{OCH}_3 + 2[\text{SiO}(\text{H})\text{Al}] = 2[\text{SiO}(\text{CH}_3)\text{Al}] + \text{H}_2\text{O}$ [139, 140], were conducted. The concentration of Brønsted acid sites changed from $1.85 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ to $1.26 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ and from $3.30 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ to $2.39 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$, respectively, when ALD-Si was applied to PMFI and PMWW zeolites (Table 5.1). The decreases in number of active Brønsted acid sites in Si-PMFI (by 32%) and Si-PMWW (by 28%) can be ascribed to the concealment of external acid sites by the deposited Si-species. The ALD-Al modifications, however, increased the number of active Brønsted acid sites to $4.19 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ and $3.66 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ in Al-PMFI and Al-PMWW, respectively (Table 5.1). The emergence of new acid sites in Al-PMFI (by 126%) and Al-PMWW (by 11%) via ALD-Al processes might be due to the bridging hydroxyls ($\text{Si-O}(\text{H})\text{-Al}$) on pillared zeolites bonded to distorted Al tetrahedral with links to oxygen atoms of the zeolite framework. Similar phenomena have been reported for ALD-Al of FAU [188, 192] and OKO [184] zeolites in literature.

Solid state ^{27}Al MAS NMR was employed to investigate the local bonding environment in the ALD-Si and ALD-Al modified PMFI and PMWW zeolite catalysts (Figure 5.3). In Si-PMFI and Si-PMWW samples, ^{27}Al MAS NMR signals were

observed at 55 ppm and 0 ppm, which can be ascribed to tetrahedral framework Al (Al_T) and octahedral extra framework Al (Al_O), respectively [62, 193-195]. The ^{27}Al MAS NMR spectra of Si-PMFI and Si-PMWW are consistent with their parent counterparts, PMFI and PMWW zeolites [62]. The ^{27}Al MAS NMR spectra of ALD-Al modified PMFI and PMWW zeolites contain not only the Al_T and Al_O peaks, but also an additional peak centered at 30 ppm (Figure 5.3). The appearance of the new peak at ~ 30 ppm in Al-PMWW and Al-PMFI can be assigned to distorted tetrahedral framework and pentacoordinated Al species that were introduced via ALD-Al process [188]. The inclusion of new types of acid sites in ALD-Al process indicated by ^{27}Al MAS NMR analysis is consistent with the composition and N_{total, H^+} analyses discussed above.

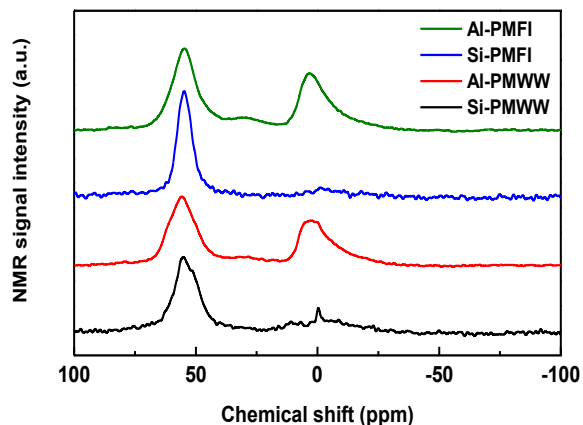


Figure 5.3. ^{27}Al MAS NMR spectra of Al-PMFI, Si-PMFI, Al-PMWW and Si-PMWW.

The types of acid sites in ALD-modified PMFI and PMWW zeolites were further characterized using FTIR spectra of adsorbed pyridine (Figure 5.4). Pyridine bound to Lewis acid sites is associated with the characteristic absorption band at 1460 cm^{-1} and that bound to Brønsted acid sites is affiliated with the band at 1545 cm^{-1} in the FTIR spectra [196-198]. In Figure 5.4(A), the absorption band at 1545 cm^{-1} of

PMWW is similar to that of Si-PMWW, but slightly smaller than Al-PMWW. On the contrary, the adsorption band at 1460 cm^{-1} broadens from PMWW to Si-PMWW and Al-PMWW. In addition, the absorption peak in this band splits into multiple peaks with irregular shapes. The non- or slight change in absorption band for Brønsted acid sites in Figure 5.4(A) indicates that ALD-Si did not obviously modify the properties of Brønsted acid sites in PMWW zeolite. The “inhomogeneous broadening” in the Lewis acid band indicates the formation of various types of Lewis acid sites in PMWW zeolite materials via the ALD-Si or ALD-Al process [184, 192].

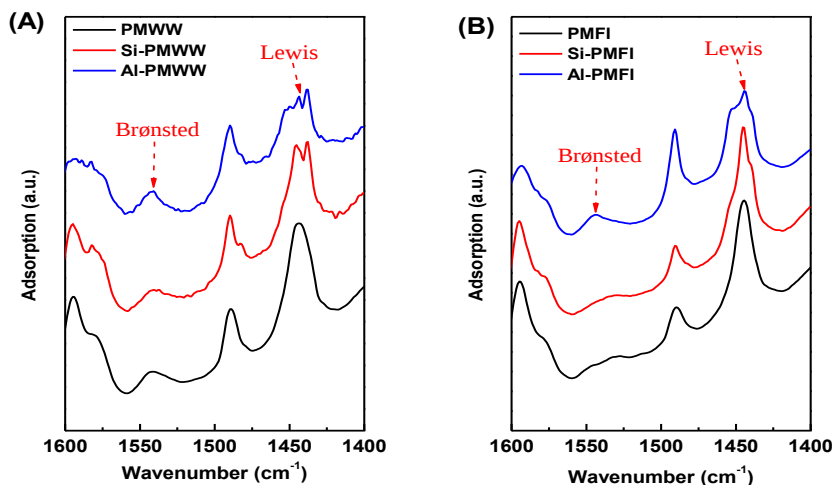


Figure 5.4. FTIR spectra of adsorbed pyridine of (A) PMWW and (B) PMFI zeolites before and after ALD modifications.

Figure 5.4(B) shows the FTIR spectra of adsorbed pyridine on PMFI zeolite before and after ALD modifications. Similarly, the band associated with Brønsted acid sites does not change obviously, while the band affiliated with Lewis acid sites exhibits “inhomogeneous broadening” and “peak splitting”. It should be noted that the peak intensity of Al-PMFI at 1545 cm^{-1} is much higher and more obvious than that of PMFI and Si-PMFI, which suggests the presence of a higher number of Brønsted acid sites.

This evidence is in consistence with the higher number of acid sites in Al-PMWW determined from DME titrations above.

5.3.4. External acid sites in pillared zeolites after ALD modifications

Our previous studies indicated that a comparable number of acid sites reside on the external surface of zeolite nanosheets in unit-cell thick 2D PMWW and PMFI zeolites, which can be accessed by organic base (DTBP) probe molecules [62, 71, 101]. ALD modifications preferentially deposit Si- or Al-species on the external surface or in mesopores of pillared zeolites. It is expected that such modifications will abruptly influence the surface acidity and accessibility of external acid sites to bulky molecules of the pillared zeolite catalysts. To determine the number of Brønsted acid sites on external surface or in mesopores ($N_{\text{ext, H}^+}$), and the fraction of external acid sites ($f_{\text{ext, H}^+} = N_{\text{ext, H}^+} / N_{\text{total, H}^+}$) in ALD modified PMFI and PMWW zeolites, methanol reaction to DME in the presence of DTBP organic base was carried out. The rate loss upon DTBP saturation of external acid sites reflects the degree of accessibility of acid sites to bulky DTBP molecules, and hence, the number and fraction of external acid sites can be evaluated [47].

Table 5.1 lists $N_{\text{ext, H}^+}$ and $f_{\text{ext, H}^+}$ in PMWW and PMFI zeolites before and after ALD-Si and ALD-Al modifications. In Si-PMWW zeolite, $f_{\text{ext, H}^+}$ decreased to 45% (was 67% in PMWW), reflecting $1.12 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ diminishment of external acid site ($N_{\text{ext, H}^+}$) after ALD-Si process. From DME titration data, the decrease in total number of acid sites ($N_{\text{total, H}^+}$) was $0.91 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$, quite close to the number of dismissing external acid sites. In Si-PMFI zeolite, $N_{\text{ext, H}^+}$ is reduced by $0.35 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ and $N_{\text{total, H}^+}$ is decreased by $0.59 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$. The similarity in

reduction of $N_{\text{ext, H}^+}$ and $N_{\text{total, H}^+}$ in both Si-PMFI and Si-PMWW zeolites signifies that Si-species is preferentially deposited on or near external acid sites of the catalysts, and thus influences acid site accessibility to DTPB titrants.

DME titration for the total number of acid sites in Al-PMWW sample shows that $N_{\text{total, H}^+}$ is increased by $0.36 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$ (Table 5.1). The DTBP titration in methanol reaction experiment illustrates that $N_{\text{ext, H}^+}$ is reduced by $0.93 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$. The opposite trends, increase in total number of acid sites and reduction in external acid sites, in Al-PMWW zeolite indicates that acid site accessibility to bulky molecules is reduced. The material deposited on PMWW in ALD-Al is ~ 3 times more than that of ALD-Si, which might narrow down the micropore openings (blocking pore mouth acid sites) or mesopores existing between two zeolite nanosheets, and consequently, lead to incapability of external acid sites to access large molecules. For Al-PMFI zeolites, the increase in $N_{\text{total, H}^+}$ is $2.34 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$, and $N_{\text{ext, H}^+}$ is also enhanced by $0.25 \times 10^{-4} \text{ mol H}^+ \text{ g}^{-1}$, compared to those in PMFI zeolite (Table 5.1). The increase in $N_{\text{ext, H}^+}$ reflects that more Brønsted acid sites generated on the external surface of the PMFI zeolite, similar to the inclusion of acidity into siliceous zeolites reported previously [184]. The decrease in $f_{\text{ext, H}^+}$ in Al-PMFI hints that accessibility of acid sites to bulky molecules is also reduced. The overall analysis shows that ALD is a tool that can insert acid sites and tune their distribution and accessibility to reactant molecules in 2D zeolite materials that have unit-cell thick nanosheets and high fractions of external surfaces.

5.3.5. Catalytic tests in acid catalyzed reactions

5.3.5.1. Ethanol dehydration reaction

Ethanol dehydration to diethyl ether (DEE) was used as a probe reaction to evaluate the intrinsic activity of PMFI and PMWW zeolites after ALD-Al and ALD-Si modifications. Under strict kinetic control, the transport artifacts on the kinetic data in ethanol dehydration reaction are expected to be eliminated, and thus catalyst activity should be directly related to the intrinsic behaviors of Brønsted acid sites in the zeolite catalysts [62, 199, 200]. In our tested conditions, DEE was the only product formed over the PMFI- and PMWW zeolites and their derived structures after ALD modifications, indicating that ethanol dehydration reaction occurred through a bimolecular pathway, consistent with reports on DEE formation on medium- or large-pore zeolites [199, 200]. These results indicate that ALD-Si or ALD-Al treatments of PMFI and PMWW zeolites did not create new type of pore topology or significantly reduce the environment of active acidic hydroxyl groups to small pores, which lead to formation of ethylene product in ethanol dehydration reactions.

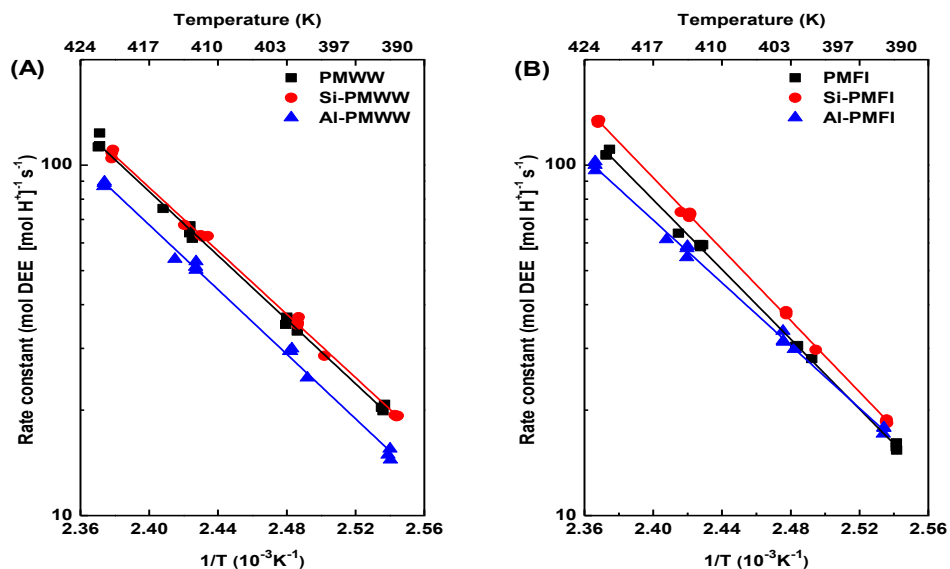


Figure 5.5. Measured rate constants of DEE production over PMWW (A) and PMFI (B) zeolite catalysts before and after ALD modifications.

Figure 5.5 shows the Arrhenius plots (the natural logarithm of regressed rate constants versus the inverse temperature) of ethanol dehydration rates over PMWW and PMFI zeolite catalysts before and after ALD modifications, respectively. The plots in both Figure 5.5(A) and (B) are parallel to each other, which indicates that all the studied zeolite samples have similar activation energies for ethanol dehydration. Table 5.2 lists the activation energy (ΔE_{meas}), entropies (ΔS_{meas}), and rate constants at 383 K (k_{meas}) for DEE formation over these six pillared zeolite samples. The site time yield of DEE differs among the zeolites by up to a factor of 1.2. Activation energies (90-99 kJ mol⁻¹) and entropies (within a range of -90 to -67 J mol⁻¹ K⁻¹) are comparable. These results imply that Brønsted acid sites in pillared 2D zeolite materials possessing Al- or Si-species incorporated by ALD processes have similar catalytic activities compared to the parent pillared 2D PMWW and PMFI zeolites when measured under strict kinetic control conditions.

Table 5.2. Rate constants (k_{meas}) of DEE production at 383 K, measured activation energy (E_{meas}) and entropy (ΔS_{meas}) of DEE synthesis over PMWW and PMFI zeolites before and after ALD-Si and ALD-Al modifications, respectively.

Catalyst	PMWW	Si- PMWW	Al- PMWW	PMFI	Si- PMFI	Al- PMFI
k_{meas} (10 ⁻⁵ mol [mol H ⁺] ⁻¹ s ⁻¹)	36.1	35.8	29.6	30.4	38.0	31.6
E_{meas}^a (kJ mol ⁻¹)	91.9	91.5	92.7	99.5	99.1	90.4
ΔS_{meas}^b (J mol ⁻¹ K ⁻¹)	-84.8	-85.6	-84.7	-67.1	-66.8	-90.0

^a Errors are ± 3 kJ mol⁻¹; ^b Errors are ± 4 J mol⁻¹ K⁻¹.

5.3.5.2. Alkylation of benzyl alcohol in mesitylene

While ethanol dehydration reaction measures the intrinsic activity of the catalysts, alkylation of benzyl alcohol in mesitylene depends on the accessibility of the

bulky molecules to the acid sites in zeolite catalysts. Here, we compared the catalytic performance of external surfaces of PMWW and PMFI zeolites after ALD modifications using the liquid phase parallel catalytic conversions of benzyl alcohol in mesitylene (etherification to dibenzyl ether and alkylation to 1,3,5-trimethyl-2-benzylbenzene) as probe reactions. The apparent rate constants of the parallel alkylation and etherification reactions were evaluated at 348 K, with less than 10% conversion of benzyl alcohol, under rigorous agitation, and in excess amount of mesitylene (molar ratio of mesitylene to benzyl alcohol = 45:1) to eliminate the effect of catalyst deactivation, external mass transfer limitations, and reaction that converts dibenzyl ether to 1,3,5-trimethyl-2-benzylbenzene [71, 101].

Previous studies indicated that the parallel reactions occur exclusively on the external surface of MWW catalysts with alkylation being favored over etherification reaction [71, 101]. By applying pseudo-first order reaction model on the reaction data, the external alkylation and etherification rate constants ($k_{\text{alk,ext}}$ and $k_{\text{eth,ext}}$), respectively, can be readily analyzed. The model for the alkylation reaction is:

$$\ln \frac{C_A^0}{C_A} = k_{\text{alk,ext}} N_{\text{ext, H}^+} (1 + \alpha) t, \text{ where } C_A^0 \text{ is the initial benzyl alcohol concentration in}$$

solution (mol L^{-1}), C_A is benzyl alcohol concentration in solution (mol L^{-1}), $N_{\text{ext, H}^+}$ (mol H^+) is the total moles of external Brønsted acid sites of the catalyst present in the batch reactor (Table 5.2), α is the product selectivity ($\alpha = 2C_E/C_C$, C_E and C_C are the concentrations of dibenzyl ether and 1,3,5-trimethyl-2-benzylbenzene in solution (mol L^{-1}), respectively), and t is the reaction time (s), respectively, and the constant of external acid sites ($k_{\text{alk,ext}}$ ($\text{s}^{-1} [\text{mol H}^+]^{-1}$)) can be solved using this model. Similarly, the

model for etherification reaction on PMWW-type zeolites can be derived as:

$$\ln \frac{C_A^0}{C_A} = k_{\text{eth,ext}} N_{\text{ext, H}^+} \left(\frac{1+\alpha}{\alpha} \right) t, \text{ in which } k_{\text{eth,ext}} (\text{s}^{-1} [\text{mol H}^+]^{-1}) \text{ is the rate constant. The}$$

selectivity between the parallel etherification and alkylation reactions, defined as

$k_{\text{eth,ext}} / k_{\text{alk,ext}}$ across PMWW, Si-PMWW and Al-PMWW zeolites can be compared.

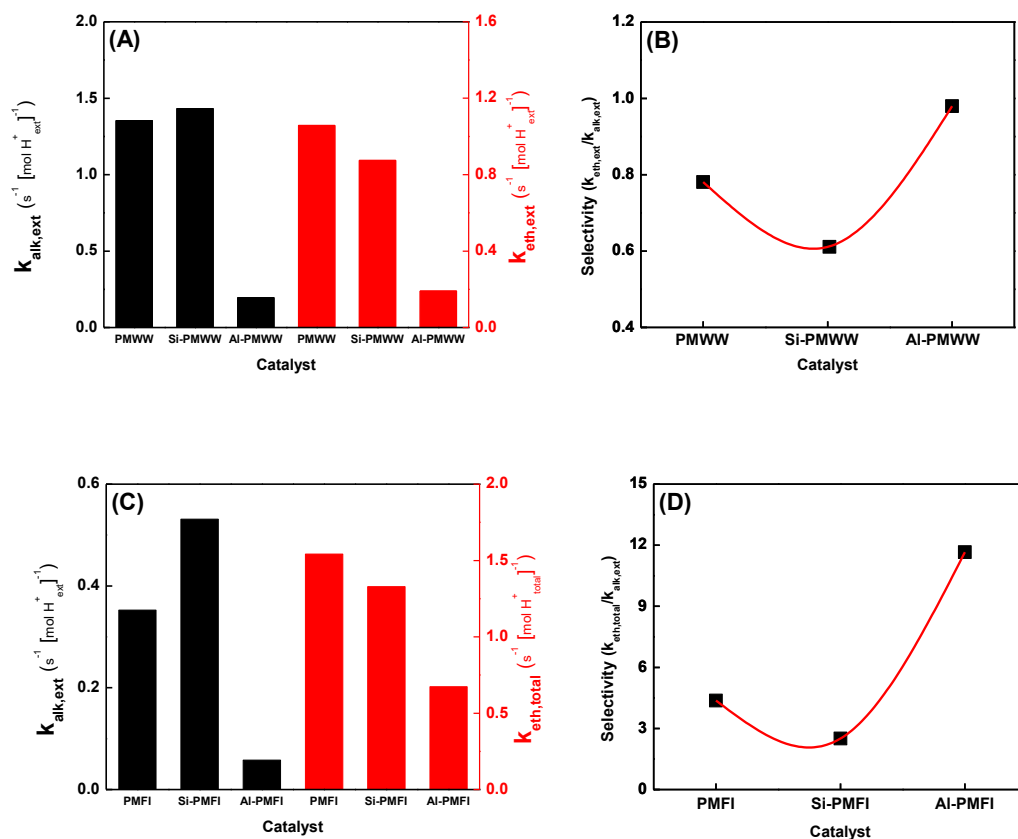


Figure 5.6. Catalytic conversion of benzyl alcohol in mesitylene over PMFI and PMWW zeolites before and after ALD modifications: (A) Alkylation and etherification reaction on external acid site of PMWW-based zeolite catalysts, (B) Selectivity for alkylation and etherification reactions on external acid site of PMWW-based zeolite catalysts, (C) Alkylation on external acid site and etherification reaction on entire acid site of PMFI-based zeolite catalysts, and (D) Selectivity for alkylation on external acid site and etherification reaction on entire acid site of PMFI-based zeolite catalysts.

Figure 5.6(A)-(B) shows the reaction rate constants and selectivity of the parallel etherification and alkylation reactions over PMWW, Al-PMWW and Si-PMWW catalysts. The alkylation and etherification rate constants of PMWW zeolite are lower and higher, respectively, in comparison with the corresponding ALD-Si and ALD-Al modified Si-PMWW and Al-PMWW zeolites (Figure 5.6(A)). Although ALD-Al introduced new types of acid sites on the PMWW zeolite, it did not enable efficient catalysis, which might be due to weak acid strength as evidenced by FTIR spectra of adsorbed pyridine in Figure 5.3(A). The selectivity towards the parallel reactions, shown in Figure 5.6(B), indicates that the alkylation reaction was slightly favored over the Si-PMWW while the etherification reaction was favored over the Al-PMWW in comparison with PMWW zeolite. These studies indicate that the activity and selectivity of external acid sites in 2D pillared zeolites can be tuned by ALD modifications.

The studies on parallel etherification and alkylation reactions over PMFI-type zeolites show that alkylation reaction only corresponds to external acid sites (similar to PMWW-type zeolites) while etherification reaction contains two contributions: one from external acid sites and the other from reaction inside the micropores (internal) [71, 101]. External alkylation rate constant can be readily analyzed using pseudo-first order reaction model discussed above to provide an understanding of catalytic behavior of external acid sites in PMFI, Si-PMFI and Al-PMFI zeolites. Analysis of external etherification reaction rate constants over PMFI-type zeolites needs tremendous model development and verifications [71, 101]. Here, we simply used the equation,

$$\ln \frac{C_A^0}{C_A} = k_{\text{eth,total}} N_{\text{total, H}^+} \left(\frac{1+\alpha}{\alpha} \right) t, \text{ to evaluate the etherification rate constant of the entire}$$

catalyst particle ($k_{\text{eth,total}}$ ($\text{s}^{-1} [\text{mol H}^+]^{-1}$)) and selectivity ($k_{\text{eth,total}} / k_{\text{alk,ext}}$) of the parallel reactions over ALD modified PMFI zeolite catalysts. Figure 5.6 (C) and (D) show similar trends in changing of activity and selectivity in PMFI-based catalysts to those of PMWW-based zeolites, further confirming that ALD can be an effective tool in tuning surface catalytic properties of the unit-cell thick 2D zeolite catalysts.

5.3.5.3. Catalytic performance in the DMA reaction

In the DMA reaction, active sites on external surfaces of zeolite catalysts are easily accessed by reactants and are not protected against undesired side reactions by the shape-selective environment within zeolite channels, which causes coke and large hydrocarbons formation and leads to fast catalyst deactivation [76, 77, 201, 202]. Studies have explored surface silanation method to deactivate external surface acid sites of zeolite catalysts [76, 77, 112], which were realized by the selective deposition of Si-species using large organosilane molecules that cannot enter zeolite channels. An enhancement in product formation rates and catalyst durability in the DMA reaction has been observed over Mo/MFI zeolite catalysts after silanation treatments. Given the capability of selective controlling surface composition and acidity of 2D pillared zeolites by ALD processes, we modified the PMFI with ALD-Si process to passivate the surface active sites and tested its implications on the catalytic activity and selectivity of the Mo/Si-PMFI catalysts in the DMA reaction.

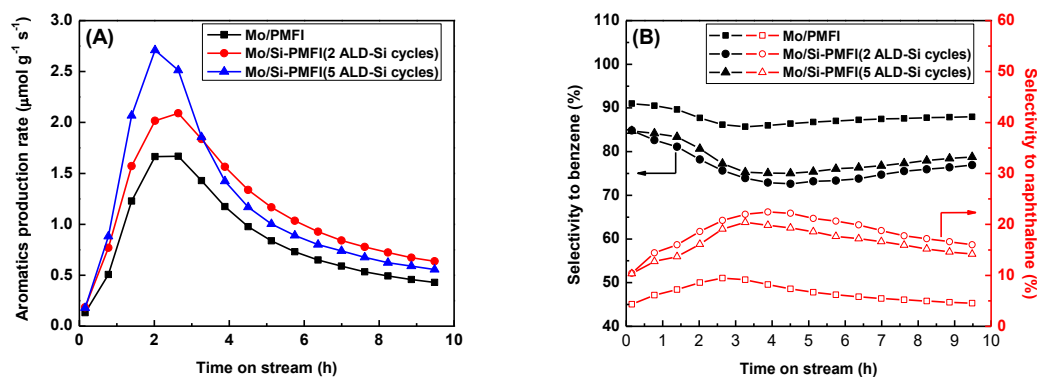


Figure 5.7. Aromatic product formation rate (A) and product selectivity (B) of the DMA reaction as a function of time on steam on 2wt% Mo/PMFI and 2wt% Mo/Si-PMFI catalysts, in which two and five ALD-Si cycles were applied to PMFI.

Figure 5.7(A) shows the formation rate of aromatic products (a sum of benzene, toluene and naphthalene) over the 2 wt% Mo/Si-PMFI catalyst, in which Si-PMFI were prepared after two and five ALD-Si cycles, respectively. For comparison purpose, the DMA reaction over the Mo/PMFI zeolite was also studied, and the data was included in Figure 5.7(A). The rate of aromatic product formation in the DMA reaction increased and then decreased after ALD-Si modification of PMFI zeolite for two and five cycles. The molecular size of Si-species precursor, TDMAS, is larger than the 10-MR micropores of PMFI zeolite, and thus the external surface active sites were selectively passivated in ALD-Si process. The removal of external acid sites of PMFI by ALD-Si successfully mitigated the anchoring of MoOx precursors and MoCx active species on external surfaces. This explains the reason for the catalytic activity improvement in Mo/Si-PMFI compared to Mo/MFI catalyst. With five ALD-Si cycles, a thicker film of Si-species might form on the external surface of PMFI zeolite, which blocked the entrance of reactant into or exit of product out of the zeolite micropores. A reduction in catalytic activity in the DMA reaction is therefore observed. Figure 5.7(B) shows

the product selectivities in the Mo/PMFI and Mo/Si-PMFI catalysts. After two and five cycles of ALD-Si modification, the 2 wt% Mo/Si-PMFI catalyst showed a lower selectivity to benzene and a higher selectivity to naphthalene products. The selectivity towards heavier naphthalene product in the DMA reaction over Mo/Si-PMFI catalyst might result from longer transport pathways of reaction species in Si-PMFI compared to PMFI zeolite. The ALD-Si process may partially block the 10-MR aperture of PMFI zeolite, and thus the residence time of reaction intermediate in micropores is prolonged. As a result, the product grows into heavier naphthalene instead of lighter benzene. The DMA reaction results demonstrate that ALD-process improves catalytic activity and tunes the product selectivity of Mo/PMFI catalyst by the selective elimination of active sites from external surfaces of PMFI zeolite surfaces.

5.4. Conclusion of Chapter 5

The external surface composition and acidity of PMWW and PMFI, a type of pillared zeolites comprised of unit-cell thick zeolitic nanosheets with micropore within each layer and mesopore between zeolitic layers, were modified by ALD-Si and ALD-Al, respectively. The ALD modifications kept micropore almost intact, but considerably decreased mesopore volume in both zeolite materials. The ALD-Si moderately decreased the external surface acidity, while ALD-Al increased the surface acidity and diversified the types of acid sites. The composition and acidity of 2D pillared zeolites were spatially modulated by ALD processes. The implications of the ALD modifications of PMWW and PMFI zeolites on catalytic reactions were tested using ethanol dehydration under kinetically controlled condition, alkylation of benzyl alcohol in mesitylene in liquid phase condition, and the DMA reaction. Both ALD-Al

and ALD-Si operations did not influence the intrinsic catalytic behaviors Brønsted of acid sites in PMWW and PMFI zeolites, but they tuned the catalytic selectivity of external acid sites in alkylation of benzyl alcohol with mesitylene reactions. The elimination of external surface active sites by ALD-Si of PMFI zeolite improved Mo/Si-PMFI catalyst activity and tuned the product selectivity. The present study exemplified for the first time that the external composition and acidity in 2D unit-cell thick zeolites were tailored by ALD modifications to impact their activity and selectivity in catalytic reactions at different levels.

Chapter 6: Overgrowth of Lamellar Silicalite-1 on MFI and BEA zeolites and its Consequences on Non-oxidative Methane Aromatization Reaction

6.1. Introduction

External acid sites in zeolites is less shape selective compared to those enclosed in zeolite micropores (i.e. internal acid sites) and consequently lead to an inferior selectivity to desired products. For example, in the alkylation of toluene by methanol, the external acid sites on ZSM-5 zeolite favored the formation of o- or m-xylene and thus lowered the selectivity to the desired p-xylene, while o- or m-xylene formation was commonly excluded from the acid sites in micropores due to steric constraints [203]. In the fructose transformation, the external acid sites of MFI zeolite lowered the selectivity to desired 5-hydroxymethylfurfural (HMF) product by facilitating the oligomerization of HMF to by-products [204]. Similarly, in the DMA reaction, the presence of external acid sites in Mo/ZSM-5 catalysts aggravated the formation of carbonaceous deposits, resulting in rapid catalyst deactivation [77, 78].

To overcome the inferior zeolite catalyst performances caused by the presence of external acid sites, passivation of these external acid sites on zeolite catalysts has been intensively explored [76, 77, 112, 204-206]. Silanation of the exterior of zeolite catalysts has been one of the most widely practiced methods to deactivate external acid sites. In the silanation process, a bulky, silicon-containing precursor compound is introduced onto the zeolites, reacts with the external surface silanol (-OH) groups, and deposits a catalytically inactive silica layer against the external surface acid sites.

Chemical liquid deposition [74, 76, 77, 112, 204, 207], chemical vapor deposition [38, 208, 209] [208, 209] and atomic layer deposition [46], etc., have been employed to introduce the silica precursors into the silanation process. The resultant passivation of external acid sites promoted the reaction on the acid sites in the shape-selective micropores rather than on the unselective external surface, which led to high selectivity to desired products and suppression of the catalyst deactivation. For example, in xylene isomerization, surface modified MFI zeolite showed a much higher selectivity to p-xylene compared to unmodified MFI zeolite due to the suppression of xylene isomerization to m-xylene on the external acid sites [207]. It should be noted that the silanation method often causes a full coverage of the zeolite exterior by silica-based materials, which narrows the pore opening or even blocks the pore entrance of the zeolite catalysts and consequently slows down the mass transport in catalytic reactions.

The synthesis of an inactive zeolite shell on the active zeolite core (i.e., core@shell zeolite composite) is another method practiced for passivation of the external acid sites in zeolite catalysts. The core@shell zeolite composites are usually prepared via overgrowth [125, 210-212] and epitaxial overgrowth methods. For example, the overgrowth has been successfully conducted by coating SAPO-34 zeolite onto MFI zeolite to form MFI@SAPO-34 as well as growing MFI zeolite onto MOR zeolite to form MOR@MFI. The epitaxial overgrowth has been exemplified by FAU@LTA, MFI@Silicalite-1 and EMT@FAU core-shell zeolites. Similarly, the overgrowth of a zeolite shell onto the core zeolite is likely to cause the blockage of pore openings and aggravate the diffusion limitation, leading to the slow mass transport and poor catalytic performance.

Introduction of mesopores via silanation or overgrowth method has been investigated to overcome the mass transport limitation in the as-prepared zeolite catalysts. The silanation followed by desilication has been explored to maintain mass transport while deactivating the external acid sites in Mo/MFI catalysts [74]. The resultant zeolite was used for the DMA reaction, in which the silanation helped to increase the methane conversion and lower the selectivity to coke, but the introduction of mesoporosity via desilication did not improve the catalytic performance [74]. Additionally, it should be mentioned that the catalyst prepared using this method included an additional desilication step aside from silanation, which complicated the catalyst synthesis procedure. Creation of mesopores in zeolite composites has been realized by overgrowth of mesoporous SAPO-34 over bulk MFI zeolite [210] and epitaxial growth of lamellar MFI over bulk MFI zeolite [213, 214]. The interconnected microporous and mesoporous components have complementary features: acid sites in the micropores and fast diffusion paths in the mesopores. However, the passivation of external acid sites and the creation of mesoporosity for facile mass transport of bulky molecules have not been exclusively explored in literature.

In this study, we report a simple one-step synthesis strategy to create the zeolite catalysts with passivated external acid sites and mesoporosity. The synthesis was conducted via overgrowth of the lamellar silicalite-1 onto bulk zeolite materials with the assistance of the diquaternary ammonium template C_{22-6-6} to form a zeolite composite. The commercial MFI and BEA zeolites were employed as the active zeolite in the composite. An epitaxial growth of lamellar mesoporous silicalite-1 nanosheets on the commercial MFI zeolite was observed, resulting in the hierarchical meso-

/microporous lamellar silicalite-1/MFI (L-Si/MFI) zeolite composite. Different from the epitaxial growth of lamellar silicalite-1 in L-Si/MFI, the lamellar mesoporous silicalite-1 nanosheets were laid over the surface of or partially interdigitated into the commercial BEA zeolite, which formed the hierarchical meso-/microporous lamellar silicalite-1/BEA (L-Si/BEA) zeolite composite. Physicochemical properties of the as-prepared zeolite composites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Ar adsorption-desorption isotherm and NH₃-temperature programmed desorption (NH₃-TPD) analyses. The catalytic performance of the L-Si/MFI and L-Si/BEA zeolite composites was examined in the DMA reaction over 2 wt% Mo-loaded L-Si/MFI and L-Si/BEA catalysts.

6.2. Experiments

6.2.1. Materials

2,6-Di-tert-butylpyridine (DTBP, 98% purity), triphenylphosphine (TPP, 99% purity) and tetraethyl orthosilicate (TEOS, 98% purity) were purchased from Alfa Aesar. Sodium hydroxide (NaOH, 97+% purity), sulfuric acid (H₂SO₄, 98% purity) and ammonium nitrate (NH₄NO₃, 99+% purity) were bought from Sigma-Aldrich. Diquaternary ammonium surfactant (C₂₂₋₆₋₆) was synthesized based on the method reported by Ryoo et al. which has also been described in our previous work [123]. Deionized (DI) water was used throughout the experiment. Commercial MFI with Si/Al ratio of 15 and commercial BEA with Si/Al ratio of 19, both in the NH₄⁺ form, were purchased from Alfa Aesar. Prior to the hydrothermal overgrowth of lamellar silicalite-

1, the commercial MFI and BEA zeolites in NH_4^+ form were treated in flowing air (1.67 mL s^{-1} , Airgas) while increasing the temperature from ambient temperature to 823 K at ramp rate of 0.0167 K s^{-1} and holding at 823 K for 4 h to thermally decompose NH_4^+ to NH_3 and H^+ .

6.2.2. Synthesis of zeolite composites

The recipe used for the hydrothermal synthesis of the L-Si/MFI and L-Si/BEA was as follows: $30\text{Na}_2\text{O}/100\text{SiO}_2/10\text{C}_{22-6-6}/18\text{H}_2\text{SO}_4/4000\text{H}_2\text{O}/5.8$ commercial MFI or 8.8 commercial BEA zeolite. The mass quantify of silicalite-1 calculated from its precursor (TEOS) was set to 22.6 wt% of that of the commercial bulk MFI or BEA zeolite under the assumption of 100% conversion of TEOS into silicalite-1. A NaOH solution was prepared by dissolving 0.36 g NaOH in 1.59 g DI water and a H_2SO_4 solution was prepared by mixing 0.21 g H_2SO_4 and 2.17 g DI water. Subsequently, the NaOH solution was added dropwise to the H_2SO_4 solution under vigorous stirring. 3.14 g TEOS was added into the above mixture, and the resultant mixture was magnetically stirred for 24 h at room temperature. Afterwards, 4 g commercial MFI or BEA zeolite was added. After the mixture was stirred for 0.5 h, a C_{22-6-6} solution, prepared by dissolving 1.09 g C_{22-6-6} in 7.5 g DI water at 333 K, was added. After continuous stirring for 2 h at room temperature, the resultant gel was transferred into a Teflon-lined, stainless-steel autoclave, followed by hydrothermal synthesis for 5 days by tumbling the autoclave vertically at 30 rpm in an oven heated at 423 K. After the synthesis, the zeolite product was collected by centrifugation, washed with DI water, and dried at 343 K overnight.

All of the as-prepared zeolite composite samples were calcined in flowing air (1.67 mL s^{-1}) while increasing the temperature from ambient temperature to 873 K at a ramp rate of 0.0167 K s^{-1} and holding at 873 K for 6 h. The calcined zeolite samples were then ion-exchanged three times using 1 M aqueous NH_4NO_3 (weight ratio of zeolite to NH_4NO_3 solution = 1:10) at 353 K for 12 h and subsequently collected by centrifugation, washed with DI water three times, and dried at 343 K overnight. The calcination in dry air (1.67 mL s^{-1}) was conducted again on the ion-exchanged samples by increasing the temperature from ambient temperature to 823 K at a ramp rate of 0.0167 K s^{-1} and holding at 823 K for 4 h to thermally decompose NH_4^+ to NH_3 and H^+ . Eventually, the zeolite composite samples in the H^+ -form were used for physicochemical characterizations.

The wetness impregnation method was used to prepare the 2 wt% Mo-loaded L-Si/MFI and L-Si/BEA catalysts for the DMA reaction. 0.0378 g of ammonium molybdenum tetrahydrate (99% purity, Sigma-Aldrich) was dissolved in 0.5 g DI water at room temperature to form a solution, which was then added dropwise to 1 g L-Si/MFI or L-Si/BEA zeolite composite. The as-prepared Mo/L-Si/MFI or Mo/L-Si/BEA catalyst was dried at 393 K overnight, followed by a two-stage calcination procedure reported in our previous work [45, 47]. In the first stage, the sample was heated from room temperature to 623 K at 0.0167 K s^{-1} in flowing air (1.67 mL s^{-1}) and hold at 623 K for 16 h. For the subsequent stage, the sample was heated to 973 K at 0.167 K s^{-1} and hold at 973 K for 10 h. The resultant Mo/zeolite composite catalyst was pelletized, crushed, and sieved to retain the particle sizes between 180 and 425 μm (40–80 mesh) for the subsequent DMA reaction. For simplicity, 2 wt% Mo-loaded L-Si/MFI and L-

Si/BEA catalysts were designated as Mo/L-Si/MFI and Mo/L-Si/BEA, respectively. For comparison purpose, 2 wt% Mo-loaded commercial MFI zeolite and commercial BEA zeolite catalysts were also prepared using the same method, which were designated as Mo/MFI and Mo/BEA, respectively.

6.2.3. Characterization of zeolite composites

6.2.3.1. Morphology, crystallinity, composition and textural property analyses

The morphologies of the L-Si/MFI and L-Si/BEA zeolite composite samples were observed using both SEM (FEI QUANTA 200) and TEM (JEM2100 LaB6). The crystalline phases of the zeolite composite samples were analyzed by the powder XRD patterns using the Rigaku Ultima III instrument with CuK α radiation. The elemental compositions (Si, Al and Mo) of the catalyst samples were determined by the inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 4300 DV instruments, Perkin–Elmer). The surface elemental compositions were measured using an X-ray photoelectron spectroscopy (XPS, ESCA 5600 equipped with 16 channel-hemispheric detector, Physical Electronics). The textural properties of the catalyst samples were analyzed using the Ar adsorption-desorption isotherms, measured at 87 K with an Autosorb-iQ analyzer (Quantachrome Instruments). Prior to the isotherm measurement, all the zeolite samples were evacuated overnight at 623 K and 1 mm Hg.

6.2.3.2. Acidity determination

The total number of Brønsted acid sites in the commercial MFI and BEA zeolites as well as the L-Si/MFI and L-Si/BEA zeolite composites was measured via dimethyl ether (DME) titration experiments since the Brønsted acid sites participate in the reaction between DME and H^+ to form surface methyl groups, $CH_3OCH_3 +$

$2[\text{SiO}(\text{H})\text{Al}] = 2[\text{SiO}(\text{CH}_3)\text{Al}] + \text{H}_2\text{O}$ [139, 140]. The experiments were carried out in a tubular packed-bed quartz reactor (10 mm inner diameter) under atmospheric pressure. The temperature of the reactor was held constant by a resistively heated furnace (National Electric Furnace FA120 type) where the temperature was controlled by a Watlow Controller (96 series). The catalyst temperature was measured using a K-type thermocouple touching the bottom of a well on the external surface of the quartz reactor. Details on the DME titration experimental setup and reaction conditions were described in our previous work [45, 47]. The same setup was used for the following organic base titration and gas-phase catalytic reaction study.

The acidity of the zeolite and Mo-loaded zeolite samples was measured by NH_3 -TPD using a mass spectrometer (MS, Ametek Proline) and the set-up described in the DME titration experiment above. Prior to the measurement, 0.1 g of sample was loaded into a quartz reactor and heated at a rate of 0.05 K s^{-1} to 823 K under He flow (0.5 mL s^{-1}) and hold at 823 K under the same flow condition for 2 h. After being cooled to 393 K under He flow (0.5 mL s^{-1}), the catalyst sample was exposed to an NH_3 (0.5 mL s^{-1} , ultrapure, Airgas) stream for 0.5 h. Physisorbed NH_3 was then removed by flowing He gas (0.5 mL s^{-1}) for 2 h. Afterwards, the catalyst sample was heated to 1023 K at a ramp rate of 0.167 K s^{-1} , and the NH_3 -TPD profile was recorded during this step.

6.2.3.3. Determination of external acid sites

The number of external Brønsted acid sites on the commercial zeolites and synthesized zeolite composites was measured by organic base titration during methanol dehydration reactions. Particularly, the amount of external Brønsted acid sites in the MFI and L-Si/MFI samples was measured using phenanthridine titrant while that of

BEA and L-Si/BEA was carried out using triphenylphosphine (TPP) titrant. It has been reported that the kinetic diameter of phenanthridine (~ 0.71 nm [110, 215]) is larger than the 10 MR micropores (0.51×0.55 nm and 0.53×0.56 nm) in the MFI zeolite. Therefore, phenanthridine can only access the external acid sites or acid sites in the mesopores of these two samples. Similarly, the 12 MR microporous channels (0.56×0.56 nm and 0.66×0.67 nm) in BEA zeolite are not accessible to TPP titrant, which has a kinetic diameter of ~ 0.94 nm [119, 120, 130]. The degree of loss in the dehydration rate with the cumulative addition of phenanthridine or TPP titrant molecules reflects the percentage of external acid sites. The experimental setup and reaction conditions for chemical titration of acid sites were same as those described in our previous publication [216]. The Brønsted acid sites only accessible to the DME titrant were defined as the internal acid sites. The fraction of external Brønsted acid sites was calculated by the ratio of the number of Brønsted acid sites accessible to phenanthridine or TPP titrant to the number of Brønsted acid sites accessible to the DME titrant.

6.2.4. DMA reactions over 2 wt% Mo-loaded zeolite composites

The DMA reaction was conducted in a quartz reactor described in Section 6.2.3.2. 2 wt% Mo- loaded zeolite catalyst (0.30 g) was heated from ambient temperature in He flow (0.5 mL s^{-1}) at 950 K at ramp rate 0.167 K s^{-1} under atmospheric pressure. After the temperature of the catalyst reached 950 K, the DMA reaction was carried out by introducing methane into the catalyst at a flow rate of 0.133 mL s^{-1} and Ar at a flow rate of 0.033 mL s^{-1} as internal standard. The transfer lines were maintained at temperatures greater than 473 K by resistive heating to prevent product condensation.

The effluents from the reactor were analyzed by the gas chromatograph (Agilent 7890 A GC) equipped with a methyl-siloxane capillary column (HP-1, 50.0 m $\times$ 320 μ m $\times$ 0.52 μ m) connected to a flame ionization detector (FID) and a packed column (ShinCarbon ST Columns, 80/100 mesh, 6 feet) connected to a thermal conductivity detector (TCD).

The coke formation on the spent catalysts in the DMA reaction (after time-on-stream of 10 h) was determined by the thermo-gravimetric analysis (TGA, TA Instrument, SDT Q600). 0.01 g of the spent catalyst was heated from ambient temperature to 393 K under flowing air (1 mL s⁻¹), hold at 393 K for 0.5 h and then heated to 1073 K at a ramp rate of 0.167 K s⁻¹ at the same flow condition. The weight loss versus the temperature was recorded to quantify the total amount of coke in the catalyst.

6.3. Results and discussion

6.3.1. Morphology and XRD patterns of zeolite composites

Figure 6.1 shows SEM and TEM images of the L-Si/MFI and L-Si/BEA zeolite composites together with the commercial MFI and BEA zeolites for comparison purpose. The commercial MFI contains irregular-shaped particles with an average size at 146 nm (Figure 6.1(A-B)). The L-Si/MFI zeolite composite (Figure 6.1(C-D)) inherits the irregular shape from the commercial MFI zeolite with an average size at 257 nm, but its surface turns into roughness due to the overgrowth of lamellar silicalite-1 nanosheets. Apparently, the overgrowth of silicalite-1 resulted in an increase of the MFI particle size by a factor of 1.7. Furthermore, a closer observation shows that the particle size of the core components of the L-S/MFI is similar to that of the original commercial MFI particles, indicating that commercial MFI remained almost intact in the overgrowth of lamellar silicalite-1 nanosheets. TEM image of the L-Si/MFI sample clearly shows that the lamellar silicalite-1 nanosheets protruded from surface of the commercial MFI particles (Figure 6.1(D)), consistent with the work reported by Kim et al. [214] and our previous work [213]. The lamellar silicalite-1 domains in the L-Si/MFI all appeared to be morphologically aligned on the surface, which suggests an epitaxial (lattice-matched) growth rather than a random surface deposition and overgrowth occurred in the synthesis process. Therefore, it is expected that external surface of the commercial MFI is covered by the lamellar silicalite-1, while mesopores existing in the lamellar silicalite-1 allow the facile mass transport of bulky molecules in the catalytic reactions (inset image in Figure 6.1(D)). The lamellar component in the

composite provides a combined mesoporous/microporous network and controlled surface acid sites of the bulk zeolite component.

The commercial bulk BEA zeolite is consisted of nearly spherical particles with smooth surfaces and an average particle size at 720 nm (Figure 6.1(E-F)). Different from the aligned lamellar silicalite-1 structure on the commercial MFI zeolite, the lamellar silicalite-1 grew into an intertwined structure which might be due to the random overgrowth of lamellar silicalite-1 on the surface of the BEA particles as shown in its SEM image in Figure 6.1(G). The lattice mismatch between MFI and BEA zeolite frameworks is one of the most contributing factors causing this growth pattern and surface morphology of L-Si/BEA zeolite composite. After overgrowth of lamellar silicalite-1 on the bulk BEA particles, the resultant L-Si/BEA has rough surface and the particle size was increased to 880 nm, as shown in its TEM image in Figure 6.1(H). A closer examination of the structure of the L-Si/BEA composite particles shows that the lamellar silicalite-1 not only lays on the surface of the BEA but also slightly penetrates the interior of BEA (Figure 6.1(H)). In addition, the presence of internal voids with a diameter of 10~20 nm (inset image of Figure 6.1(H)) on the edge of BEA zeolite, forming a partial nanosponge structure, indicates a partial dissolution of the bulk BEA zeolite in hydrothermal synthesis. Consequently, the lamellar component in the L-Si/BEA composite provides a combined mesoporous/microporous network, while the bulk BEA component went through a partial dissolution. Additionally, the external acid sites in the bulk BEA zeolite are expected to be modulated by the overlaid lamellar silicalite-1 structure.

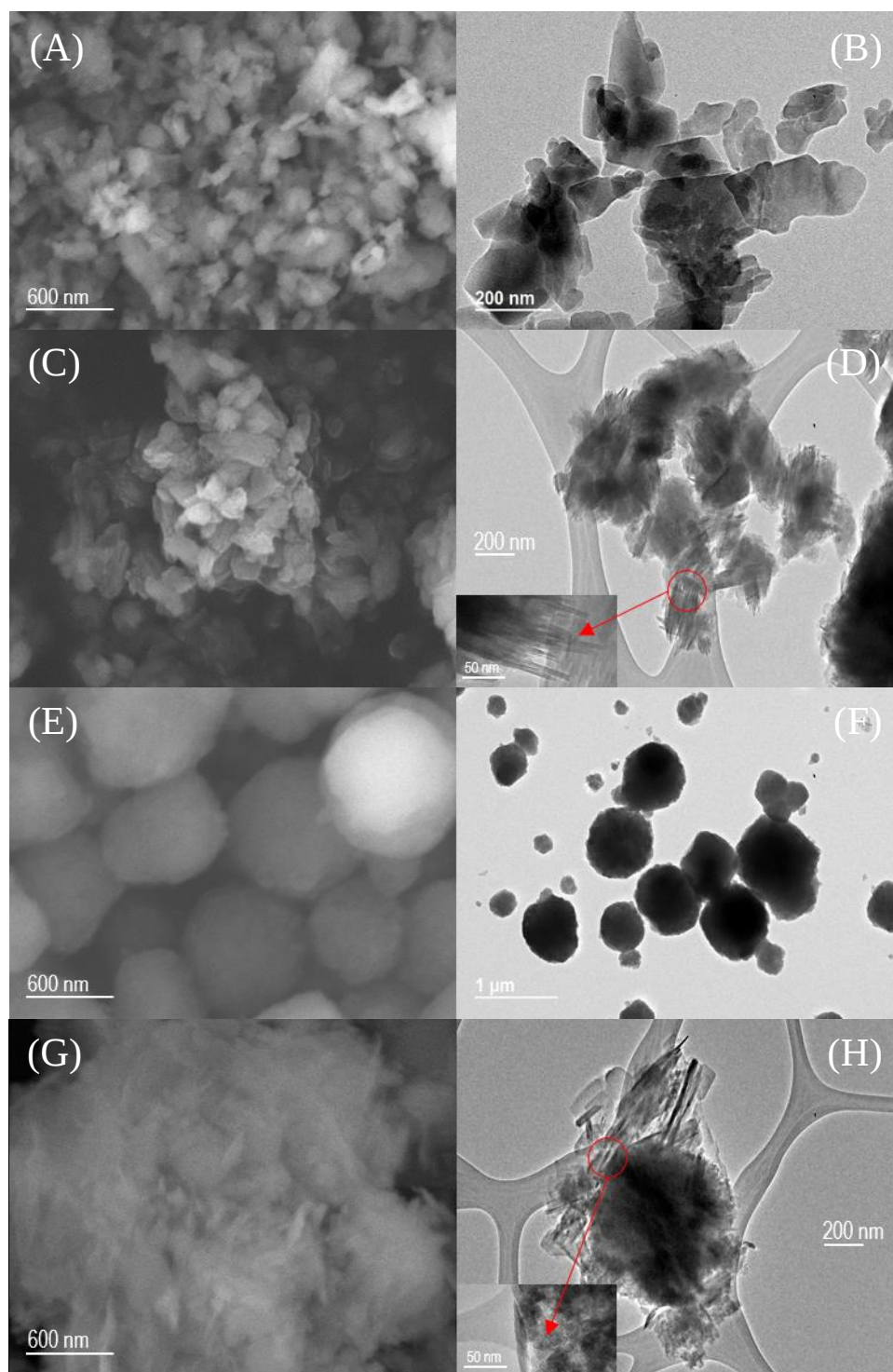


Figure 6.1. SEM images of MFI (A), L-Si/MFI (C), BEA (E) and L-Si/BEA (F) as well as TEM images of MFI (B), L-Si/MFI (D), BEA (F) and L-Si/BEA (H).

Figure 6.2 shows the XRD patterns of the L-Si/MFI and L-Si/BEA zeolite composites. For comparison purpose, the XRD patterns of commercial MFI and

commercial BEA zeolite are also included. Both commercial bulk MFI and BEA zeolites show the characteristic signature diffraction patterns of their crystalline structures [102, 217]. After the epitaxial overgrowth of the lamellar silicalite-1 shell, the resultant L-Si/MFI exhibits the same XRD pattern as that of MFI, suggesting that the development of the sole MFI crystalline structure was successful in the zeolite composite. However, for the synthesized L-Si/BEA composite zeolite, the XRD pattern, consists of both characteristic diffraction peaks of silicalite-1 ($2\theta = 8.8^\circ$, 23° and 24°) and BEA ($2\theta = 8.0^\circ$ and 22°) zeolites. This implies the successful synthesis of silicalite-1 structure in the presence of BEA particles. The XRD and electron microscopy (SEM and TEM) characterizations both confirm the successful synthesis of L-Si/MFI and L-Si/BEA zeolite composites in which the presence of mesoporosity and partial coverage of the external surface of the MFI and BEA zeolites were concurrently realized via the simple one-step hydrothermal synthesis method.

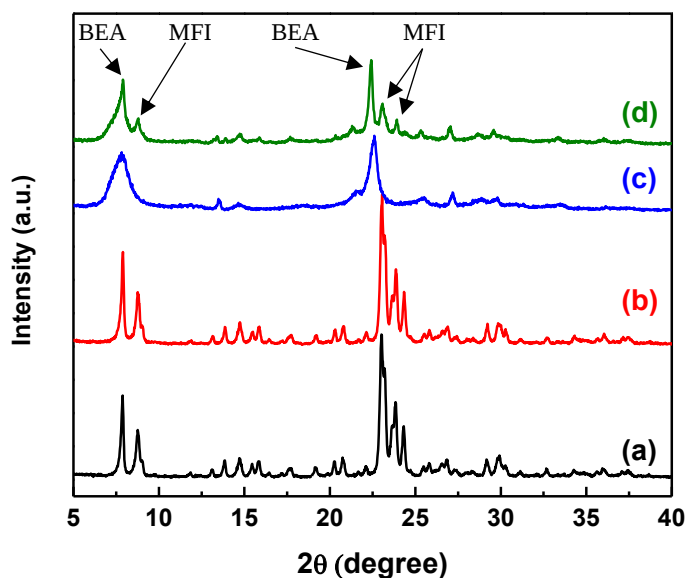


Figure 6.2. XRD patterns of MFI (a), L-Si/MFI (b), BEA (c) and L-Si/BEA (d).

6.3.2. Textural property of zeolite composites

Figure 6.3 shows the Ar isotherms (Figure 6.3(A)) and the non-local density function theory (NLDFT) pore size distribution (Figure 6.3(B)) of the L-Si/MFI and L-Si/BEA composite zeolites. For comparison, the Ar isotherms and pore size distributions of commercial MFI and BEA zeolites are also shown in Figure 6.3. At lower relative pressures ($P/P_0 < 0.05$), L-Si/MFI zeolite shows similar Ar uptake to that of MFI zeolite, indicating that both materials have similar microporosity due to the fact that they share the same microporous topology (Figure 6.3(A)). In contrast, within the same pressure range, the L-Si/BEA zeolite has a lower Ar uptake than the bulk BEA zeolite, which is caused by the different microporous topology between BEA and MFI zeolites. It is known that MFI zeolite consists of two interconnected, 10-membered ring (MR) channel systems, one running straight along the b-axis direction (0.53×0.56 nm) and the other one running zigzagly in the direction parallel to the a-axis (0.51×0.55 nm). The BEA zeolite contains two straight intersecting 12 MR microporous channels, one running in the a-axis direction (0.66×0.67 nm) and the other one running in the c-axis direction (0.56×0.56 nm). The smaller micropore sizes of MFI than BEA lead to the lower Ar uptake in this range of the L-Si/BEA composite compared to that of the bulk BEA zeolite. At higher relative pressures ($0.4 < P/P_0 < 1$) in Figure 6.3(A), the Ar uptake increases from MFI to L-Si/MFI due to the presence of mesoporosity in the L-Si/MFI composite that resulted from the epitaxial growth of lamellar silicalite-1 on the surface of the commercial bulk MFI. L-Si/BEA has comparable Ar uptake to that of commercial bulk BEA in this pressure range. However, a hysteresis loop is clearly seen in the L-Si/BEA, reflecting the Ar capillary condensation in the mesopores that results

from the lamellar silicallite-1 and nanosponge BEA structure in this zeolite composite. The absence of a recognizable hysteresis loop in the Ar isotherm of L-Si@MFI is probably due to the low fraction of lamellar silicalite-1 shell, which is consistent with a previous report [218].

The NLDFT pore size distributions of the L-Si/MFI and L-Si/BEA zeolite composites, in comparison with the commercial bulk MFI and BEA, respectively, further indicate the presence of mesoporosity after the hydrothermal overgrowth of lamellar silicalite-1 in these composites. In Figure 6.3(B), the peaks centered at 0.51 nm and 0.61 nm are assigned to the micropores of MFI and BEA, respectively. The lamellar silicalite-1 has the same micropore size as that of MFI. Therefore, the L-Si/MFI zeolite composite also has the micropore peak centered at 0.51 nm. The micropore size peak of the L-Si/BEA zeolite composite, which is also centered at 0.61 nm along with BEA zeolite, slightly shifts to the lower size due to the smaller micropore size of lamellar MFI compared to that of BEA zeolite in this composite. This confirms the composite nature of the L-Si/BEA zeolite. The peaks centered at ~ 0.90 nm in Figure 6.3(B) might be due to the reminiscence of a phase transition in the Ar adsorption, which has been previously reported for MFI zeolite samples [173-175, 219]. The peaks in the range of 3 nm - 6 nm correspond to the mesopores in the composite zeolites. Apparently, L-Si/MFI and L-Si/BEA zeolite composites have higher mesoporosity than the corresponding commercial MFI and BEA zeolites. The slightly larger mesopore size and higher mesopore volume (indicated by the peak intensity in Figure 6.3(B)) of L-Si/BEA than those of L-Si/MFI can be attributed to the

nanosponge structure of BEA, which resulted from the random overgrowth of lamellar silicalite-1 on the commercial bulk BEA zeolite.

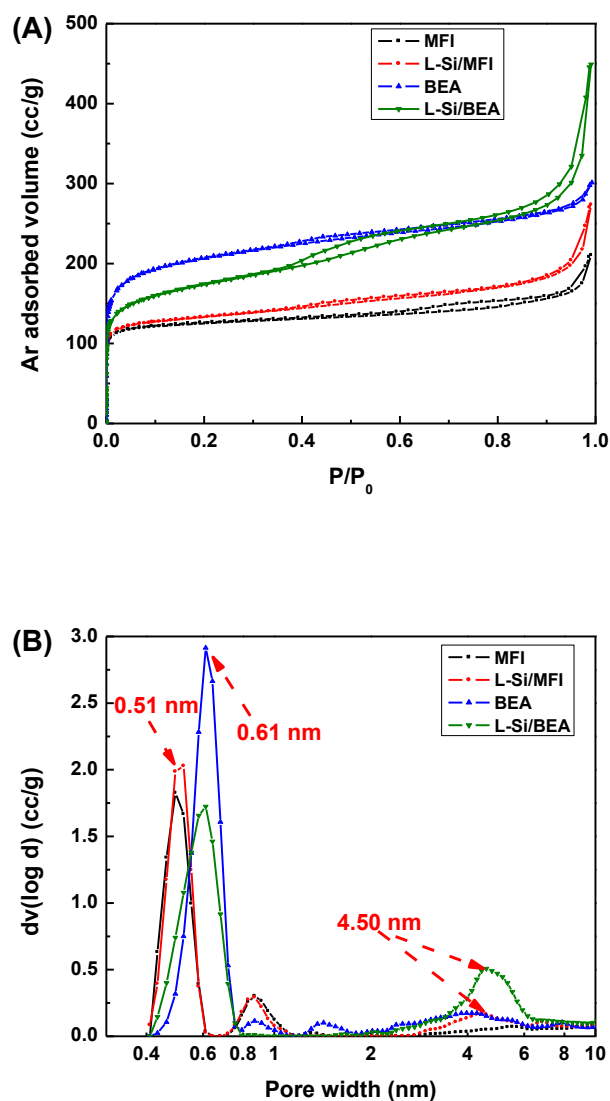


Figure 6.3. Ar adsorption-desorption isotherms (A) and NLDFT pore size distribution (B) of MFI, L-Si/MFI, BEA and L-Si/BEA.

Table 6.1. Textual property of MFI, L-Si/MFI, BEA and L-Si/BEA zeolite samples.

Zeolite	S_{BET}^a	S_{micro}^b	S_{ext}^b	V_{total}^c	V_{micro}^b	V_{meso}^d	$f_{\text{ext,shell}}^e$
	$(\text{m}^2 \text{ g}^{-1})$			$(\text{cm}^3 \text{ g}^{-1})$			(%)
MFI	431	369	62	0.21	0.132	0.078	--
L-Si/MFI	450	340	110	0.251	0.121	0.13	16
BEA	677	524	154	0.346	0.199	0.147	--
L-Si/BEA	559	325	233	0.384	0.119	0.265	59
Lamellar MFI ^f	310	141	169	0.462	0.063	0.399	--

^a Determined from Brunauer, Emmett, and Teller (BET) method; ^b Determined from *t*-plot method; ^c Obtained from the adsorption branch of the isotherms at $P/P_0=0.95$; and ^d $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$; ^e $f_{\text{ext,shell}} = (V_{\text{micro-MFI}} - V_{\text{micro-L-Si/MFI}}) / (V_{\text{micro-MFI}} - V_{\text{micro-Lamellar MFI}})$ for L-Si/MFI and $(V_{\text{micro-BEA}} - V_{\text{micro-L-Si/BEA}}) / (V_{\text{micro-BEA}} - V_{\text{micro-Lamellar MFI}})$ for L-Si/BEA; ^f Obtained from Laleh et al's paper for the comparison purpose.

Table 6.1 summarizes the Brunauer, Emmett, and Teller (BET) surface area (S_{BET}), micropore surface area (S_{micro}), external surface area (S_{ext}), total pore volume (V_{total}), micropore volume (V_{micro}) and mesopore volume (V_{meso}), which were extracted from the Ar isotherms in Figure 6.3. The higher external surface area and larger mesopore volume of L-Si/MFI and L-Si/BEA than their microporous counterparts further confirm the successful overgrowth of lamellar silicalite-1 on both MFI and BEA zeolites. It should be noted that the measured micropore volumes of the zeolite composites lie between the micropore volumes of the bare BEA ($0.199 \text{ cm}^3 \text{ g}^{-1}$) and lamellar silicalite-1 ($0.063 \text{ cm}^3 \text{ g}^{-1}$) [220]. Based on the micropore volume in Table 6.1, mass fractions of the bulk MFI and BEA components in the composites were calculated to be 85% and 41%, respectively, according to the method reported in our previous work [220]. It should be noted that the mass fractions of the commercial bulk MFI and BEA were set to be 81.6% in the synthesis recipe under the consumption of 100% conversion of TEOS to lamellar silicalite-1 without dissolution of bulk MFI or BEA core zeolite. The slight difference between the designed mass fraction and estimated value of MFI bulk zeolite in L-Si/MFI indicates that bulk MFI zeolite remained almost intact in the hydrothermal synthesis. In contrast, the dramatic decrease in the mass

fraction of BEA bulk zeolite in L-Si/BEA from the designed value to the estimated value implies either the BEA zeolite went through a significant dissolution in the hydrothermal synthesis or the random overgrowth of the lamellar silicalite-1 shell partially blocked the pore openings of the BEA bulk zeolite, since the pore blockage can lead to a lower micropore volume and consequently a lower estimated mass fraction of BEA bulk zeolite. As discussed above, bulk BEA zeolite went through a dissolution in the hydrothermal overgrowth of the lamellar silicalite-1 shell, which led to a formation of nanosponge structure consisting of internal voids with a diameter of 10-20 nm on the edge of BEA bulk zeolite. However, given the fact that the lamellar silicalite-1 shell lies on the surface of or is interdigitated into BEA bulk zeolite, the partial blockage of the micropores in the BEA bulk zeolite cannot be excluded during the overgrowth of the lamellar silicalite-1 shell, which requires further evidence.

6.3.3. Composition and acidity of zeolite composites

The Si and Al compositions (represented by Si/Al ratio) of the synthesized L-Si/MFI and L-Si/BEA zeolite composites were analyzed by the ICP-OES technique. Table 6.2 shows the Si/Al ratios of these two zeolite composites together with the commercial bulk MFI and BEA zeolites. The epitaxial overgrowth of lamellar silicalite-1 on the commercial MFI zeolite increased the Si/Al of MFI from 17 to 23 for L-Si/MFI zeolite composite. Similarly, the Si/Al ratio of BEA was increased from 25 to 40 in the L-Si/BEA zeolite composite due to the presence of the silicalite-1 component in the composite. The surface Si and Al compositions of these four zeolite samples were examined by the XPS technique. It was shown that the Si/Al ratios (the fourth entry in Table 6.2) of MFI, BEA, L-Si/MFI and L-Si/BEA were 23, 27, 74 and

49, respectively. Apparently, the surface and bulk compositions of the commercial bulk MFI and BEA zeolites are similar. After the hydrothermal overgrowth, the resultant L-Si/MFI has a much lower Al content on the surface component compared to that of the bulk MFI component. This result clearly indicates the epitaxial growth of the lamellar silicalite-1 on the surface of the bulk MFI, which did not cause the obvious dissolution and recrystallization of MFI component in the synthesis process. On the contrary, the L-Si/BEA zeolite composite shows similar surface and bulk Si and Al compositions, different from the expectation for the siliceous silicalite-1 surface in the composite. The presence of Al species on the external surface of silicalite-1 layer might be due to the fractioning of bulk BEA into a nanosponge-like structure on its edge as evidenced in Figure 6.1(H), serving as the nutrients for the formation of mesoporous 2D lamellar MFI nanosheets directed by the C₂₂₋₆₋₆ template in the hydrothermal overgrowth process.

Based on the changes in Si/Al ratios before and after overgrowth of the lamellar silicalite-1 shell, the mass fractions of the bulk MFI or BEA zeolite component in the core-shell zeolite composites can be calculated. The calculation shows that the mass fractions of MFI and BEA bulk zeolites are 75% and 63%, respectively, in L-Si/MFI and L-Si/BEA. The similarity among this estimated value of 75% from elemental analysis, the estimated value of 85% from Ar isotherms and the designed value of 81.6% in the synthesis recipe further confirmed that bulk MFI zeolite remained almost intact during hydrothermal synthesis. On the contrary, for the mass fraction of BEA bulk zeolite in L-Si/BEA, the determined value of 63% from elemental analysis is higher than that estimated from Ar isotherms (41%) but lower than the designed value of 81.6%

in the recipe. As discussed in Section 6.3.2, the much lower mass fraction of BEA bulk zeolite estimated from Ar isotherms than the designed value in the recipe is due to the partial dissolution of BEA bulk zeolite but whether the partial pore blockage of BEA bulk zeolite exists and contributes to this difference remains uncertain. Since the mass fraction of BEA core zeolite in L-Si/BEA estimated from elemental analysis is not affected by the pore blockage and sits between that estimated value from Ar isotherms and the designed value in the recipe, we propose that the partial pore blockage of BEA zeolite could be the reason for the lower mass fraction of BEA bulk zeolite estimated from Ar isotherms than that determined by element analysis. Hence, the overgrowth of lamellar silicalite-1 shell led to a partial dissolution of bulk BEA zeolites in the hydrothermal synthesis and a partial pore blockage of BEA bulk zeolite.

Table 6.2. Composition and acid site concentration of MFI, L-Si/MFI, BEA and L-Si/BEA zeolites.

Zeolites	Si/Al ^a	f _{ext,shell} ^b (%)	Si/Al ^c	N _{Al} ^a (x10 ⁻⁴ mol g ⁻¹)	N _{total,H⁺} ^d (x10 ⁻⁴ mol g ⁻¹)	f _{ext, H⁺} ^e (%)	N _{ext,H⁺} ^f (x10 ⁻⁴ mol g ⁻¹)
MFI	17	--	23	8.7	8.4	26	2.2
L-Si/MFI	23	25	74	6.9	5.8	20	1.2
BEA	25	--	27	6.5	6.4	24	1.6
L-Si/BEA	40	37	49	4.5	3.5	29	1.0

^a Measured by ICP-OES analysis; ^b Mass fraction of lamellar MFI determined from changes of Si/Al ratios before and after lamellar silicalite-1 growth on MFI or BEA sample; ^c Measured by XPS analysis; ^d Concentration of Brønsted acid sites in entire catalyst particles, determined by DME titration; ^e Fraction of external Brønsted acid sites, determined by degree of the loss in methanol dehydration rate in presence of phenanthridine titrant (MFI and L-Si/MFI zeolites) or TPP titrant (BEA and L-Si/BEA zeolites); ^f $N_{\text{ext,H}^+} = f_{\text{ext,H}^+} \times N_{\text{total,H}^+}$.

The number of active Brønsted acid sites ($N_{\text{total,H}^+}$) in the commercial and synthesized zeolite composite samples was measured by the DME titration method, and the result is shown in Table 6.2. The number of Brønsted acid sites in MFI and BEA zeolites are 8.4×10^{-4} mole H⁺ g⁻¹ and 6.4×10^{-4} mole H⁺ g⁻¹, respectively. After the overgrowth of the Al-free lamellar silicalite-1 shell, the number of Brønsted acid

sites were decreased to 5.8×10^{-4} mole $H^+ g^{-1}$ and 3.5×10^{-4} mole $H^+ g^{-1}$, respectively, in L-Si/MFI and L-Si/BEA composite zeolites. Both the bulk MFI and BEA zeolites show similar numbers of Brønsted acid sites to those of Al sites, while both L-Si/MFI and L-Si/BEA zeolite composites show significantly lower numbers of Brønsted acid sites than those of Al sites, reflecting the acid sites passivation caused by the overgrowth of lamellar silicalite-1 shell. Table 6.2 also shows that the fractions of external acid sites (f_{ext,H^+}) in MFI and L-Si/MFI are 26% and 20%, respectively. In combination with the total number of acid sites in these two zeolite composites, the number of external acid sites ($N_{ext,H^+} = N_{total,H^+} \times f_{ext,H^+}$) of MFI and L-Si/MFI were 2.2×10^{-4} mole $H^+ g^{-1}$ and 1.2×10^{-4} mole $H^+ g^{-1}$, respectively. Similarly, the fractions of external acid sites in BEA and L-Si/BEA are ~24% and ~29%, respectively. The number of external acid sites in BEA and L-Si/BEA were determined to be 1.6×10^{-4} mole $H^+ g^{-1}$ and 1.0×10^{-4} mole $H^+ g^{-1}$, respectively. The organic base titration data shows that the fraction of external acid sites in bulk MFI was reduced by 6% when the silicalite-1 shell was developed on its surface to form the L-Si/MFI zeolite composite. On the contrary, the fraction of external acid sites in BEA zeolite was increased by 5% after the random overgrowth of silicalite-1 on BEA to form the L-Si/BEA zeolite composite. Therefore, the epitaxial growth of silicalite-1 onto MFI led to the concurrent passivation of external surface acid sites and generation of mesoporosity. However, the same process only led to the formation of mesoporosity in the L-Si/BEA zeolite composite. The dissolution and re-crystallation process in the random overgrowth of silicalite-1 on BEA results in the migration of Al sites from BEA to silicalite-1 (i.e., MFI) structure.

The acidity of the L-Si/MFI and L-Si/BEA was further examined by the NH_3 -TPD measurement. For comparison purpose, the NH_3 -TPD profiles of the commercial MFI and commercial BEA were also measured. The lamellar MFI that was synthesized according to the procedure reported by Ryoo's group [102] was also measured with the NH_3 -TPD profile. Figure 6.4(A) shows the NH_3 -TPD profiles of MFI, L-Si/MFI and lamellar MFI zeolite samples. These three samples exhibit the typical double-peak characteristics of MFI zeolites in the NH_3 -TPD process [38, 47, 176, 220]. The NH_3 -TPD profile of the MFI sample can be further deconvoluted into three peaks, centering at ~ 438 K, ~ 514 K and ~ 640 K (Figure 6.4 (C)) by using the Gauss curve fitting method, which corresponds to physisorbed NH_3 , chemisorbed NH_3 with medium-strength acid sites or Lewis acid sites and chemisorbed NH_3 with strong Brønsted acid sites, respectively [38, 152]. The area of each deconvoluted peak corresponds to the amount of ammonia that desorbs from the sample, which can be used to estimate the acidity of the zeolite samples. Clearly, the number of acid sites decreases from the bulk MFI, L-Si/MFI and then to lamellar MFI ($\text{Si}/\text{Al} = 50$) as indicated by the decrease in their peak areas in Figure 6.4(A), which is consistent with the results determined from the DME titration experiment above. The shifting of the desorption peaks to the lower temperatures from bulk MFI, L-Si/MFI and then to lamellar MFI suggests that acid strength of L-Si/MFI is lower than that of the bulk MFI but higher than lamellar MFI. Figure 6.4(B) shows the NH_3 -TPD profiles of the BEA and L-Si/BEA together with the lamellar MFI sample. The peak intensity in the NH_3 -TPD profiles follows the order of $\text{BEA} > \text{L-Si/BEA} > \text{lamellar MFI}$, which is consistent with the ranking of the number of acid sites in these three samples. The left-shift of the peak position in L-Si/BEA

compared to that of BEA indicates that the acid strength is weakened after the random overgrowth of zeolite on the commercial bulk BEA zeolite. Compared to that of lamellar MFI zeolite, the L-Si/BEA has fewer strong acid sites, which might be due to the mesoporous nanosponge-like structure present in the L-Si/BEA zeolite composite. Overall, the epitaxial overgrowth of silicalite-1 onto the bulk MFI or random overgrowth of silicalite-1 onto the bulk BEA zeolites resulted in weaker acid sites compared to those in the bulk microporous zeolite structures.

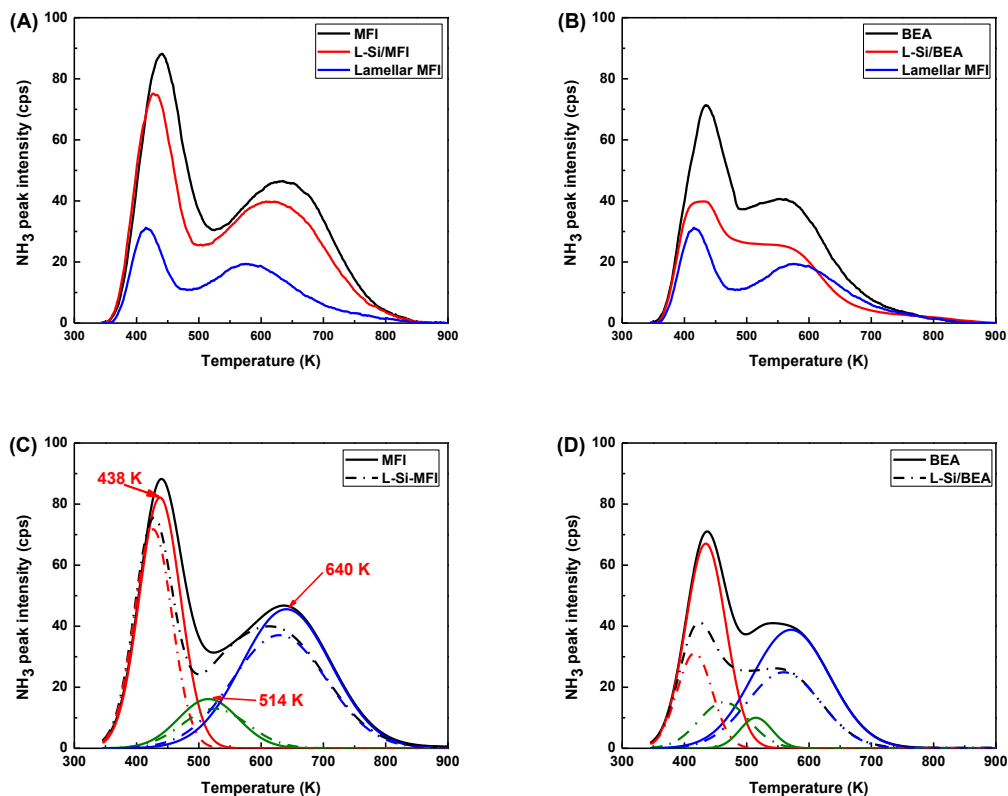


Figure 6.4. NH₃-TPD profiles of MFI and L-Si/MFI (A), BEA and L-Si/BEA (B) with that of lamellar MFI as reference; deconvoluted NH₃-TPD profiles of MFI and L-Si/MFI (C), BEA and L-Si/BEA (D).

6.3.4. Catalytic performance of 2 wt% Mo-loaded L-Si/MFI and L-Si/BEA zeolite composites

The DMA reaction was used to probe the catalytic consequences of the overgrowth of the lamellar silicalite-1 on the commercial bulk MFI and BEA zeolites, in which the 2 wt% Mo-loaded L-Si/MFI and L-Si/BEA zeolite composites were used as catalysts. The Mo-loaded MFI or BEA zeolites have been often studied as catalysts for the DMA reaction. It is believed that the unique 10MR channels in MFI and 12 MR channels in BEA zeolite, whose size is close to the kinetic diameter of benzene molecule, favors the synthesis of aromatic molecules but prevents accumulation of polycondensed aromatic substances [39, 43]. The acidity, crystal size and porosity of zeolites are also key factors that considerably influence the catalyst performance in the DMA reaction. The adjustment of zeolite acidity by selective silanation of zeolite external acid sites [76, 77, 112] or by dealumination of excess acid sites through steam treatment of zeolites enhanced catalyst performance because external or excessive acid sites, regarded as a key factor for coke formation, were deactivated or removed. The morphology and pore sizes of zeolites also played an important role in influencing the product selectivity and mass transport in the DMA reaction given the difference in the molecular size of the reactant (methane) and the products (aromatics). Given the unique structure of the as-developed L-Si/MFI and L-Si/BEA zeolite, in which the generation of mesoporosity and modulation of the external acidity were concurrently realized, we expect there to be an impact on the catalytic activity and selectivity of the catalysts in the DMA reaction.

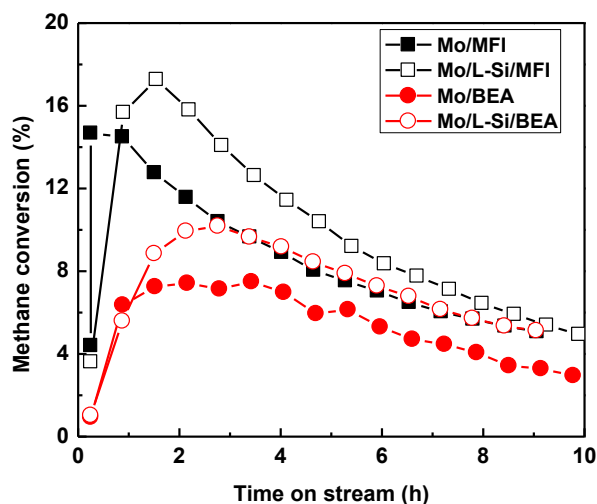


Figure 6.5. Methane conversion in the DMA reaction over 2 wt% Mo-loaded MFI, L-Si/MFI, BEA and L-Si/BEA catalysts.

Figure 6.5 shows the methane conversion in the DMA reaction over the 2 wt% Mo-loaded L-Si/MFI and L-Si/BEA zeolite composites as well as the 2 wt% Mo-loaded bulk MFI and BEA zeolites. For all of the investigated catalysts, the methane conversion sharply increased in the initial period of the reaction (i.e., induction period, $< \sim 1$ h), reached a maximum after about time of stream (TOS) of 2 h, and then decreased with the reaction time on stream. The methane conversion during the initial induction period is due to the rapid buildup of carbonaceous deposits on the Mo species to form MoC_xO_y sites that convert methane into reaction intermediates, which then react to form aromatic products over Brønsted acid sites in zeolites [27]. The overgrowth of lamellar silicalite-1 on the MFI and BEA does not apparently affect the catalyst performance in the induction period of the DMA reaction. After the induction period, both Mo/L-Si/MFI and Mo/L-Si/BEA catalysts showed higher activity than the corresponding Mo/MFI and Mo/BEA catalysts. With the progress of the reaction,

Mo/L-Si/MFI has a faster deactivation than that of Mo/MFI, which led to a similar methane conversion at TOS of 10 h. On the other hand, Mo/L-Si/BEA maintained a higher methane conversion than that of the Mo/BEA in the course of the reaction up to TOS of 10 h. The different deactivation behavior of both zeolite composite catalysts might be due to the different morphological and acidity distribution as discussed above.

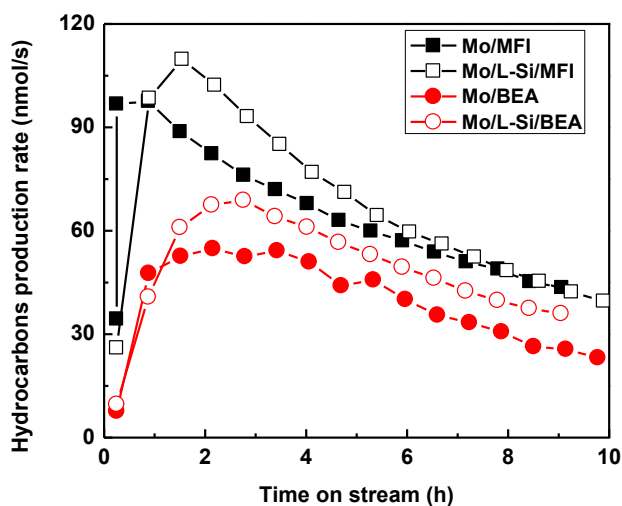


Figure 6.6. Production rate of hydrocarbons (a sum of benzene, toluene, naphthalene, ethylene and ethane) in the DMA reaction over 2 wt% Mo-loaded MFI, L-Si/MFI, BEA and L-Si/BEA catalysts.

Figure 6.6 shows the formation rate of hydrocarbon products, including benzene, toluene, naphthalene, ethylene and ethane, in the DMA reaction. Similar to the methane conversion in Figure 6.5, the hydrocarbon production rate increased rapidly during the induction period and gradually decreased with the reaction progress due to the deactivation caused by coke accumulation. Mo/L-Si/MFI showed a higher hydrocarbon production rate than Mo/MFI and a faster deactivation rate. In contrast, Mo/L-Si/BEA showed a higher hydrocarbon production rate than Mo/BEA up to TOS of 10h. The higher methane conversion and hydrocarbon production rate over both

Mo/L-Si/MFI and Mo/L-Si/BEA zeolite composite catalysts than their microporous MFI and BEA counterparts can be attributed to the enhanced mass transport resulting from the overgrowth of lamellar silicalite-1 shell.

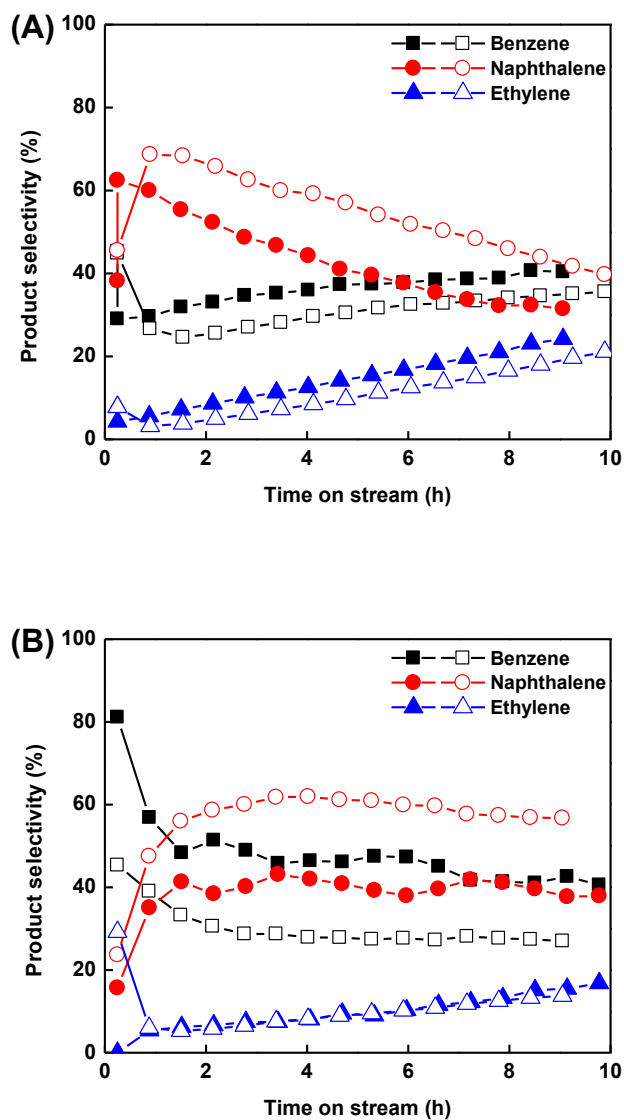


Figure 6.7. Selectivity of benzene, naphthalene and ethylene in the DMA reaction over 2 wt% Mo-loaded MFI (filled symbol) and L-Si/MFI (open symbol) (A) and over 2 wt% Mo-loaded BEA (filled symbol) and L-Si/BEA (open symbol) (B).

Benzene, naphthalene and ethylene are the three major hydrocarbon products in the DMA reaction, and their selectivities are shown in Figure 6.7. Compared to the bulk microporous MFI and BEA zeolites, the presence of lamellar silicalite-1 and the resultant higher mesoporosity and acidity distribution in the zeolite composites led to an increase in naphthalene selectivity and a decrease in selectivity to benzene and ethylene over Mo/L-Si/MFI and Mo/L-Si/BEA catalysts. The higher selectivity towards the heavier naphthalene product over Mo/L-Si/MFI and Mo/L-Si/BEA catalysts than Mo/MFI and Mo/BEA zeolites, respectively, can be attributed to the enhanced mass transport resulting from the mesoporosity in the zeolite composites.

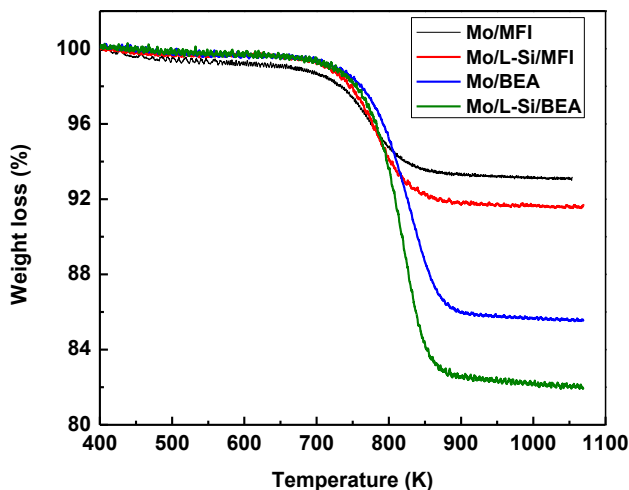


Figure 6.8. TGA analysis of the spent 2 wt% Mo-loaded MFI, L-Si/MFI, BEA and L-Si/BEA catalysts after TOS of 10 h in the DMA reaction.

The coke deposition in the catalysts was also analyzed by TGA after the TOS of 10 h in the DMA reaction. Figure 6.8 shows that the weight fractions of coke are 6%, 9%, 15% and 18% in the spent Mo/MFI, Mo/L-Si/MFI, Mo/BEA and Mo/L-Si/BEA catalysts, respectively. It has been reported that passivation of external acid

sites by depositing silica or coating a silicalite-1 shell onto the zeolite surface can reduce the amount of coke formed during the DMA reaction [38, 76-78]. The opposite trend observed in the present study can be ascribed to the mesoporosity in the zeolite composites created in the overgrowth process, which functioned as a coke reservoir [47, 171] and led to a slightly higher coke deposition compared to that of the bulk MFI or BEA zeolite-based catalysts.

6.4. Conclusion of Chapter 6

The zeolite composites that consist of two compositionally and/or structurally different zeolite components were prepared via a simple one-step hydrothermal overgrowth method. Two representative zeolite composites, lamellar silicalite-1 epitaxially grown on commercial bulk MFI (L-Si/MFI) and lamellar silicalite-1 randomly grown on commercial bulk BEA (L-Si/BEA), were synthesized via this method. The morphological characterizations showed that lamellar silicalite-1 formed an ordered, layered structure on the surface while the bulk MFI zeolite kept intact in the interior of the L-Si/MFI composite. On the contrary, lamellar silicalite-1 formed an intertwined layer on the surface, and the bulk BEA was turned into a nanosponge-like structure in the L-Si/BEA composites. The epitaxial growth of silicalite-1 on bulk MFI did not cause obvious dissolution of the bulk zeolite domain, and thus created the mesoporous lamellar surface and partially passivated the external surface acid sites in L-Si/MFI zeolite. The random overgrowth, however, caused the dissolution and re-crystallization of the BEA component and consequently led to the formation of mesoporosity in bulk MFI and the mitigation of aluminum content onto the external surface of the L-Si/BEA zeolite composite. The composition and acidity analyses

confirmed the concurrent formation of mesoporosity and migration of acid sites in the formation of the zeolite composites. The implications of the presence of mesoporosity and acid site migration on the catalytic reactions were probed by the DMA reaction over the 2 wt% Mo-loaded L-Si/MFI and L-Si/BEA zeolite composites. It was shown that methane conversion, hydrocarbon production, and coke formation were all increased in Mo/L-Si/MFI and Mo/L-Si/BEA catalysts compared to those of Mo/MFI and Mo/BEA catalysts. The product selectivity analysis shows that naphthalene and coke were slightly favored in the Mo-loaded zeolite composite catalysts. The enhanced mass transport, as a consequence of mesoporosity and the passivation of external acid sites of the zeolite composites, contributed to the higher methane conversion and hydrocarbon production. The mesoporosity introduced by the overgrowth of lamellar silicalite-1 on the bulk zeolites functioned as a coke reservoir and thus enhanced the formation of heavier aromatic products and coke deposition in the catalysts.

Chapter 7: Conclusion remarks and Future work

7.1. Conclusion remarks

In this study, we have systematically and rigorously evaluated the application of 2D lamellar zeolites in the DMA reaction. The interlayer mesoporosity originating from the 2D lamellar structure that comprises ultra-thin zeolitic nanosheets with micropores within each layer and mesopores between zeolitic layers facilitated the mass transport of bulky molecules, enhanced the accessibility of active sites and increased the tolerance for harmful coke deposition, leading to significant improvement in the catalytic activity, stability and selectivity of Mo-loaded 2D zeolite catalysts in the DMA reaction.

On the other hand, compared to conventional microporous zeolites, the high external surface area of 2D zeolites provides a large amount of external acid sites, which have inferior selectivity to desired products compared to those inside the micropores due to the lack of the shape selective environment. Given the importance of the acid site distribution to the catalytic performance of 2D zeolites, the other part of this study was focused on the identification, quantification and performance evaluation of the external acid sites in 2D zeolites. In this study, we deactivated the external acid sites by using the state-of-art ALD technique and found that ALD modification did not alter the intrinsic activity of acid sites or block the porous channels and was capable of promoting the catalytic performance of 2D zeolites in the DMA reaction. Furthermore, we have identified and quantified the spatial distribution of a third type of acid site, the pore mouth acid sites located at the pore openings in 2D

zeolites, and studied its distinct catalytic activity and selectivity in acid catalyzed reactions. Lastly, we proposed to grow lamellar silicalite-1 nanosheets onto the commonly employed microporous MFI and BEA zeolites to form a lamellar silicalite-1/MFI or BEA zeolite composite. This composite structure was capable of deactivating the external acid sites in the MFI and BEA zeolites and simultaneously retained the facile mass transport of bulky molecules due to the mesoporosity in the lamellar silicalite-1 nanosheets.

(1) In Chapter 2, we identified and quantified the spatial distribution of acid sites on the external surface (external surface acid sites), at the pore openings (pore mouth acid sites) and inside the micropores (internal acid sites). These three types of acid sites have distinct selectivities and activities due to the difference in their local shape-selective environments. The quantification of acid sites on the external surface and at the pore mouth regions in 2D PMFI and PMWW zeolites was conducted via three approaches: DME titration of acid sites before and after the external surface of zeolites passivated by SiO₂-species, methanol dehydration over PMFI and PMWW with cumulative addition of TPP or DTBP titrants, and methanol dehydration over Si-PMFI and Si-PMWW with cumulative addition of DTBP titrants. The fractions of external surface or pore mouth acid sites identified by these methods consistently showed that PMFI and PMWW had 32% and 33% external surface acid sites, and 6% and 31% pore mouth acid sites, respectively. The catalytic behavior of the individual external surface or pore mouth acid site was evaluated by alkylation of benzyl alcohol in mesitylene with the cumulative addition of DTBP or TPP titrants, and the results

showed that the pore mouth acid sites and external surface acid sites had different rate constants in the alkylation reaction.

(2) In Chapter 3, we evaluated the catalytic performance of 4.7 wt% Mo/lamellar MFI and Mo/lamellar MWW catalysts in the DMA reaction in order to study the effect of mesoporosity on the activity, stability and selectivity of catalysts. Compared to their corresponding Mo-loaded microporous zeolites, the Mo-loaded lamellar zeolites showed a higher methane conversion, a higher aromatic production, and more coke accumulation in the initial stage of the reaction. This promoting effect of mesoporosity can be attributed to the easy access of the active sites, enhanced mass transport of bulky aromatics products and increased tolerance to the coke accumulation in Mo-loaded lamellar zeolites. However, in the long term, the catalytic performance of Mo/lamellar zeolite catalysts gradually became comparable to their microporous counterparts because the formation of coke blocked the mesopores and thus offset the beneficial effects of mesoporosity.

Inspired by the positive effect of mesoporosity in 2D zeolites and its limitation in the long term, in Chapter 4, we systematically studied implications of the tunable meso-/microporosity on the spatial distribution and catalytic performance of metal-acid sites in Mo/lamellar MFI catalysts in the DMA reaction. The meso-/microporous lamellar MFI zeolite was prepared by a dual template synthesis strategy with C₂₂₋₆₋₆ as the mesopore-forming agent and the TPAOH as the micropore-forming agent, and the ratio of meso-/microporosity in these lamellar MFI zeolites was tailored by simply tuning the ratio of C₂₂₋₆₋₆/TPAOH. A volcano-type dependence between the hierarchy factor ($\frac{V_{\text{micro}}}{V_{\text{total}}} \times \frac{S_{\text{ext}}}{S_{\text{total}}}$), distribution of Brønsted acid sites and Mo sites, and aromatics production rate,

respectively, with the ratio of C₂₂₋₆₋₆/TPAOH in the hydrothermal synthesis suggest that a balance between the meso- and microporosity is essential to achieve the desired textural properties and active site distribution as well as to optimize the catalytic performance in the DMA reaction. This work demonstrated that, for the first time, optimization of the contributions from the meso- and micropores in hierarchical zeolites to the catalytic reactions can be achieved by the one-step simple and versatile dual template synthesis method.

(3) In Chapter 5, in order to deactivate the external acid sites in 2D zeolites and study the consequent effect on their catalytic performance, we modified the external surface composition of 2D PMWW and PMFI zeolites via ALD of silica species or alumina species. By selecting proper ALD precursors with kinetic diameters larger than the micropore sizes of PMFI and PMWW zeolites, we found that ALD modifications kept micropores almost intact but considerably decreased mesopore volume in both 2D zeolites. It is worth noting that the ALD-Si moderately decreased the external surface acidity but ALD-Al increased the surface acidity and diversified the types of acid sites. By using ethanol dehydration and alkylation & etherification of benzyl alcohol in mesitylene as probe reactions, we found that both ALD-Al and ALD-Si modifications did not influence the intrinsic catalytic behaviors of Brønsted acid sites in PMWW and PMFI zeolites but were capable of tuning the catalytic selectivity of external acid sites in the alkylation of benzyl alcohol with mesitylene. The elimination of external active sites by ALD-Si of PMFI zeolite improved the activity of Mo-loaded PMFI catalyst and tuned its selectivity in the DMA reaction. The present study exemplified for the first time that the external composition and acidity of 2D zeolites were tailored by ALD

modification to impact their activity and selectivity in catalytic reactions at different levels.

(4) In Chapter 6, the overgrowth of lamellar silicalite-1 nanosheets on the surface of microporous MFI and BEA zeolites was carried out via a simple one-step hydrothermal overgrowth method to form L-Si/MFI and L-Si/BEA zeolite composites in order to deactivate the external acid sites in MFI and BEA zeolites while avoiding pore blockage. The lamellar silicalite-1 formed an ordered, layered structure on the surface of L-Si/MFI, and the bulk MFI zeolite kept intact in the composite. In contrast, lamellar silicalite-1 formed an intertwined layer on the surface of L-Si/BEA with the bulk BEA partially converted into a nanosponge-like structure. The epitaxial growth of lamellar silicalite-1 on bulk MFI created the mesoporous lamellar surface and partially passivated the external surface acid sites in L-Si/MFI. On the other hand, the random overgrowth of lamellar silicalite-1 on bulk BEA zeolite caused the dissolution and re-crystallization of the BEA component and consequently led to the formation of mesoporosity in L-Si/BEA. Compared to their corresponding Mo-loaded microporous MFI and BEA zeolite catalysts, 2 wt% Mo-loaded L-Si/MFI and L-Si/BEA catalysts showed a higher methane conversion, a higher hydrocarbon formation rate and more coke accumulation in the DMA reaction. Furthermore, the presence of mesopores resulted in a higher selectivity towards naphthalene. The enhanced mass transport due to the mesoporosity and the passivation of external acid sites of zeolite composites contributed to the improved catalytic performance and the enhanced selectivity to heavier aromatics.

7.2. Future directions

(1) Reaction mechanism of the DMA reaction over Fe@SiO₂ catalyst

In 2014, Bao's group reported a novel catalyst in the DMA reaction with 0.5% Fe embedded in the framework of silica to form Fe@SiO₂ catalyst. This catalyst resulted in 48% conversion of methane at 1363 K with negligible formation of coke [67]. Furthermore, the Fe@SiO₂ showed excellent selectivity to ethylene and aromatics with 50% ethylene selectivity, 25% benzene selectivity and 25% naphthalene selectivity. Despite the study of its catalytic performance, the reaction mechanism for the Fe@SiO₂ catalyst is rarely available. Therefore, in the future, we would like to prepare the Fe@SiO₂ catalyst, evaluate its catalytic performance in the DMA reaction and reveal the reaction mechanism.

(2) Spatial distribution of transition metal sites in 2D lamellar zeolites

2D lamellar zeolites are a novel type of support materials for metal oxide species. Efforts have been made to explore the performance of metal oxide species supported on 2D zeolite substrates in catalytic reactions, but the location and local structure of metal oxide species remain elusive. In the metal-loaded zeolite catalysts, acid sites function as the anchors for metal sites. Therefore, because of the difference in the local environments of acid sites, the metal sites may also have different selectivity and activity in catalytic reactions and therefore, their spatial distribution is worth a systematic study. Rhenium-loaded MFI zeolite catalyst (Re/MFI) has shown a comparable performance to Mo/MFI catalyst in the DMA reaction. Furthermore, it has been reported that, in the Re/zeolite catalyst, Re species anchored onto the Brønsted acid sites of zeolite to form isolated Re-oxo tetrahedral monomers with +7 valence,

which was independent of the loading amount of Re precursors [221, 222]. Therefore, by taking advantage of the simplicity of this Re anchoring mode in MFI zeolite, we would like to study the spatial distribution and the structure of Re species in the 2D PMFI and PMWW zeolites to reveal the correlation among distribution, structure and catalytic performance of Re active sites.

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