

SYNTHESIS OF MESOPOROUS [Al]-[B]-ZSM-5, -SSZ-13 AND -SSZ-39 FOR
METHANOL TO OLEFINS PROCESS

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FOR METHANOL TO OLEFINS PROCESS**

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ABSTRACT

SYNTHESIS OF MESOPOROUS [Al]-[B]-ZSM-5, -SSZ-13 AND -SSZ-39 FOR METHANOL TO OLEFINS PROCESS

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Light olefins such as ethylene and propylene are important building blocks for modern chemistry. Traditionally they are produced from steam cracking and fluid catalytic cracking (FCC), which are energy intensive and give low olefin yields. Increasing demand of light olefins and decreasing petroleum resources give rise to development of new methods to produce light olefins. Methanol to olefins (MTO) reaction, known as a non-oil route, has attracted huge attention in the last decades as an alternative for converting methanol to light olefins using solid acid catalysts; i.e., zeolites. In this thesis, boron containing mesoporous ZSM-5, SSZ-13 and boron containing SSZ-39 were synthesized using bottom-up approaches to increase the lifetime and olefin selectivity observed on the conventional zeolite catalysts. For ZSM-5, methods such as hard-templating, soft-templating and nanosized crystals were used. For SSZ-13, soft-templating using cetyltrimethylammonium bromide was used. Amongst the synthesized ZSM-5 zeolites, highest mesopore volume was obtained from nanosized crystals; i.e., NS-[Al]-[B]-ZSM-5 which was 0.185 cm³/g; whereas, NS-[Al]-[B]-SSZ-13 (3) showed the highest mesopore volume which is 0.417 cm³/g among SSZ-13 zeolites. The increased mesopore volume in the NS-[Al]-[B]-ZSM-5 resulted in

one-and-a-half-time increase in the lifetime of conventional ZSM-5 in the methanol to olefins (MTO) reaction. On the other hand, the highest propylene selectivity (41%) is observed on mes-[Al]-[B]-ZSM-5 due to selective incorporation of Al atoms and low defect-concentration of the synthesized zeolite.

Keywords: Zeolite, Methanol to Olefins Reaction, Boron, Mesoporous Zeolites, Nanosized Zeolites



ÖZ

METANOLDEN OLEFİN REAKSİYONU İÇİN MEZOFOR [Al]-[B]-ZSM-5, -SSZ-13 VE –SSZ-39 SENTEZİ

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Etilen ve propilen gibi hafif olefinler modern kimyanın önemli yapıtaşlarıdır. Günümüzde hafif olefinler yüksek enerji gerektiren dizel ve nafta gibi petrol ürünlerinin termal ve katalitik parçalanmasından oluşurlar. Nüfusun hızla artması ve petrol kaynaklarının azalması hafif olefin üretimi için başka yolları geliştirmiştir. Bu yollardan biri de metanolden olefin üretilmesidir. Bu tezde, katalizör ömrünü ve olefin seçiciliğini artırmak için aşağıdan yukarıya sentez yöntemleri kullanılarak bor içeren mezo-gözenekli ZSM-5 ve SSZ-13 ile bor içeren SSZ-39 sentezlenmiştir. ZSM-5 sentezi için katı kalıp ve yumuşak kalıp kullanılmıştır. Ayrıca kalıp kullanılmadan kristal boyutunu nano boyutta küçülterek çok küçük boyutta ZSM-5 sentezlenmiştir. SSZ-13 sentezinde ise yumuşak kalıp olarak setiltrimetil amonyum bromür kullanılmıştır. Sentezlenen ZSM-5 zeolitlerinin arasında en yüksek mezo-gözenek hacmi NS-[Al]-[B]-ZSM-5’de görülmüş olup hacmi $0.185 \text{ cm}^3/\text{g}$ olarak bulunmuştur. SSZ-13 zeolitleri arasında ise NS-[Al]-[B]-SSZ-13 (3) en yüksek hacme sahiptir ve değeri $0.417 \text{ cm}^3/\text{g}$ olarak hesaplanmıştır. Normal ZSM-5 ile karşılaştırıldığında, NS-[Al]-[B]-ZSM-5’de mezo-gözenek hacminin artması katalizör ömrünü bir buçuk kat arttırmıştır. En yüksek propilen seçiciliği ise seçici Al yerleştirilmesi ve düşük kusurlu derişimi sayesinde mes-[Al]-[B]-ZSM-5’de görülmüştür.

Anahtar Kelimeler: Zeolit, MTO reaksiyonu, bor, mezo-gözenekli zeolitler, nano-boyutlu zeolitler





To My Family

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LIST OF ABBREVIATIONS

ABBREVIATIONS

MTO	Methanol to Olefin
DME	Dimethyl ether
MeOH	Methanol
WHWV	Weight hourly space velocity
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-Ray Spectroscopy
ICP-OES	Inductively coupled plasma-optical emission spectrometer
FTIR	Fourier Transform Infrared
BJH	Barrett–Joyner–Halenda Adsorption model
MAS-NMR	Magic angle spinning neutron magnetic resonance spectroscopy
HTI	Hydrogen transfer index
TGA	Thermal gravimetric analysis
SDA	Structure direction agent
CTABr	Cetyltrimethylammonium bromide

LIST OF SYMBOLS

SYMBOLS

T	temperature, °C
λ	wavelength, Å
F	molar flow rate, mol/min
P	pressure, Pa
MW	molecular weight, g/mol
Q	flow rate, cm ³ /min
R	gas constant, $\frac{Pa \cdot m^3}{gmol \cdot K}$
RF	response factor, $\frac{ppm}{area}$
WHSV	weight hourly space velocity, h ⁻¹

CHAPTER 1

INTRODUCTION

Zeolites are crystalline aluminosilicates having three dimensional framework structures composed of corner tetrahedral T atoms linked to oxygen atoms (TO_4 , $\text{T}=\text{Si}$, Al). They contain highly ordered pores with uniform size in the range of ~ 0.4 nm to 1.5 nm [1]. General formula of the zeolite is $\text{M}^{n+} x/n \cdot (\text{AlO}_{4/2})^- x (\text{SiO}_{4/2}) y \cdot z \text{H}_2\text{O}$.

Zeolites are found in nature and they can be synthesized. First natural zeolites were discovered in 1756 by the Swedish mineralogist A. F. Cronstedt [2]. He gave the name 'zeolite' coming from the Greek words meaning 'boiling stone'. They were found in vugs and cavities of basaltic rocks and in sedimentary rocks [3]. Faujasite, mordenite, chabazite, erionite, ferrierite and clinoptilolite are some of the examples of natural zeolites. These zeolites are used as adsorbents and ion-exchangers. Also they can be used for separation and purification reactions. However, natural zeolites contain impurity phases and therefore they do not have uniform pore sizes so their application fields are limited especially in catalysis. For this reason, mainly synthetic zeolites are used in catalytic applications.

1.1 Properties of Zeolites

Zeolites have fascinating and special properties such as physical and chemical stability, tunability of the pore size, composition and acidity. Zeolites have uniform tunable pores. Tunability of pore size is a very important property for catalytic applications because the pore size affects reactant, product and transition state selectivity. Uniform pores of zeolites enable zeolites to act as molecular sieves. The molecules having larger size than zeolite pores are not allowed inside the zeolite crystals; however, the small size molecules can enter the zeolite crystals providing

reactant selectivity. Product and transition state selectivity are not only determined by pore size but also by the shape of the pore structure. Shape and size of the zeolite pores prevents the formation of a molecule that does not fit inside the zeolite framework. Also, products that are too large does not desorb from the pores. In addition to shape selectivity and size of the zeolites pore, thermodynamic effects must also be considered. According to thermodynamics, the molecule having lowest free energy of adsorption can be adsorbed and then can react. Also, the molecules having lowest free energy of formation in the adsorbed phase can form as transition state molecules and products having highest adsorption free energy can be desorbed. Review article written by Smit gives more information about thermodynamic effects and shape selectivity [4].

Tunability of composition is another important property of zeolites. According to Loewenstein's Rule, the linkage of two tetrahedral Al atoms is forbidden [5] so Si/Al ratio can range from 1 to infinity. This wide range of the Si/Al ratio facilitates the application of zeolites (details will be given in the next section). Low Si/Al ratio (high Al concentration) causes a higher density of negative charge in the zeolite framework, which can be compensated by extraframework cations such as H^+ , alkali, alkaline earth and transition metal cations as shown in Figure 1.1.

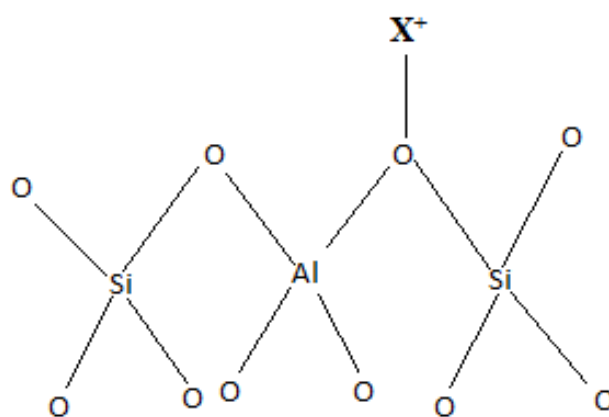


Figure 1.1. Common representation of extraframework cation of zeolite

Acidity is very important for zeolites. There are two types of acid site in the zeolites, which are Bronsted and Lewis acid sites. Isomorphous substitution of Si^{4+} by trivalent metal cation such as Al^{3+} results in negative charges in the framework. These negative charges are compensated by hydroxyl protons or metal cations occurring Bronsted acid sites or Lewis acid sites, respectively [6].

Because of all of these properties, zeolites are very important and they have large usage areas for many applications.

1.2 Applications of Zeolites

Zeolites are widely used in chemical industry with many applications such as ion-exchangers, adsorbents, catalysts, in separation and purification processes.

Zeolites having maximum cation exchange capacity are preferred as ion-exchangers and adsorbents. To have maximum cation exchange capacity, a zeolite should contain an equal number of aluminum and silicon atoms linked to an oxygen atom [7]. The largest ion exchange market for zeolites is detergents [8]. Zeolite A, Zeolite P and Zeolite X have been mostly used for detergents [9]. Some of the adsorption examples may include: adsorption of carbon dioxide and methane on different zeolites such as ZSM-5 [10], zeolite 13X [11] and zeolite 5A [12], separation of CO_2 from flue gas using SSZ-13 [13] and NaK-Zeolite A [14] as adsorbents and H_2 storage on Cu-exchanged and boron containing zeolites such as ZSM-5 and SSZ-13 [15], [16]. Also zeolite membranes have been used for separation processes. For example, isopropyl alcohol/ H_2O mixture was separated using MOR zeolite membrane [17] and CO_2 and CH_4 were separated using CHA membrane [18].

Zeolites having high adsorption capacity such as zeolite X and A were used to purify water from heavy metals [19]. Also, HEU type zeolite membranes can remove metal cations and toluene from synthetic seawater [20].

Zeolites are mostly used as catalyst so they are very important for chemical industry. For catalytic application purposes, zeolites having high silica content are interesting

because higher silicon atom concentration makes them resistant to high temperatures. Apart from their thermal stability, the reasons for their importance in catalysis is due to the following features. Firstly, they are non-toxic. Also, they have high surface area so they have high density of active sites [21]. Moreover, the adsorption properties of zeolites can be varied from hydrophobic to hydrophilic type materials and their adsorption capacity is very high [22]. They have channels and cavities which are in the range of 5–15 Å [22] and uniform pores, which allow shape-selective catalysis. Furthermore, they have varying diffusion path length due to different crystal sizes of zeolites. Variable Si/Al ratio that can be changed during synthesis and using post-synthesis method, enables tuning of zeolite acidity. In addition to that, substitution of Al atom by B, Ga, Fe and Ti can change the acidity of zeolites (additional information given in the next chapter) [23].

In refinery and petrochemical industry, zeolites are used for fluid catalytic cracking and hydrocarbon cracking reactions [8]. Also, they can catalyze some reactions such as methanol to olefin [24], isomerization [25] and alkylation of hydrocarbons [26].

1.3 Synthesis of Zeolites

Zeolites can be synthesized in laboratory via hydrothermal conditions. Hydrothermal synthesis occurs under high temperature (100~1000 °C) and pressure (1~100 MPa) in aqueous solution using a high pressure autoclave. In a typical hydrothermal synthesis procedure, a source of alumina and a source of silica are dissolved in a basic aqueous solution. Mostly, water is used as the solvent. Water plays significant roles for hydrothermal synthesis. For example, it acts as a solvent and accelerates the reactions. Zeolites are formed by building of corner sharing SiO_4 and AlO_4^- tetrahedra giving rise to three dimensional four connected different types of frameworks. Up to the present, thousands of zeolites have been synthesized. Zeolites have been grouped as their structure types. The Structure Commission of the International Zeolite Association (IZA) has assigned to three-letter codes for each of them. There exist 248 structure types of zeolites and zeotype framework approved by IZA [27].

1.3.1 Important Parameters in Zeolite Synthesis

There are lots of variables that affect the synthesis of zeolites. Some of them are silicon and aluminum sources, Si/Al ratio, alkalinity, amount of water, structure directing agent, crystallization temperature and time, aging, seeding and stirring.

1.3.1.1 Silicon and Aluminum Sources

Colloidal silica, fumed silica, tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) are commonly used silica sources. Silica sources affect the nucleation and crystallization of zeolites so they influence the size and morphology of zeolite crystals. Each silica source has different surface areas. Silica sources having high surface area are dissolved easily. They give rise to faster nucleation, forming small crystals. On the other hand, to form large crystals, silica sources having low surface area and low solubility are necessary. These silicon sources are less reactive so they cause less nucleation [28]. Sodium aluminate, aluminum isopropoxide, aluminum nitrate and aluminum hydroxide are some of the aluminum sources using synthesis of zeolite. Different aluminum source may change the framework of zeolite because it affects the crystallization of zeolites [29]. For example, Sano et al. synthesized MOR type zeolites using different aluminum source. He observed that when aluminum chloride (AlCl_3) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) were used as an Al source, pure MOR-type zeolite was obtained. On the other hand, beta type zeolite was synthesized using aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) [30].

1.3.1.2 Si/Al Ratio

Si/Al ratio is very important variable for synthesis of zeolites because it determines the application field of zeolites. As mentioned before, for ion exchange process, zeolites having same amount of aluminum and silicon ($\text{Si/Al} \sim 1$) are necessary while high silica content zeolites are used as catalyst. Si/Al ratio in the synthesized zeolite

cannot be easily arranged by changing the Si/Al ratio in the synthesis gel. To get desired Si/Al ratio in the obtained product, some additional conditions are required such as specific SDA and fluoride synthetic medium [31].

1.3.1.3 Alkalinity

Zeolites are mostly synthesized under basic conditions. Alkalinity increases the solubility of the silicon and aluminum sources so when alkalinity increases, the induction and nucleation periods decrease and the crystallization of zeolites accelerates. Because of the high crystallization rates, smaller particles are produced [32]. Also, increasing alkalinity leads to form aluminum rich zeolites.

1.3.1.4 Amount of H₂O

The most used solvent for synthesis of zeolite is water. When water content changes, reactants concentration also changes, affecting the crystallization of zeolites. If water content increases, larger crystals can be produced because crystal growth is favored [2].

1.3.1.5 Structure Directing Agent (SDA)

SDAs are very important parameter for zeolite synthesis. They influence the formation of zeolites. Certain framework is formed from a specific SDA (see Table 1.1). Different SDAs direct to different structural units, cavities and cages. Thus, proper SDA must be chosen to obtain desired zeolite framework. Also, SDA is a critical parameter to synthesize high silica zeolites [33].

Table 1.1 Structure direction agents for different zeolites structure

Zeolite Structure Types	SDAs
MFI	tetrapropylammonium bromide (TPABr) tetrapropylammonium hydroxide (TPAOH)
CHA	N,N,N-trimethyladamantanammonium hydroxide (TMAdaOH)
AEI	Cis, trans-1,1,3,5-Tetramethylpiperidinium hydroxide

1.3.1.6 Crystallization Temperature

Crystallization temperature is also an important factor for zeolite synthesis because it affects the nucleation, crystal growth and morphology. Nucleation rate and crystal growth rate increases with increasing crystallization temperature, particularly the crystal growth rate over the nucleation rate. Thus, zeolite crystals get larger with increasing temperature [34]. Also, during the synthesis, many factors change with crystallization temperature such as polymerization reaction between the polysilicate and aluminate anions, formation, dissolution and transformation of the gel and the phase transition of metastable phases. These factors result in formation of different zeolites having different pore diameter, volume and framework density [3]. Therefore, to obtain desired zeolite, it must be synthesized within a specific temperature range.

1.3.1.7 Crystallization Time

Crystallization time affects the crystallinity and it improves with time [34]. However, thermodynamically, zeolites are metastable phases. Firstly, one metastable phase occurs then more stable phases replace it and each other so a zeolite can become another zeolite with increasing time. For example, a prolonged crystallization time leads to phase transformation from NaA zeolite (LTA framework) to sodalite (SOD framework) [35]–[37]. For this reason, to obtain desired zeolite, suitable time is determined [2].

1.3.1.8 Aging

Aging, the period between the formation of homogeneous mixing of the zeolite gel and the beginning of the crystallization, is another variable to affect the nucleation and crystal growth of zeolites. It has commonly been assumed that first nuclei are formed during aging period. While nucleation is accelerated, induction period and crystallization time decrease with aging. Thus, the crystal size can be reduced and crystal population increases with the help of the aging [38].

1.3.1.9 Stirring

Stirring can affect crystallization kinetics and the crystal size. In a stirred system, because of faster mass transfer rates, rapid supersaturation is obtained. This causes getting smaller zeolite crystals. Also, stirring can result in formation of different zeolite phases. To illustrate, while TON zeolite can synthesize with stirring, MEL zeolite form statically at the same conditions [39].

1.3.1.10 Seeding

A small amount of zeolite is used in the synthesis mixture for seeding method. Seeding results in faster crystallization and small crystals for slightly supersaturated system [40].

1.4 Mesoporous Zeolites

As mentioned before, zeolites have interconnected micropores displaying narrow pore size distribution ranging between ~0.4 nm to 1.5 nm. Although these order pores make them suitable molecular sieve and shape selective catalysts, small micropores cause some problems especially in the area of catalysis. Firstly, molecules with sizes larger than about 1.5 nm do not enter the internal surface of the zeolites so these larger

molecules are converted on the external surface of the zeolites, which is causing low conversion of the reactants [41]. Also, even if reactants are small enough to enter the zeolite pores, small micropores cause slow mass transport to and away from the catalytic centers due to larger diffusion path length [42]. Slow mass transport can decrease the catalytic conversions and cause unwanted secondary reactions and coke formation [42]. This results in the accumulation of coke in the zeolite micropore and deactivation of catalysts, which reduces lifetime of catalysts [43]. To solve these problems, recently, supplementary mesopores are introduced into zeolite materials without sacrificing the zeolite structure. According to IUPAC (International Union of Pure and Applied Chemistry) classification of pores, pores in the range of 2 to 50 nm are called mesopores [44]. Additional mesopores enable larger molecules to enter the zeolite internal surfaces. Also, they accelerate catalytic conversions by a faster diffusion and mass transport [45]. Moreover, unwanted secondary reactions and coke formation can be avoided. For these reasons, recently some methods have been developed to synthesize mesoporous zeolites. There are two methods to create mesoporous zeolites, which are bottom-up and top down methods (see Figure 1.2).

1.4.1 Bottom-up Methods

For bottom-up synthesis of mesoporous zeolites, a secondary porosity is added during synthesis of zeolites using templates (hard-templating and soft-templating) or relying on reaction conditions without using any template (non-templating method). While carbon compounds such as carbon nanotubes and nanoparticles [46], CaCO_3 [47] and aerogel [48] are the example of hard templates, surfactants [49] and polymers [50] are used as soft templates. For both soft and hard templating methods, templates are added to the standard synthesis zeolite gel. The zeolite is formed around template. Then template is removed by calcination. Finally, intracrystalline mesopores are generated within zeolite crystals. If synthesis conditions enable the formation of nanosized zeolites, templates are not necessary to synthesize mesoporous zeolites [51]. When the nucleation rate is faster than crystallite growth, nanosized zeolites having small crystal

size can be synthesized. Between these small crystal intercrystalline mesoporosity can be created.

1.4.2 Top-Down Methods

In contrast to bottom-up methods, in top-down methods, after the microporous zeolite is synthesized, secondary porosity is created by leaching procedures. They are also called post-treatment methods. They consist of dealumination and desilication. Although both of them have been used to create mesoporosity, major drawback of these methods is losing significant part of the zeolite mass. Dealumination is achieved by steam treatment at high temperature and acid leaching with nitric acid and hydrochloric acid to extract aluminum atoms from zeolite framework [52]. Extraction of aluminum atoms create intracrystalline mesoporosity. This method is used not only to create mesopore but also to increase Si/Al ratio. The zeolite with a higher Si/Al ratio is more stable and has higher acid strength so this method can be used for catalytic application [53]. For example, ultrastable zeolite Y with high Si/Al ratio can be synthesized using dealumination to use catalytic cracking reactions [54].

On the other hand, zeolites can be treated in an alkaline medium to remove silicon atoms from the crystal structure, which is called desilication. Under basic conditions, removing silicon atoms leads to the formation of intracrystalline mesoporosity and decreases the Si/Al ratio [45]. However, aluminum atoms in the framework suppress the extraction of silicon atoms so initial Si/Al ratio affects the desilication. For example, if Si/Al ratio of ZSM-5 zeolite is less than 15, high concentration of Al atoms in the zeolite framework prevent the extraction of Si atoms [55]. Optimal Si/Al ratio for desilication is between 25 to 50 [45].

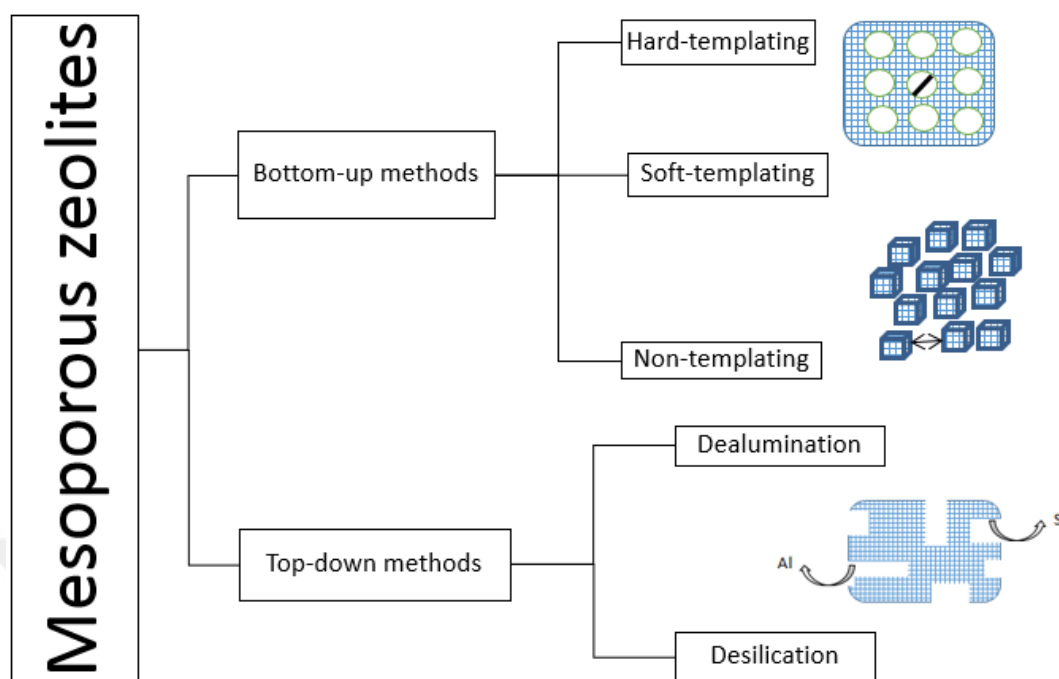


Figure 1.2. Schematic representation of synthesis methods for mesoporous zeolites

1.5 Synthesis of Mesoporous ZSM-5

ZSM-5 is a versatile zeolite having MFI topology showing a 3-dimensional two intersecting 10-ring channel system. Straight channels are interconnected by sinusoidal channels. ZSM-5 has 4-MR, 5-MR and 6-MR cage structures. These cages form two elliptical pores of $5.1 \text{ \AA} \times 5.5 \text{ \AA}$ and $5.3 \text{ \AA} \times 5.6 \text{ \AA}$. While typical crystal shape of MFI is hexagonal prismatic, referred to as a coffin shaped, unit cell of MFI structure is orthorhombic. ZSM-5 has been widely used in chemical applications as catalyst and adsorbent. However, especially when ZSM-5 is used as a catalyst, micropores are the major limitation for many reactions as mentioned before. To overcome this problem, recently, mesoporous ZSM-5 has been created using different methods.

Madsen and Jacobsen synthesized nanosized ZSM-5 using carbon black and they created intercrystalline mesopores [56]. Then Jacobsen used carbon nanotubes and produced large zeolite crystals with intracrystalline mesopores and the mesopore

volume reached $1.01 \text{ cm}^3/\text{g}$ [57]. Moreover, Wang synthesized mesoporous ZSM-5 using two different soft templates, namely, dimethyl octadecyl [3-(trimethoxysilyl)propyl]ammonium chloride (TPOAC) and hexadecyl trimethyl ammonium bromide (CTAB) [58]. Also, Wan reported a simple method for the synthesis of mesoporous ZSM-5 without using additional template [59]. While he used TPAOH as SDA for synthesis of mesoporous ZSM-5, TPAOH and TPABr were used as SDA to synthesize conventional ZSM-5. Also, different reactants ratios were used. He created highly crystalline, nanosized particles and between these particles intercrystalline mesopores were created.

In addition to bottom-up methods, using top-down methods mesoporous ZSM-5 have been synthesized. For example, while Rutkowska obtained mesoporous ZSM-5 by removing silicon atoms from the zeolite framework (Si/Al ratio of parent zeolite was ~ 16.5 because high concentration of aluminum prevents the extraction of silicon from the zeolite framework) [60], Li used acid treatment to extract aluminum atoms from zeolite structure and he prepared mesoporous ZSM-5 [61].

1.6 Synthesis of Mesoporous SSZ-13

SSZ-13, which is a zeolite with chabazite (CHA) structure, has 3-dimensional pore system composed of large cavities with the size of $7.3 \text{ \AA} \times 12 \text{ \AA}$ connected by small 8-ring pore openings ($3.8 \text{ \AA} \times 3.8 \text{ \AA}$). When compared to medium and large pore zeolites, these small pore openings have advantages because only small molecules diffuse in and out of the pores and selectivity toward these molecules is higher such as in the case of selective catalytic reduction of NO_x by NH_3 [62]. However, diffusion limitations can restrict reaction rates. Also, the formation of coke deposits in the cages of SSZ-13 give rise to faster deactivation and lower catalyst efficiency [63]. Introducing mesopores additional to the micropores and reduction of the crystallite size of the zeolite deal with these problems. Olsbye and co-authors used alkaline treatment to form mesoporous in the SSZ-13 crystals [64]. Moreover, Kumar obtained small zeolite crystals using CTAB in the synthesis of SSZ-13 [65]. Also, Hensen used

different templates such as diquatamary ammonium-type surfactant $C_{22-4-4}Br_2$ resulting in increasing mesoporosity [66]. However, synthesis of such diquatamary ammonium-type surfactants is rigorous.

1.7 MTO Reactions

Light olefins such as ethylene and propylene are important intermediates and building blocks in chemical industry. They can be used as the essential feedstock for the production of petrochemicals. Polymer productions such as polyethylene and polypropylene constitute the majority of olefins consumption. Also, ethylene is used to synthesize styrene, ethane oxide, vinyl chloride and some functionalized hydrocarbons such as dichloroethane, ethylbenzene and ethanol [67]. On the other hand, propylene derivatives are acrylonitrile, oxoalcohols, propylene oxide and cumene [68]. Recently, they have been produced from steam cracking [69] and fluid catalytic cracking reactions [70] using naphtha, diesel and other petroleum products. However, these methods are very energy consuming with low olefin yields [71]. Also, cracking reactions result in high amount of CO_2 [71]. Furthermore, increasing demands of light olefins, in particular, for propylene and the shortage of petroleum resources in the future give rise to development of new methods to produce high yield of olefins [72].

Instead of petroleum route, methanol-to-olefins (MTO) is one of the most promising alternative for the production of olefins, which provides producing basic petrochemicals from nonoil resources since methanol is made from synthesis gas (CO_2 and H_2), which can be produced from steam reforming of natural gas [73] and gasification of coal [74]. Therefore, the fundamental study of the MTO have attracted attention of many researchers since Mobil discovered methanol to gasoline reaction using zeolites in 1977 [75]. Then, after silicoaluminophosphate (SAPO) molecular sieves were found by scientists from Union Carbide in 1984 [76], Dalian Institute of Chemical Physics (DICP) and Chinese Academy of Sciences found that methanol could be converted to olefins by SAPO-34 [77]. The world's first MTO commercial

plant based on the DICP's MTO technology (DMTO) was constructed in August 2010 in China [78]. This is an important milestone for MTO process development. UOP and Norsk- Hydro (now INEOS) developed the SAPO -34 based MTO process in 1990s and they built a fluidized bed MTO pilot plant in 1995 [79]. In addition to Mobil, DICP and UOP, SINOPEC have developed SAPO-34 based MTO process (SMTO) since 2000 [80]. Besides all SAPO-34 based MTO process, Lurgi developed by Mobil focused on increasing propylene yield and started the development of methanol to propylene (MTP) process using ZSM-5 in 1993 [81] and first industrial MTP process was developed by Lurgi in 2010 [82].

Acidic catalyst such as zeolites are the most widely used materials for MTO since methanol has high activity over different acidic zeolites with a variety of morphologies, topologies and compositions. The MTO process has been evaluated over several types of zeolites under different reaction conditions. Some of them are ZSM-5 [83], SAPO-34 [84], MOR [85], SSZ-13 [63] and NaY [86]. ZSM-5 and SAPO-34 are mostly used zeolites for MTO process. SAPO-34 having CHA topology shows high selectivity to ethylene and propylene because of its mild acidity, shape selectivity property and effective pore size that hinder the diffusion of aromatics [87]. However, small pore openings result in the diffusion limitations of reactant and products and coke formation so it could be deactivated in several hours so a continuous regeneration is required [88]. As mentioned before, ZSM-5 has 3- dimensional interconnected straight and sinusoidal 10-ring medium sized channels. It has a higher resistance towards coke formation and higher propylene selectivity than SAPO-34 in MTO reaction due to medium pore openings. However, ZSM-5 still suffers from rapid and severe deactivation due to the coke formation, which cause shorter lifetime of catalyst and lower light olefins selectivity [89]. Many researchers have attempted to improve the selectivity of light olefins. Detailed information will be given in the next section.

1.7.1 MTO Reaction over ZSM-5 Catalyst

ZSM-5 is a high-silica zeolite, which is a promising candidate catalyst for MTO reaction due to having 10-ring medium sized channels, well-defined microporosity, high surface area, high catalytic activity, high thermal stability and high resistance to coke formation. In spite of these unique properties, due to these micropores and strong acidity, lower selectivity of propylene and catalyst deactivation because of coke formation are still an ongoing challenge in MTP process. Acidity and pore structure influence the catalytic activity and products selectivity so great efforts have been made for adjusting acidity and pore structure of ZSM-5.

1.7.1.1 Mesoporosity

As mentioned before, microporosity causes intracrystalline diffusion limitations. To overcome these problems, two different strategies have been developed in recent years. First one is to prepare nanosized ZSM-5 by reducing the crystal size of the ZSM-5 to nanometer scale, which decreases the diffusion path length, increases the external surface area and improves diffusion rate of reactants [40]. For example, Chen et al. synthesized nanocrystalline ZSM-5 by seed-induced method with CTAB. According to that article, when methanol conversions decreased to around 95 %, catalytic lifetime of nanosized ZSM-5 and conventional ZSM-5 were 40 h and 15 h, respectively [90]. Also, average value of selectivity towards propylene for nanosized and conventional ZSM-5 were 39.5 % and 35.7 %, respectively [90]. Thus, nanosized ZSM-5 had higher catalytic lifetime, higher stability and more propylene selectivity than those of conventional one. Moreover, Zhang et al. prepared mesopore containing ZSM-5 with small crystal size. Catalytic lifetime of nanosized ZSM-5 (325 h) was nearly three times longer than conventional ZSM-5 (120 h) and propylene selectivity for former ZSM-5 (46.3 %) was higher than latter one (39.8 %) [91].

Second one is to introduce secondary pores in addition to micropores to create mesoporous ZSM-5. Mesoporous ZSM-5 possesses higher catalytic activity compared

to microporous ZSM-5 because it has faster diffusion and mass transport to and away from catalytic centers, which accelerate catalytic conversions and avoid unwanted secondary reactions and coke formation. As mentioned before Wang et. al synthesized mesoporous ZSM-5 zeolite using soft template (TPOAC) for methanol to olefins reaction. It had high mesopore volume and high surface area ($0.34 \text{ cm}^3/\text{g}$, and $508 \text{ m}^2/\text{g}$). According to that article, although 100% methanol conversion was kept around 11 h for conventional ZSM-5, methanol conversion of 100% remained constant for more than 67 h for mesoporous ZSM-5 [58]. Also, propylene selectivity increased from 14.59 % to 20.83 % with increasing mesoporosity [58].

1.7.1.2 Acidity

Strong acidity initiates MTO reaction but it also accelerates the coke formation. The acidity of zeolites has a great effect on their catalytic behavior so regulation of acidity of ZSM-5 is a very important issue. There are some ways to control the acidity. One of them is that tetrahedral sites in zeolites can be isomorphously substituted by other atoms such as boron (B) [23]. Boron incorporation into ZSM-5 zeolite framework leads to an increase in the amount of weak acid sites without changing the MFI structure. Yang et al. reported that B substitution in ZSM-5 framework increased the catalyst life time up to seven times while the same propylene selectivity (40 %) was obtained [92]. Also, Yaripour et al. synthesized boron containing ZSM-5 zeolite. He observed that lifetime of boron incorporated ZSM-5 was 1300 h, whereas the lifetime of reference zeolite ([Al]-ZSM-5) was 340 h [93]. However, almost the same propylene selectivity (47.6 %) was observed in boron containing ZSM-5. Moreover, Li et al. synthesized boron containing ZSM-5 zeolite and it was deboronated to control Al distribution in the zeolite framework and get a larger concentration of acid sites in 10R channels [94]. Al-ZSM-5 enriched with Al in the 10R channels was produced by removing of B atoms. According to results, deboronated ZSM-5 was more selective to propylene (40%) and it had higher catalytic lifetime (~42 h) than conventional Al-

ZSM-5 whose propylene selectivity and lifetime of catalyst were 25 % and 20 h, respectively.

In addition to boron substitution, acidity can be adjusted by changing Si/Al ratio. Lower Si/Al ratio causes larger numbers of acid sites so methylated aromatic species formation increases. This results in higher coke formation [95]. Thus, ZSM-5 zeolite with high Si/Al ratio have been synthesized to increase selectivity of propylene and enhance lifetime of catalyst. Li et al. synthesized ZSM-5 zeolite with different Si/Al ratios and those ZSM-5 zeolites were evaluated in MTO reaction. He observed that increasing Si/Al ratio up to 220 enhanced the lifetime of catalyst and propylene selectivity. While lifetime of that zeolite was 164 h, ZSM-5 with lowest Si/Al ratio (15) has shorter lifetime of 13 h. When Si/Al ratio reached 300, lifetime decreased to 80 h but it was still higher than ZSM-5 with lowest Si/Al ratio. However, highest propylene selectivity (50.6 %) was obtained over the ZSM-5 having highest Si/Al ratio [96]. Also, Mei et al. synthesized ZSM-5 zeolites with different Si/Al ratios. According to that article, increasing Si/Al ratio decreased the Bronsted acidity and favored the formation of propylene [97]. When Si/Al ratio increased, propylene selectivity and lifetime of catalyst also increased. When Si/Al ratio increased from 11 to 72, propylene selectivity also increased from 26.7 % to 37 % and lifetime of catalyst also increased from 20 h to 140 h.

Table 1.2 MTO reaction on different ZSM-5

Zeolite	Si/Al, Si/B	Reaction conditions	CH ₃ OH conversion (%)	Propylene selectivity (%)	Lifetime (h)	Ref
Nano-Al-ZSM-5	78.5	Activated at 470 °C in 100 % N ₂ flow of 60 ml/min for 1 h, WHSV=8 h ⁻¹ with a MeOH/H ₂ O molar ratio=1:1, catalyst weight=0.5 g, reaction T=470 °C and P=1 atm	100	39	40	[90]
Mes-Al-ZSM-5	22.5	Activated at 500 °C in 100 % He flow of 30 ml/min for 1 h, WHSV=6 h ⁻¹ with carrier gas (24 ml/min), catalyst weight=100 mg, reaction T=450 °C and P=1 atm	100	21	67	[58]
Mes-Al-ZSM-5	156	WHSV=1.25 h ⁻¹ with a MeOH/H ₂ O molar ratio=1:5, reaction T=460 °C and P=1 atm	100	45	400	[98]
B-Al-ZSM-5	201, 335	WHSV=1.8 h ⁻¹ with a MeOH/H ₂ O molar ratio=1:3, catalyst weight=1 g, reaction T=460 °C and P=1 atm	100	40	700	[92]
B-Al-ZSM-5		Activated at 300 °C in 100 % N ₂ flow of 30 ml/min for 2 h, WHSV=0.9 h ⁻¹ with a MeOH/H ₂ O mass ratio=1:1, catalyst weight=4 g, reaction T=480 °C and P=1 atm	99.2	47.6	1300	[93]
Mes-Al-ZSM-5	168	Activated at 500 °C for 5 h in 100 % N ₂ flow of 30 ml/min for 2 h, WHSV=2 h ⁻¹ with a MeOH/H ₂ O molar ratio=1:1, catalyst weight=1 g, reaction T=470 °C and P=1 atm	100	46.3	335	[91]
Nano-B-Al-ZSM-5	162	WHSV=4 h ⁻¹ with a MeOH/H ₂ O molar ratio=1:3, catalyst weight=0.5 g, reaction T=460 °C and P=1 atm	100	42	725	[99]

1.7.1.3 Mechanism of MTO

MTO reaction mechanism has seen interest in recent years but it is still challenging because of some reasons. First of all, it has complex reaction network. Also, getting information about gas-phase products are difficult. Moreover, different reaction intermediates are confined within the different zeolite pores and cavities so identification of reaction intermediates are also difficult.

In a simplified route of the methanol to hydrocarbon (MTH) reaction, the methanol conversion consists of three steps [100]. Firstly, methanol is dehydrated to dimethyl ether. In the second step, equilibrium mixture of methanol, dimethyl ether and water are converted to light olefins. Then, light olefins can be converted to high olefins, naphthenes, aromatics and paraffins via oligomerization, cyclization and hydrogen transfer reaction. These reaction steps are summarized in Figure 1.3.

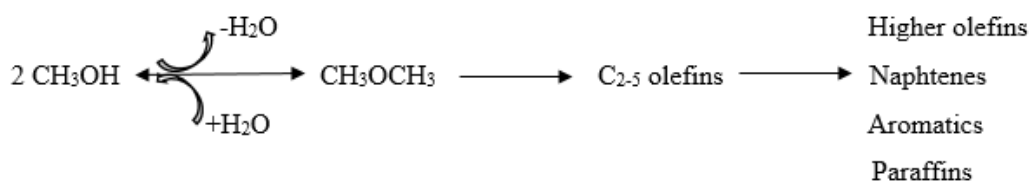


Figure 1.3. Schematic representation of MTO reaction pathway [100]

In the first step, a surface methoxyl is formed when a methanol molecule reacts with a hydroxyl group on solid acid catalyst and then it is subject to a nucleophilic attack by another methanol molecule. In the third step, higher olefins, naphtenes, aromatics and paraffins are converted from light olefins via carbenium ion mechanisms. However, mechanism of second step, the initial C-C bond formation, has been discussed and researchers have been focus on the formation of first C-C bond from methanol or DME in the MTO process. Although more than 20 possible mechanisms for initial C-C bonds have been offered such as oxonium ylides, carbocations, carbenes and free radicals, there have been little experimental evidence for these mechanisms [100].

According to hydrocarbon pool mechanism proposed by Dahl and Kolboe, light olefins, alkenes and aromatics are produced from a pool of $(CH_2)_n$ species formed from methanol as shown in Figure 1.4. This mechanism has been described for SAPO-34. The higher methylated benzenes or their protonated counterparts were the main catalytic engines of hydrocarbon pool and hexamethylbenzene displays the greatest reactivity for alkene formation for SAPO-34 [101].

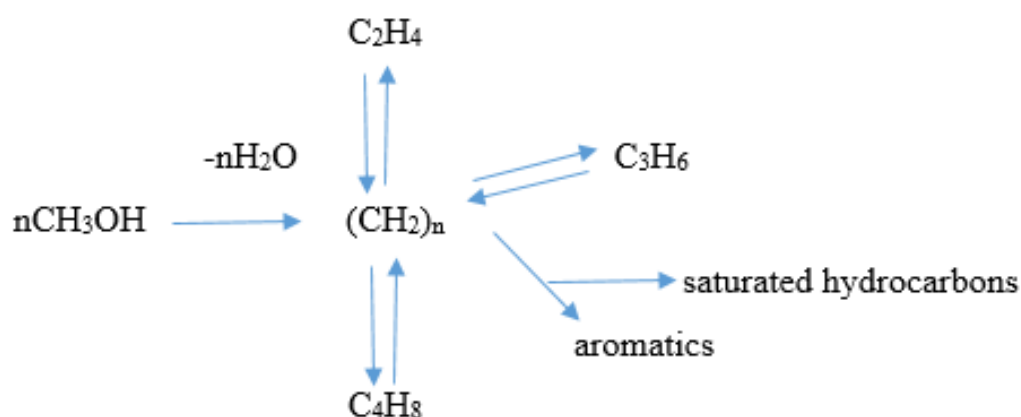


Figure 1.4. Schematic representation of Hydrocarbon Pool Mechanism proposed by Dahl and Kolboe [101]

According to the dual-cycle, two catalytic cycles operate simultaneously over ZSM-5 as shown in Figure 1.5. The first cycle is the aromatics/ ethylene cycle and the second cycle is alkene-based cycle. While alkene methylations and interconversions such as cracking reactions produce propylene and higher alkenes, ethylene are formed from lower methylbenzenes. Thus propylene/ ethylene ratio can be controlled [102].

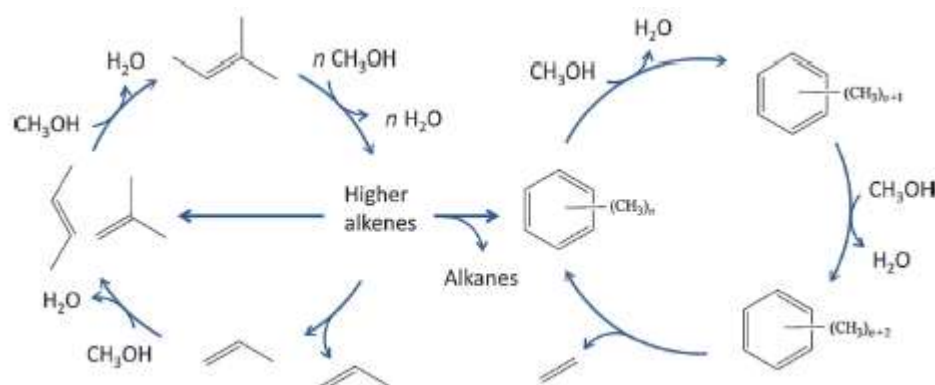


Figure 1.5. Schematic representation of Dual-cycle Mechanism for methanol conversion over ZSM-5 [102]

1.7.2 MTO Reaction over SSZ-13 Catalyst

SSZ-13 zeolite, having CHA topology, is the aluminosilicate analogue of SAPO-34. As mentioned before, due to small pore openings CHA framework has some advantages such as only small molecules can diffuse in and out of the pores. Thus, propylene and ethylene are obtained at high and similar selectivity. However, these small pores cause faster deactivation and lower catalyst efficiency so frequent regeneration is required. SSZ-13 has stronger acidity than SAPO-34 [103] so former tends to deactivate more quickly due to forming more carbonaceous deposits in the zeolite pores [64]. However, while MTO reaction can start at a higher temperature (400 °C) for SAPO-34 [103], a lower temperature (350 °C) [63] is sufficient for SSZ-13 rendering SSZ-13 a good alternative catalyst for MTO reactions.

To overcome the diffusion problems, Olsbye et al. synthesized mesoporous SSZ-13 by alkaline treatment. However, lifetime of microporous SSZ-13 is higher than mesoporous SSZ-13 because of decreasing in surface area after alkaline treatment [64]. Moreover, Zhu et al. synthesized mesoporous SSZ-13 by adding diquarternary ammonium type surfactant as a mesoporegen and fluoride anions. According to that article, while methanol conversion decreases to 50 % after 14 h for mesoporous SSZ-13, methanol conversion reached around 50 % after 2 h for conventional SSZ-13

[104]. Furthermore, Li used CTAB as mesoporegen to produce nanosized SSZ-13. Due to the presence of intercrystalline mesopores and shorter diffusion length, nano-SSZ-13 showed around two-times longer lifetime than conventional SSZ-13. Methanol conversion decreased to 50 % at 310 min for conventional SSZ-13 but 50 % conversion was obtained after 760 min for nano-SSZ-13 [63].



CHAPTER 2

EXPERIMENTAL METHODS

In this thesis, boron containing mesoporous ZSM-5, SSZ-13 and boron containing SSZ-39 were synthesized using bottom-up approaches to increase the lifetime and olefin selectivity observed on the conventional zeolite catalysts. The schematic drawing for the summary of the zeolites synthesized are given in Figure 2.1.

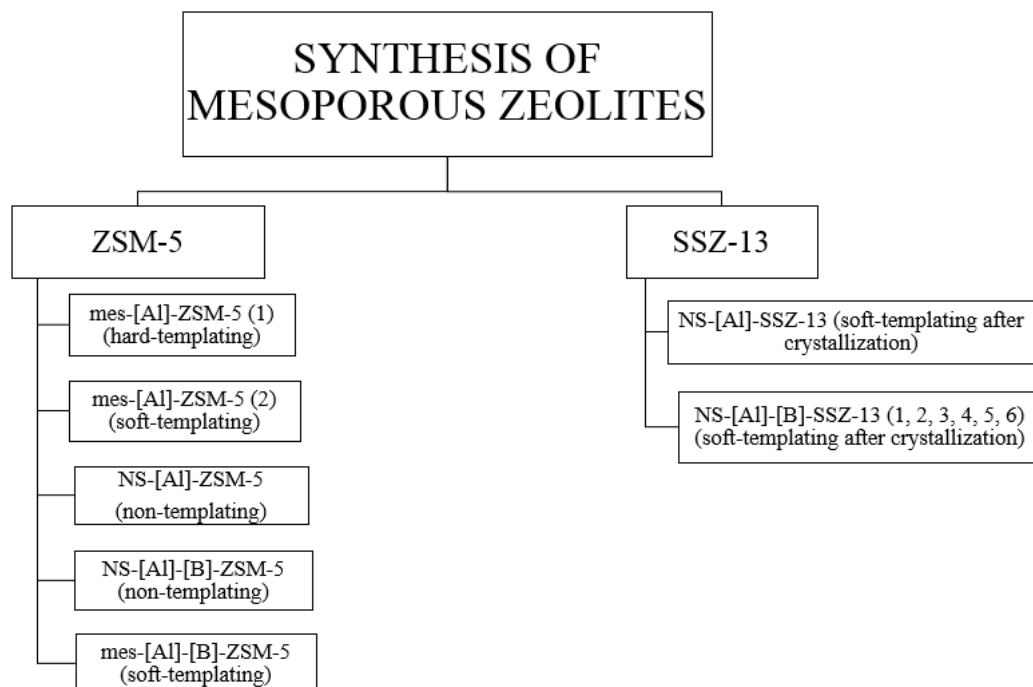


Figure 2.1. Synthesis methods for mesoporous zeolites

2.1 ZSM-5 Synthesis Procedures

2.1.1 Conventional [Al]-ZSM-5

Conventional [Al]-ZSM-5 was synthesized hydrothermally following a similar procedure reported by Zhang et al. [105] using a gel formula of 1 SiO₂: 0.00877 Al₂O₃: 0.255 Na₂O: 0.2562 TPABr: 182.45 H₂O. Firstly, 0.05 g sodium aluminate (Reidel De Haen, 44 wt.% Na₂O, 55 wt.% Al₂O₃, 1 wt.% H₂O, NaAlO₂) and 0.6 g of sodium hydroxide (Merck, 99 wt.%, NaOH) were dissolved in 101.25 mL H₂O and stirred for 12 hours at 25 °C. 6.425 g of tetraethyl orthosilicate (Merck, 98 wt.%, TEOS) was then added dropwise under agitation, followed by 2.1 g of tetrapropylammonium bromide (Merck, >99 wt.%, TPABr) as the structure direction agent (SDA) and stirred for additional 12 hours. Then, the mixture was transferred into 35 mL Teflon-lined autoclaves and statically heated at 175 °C for 3 days. After crystallization, the solid was separated using vacuum filtration, washed with de-ionized water, dried at 100 °C for 12 hours and calcined at 550 °C using a heating rate of 1 °C /min for 5 hours using muffle furnace.

2.1.2 Mesoporous [Al]-ZSM-5 (Using Hard Template) (Mes-[Al]-ZSM-5 (1))

The hierarchical [Al]-ZSM-5 was synthesized hydrothermally using a modified version of a procedure reported by Zhang et al. [105]. Molar composition of the mixture was 1 SiO₂: 0.00877 Al₂O₃: 0.255 Na₂O: 0.2562 TPABr: 182.45 H₂O. Firstly, 0.1 g of NaAlO₂ (Reidel De Haen, 44 wt.% Na₂O, 55 wt.% Al₂O₃, 1 wt.% H₂O) and 1.2 g of NaOH (Merck, 99 wt.%,) were dissolved in 202.5 mL H₂O and stirred for 12 hours at 25 °C. Then 12.85 g of TEOS (Merck, 98 wt.%) was added dropwise under agitation followed by, 6 g of carbon template (Printex U, carbon black 25 nm) as mesoporegen and 4.2 g of TPABr (Merck, >99 wt.%) as SDA were added and stirred for additional 12 hours. Then, the mixture was transferred into 35 mL Teflon-lined

autoclaves and heated at 175 °C for 3 days. After crystallization, the solid was vacuum filtered and washed with 250 mL de-ionized water. Obtained product was dried at 100 °C for 12 hours and calcined at 600 °C using a heating rate of 1 °C/min for 24 hours using muffle furnace.

2.1.3 Mesoporous [Al]-ZSM-5 (Using Soft Template) (Mes-[Al]-ZSM-5 (2))

Mesoporous [Al]-ZSM-5 was synthesized hydrothermally following a procedure similar to Xue et al. [106] using a gel mixture with the molar composition of 1 SiO₂: 0.0167 Al₂O₃: 0.13 Na₂O: 0.14 HDA: 0.1 CTABr: 60 H₂O. Firstly, 0.87 g of NaOH (Merck, 99 wt.%) and 0.31 g of NaAlO₂ (Sigma Aldrich, 50-56 wt.% of Al₂O₃, 37-45 wt.% of Na₂O) were dissolved in 108 g of hot de-ionized water. After the mixture cooled to room temperature, 3.72 g of cetyltrimethylammonium bromide (Sigma Aldrich, 98 wt.%, CTABr) as mesoporegen and 1.66 g of 1, 6-diaminohexane (Sigma Aldrich, 98 wt.%, HDA) as SDA were added and dissolved. Then, 6.01 g of fumed silica (Sigma Aldrich, 99.8 wt.%) was added. After the obtained homogeneous white mixture was stirred for 6 hours at 25 °C, it was transferred into a 35 mL Teflon-lined autoclave and statically heated at 150 °C for 28 days. The product was recovered by vacuum filtration and washed with de-ionized water. Then, synthesized zeolite was dried at 70 °C, and calcined under flowing air (40 cm³/min flow rate) at 580 °C for 10 hours with a heating rate of 1 °C/min.

2.1.4 Nanosized [Al]-ZSM-5 (NS-[Al]-ZSM-5)

Nanosized [Al]-ZSM-5 was synthesized hydrothermally according to procedure reported by Wan et al. [59]. 0.235 g of NaAlO₂ (Sigma Aldrich, 50-56 wt.% of Al₂O₃, 37-45 wt.% of Na₂O), 25.3 g of tetrapropylammonium hydroxide solution (Merck, 40 wt.% solution in water, TPAOH) as SDA were firstly dissolved in 150 mL of de-ionized water and they were stirred for 30 minutes at room temperature. Then, 27.4 g of TEOS (Merck, 98 wt.%) was added dropwise followed by, the mixture was stirred

at room temperature for 21 hours. The chemical composition of synthesis gel was Na_2O : 1 Al_2O_3 : 101 SiO_2 : 39 TPAOH: 7215 H_2O . Then, the clear mixture was transferred to a Teflon-lined autoclave, and heated at 180 °C for 3 days. The solid product was recovered by vacuum filtration and washed with deionized water. Obtained zeolite was dried at 80 °C and calcined at 550 °C using a heating rate of 1 °C/min for 5 hours under flowing 40 cm^3/min air.

2.1.5 Conventional [B]-ZSM-5

Conventional [B]-ZSM-5 was synthesized with hydrothermal technique using a similar procedure reported by Sanhoob et al. [107]. In a typical synthesis of [B]-ZSM-5, 0.96 g of NaOH (Merck, 99 wt.%) was dissolved in 124.3 g of de-ionized water. Then, 12.2 g of TPAOH (Merck, 40 wt.% solution in water) as SDA was added and stirred for a few minutes until completely homogeneous solution was obtained. After 36 g of colloidal silica (Sigma Aldrich, 40 wt.% suspension in water, LUDOX AS-40) was added dropwise under agitation, 1.48 g of boric acid (Merck, 99.5 wt.%, H_3BO_3) was added to the mixture. The resulted mixture had a molar composition of 1 SiO_2 : 0.1 TPAOH: 0.1 NaOH: 0.1 H_3BO_3 : 35.5 H_2O . The clear solution was stirred for 2 hours at room temperature and then transferred into Teflon-lined autoclaves and heated at 180 °C for 3 days. The product was recovered by vacuum filtration and washed with de-ionized water. Then, the solid was dried at 80 °C, and calcined using muffle furnace at 550 °C for 6 hours using a heating rate of 1 °C/min.

2.1.6 Mesoporous [B]-ZSM-5 (Using Soft Template) (mes1-[B]-ZSM-5, mes2-[B]-ZSM-5 and mes3-[B]-ZSM-5)

Mesoporous [B]-ZSM-5 zeolites were synthesized using a modified version of a procedure reported by Xue et al. [106]. Molar composition of the mixture was 1 SiO_2 : x H_3BO_3 : 0.13 Na_2O : 0.14 HDA: 0.1 CTABr: 60 H_2O (x is 0.032 (mes1-[B]-ZSM-5), 0.064 (mes2-[B]-ZSM-5) and 0.128 (mes3-[B]-ZSM-5)). In a synthesis of mes3-[B]-

ZSM-5, 1.5 g of NaOH (Merck, 99 wt.%) and 1.1 g of H₃BO₃ (Merck, 99.5 wt.%) were firstly dissolved in 156 g of distilled water. Then, 5.37 g of CTABr (Sigma Aldrich, 98 wt.%) as mesoporegen and 2.39 g of HDA (Sigma Aldrich, 98 wt.%) as SDA were added and dissolved. After 8.67 g of fumed silica (Sigma Aldrich, 99.8 wt.%) was added, the resulting mixture was stirred for 6 hours at 25 °C to obtain homogeneous white solution. Then, it was transferred into a Teflon-lined autoclave and heated at 150 °C for 14 days. The product was separated by vacuum filtration, washed with de-ionized water and dried at 70 °C. Mes3-[B]-ZSM-5 was calcined using the calcination procedure given for mes-[Al]-ZSM-5 (2).

2.1.7 Nanosized [B]-ZSM-5 (NS1-[B]-ZSM-5, NS2-[B]-ZSM-5 and NS3-[B]-ZSM-5)

Nanosized [B]-ZSM-5 zeolites were synthesized hydrothermally using a modified version of the procedure reported by Wan et al. [59] using a mixture with the molar composition of 1 Na₂O: x H₃BO₃: 101 SiO₂: 39 TPAOH: 7215 H₂O (x is 2 (NS1-[B]-ZSM-5), 4 (NS2-[B]-ZSM-5), 8 (NS3-[B]-ZSM-5)). For synthesis of NS1-[B]-ZSM-5, firstly, 0.027 g of H₃BO₃ (Merck, 99.5 wt.%), 0.05 g of NaOH (Merck, 99 wt.%) and 4.36 g of TPAOH solution (Merck, 40 wt.% solution in water) as SDA were dissolved in 25.8 g of de-ionized water at room temperature for 30 minutes. Then, 4.7 g of TEOS (Merck, 98 wt.%) was added dropwise. After the clear solution was stirred at room temperature for 20 hours, it was transferred to a Teflon-lined autoclave and heated at 180 °C for 3 days. Then, the product was cooled and it was recovered by vacuum filtration and washed with de-ionized water. The solid was then calcined with a similar procedure for NS-[Al]-ZSM-5.

2.1.8 Mesoporous [Al]-[B]-ZSM-5 (Using Soft Template) (Mes-[Al]-[B]-ZSM-5)

Mesoporous [Al]-[B]-ZSM-5 was synthesized hydrothermally following a modified procedure given for mes-[Al]-ZSM-5 (2) by Xue et al. [106] using a mixture with the molar composition of 1 SiO₂: 0.005Al₂O₃: 0.01 H₃BO₃: 0.01 Na₂O: 0.14 HDA: 0.1 CTABr: 60 H₂O. Firstly, 0.024 g of NaOH (Merck, 99 wt.%) and 0.081 g of NaAlO₂ (Sigma Aldrich, 50-56 wt.% of Al₂O₃, 37-45 wt.% of Na₂O) were dissolved in 94.8 g of de-ionized water. After 0.054 g of H₃BO₃ was added to the mixture, 3.26 g of CTABr (Sigma Aldrich, 98 wt.%) as mesoporegen and 1.45 g of HDA (Sigma Aldrich, 98 wt.%) as SDA were added and dissolved. Then, 5.28 g of fumed silica (Sigma Aldrich, 99.8 wt.%) was added. The obtained mixture was stirred for 6 hours at 25 °C. After it was transferred into a 35 mL Teflon-lined autoclave and heated at 150 °C for 34 days, temperature was increased to 170 °C and the hydrothermal synthesis continued for 22 more days. The product was recovered by vacuum filtration and washed with de-ionized water. Then synthesized zeolite was dried at 70 °C, and calcined at 580 °C for 10 hours using a heating rate of 1 °C/min using muffle furnace.

2.1.9 Nanosized [Al]-[B]-ZSM-5 (NS-[Al]-[B]-ZSM-5)

Nanosized [Al]-[B]-ZSM-5 was synthesized hydrothermally using a modified procedure reported by Wan et.al [59]. The chemical composition of the mixture was 1 Na₂O: 1 Al₂O₃: 20 H₃BO₃: 101 SiO₂: 39 TPAOH: 7215 H₂O. Firstly, 0.202 g of NaAlO₂ (Sigma Aldrich, 50-56 wt.% of Al₂O₃, 37-45 wt.% of Na₂O) was dissolved in 128.3 g of de-ionized water. After 21.65 g of TPAOH solution (Merck, 40 wt.% solution in water) as SDA was added to the mixture, 1.35 g of H₃BO₃ (Merck, 99.5 wt.%) was added to the mixture. The mixture was stirred at room temperature for 30 minutes. After 23.44 g of TEOS (Merck, 98 wt.%) was added dropwise, the clear solution was stirred at room temperature for 20 hours. Then, it was transferred to a Teflon-lined autoclave and heated at 180 °C for 3 days. The obtained product was

cooled and recovered using vacuum filtration and washed with de-ionized water. Then, zeolite was calcined using the same procedure given for NS-[Al]-ZSM-5.

2.2 SSZ-13 Synthesis Procedures

2.2.1 Conventional [Al]-SSZ-13

Conventional [Al]-SSZ-13 was synthesized hydrothermally using a modified procedure reported by Pham et al. [108]. Firstly, 3.58 g of aluminum ethoxide (Sigma Aldrich, 97 wt.%) was dissolved in 161.8 g of N,N,N trimethyl-1 adamantanammonium hydroxide solution (Sachem, 20 wt.%, TMAdaOH), which was used as SDA, and they were stirred with magnetic stirrer for 35 minutes at 25 °C. Then, 65.1 g of TEOS (Merck, 98 wt.%) was added dropwise to the mixture and the resulting mixture was stirred at room temperature for 90 minutes to obtain a homogeneous gel with the molar composition of 1 SiO₂: 0.035 Al₂O₃: 0.5 TMAdaOH: 20 H₂O. The synthesis gel was then transferred to 35 mL Teflon-lined autoclaves and heated at 150 °C for 7 days. After crystallization, the product was recovered by vacuum filtration and washed with de-ionized water. Then, it was dried at 80 °C and calcined at 580 °C for 7 hours with a heating rate 1 °C/min under flowing air (40 cm³/min flow rate).

2.2.2 Conventional [B]-SSZ-13

Conventional [B]-SSZ-13 was synthesized hydrothermally according to the procedure reported by Regli et al. [109]. Molar composition of the mixture was 1 SiO₂: 0.08 H₃BO₃: 0.244 TMAdaOH: 31 H₂O. In a typical synthesis procedure, firstly, 80.26 g of TMAdaOH (Sachem, 20 wt.%) as SDA, 109.5 g of de-ionized water and 1.54 g of H₃BO₃ (Merck, 99.5 wt.%) were stirred at room temperature for 30 minutes until having a homogeneous mixture. Then, 18.7 g of fumed silica (Sigma Aldrich, 99.8

wt.%) was added to the mixture and stirred for one more hour. The homogeneous mixture was then transferred to a Teflon-lined autoclave and heated at 160 °C for 6 days with a tumbling rate of 75 rpm. After crystallization, the product was recovered by vacuum filtration and washed with de-ionized water, dried at 80 °C and calcined under flowing air at 560 °C for 8 hours using a heating rate 1 °C/min using muffle furnace.

2.2.3 Nanosized [Al]-SSZ-13 (NS-[Al]-SSZ-13)

Nanosized [Al]-SSZ-13 was synthesized hydrothermally using a procedure reported Li et al. [63]. Chemical composition of the mixture was 0.1 Na₂O: 1 SiO₂: 0.025 Al₂O₃: 0.2 TMAOH: 44 H₂O: 0.12 CTABr. 38.9 g of TMAOH (Sachem, 20 wt.%) as SDA was firstly mixed with 0.97 g of NaOH (Merck, 99 wt.%) and 114.8 g of de-ionized water at room temperature until it was dissolved completely. Then, 11.07 g of fumed silica (Sigma Aldrich, 99.8 wt.%) was added to the solution. Finally, 0.85 g of NaAlO₂ (Sigma Aldrich, 50-56 wt.% of Al₂O₃, 37-45 wt.% of Na₂O) was added. The resulting gel was stirred at room temperature for one hour. After it was transferred into Teflon-lined autoclaves and heated at 160 °C for one day, 8.23 g of CTABr (Sigma Aldrich, 98 wt.%) as mesoporegen was mixed with the solution and stirred until it was completely mixed. The mixture containing CTABr was transferred into the Teflon-lined autoclave again and heated at 160 °C for 13 days. The product was recovered by vacuum filtration and washed with de-ionized water, dried at 70 °C, and calcined as explained for mes-[Al]-ZSM-5 (2).

2.2.4 Nanosized [Al]-[B]-SSZ-13 (1) (NS-[Al]-[B]-SSZ-13 (1))

NS-[Al]-[B]-SSZ-13 (1) was synthesized hydrothermally using a modified version of the procedure reported by Li et al. [63] using 1 SiO₂: 0.04 H₃BO₃: 0.04 Al₂O₃: 0.244 TMAOH: 40 H₂O: 0.06 CTABr. 10.44 g of TMAOH (Sachem, 20 wt.%) and 20.8 g of de-ionized water was firstly stirred at room temperature and 2.43 g of fumed silica

(Sigma Aldrich, 99.8 wt.%) was added slowly. Then, 0.1 g of H_3BO_3 (Merck, 99.5 wt.%) and 0.3 g of NaAlO_2 (Sigma Aldrich, 50-56 wt.% of Al_2O_3 , 37-45 wt.% of Na_2O) were added to the solution and stirred for one hour. After the mixture was transferred into Teflon-lined autoclaves and heated at 160 °C for one day using a tumbling rate of 75 rpm, 0.9 g of CTABr (Sigma Aldrich, 98 wt.%), which was used as mesoporegen, was mixed with the solution and stirred until it was completely mixed. The mixture containing CTABr was transferred into the Teflon-lined autoclave again and heated at 160 °C for 10 days using a tumbling rate of 75 rpm. The product was recovered by vacuum filtration and washed with de-ionized water, dried in air, and calcined using the same procedure given for mes-[Al]-ZSM-5.

2.2.5 Nanosized [Al]-[B]-SSZ-13 (NS-[Al]-[B]-SSZ-13 (2, 3, 4, 5, 6))

Nanosized [Al]-[B]-SSZ-13 zeolites were synthesized hydrothermally using a modified version of the procedure reported by Li et al. [63] using 1 SiO_2 : 0.04 H_3BO_3 : 0.04 Al_2O_3 : 0.244 TMAOH: 40 H_2O : 0.12 CTABr. After 10.18 g of TMAOH (Sachem, 20 wt.%) and 20.29 g of de-ionized water was firstly stirred at room temperature, 0.09 g of H_3BO_3 (Merck, 99.5 wt.%) was added to the mixture and stirred for 30 min. Then, 2.37 g of fumed silica (Sigma Aldrich, 99.8 wt.%) was added slowly and 0.29 g of NaAlO_2 (Sigma Aldrich, 50-56 wt.% of Al_2O_3 , 37-45 wt.% of Na_2O) were added to the solution and stirred for one hour. After the mixture was transferred into Teflon-lined autoclaves and heated at 160 °C for around 65 (for NS-[Al]-[B]-SSZ-13 (2)), 50 (for NS-[Al]-[B]-SSZ-13 (3)) and 69 (for NS-[Al]-[B]-SSZ-13 (4, 5, 6)) hours with a rotation of 75 rpm, 1.76 g of CTABr (Sigma Aldrich, 98 wt.%), which was used as mesoporegen, was mixed with the solution and stirred until it was completely mixed. The mixture containing CTABr was transferred into the Teflon-lined autoclave again and heated at 160 °C for 17 days using a tumbling rate of 75 rpm. The product was recovered by vacuum filtration and washed with de-ionized water, dried in air, and calcined using the same procedure given for mes-[Al]-ZSM-5.

2.3 SSZ-39 Synthesis Procedures

2.3.1 Conventional [Al]-SSZ-39

[Al]-SSZ-39 was synthesized hydrothermally using the gel formula with a molar composition of 1 SiO₂: 0.02 Al₂O₃: 0.19 SDA: 0.25 Na₂O: 22.3 H₂O. Firstly, 23.415 g of cis, trans-1,1,3,5-tetramethylpiperidinium hydroxide (Sachem, Inc., 35.3 wt.%) as SDA was mixed with 61.8 g of de-ionized water. After 44.940 g of sodium silicate solution (Merck, 28 wt.% SiO₂, 9 wt.% Na₂O, 65 wt.% H₂O) and 3.6 gram of 1 M NaOH solution (Merck, 99 wt.%) were added and stirred for 15 minutes at room temperature, 4.49 g of NH₄-US-Y (Alfa Aesar, Zeolite Y, Si/Al=12) was added slowly to the mixture and stirred for half an hour. The synthesis gel was then transferred to Teflon-lined autoclaves and heated at 150 °C for 7 days using a tumbling rate of 45 rpm. After crystallization, the product was recovered by vacuum filtration, washed with de-ionized water and dried in air. The obtained zeolite was calcined at 560 °C for 8 hours with a heating rate 1 °C/min under flowing air with 40 cm³/min flow rate.

2.3.2 [Al]-[B]-SSZ-39 (1)

[Al]-[B]-SSZ-39 (1) was synthesized hydrothermally using the gel formula with a molar composition of 1 SiO₂: 0.038 H₃BO₃: 0.19 SDA: 0.29 Na₂O: 22 H₂O. Firstly, 5.98 g of cis, trans-1,1,3,5-tetramethylpiperidinium hydroxide (Sachem, Inc., 35.3 wt.%) as SDA was mixed with 14.5 g of de-ionized water and 0.163 g of H₃BO₃ (Merck, 99.5 wt.%) and they were stirred for 15 minutes. Then, 0.503 g of NH₄-US-Y (Alfa Aesar, Zeolite Y, Si/Al=12) and 13.85 g of sodium silicate solution (Merck, 28 wt.% SiO₂, 9 wt.% Na₂O, 65 wt.% H₂O) were added to the mixture and stirred for 30 minutes at room temperature. The synthesis gel was then transferred to Teflon-lined autoclaves and heated at 150 °C for 7 days using a tumbling rate of 45 rpm. After the product was recovered by vacuum filtration, washed with de-ionized water and

dried in air, it was calcined using the same procedure given for conventional [Al]-SSZ-39.

2.3.3 [Al]-[B]-SSZ-39 (2)

[Al]-[B]-SSZ-39 (2) was synthesized hydrothermally using the gel formula with a molar composition of 1 SiO₂: 0.038 H₃BO₃: 0.02 Al₂O₃: 0.19 SDA: 0.29 Na₂O: 22 H₂O. Firstly, 23.9 g of cis, trans-1,1,3,5-tetramethylpiperidinium hydroxide (Sachem, Inc., 35.3 wt.%) as SDA was mixed with 58 g of de-ionized water and 0.65 g of H₃BO₃ (Merck, 99.5 wt.%) and they were stirred for 15 minutes. Then, 2 g of dealuminated NH₄-US-Y and 55.4 g of sodium silicate solution (Merck, 28 wt.% SiO₂, 9 wt.% Na₂O, 65 wt.% H₂O) were added to the mixture and stirred for 30 minutes at room temperature. The synthesis gel was then transferred to Teflon-lined autoclaves and heated at 150 °C for 7 days using a tumbling rate of 45 rpm. After crystallization, the product was recovered by vacuum filtration, washed with de-ionized water and dried in air. The obtained solid was calcined using the same procedure given for conventional SSZ-39.

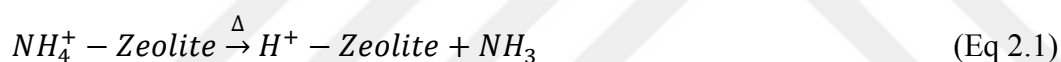
2.4 Dealumination of HH₄-US-Y

The dealumination procedure consisted of three steps. First of all, 7 g of NH₄-US-Y (Alfa Aesar, Zeolite Y, Si/Al =12) was converted to proton form (H⁺-US-Y) by heating at 550 °C for 5 hours. Proton form of the Zeolite Y was refluxed with 140 mL 2 M nitric acid solution (Merck, 65wt%, HNO₃) (solution to zeolite ratio is 20 mL/g) at 100 °C for 2 hours. Then, product was recovered by vacuum filtration, washed with de-ionized water several times and dried. Solids was heated at 550 °C for 5 hours. For second step of the dealumination procedure, remained zeolite (6 g) was refluxed with 120 mL 0.2 M NaOH (Merck, 99 wt.%) solution at 70 °C for half an hour. Again, the product was recovered by vacuum filtration, washed with de-ionized water several times and dried. For the final step, remaining Zeolite Y (~6 g) was refluxed with 120

mL 0.2 M HNO₃ solution at 50 °C for 1.5 hours. Then, the product was recovered by vacuum filtration, washed with de-ionized water several times and dried. Obtained zeolite was exchanged with ammonium nitrate three times.

2.5 Ammonium Exchange Procedure

To obtain NH₄⁺-zeolites, conventional [B]-ZSM-5, conventional [Al]-ZSM-5, mes-[Al]-ZSM-5 (2), NS-[Al]-[B]-ZSM-5, mes-[Al]-[B]-ZSM-5, NS-[Al]-SSZ-13, NS-[Al]-[B]-SSZ-13 (1, 2, 3) and [Al]-[B]-SSZ-39 (2) were exchanged with ammonium nitrate (Sigma Aldrich, >99%, NH₄NO₃). Between 1 and 3 g of calcined zeolites was mixed with 500 mL of 0.2 M NH₄NO₃ aqueous solution and the mixture was stirred at 80 °C for 3 hours. Then, the zeolites were recovered by vacuum filtration, washed with 500 mL de-ionized water and dried at 80 °C. The procedure was repeated three times. Finally, exchanged zeolites were heated at 550 °C for 5 hours using a heating rate of 2 °C/min to obtain H⁺ form of the zeolites (see equation 2.1) for MTO reaction.



2.6 Characterization Techniques

2.6.1 X-ray Diffraction (XRD) Analysis

Powder X-ray diffraction data were obtained following the calcination of the samples. Diffractograms were recorded on Rigaku Ultima-IV diffractometer located at METU Central Laboratory, using Cu K α source ($\lambda=1.5418$ Å) operated at 40 kV and 30 mA, using 2 θ angle range from 2° to 50° at a speed of 1 °/min. Measured diffractograms of [B]-ZSM-5 samples were analyzed using CelRef Unit-Cell refinement software [110], where unit cell parameters of an orthorhombic unit cell system with a space group of *Pnma* were refined for calcined samples.

2.6.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) images were obtained using a QUANTA 400F Field Emission SEM located at METU Central Laboratory with an accelerating voltage of 20 kV or 30 kV. The samples were coated by Pd-Au mixture prior to analysis.

2.6.3 Elemental Analysis

The boron, aluminum and silicon content of the catalyst samples were analyzed using inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer Optime 4300DV) located at METU Central Laboratory. The samples were digested in HF/HNO₃ mixture before the analysis.

For some of the samples, the Al and Si content was also determined using Energy Dispersive X-ray Spectroscopy (EDX) analysis using QUANTA 400F Field Emission SEM located at METU Central Laboratory operated at an accelerating voltage of 20 kV or 30 kV. Analysis was performed based on spectra obtained from at least 5 different regions.

2.6.4 Textural Analysis- N₂ Adsorption Tests

Surface area and pore volume of the calcined zeolites were analyzed using Micromeritics Tristar II 3020 analyzer located in the Department of Chemical Engineering, METU. Samples were degassed at 300 °C for 6 h under vacuum (using Micromeritics VacPrep 061) before N₂ adsorption/desorption tests were conducted at -196 °C. N₂ (Oksan, 99.999%) adsorption tests were conducted at relative pressure values between 10⁻⁵ and 0.98 following the free cell volume measurement conducted using He (Oksan, 99.999%). Micropore volumes were calculated using t-plot statistical thickness method between 3.5 Å and 5 Å with Harkins Jura thickness equation [111]. The mesopore volumes are calculated by subtracting the t-plot

micropore volume from the single point pore volume obtained at $P/P_0=0.98$. The pore size distributions were calculated using Barrett–Joyner–Halenda (BJH) Adsorption model [112].

2.6.5 Fourier Transform Infrared Spectra (FTIR)

Fourier transform infrared spectra (FTIR) for [B]-ZSM-5 samples were obtained using PerkinElmer UATR Two spectrometer equipped with an Attenuated Total Reflectance (ATR) attachment. The samples were scanned 64 times at a spectral resolution of 4 cm^{-1} . The spectrum was collected in the mid IR region from 500 cm^{-1} to 4000 cm^{-1} .

2.6.6 Magic Angle Spinning Neutron Magnetic Resonance (MAS NMR)

^{27}Al MAS NMR spectra were obtained on Bruker Superconducting FT NMR Spectrometer Avance TM 300 MHz WB located at the METU Central Laboratory, which is equipped with a high power UltrashieldTM 300 MHz magnet and 4 mm MAS probe. The samples were hydrated at 25 °C prior to analysis.

2.6.7 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Shimadzu DTG 60H) by flowing air at 60 ml/ min flow rate and increasing the temperature from 20 °C to 750 °C using a heating rate of 10 °C/min. For TGA analysis approximately 15 mg of sample was used.

2.7 Methanol to Olefins Reaction Procedure

2.7.1 Equipment Used in Reaction Set-up

The gas flow rates were controlled using a digital mass flow controller (Alicat, MC-100SCCM-D/5M). A glass bubble flow meter was used to measure the gas volumetric flow rates at the exit of the reactor. A quartz tube that has 7 mm ID and 9 mm OD was used as the reactor. A cylindrical furnace around the reactor tube was used as a heater and temperature was controlled by a controller (ORDEL, PC771) and thermocouple attached to the center of the zeolite outside the quartz cylinder tube. The methanol is fed to the reactor using a gas bubbler, through which He flow was directed to supply methanol at a vapor pressure at 25 °C (16.9 kPa at 25 °C, 16.7 mol %) (see Figure 2.2).

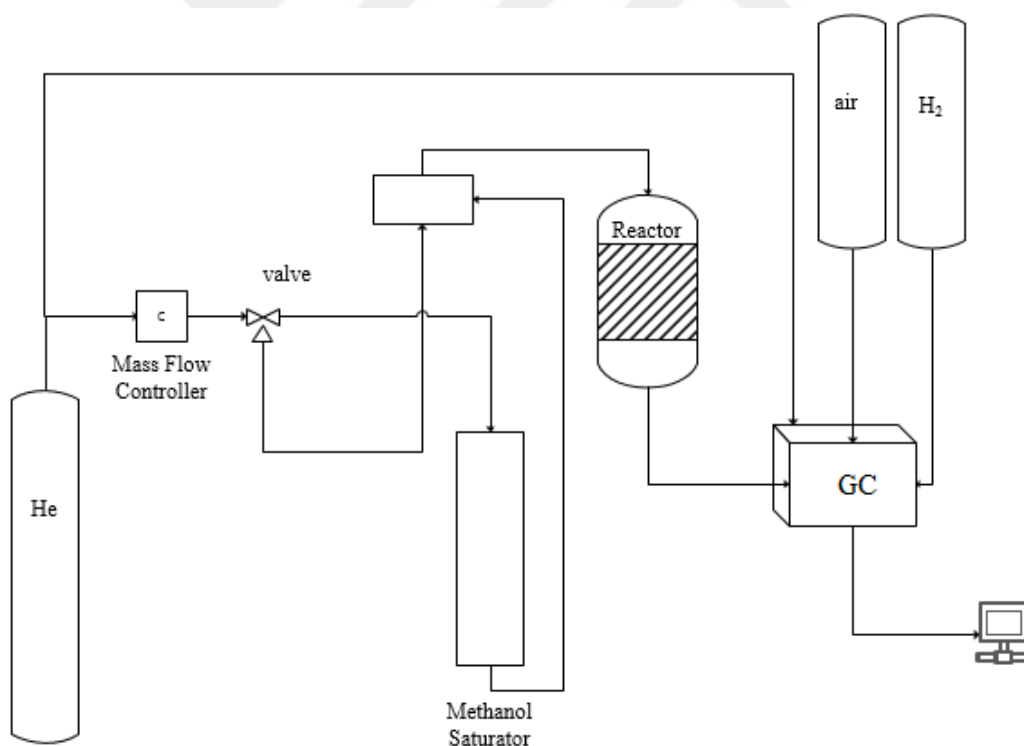


Figure 2.2. Experimental set-up for methanol to olefin reaction system

The qualification and quantification analysis of effluent gas of the reactor was done using a gas chromatograph (GC) (Agilent 7820A) equipped with a flame ionization detector (FID). The carrier inert gas of GC was He (Hatgaz, 99.999%), H₂ (Hatgaz, 99.999%) and dry air (Oksan, 99.99%) was used for FID. A HP-Plot Q column (19095P-QO4, 30 m x 0.530 mm x 40 µm) was used for separation. A thermal conductivity detector (TCD) and flame ionization detector (FID) were used simultaneously for element qualification and quantification. The split ratio of GC set to 1/5. 250 µl sample was automatically sent to the column using sampling valve each 28 min. The method used for product analysis is given in Table 2.1.

Table 2.1 The method parameters used for methanol and olefin product analysis

Inlet temperature (°C)	150
TCD temperature (°C)	250
FID temperature (°C)	300
Column pressure (psi)	13.6
Oven temperature (°C)	60 °C for 5 min, to 180 °C using 10 °C/min rate hold at 180 °C for 7 min

2.7.2 Reaction Procedure

100 mg H⁺-zeolite was placed in the quartz reactor supported by a glass wool. The zeolite was firstly activated at 540 °C for 1 hour under 75 sccm He (Hatgaz, 99.999%) flow. After cooling to room temperature, the He flow (40 sccm) was directed to methanol saturator at 25 °C before sent to the zeolite. For these conditions, the weight hourly space velocity for methanol (WHSV) was calculated to be 5.5. g CH₃OH/g zeolite/ h. The reaction temperature was set to 450 °C using a heating rate of 5 °C/min. Gas samples were taken at every 28 min for analysis using GC.

The calibration of the gases was performed using a standard gas mixture of methane, ethane, propylene, propane, i-butane, n-butane, i-pentane, n-pentane. The calculated response factors (ppm/ area) are given in Table 2.2.

Table 2.2 Calibration (response factors) for the reactants and products for FID

Gas	Response factor (ppm/area)
CH ₄	9.82
C ₂ H ₆	5.36
C ₃ H ₈	3.82
i-C ₄ H ₁₀	3.16
n-C ₄ H ₁₀	3.42
i-C ₅ H ₁₂	2.74
n-C ₅ H ₁₂	3.74

The methanol conversion was calculated taking dimethyl ether into consideration as the reactant (see Eq. 2.2). The selectivity and yield for products were calculated using the formula given in Eq. 2.3 and 2.4.

$$Conversion \% = \frac{FMeOH_{in} - (FMeOH_{out} + 2 * FDME)}{FMeOH_{in}} * 100 \quad \text{Eq. 2.2}$$

$$Selectivity \% = \frac{\alpha * F(C_{\alpha}H_y)}{FMeOH_{in} - (FMeOH_{out} + 2 * FDME)} * 100 \quad \text{Eq. 2.3}$$

$$Yield \% = \frac{\alpha * F(C_{\alpha}H_y)}{FMeOH_{in}} * 100 \quad \text{Eq. 2.4}$$

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization Results

3.1.1 Characterization Results for ZSM-5 Zeolites

3.1.1.1 XRD

Powder X-ray Diffraction patterns of [Al]-ZSM-5 and [Al]-[B]-ZSM-5 zeolites are shown in Figure 3.1. All of the synthesized zeolites have typical characteristic peaks of MFI with high crystallinity. The addition of mesopore-forming agent (carbon for MES-[Al]-ZSM-5(1) or CTABr for Mes-[Al]-ZSM-5(2)), changing synthesis conditions and incorporation of boron did not affect the crystallinity of zeolites. Lower peak intensities and wider peaks indicate smaller crystal sizes for Mes-[Al]-ZSM-5(2).

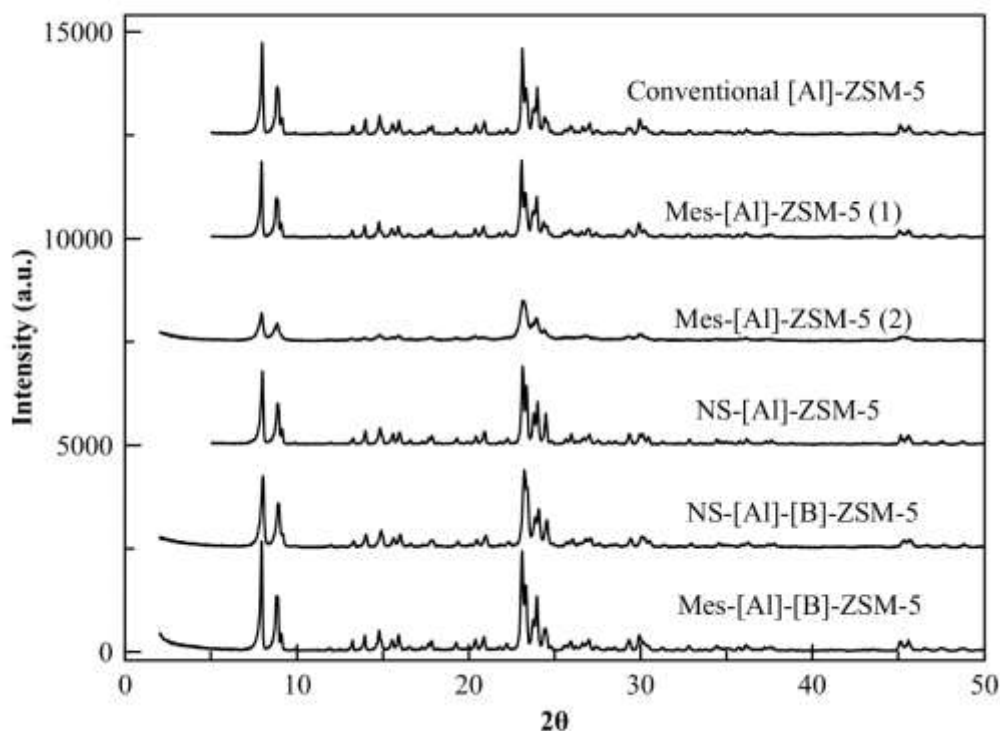


Figure 3.1. XRD patterns of [Al]-ZSM-5 and [Al]-[B]-ZSM-5 zeolites ($\lambda = 1.5418$ Å)

Boron containing zeolites, which are borosilicates do not have enough acidity to catalyze MTO reaction. However, they can be used to introduce new tetrahedral site atoms into the zeolite frameworks via post-synthetic techniques. Boron incorporated zeolites are potential intermediates for these zeolites because boron atoms can be extracted under mild acidic or thermal conditions [113]. Such deboronation and new tetrahedral substitution examples include large pore Ti containing zeolites (titanosilicates) for oxidation reactions [114], [115] and [Fe]-SSZ-24 for isopropylation of biphenyl [116]. Easy deboronation of boron containing zeolites are also useful to produce interconnected mesoporosity. Deboronation using steam treatment to create mesopores in the structure of [B]-zeolite Y are reported to provide higher catalytic activity in iso-octane and 1,3,5-triisopropylbenzene (TIPB) cracking reactions [117].

Figure 3.2 shows the XRD patterns of [B]-ZSM-5 zeolites. All of them exhibit the typical XRD patterns of zeolites with MFI framework topology and they have high crystallinity. This confirms that boron containing ZMS-5 zeolites are successfully synthesized. According to Figure 3.2, the Mes3-[B]-ZSM-5 sample has lower peak intensity because it has the smallest particle sizes.

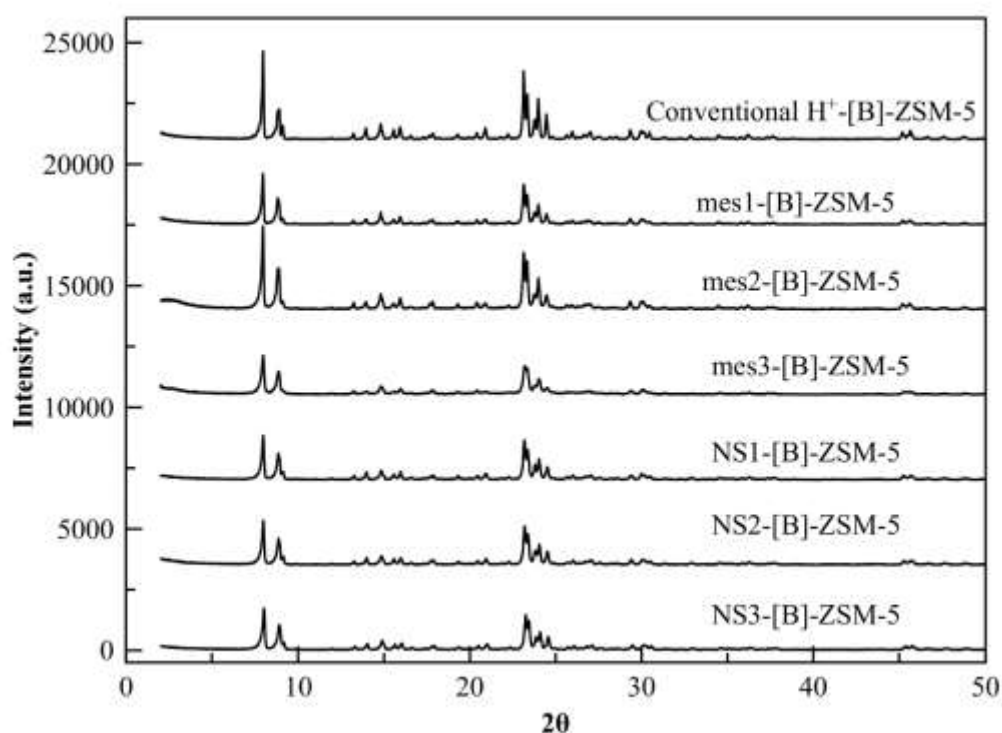


Figure 3.2. XRD patterns of [B]-ZSM-5 zeolites ($\lambda = 1.5418 \text{ \AA}$)

Boron incorporation of Mes1-[B]-ZSM-5, Mes2-[B]-ZSM-5 and Mes3-[B]-ZSM-5 samples are shown by the right shift of the 2θ values of the (501) peak of the samples (*Pnma* space group) when compared to conventional [Al]-ZSM-5 sample (23.12° for [Al]-ZSM-5, 23.14° for Mes1-[B]-ZSM-5, 23.15° for Mes2-[B]-ZSM-5 and 23.20° for Mes3-[B]-ZSM-5, see Figure 3.3). Since B–O bonds in the zeolite framework are much shorter ($1.39 \text{ \AA}$ [118]) than Si–O ($1.61 \text{ \AA}$ [119]) or Al–O ($1.75 \text{ \AA}$ [120]) bonds, a smaller unit cell volume for [B]-ZSM-5 samples are expected together with smaller d spacings and higher 2θ angle values due to Bragg's law ($n\lambda = 2d \sin\theta$).

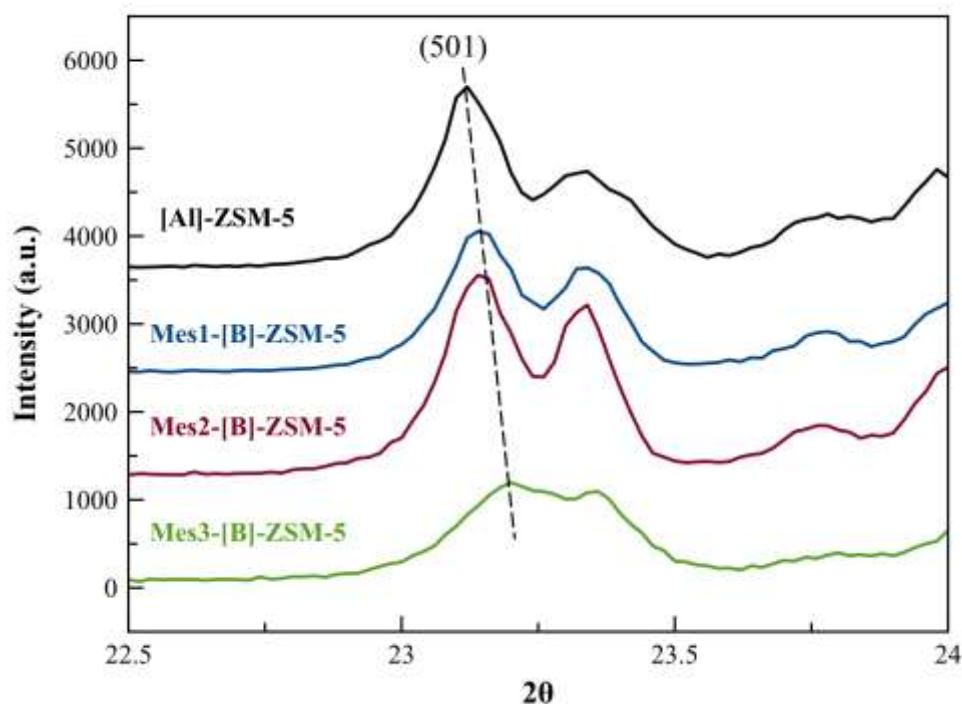


Figure 3.3. XRD patterns of conventional [Al]-ZSM-5 and Mes-[B]-ZSM-5 samples at 2θ angles between 22° and 24° ($\lambda = 1.5418 \text{ \AA}$)

In addition to the shift in 2θ angle values, successful boron incorporation can be understood from FTIR spectra of the samples (see Figure 3.4). FTIR spectra of the hydrates samples show absorption bands of lattice vibrational modes at 1216 cm^{-1} , 1044 cm^{-1} (external and internal asymmetric TOT stretch), 800 cm^{-1} (external symmetric TOT stretch), 627 cm^{-1} , 587 cm^{-1} and 543 cm^{-1} . The absorption band observed at 543 cm^{-1} is ascribed to the presence of double five membered ring vibrations, indicating formation of pentasil zeolite structure [121].

In addition to the lattice vibrational modes observed both on [Al]-ZSM-5 and [B]-ZSM-5, out-of-plane bending and stretching vibrations of B–O–Si (tetrahedrally coordinated B) at 667 cm^{-1} and 917 cm^{-1} [118] were additionally observed on Mes-[B]-ZSM-5 samples, indicating boron incorporation to the MFI framework. The intensity of the absorption bands at 667 cm^{-1} and 917 cm^{-1} were observed to increase

with increasing boron content. The vibration at 1375 cm^{-1} shows presence of trigonal B species (asymmetric B–O stretching) in the framework [118].

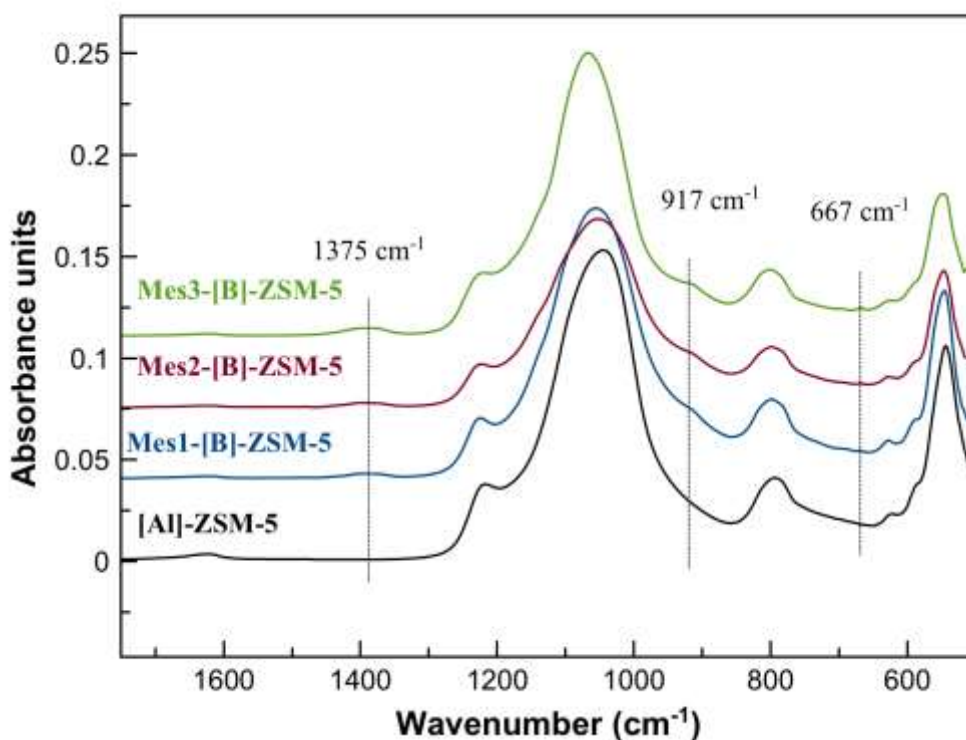


Figure 3.4. FTIR spectra of hydrated conventional [Al]-ZSM-5 and Mes-[B]-ZSM-5 samples

The formation mechanism of the microspheres of mes3-[B]-ZSM-5 is investigated using XRD analysis of calcined samples at the 7th, 10th and 14th day of synthesis. According to Figure 3.5, at the 7th day of synthesis, the peaks characteristic of MFI phase (with the most observable peaks at 8.02° and 8.94° belonging to the (101) and (020) planes of *Pnma* space group) appeared at low intensity values, indicating the starting of the crystallization. In addition to the MFI peaks, a broad peak at 2θ value of 2.92° corresponding to a d-spacing of 3 nm was observed together with a broad peak between 20° and 25° indicating a mesoporous structure. At the 10th day of synthesis, the peak at 2.92° shifted to 2.72° (d-spacing of 3.2 nm), and the characteristic MFI peaks gained more intensity. At the 14th day of synthesis, the peak

at 2.72° and the broad peak between 20° and 25° disappeared as the MFI peaks reached their maximum intensity. When the intensity of the peak belonging to the (101) plane of ZSM-5 (*Pnma* space group) observed at 7.94° was compared at the 10th day and 14th day of the synthesis, it can be said that the sample at the 10th day has 68% crystallinity with respect to the one at the 14th day.

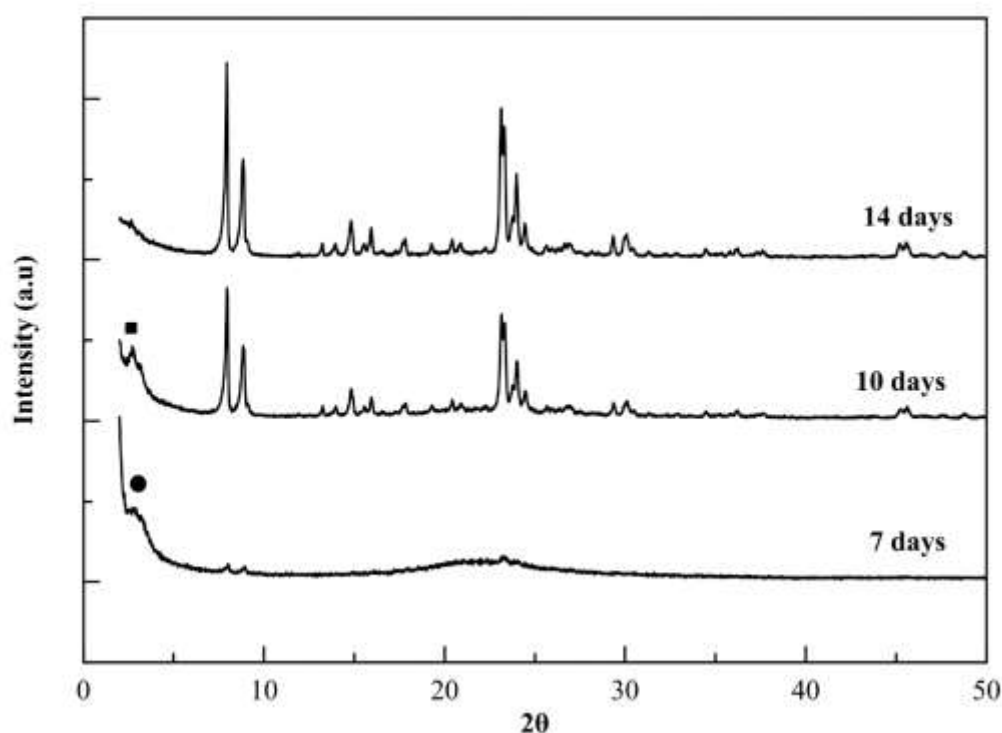


Figure 3.5. XRD pattern of Mes-B3-ZSM-5 following the 7th, 10th and 14th day of synthesis ($\lambda = 1.5418 \text{ \AA}$) ●: peak at 2.92° ■: peak at 2.72°

3.1.1.2 SEM Images

The SEM images of conventional and mes-[Al]-ZSM-5 (1) are shown in Figure 3.6 to see effect of mesoporosity on morphology and particle size. Conventional [Al]-ZSM-5 and mes-[Al]-ZSM-5 (1) have typical coffin shape crystal morphology with particle sizes around $2 \mu\text{m}$. Adding carbon template does not affect the morphology and crystal

size indicating insufficient interaction of the carbon particles with the zeolite precursors.

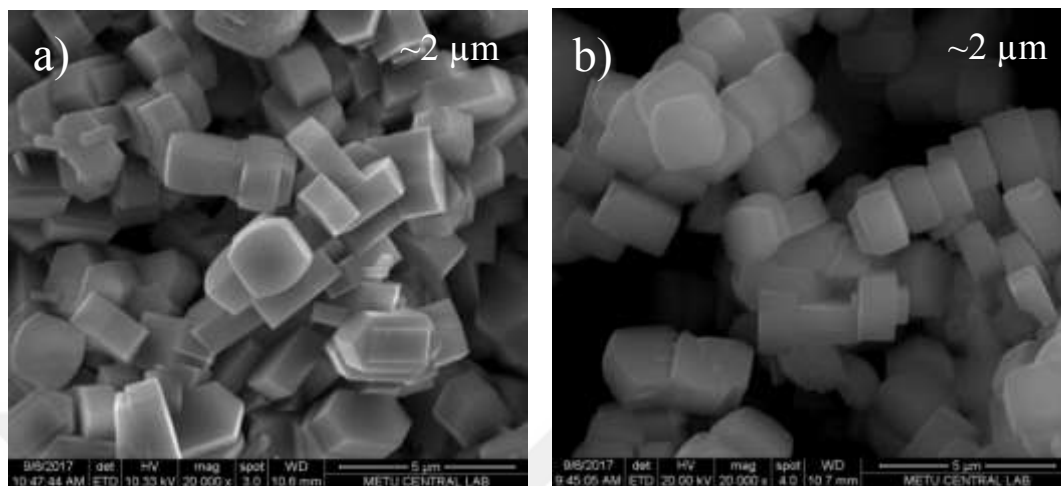


Figure 3.6. SEM images for conventional [Al]-ZSM-5 (a), Mes-[Al]-ZSM-5 (1) (b)

Adding CTABr as mesoporegen and using HDA as SDA change both morphology and crystal size. Wang et al. reported that HDA caused micron-sized spherical particles aggregated from nanoparticles, however the nanoparticles were fused together [122]. Xue et al. reported that, using CTAB in the synthesis gel together with HDA enabled loose stacking of the nanoparticles due to CTAB acting as the growth inhibitor of the nanoparticles [106]. Thus, intercrystalline mesoporosity was formed between those nanoparticles. For mes-[Al]-ZSM-5 (2), nanoparticles aggregate to create microspheres. While the primary micro spherical particles have an average crystal size of around 10 μm , average size of the nanosized particles have around 100 nm (see Figure 3.7, a and b).

NS-[Al]-ZSM-5, on the other hand, was synthesized using TPAOH as the SDA without any mesoporegen. Utilization of TPAOH rather than TPABr as SDA and TEOS as the silicon source are known to result in smaller crystals when combined with the lower H_2O content. Resulting NS-[Al]-ZSM-5 have nanoparticles of sizes around 50 nm formed clusters and size of these clusters are around 200-500 nm (see Figure 3.7, c).

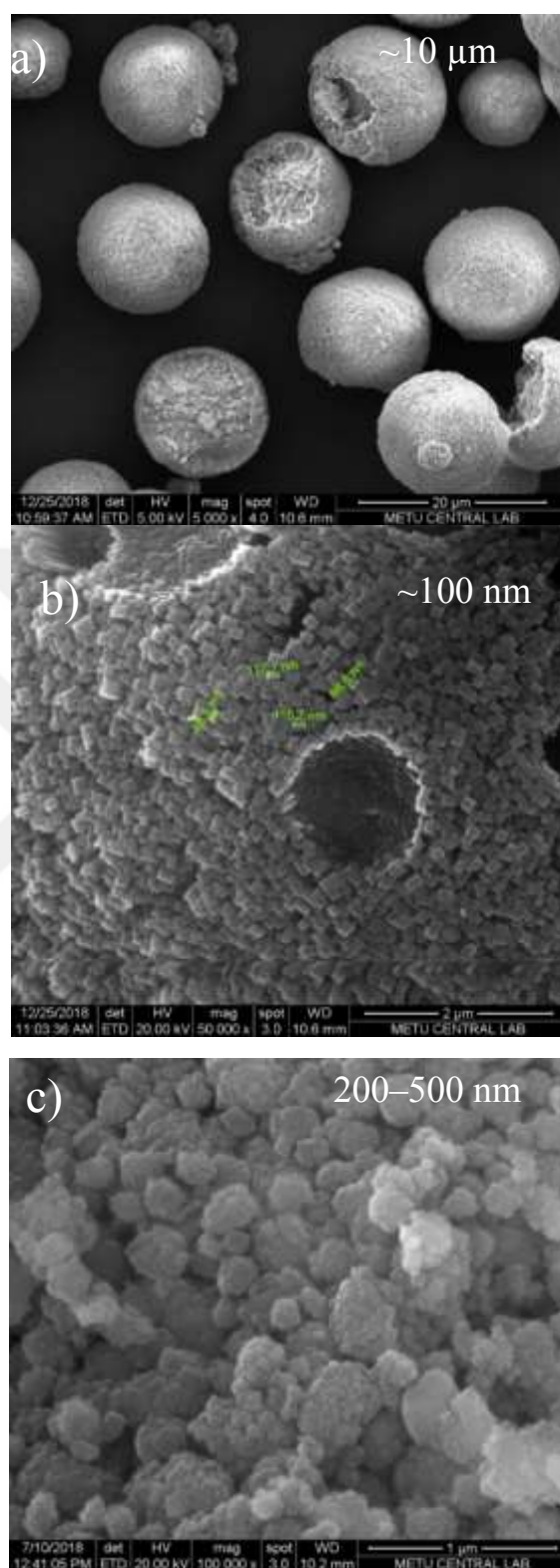


Figure 3.7. SEM images for Mes-[Al]-ZSM-5 (2) (a, b), and NS-[Al]-ZSM-5 (c)

SEM images of conventional and mesoporous [B]-ZSM-5 zeolites are shown in Figure 3.8. Conventional [B]-ZSM-5 have different shape than conventional [Al]-ZSM-5 due to larger crystal sizes (see Figure 3.8, a). Mesoporosity and boron incorporation affect both morphology and crystal size for Mes1-[B]-ZSM-5, Mes2-[B]-ZSM-5 and Mes3-[B]-ZSM-5. Varying boron content resulted in different morphology and particle sizes for these samples. Larger crystals with an average size of $30\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ was obtained from zeolite having lower boron content (mes1-[B]-ZSM-5) (Figure 3.8, b). This large crystal morphology can be explained by enhanced nucleation and growth rates in presence of higher Si content as reported by Xue et al. for Mes-[Al]-ZSM-5 [106]. Crystal sizes decrease with increasing boron content. While mes2-[B]-ZSM-5 have $20\text{ }\mu\text{m}$ particle size (Figure 3.8, c), crystal size of the mes3-[B]-ZSM-5 is $15\text{ }\mu\text{m}$ (see Figure 3.8, d). Also, higher boron content results in cauliflower-like clusters composed of nanoparticles with size of 450 nm (Figure 3.8, e). Thus, intercrystalline mesoporosity is created between nanoparticles.

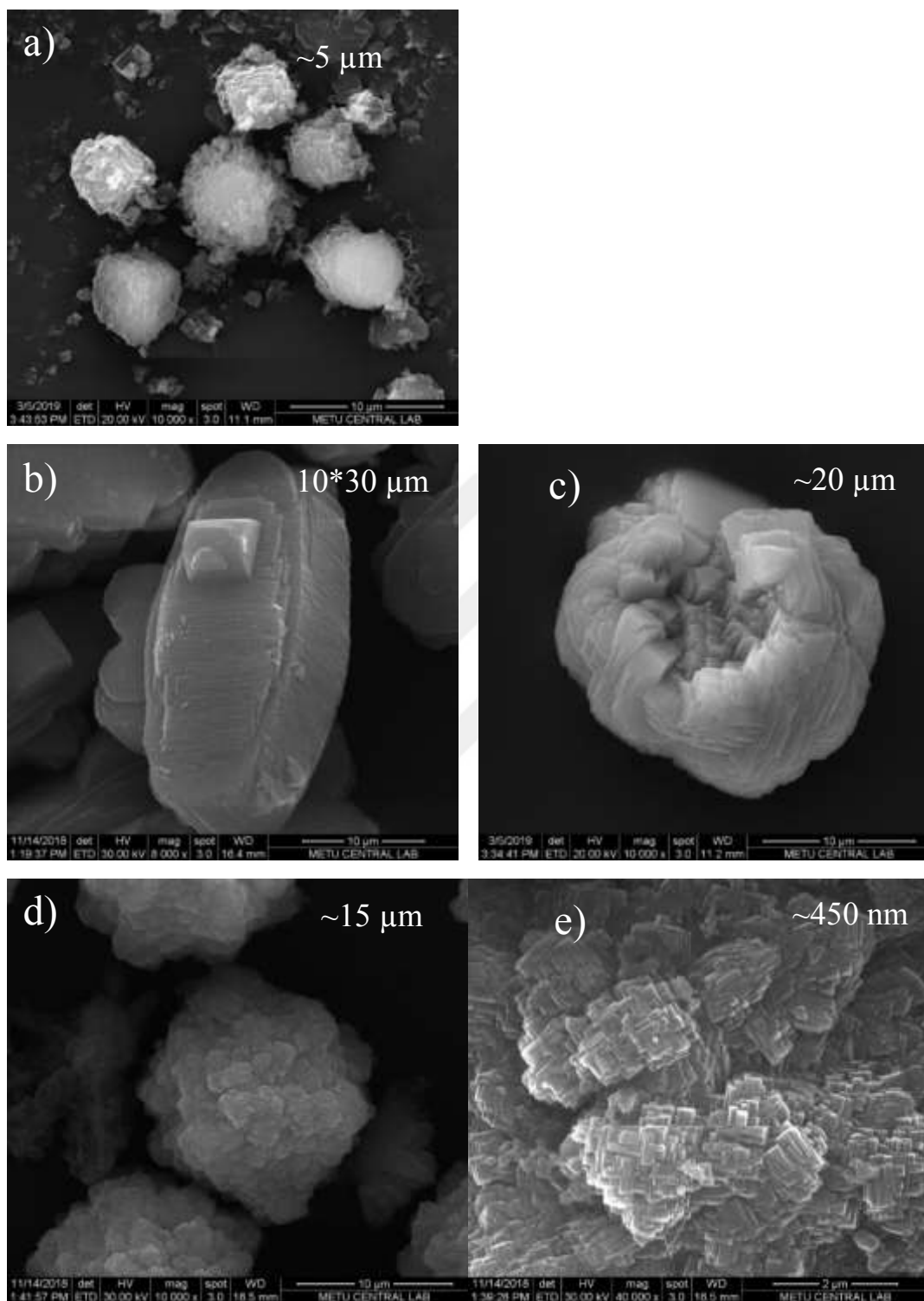


Figure 3.8. SEM images for conventional [B]-ZSM-5 (a), Mes1-[B]-ZSM-5 (b), Mes2-[B]-ZSM-5 (c) and Mes3-[B]-ZSM-5 (d, e)

The formation mechanism of the mes3-[B]-ZSM-5 is investigated using SEM images of calcined samples at the 7th, 10th and 14th day of synthesis. Figure 3.9, a shows that aggregates of spherical particles having sizes ca. 200 nm occur at the 7th day of the synthesis. This spherical structure enlarges to diameters of ~13–15 μm (see Figure 9, b). Then, further crystallization under the effect of HDA gives more defined crystals having sizes ca. 10 μm at the 14th day (see Figure 9, c).

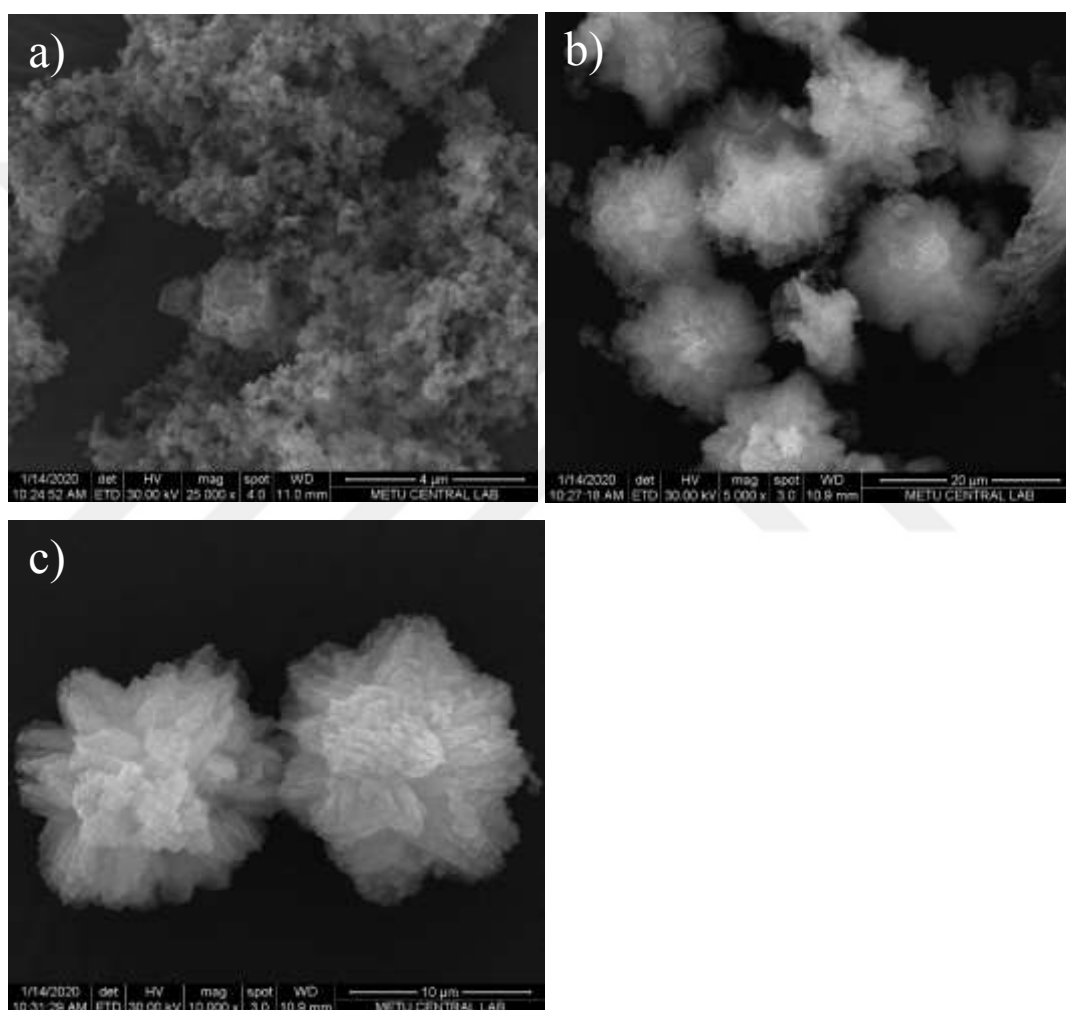


Figure 3.9. SEM images of mes3-[B]-ZSM-5 at the 7th day (a), 10th day (b) and 14th day (c) of synthesis

Figure 3.10 displays SEM images of nanosized [B]-ZSM-5 zeolites. They have typical coffin shape crystal morphology with particle sizes around 300 nm. Similar to NS-[Al]-ZSM-5 samples, utilization of TPAOH in the synthesis gel as SDA and TEOS as the silicon source are believed to result in small particle sizes. For this method, boron content does not affect the morphology and particle size.

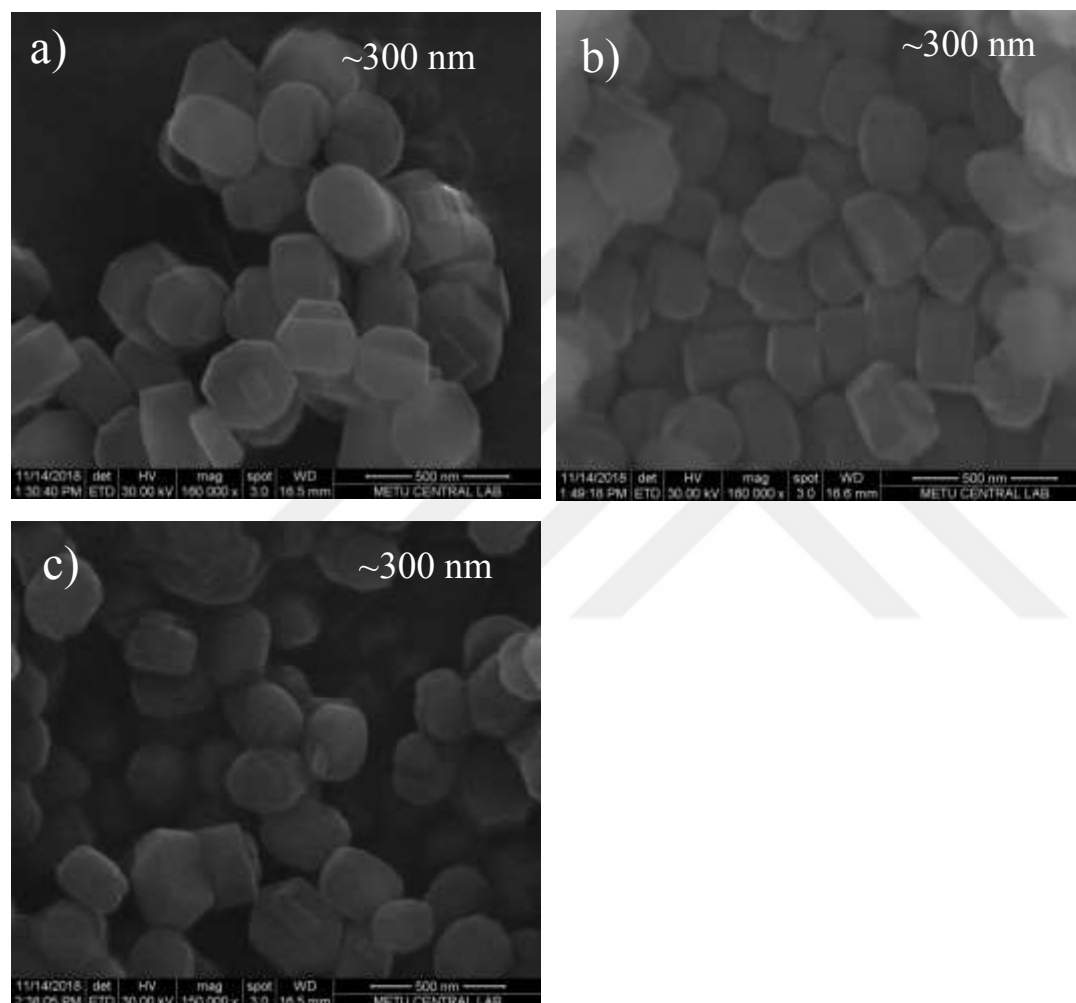


Figure 3.10. SEM images for NS1-[B]-ZSM-5 (a), NS2-[B]-ZSM-5 (b), NS3-[B]-ZSM-5 (c)

Figure 3.11 a and b show representative morphology of NS-[Al]-[B]-ZSM-5 and mes-[Al]-[B]-ZSM-5 crystals, respectively. These figures indicate that different synthesis methods lead to different crystal size and morphology. NS-[Al]-[B]-ZSM-5 have very

small cubic nanoparticles around 36 nm forming clusters of size 500 nm similar to NS-[Al]-ZSM-5. In contrast, mes-[Al]-[B]-ZSM-5 have larger crystals like snowflake with the size of 30 μm .

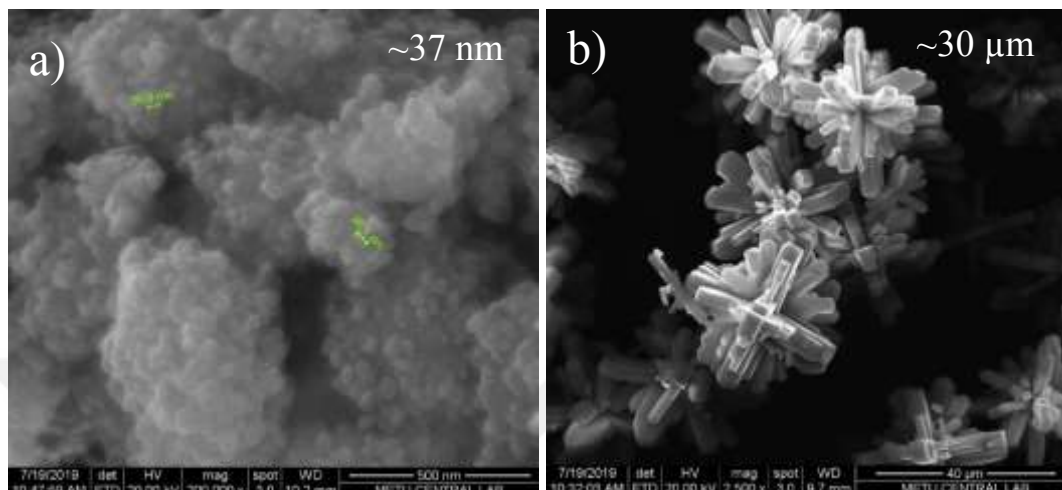


Figure 3.11. SEM image for NS-[Al]-[B]-ZSM-5 (a) and mes-[Al]-[B]-ZSM-5 (b)

3.1.1.3 N₂ Physisorption Isotherms

N₂ adsorption-desorption isotherms for [Al]-ZSM-5 zeolites are given in Figure 3.12. According to IUPAC classification, conventional-[Al]-ZSM-5 and mes-[Al]-ZSM-5 (1) exhibit typical type I (a) isotherm, reflecting traditional zeolite having only micropores. Mes-[Al]-ZSM-5 (2) shows type IV isotherm, given by mesoporous zeolites and H4 hysteresis loop, found with aggregated crystals of zeolites and some mesoporous zeolites. Also, NS-[Al]-ZSM-5 exhibits type IV isotherm.

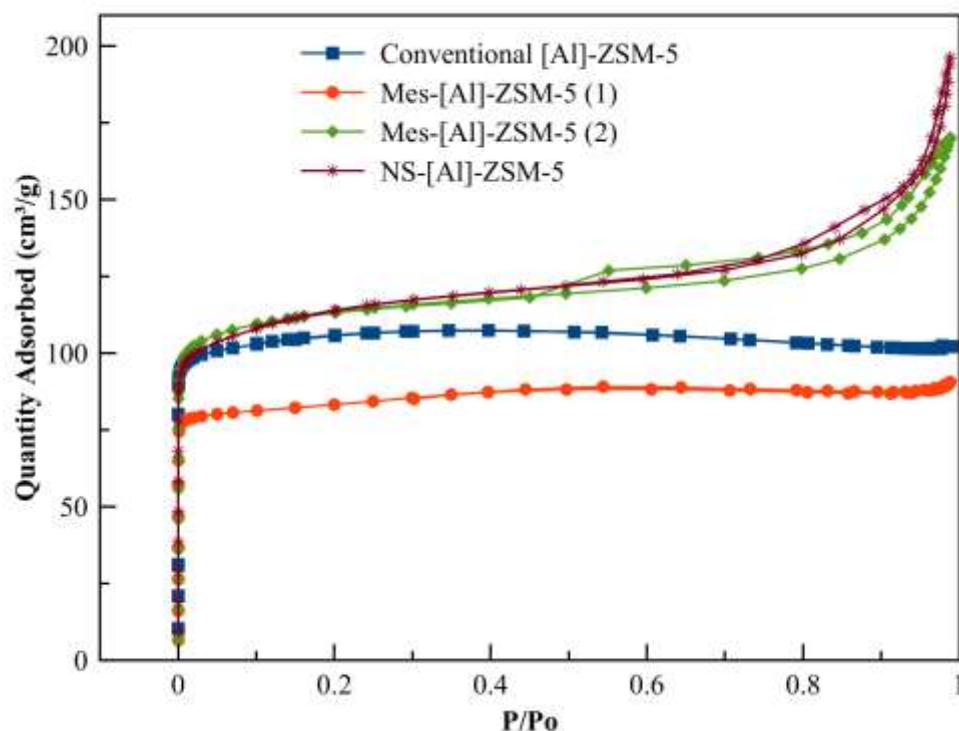


Figure 3.12. N₂ adsorption-desorption isotherms for [Al]-ZSM-5 zeolites obtained at -196 °C

Figure 3.13 represents N₂ adsorption-desorption isotherms for conventional H⁺-[B]-ZSM-5 and mesoporous [B]-ZSM-5 zeolites. According to Figure 3.13, adding mesoporosity increases the N₂ adsorption capacity. While conventional [B]-ZSM-5 exhibit a typical type I isotherm, mes1-[B]-ZSM-5, mes2-[B]-ZSM-5 and mes3-[B]-ZSM-5 show type IV isotherms with H4 hysteresis loop, which is associated with pore blocking.

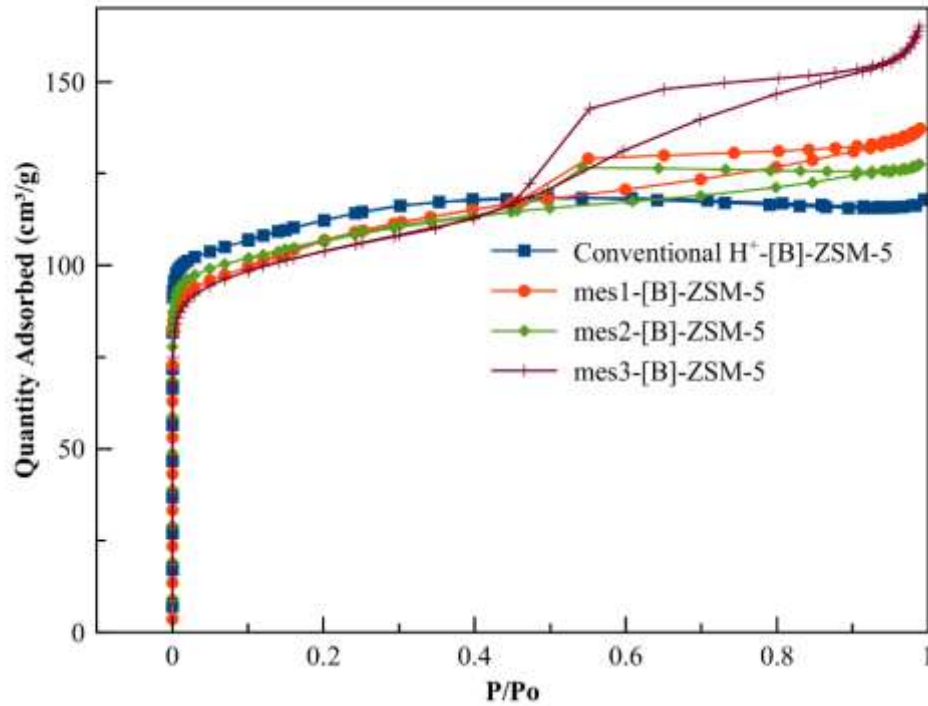


Figure 3.13. N₂ adsorption-desorption isotherms for mesoporous [B]-ZSM-5 zeolites and conventional H⁺-[B]-ZSM-5 obtained at -196 °C

Figure 3.14 shows that N₂ adsorption analysis of mes3-[B]-ZSM-5 samples at the 7th, 10th and 14th day of synthesis. According to Figure 3.14, adsorption capacity decreases with synthesis days of the mes3-[B]-ZSM-5. The highest adsorption capacity belongs to the 7th day synthesis. The hysteresis observed for the 7th day synthesis can be classified as the H2 type, which is attributed to blocked pores unlike type H1, attributed to open pores typical for MCM-41. 10th and 14th day synthesis shows type IV isotherms with H4 hysteresis loop, which is associated with pore blocking.

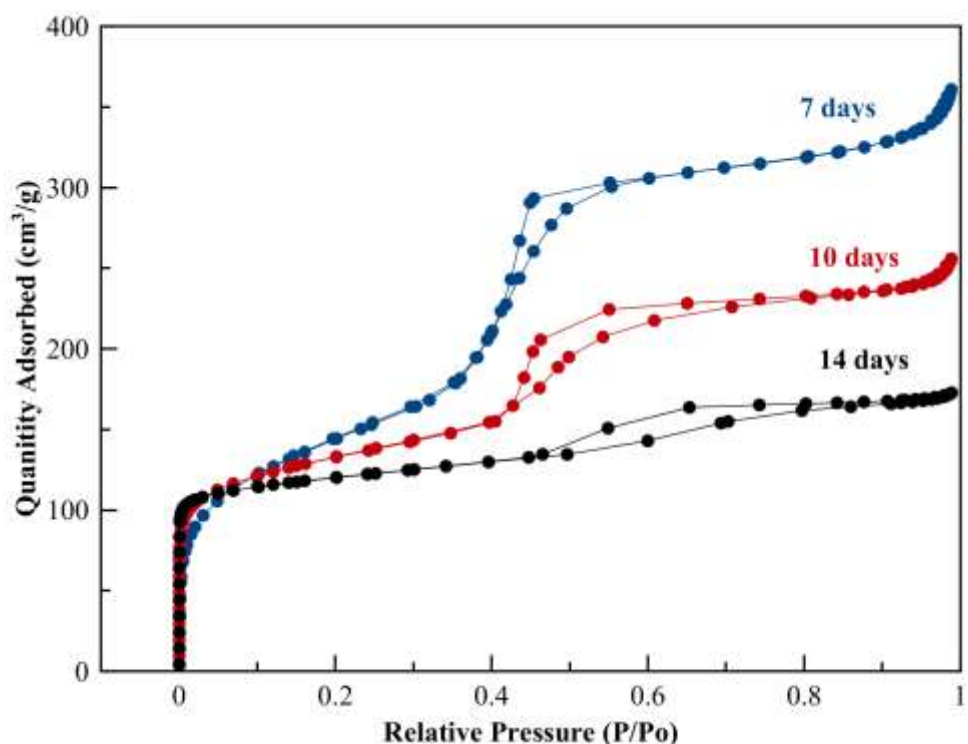


Figure 3.14. N₂ adsorption-desorption isotherm of Mes3-[B]-ZSM-5 at the 7th, 10th and 14th day of hydrothermal synthesis

Figure 3.15 shows N₂ adsorption-desorption isotherms for conventional H⁺-[B]-ZSM-5 and nanosized [B]-ZSM-5 zeolites. According to the figure, decreasing crystal size of zeolites results in increasing adsorption capacity and hysteresis. All nanosized [B]-ZSM-5 zeolites have type IV isotherm. The N₂ adsorption isotherm data of the synthesized samples can be found in Appendix A1.

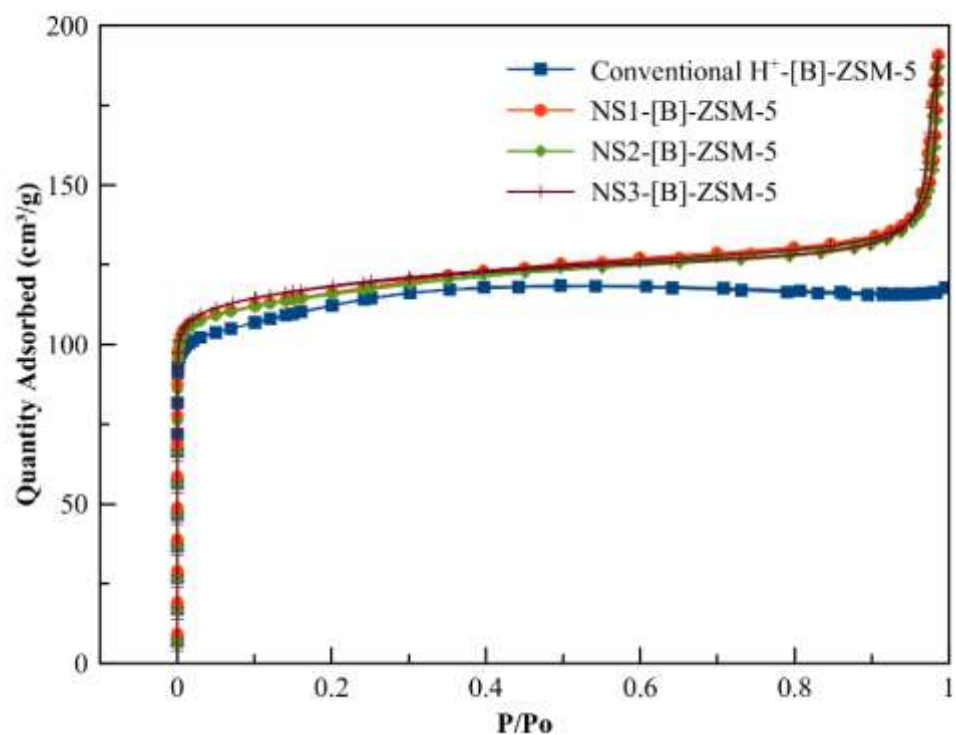


Figure 3.15. N₂ adsorption-desorption isotherms for nanosized [B]-ZSM-5 zeolites and conventional H⁺-[B]-ZSM-5 obtained at -196 °C

Figure 3.16 shows N₂ adsorption-desorption isotherms for NS-[Al]-[B]-ZSM-5 and mes-[Al]-[B]-ZSM-5. According to the Figure, NS-[Al]-[B]-ZSM-5 has high adsorption capacity. Although mes-[Al]-[B]-ZSM-5 exhibits typical type I (a) isotherm, NS-[Al]-[B]-ZSM-5 exhibits type IV isotherm.

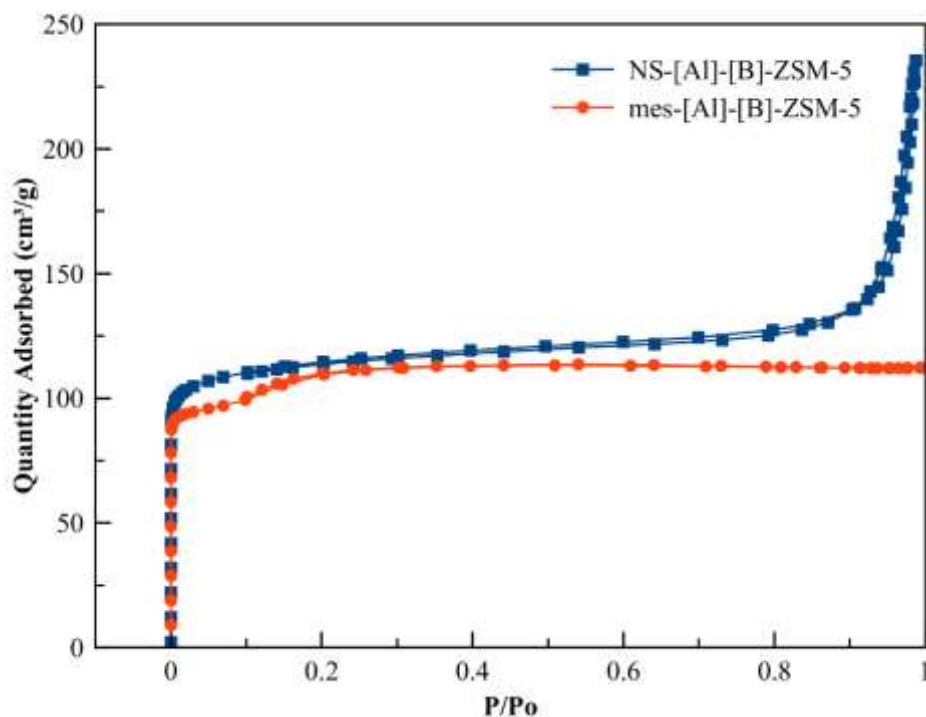


Figure 3.16. N₂ adsorption-desorption isotherms for [Al]-[B]-ZSM-5 zeolites obtained at -196 °C

3.1.1.4 Pore Size Distributions

Pore sizes of the samples were calculated using Barrett–Joyner–Halenda (BJH) adsorption. According to BJH Adsorption method, they have both mesopores and macropores. Although NS-[Al]-ZSM-5 shows a broad range of pore sizes from 5 to 140 nm, peaking at ~15 nm and ~128 nm, NS-[Al]-[B]-ZSM-5 shows pore sizes in the range of ~15-150 nm, peaking at 80 nm (see Figure 3.17).

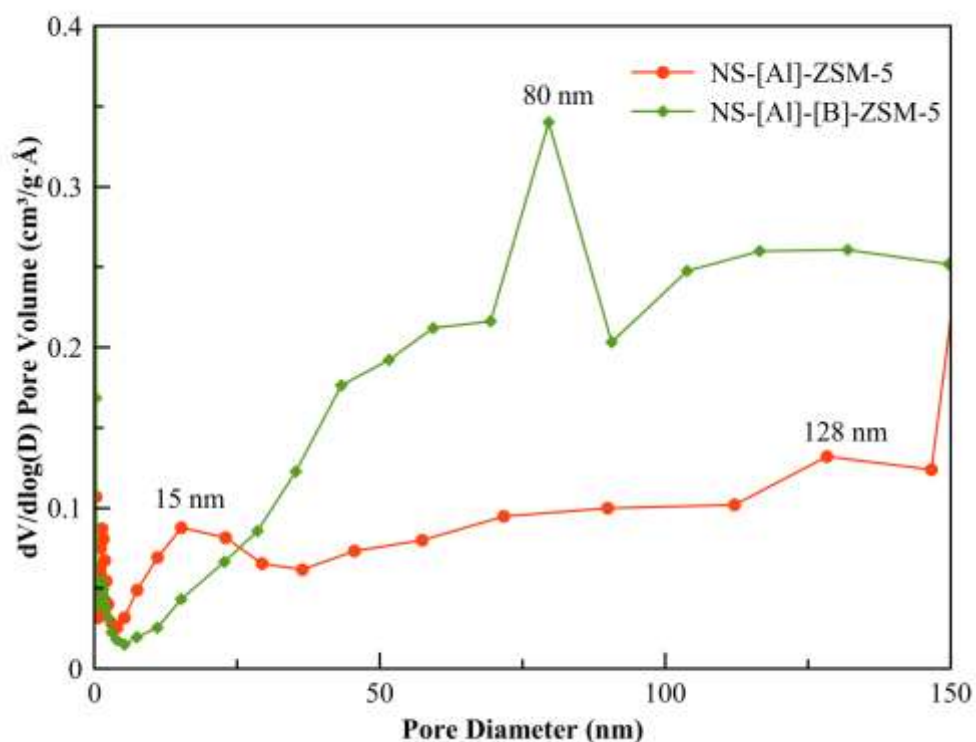


Figure 3.17. BJH adsorption branch pore size distribution of NS-[Al]-ZSM-5 and NS-[Al]-[B]-ZSM-5

BJH pore size distributions for mesoporous [B]-ZSM-5 samples are presented in Figure 3.18. According to the Figure, mes1-[B]-ZSM-5 and mes2-[B]-ZSM-5 have small pores which are ~1.5 nm and ~1.7 nm, respectively. On the other hand, mes3-[B]-ZSM-5 shows the largest pores which are 4 nm.

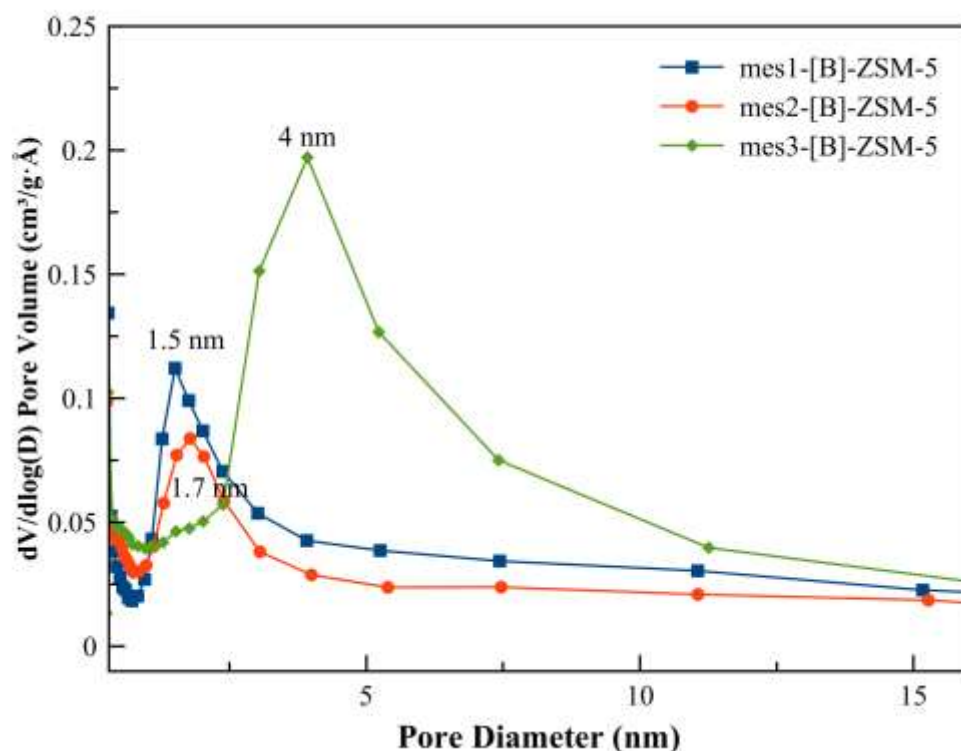


Figure 3.18. BJH adsorption branch pore size distribution of mes1-[B]-ZSM-5, mes2-[B]-ZSM-5 and mes3-[B]-ZSM-5

Figure 3.19 shows BJH pore size distributions for nanosized [B]-ZSM-5 samples. According to BJH Adsorption method, all have macropores. NS1-[B]-ZSM-5 has the largest pores which are ~132 nm. Although the diameter of the macropores for NS2-[B]-ZSM-5 are 104, for NS3-[B]-ZSM-5 are ~124 nm.

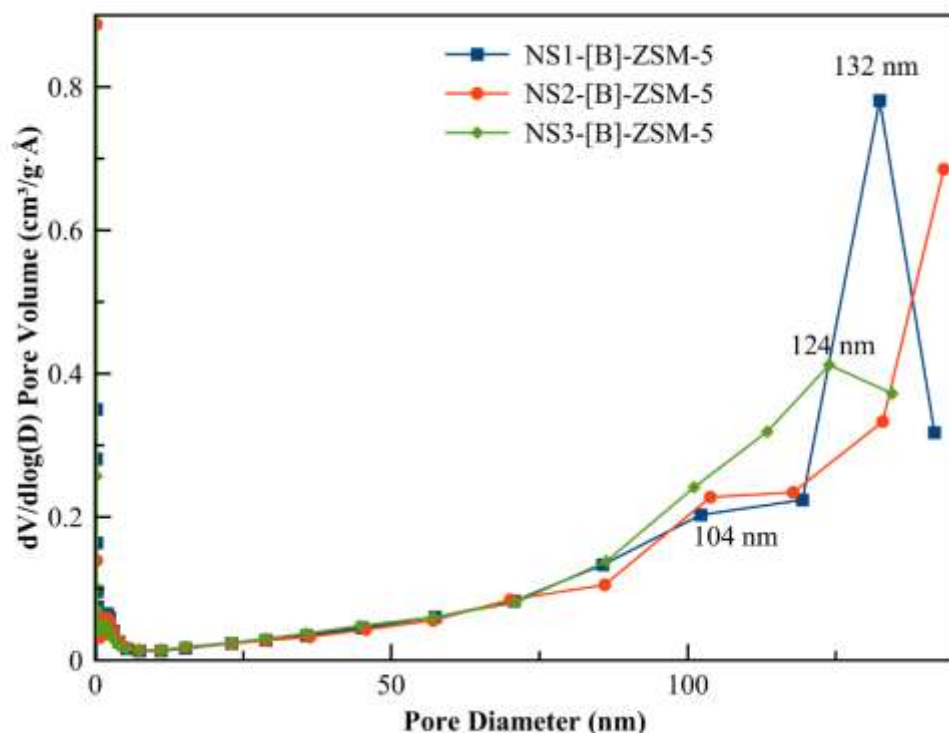


Figure 3.19. BJH adsorption branch pore size distribution of NS1-[B]-ZSM-5, NS2-[B]-ZSM-5 and NS3-[B]-ZSM-5

3.1.1.5 N₂ Physisorption Characteristic Results

Texture properties of ZSM-5 zeolites using N₂ adsorption isotherms are given in Table 3.1. According to Table 3.1, all ZSM-5 zeolites have typical MFI micropore volume reported in literatures for ZSM-5 zeolite lie between 0.126 cm³/g and 0.148 cm³/g [123]. However, mes-[Al]-[B]-ZSM-5 and mes1-[B]-ZSM-5 have relatively small micropores, which are 0.092 cm³/g and 0.098 cm³/g, respectively. NS-[Al]-[B]-ZSM-5 have the largest mesopore volume, which is 0.185 cm³/g. Hard-template (carbon) does not result in mesopore formation for mes-[Al]-ZSM-5 (1) due to insufficient incorporation of carbon particles into crystals. While soft template (CTABr) creates a mesopore volume of 0.118 cm³/g for mes-[Al]-ZSM-5 (2), mes-[B]-[Al]-ZSM-5 have relatively small mesopore volume, which is 0.098 cm³/g. Also, 0.162 cm³/g mesopore

volume is obtained from NS-[Al]-ZSM-5 by changing synthesis conditions. Moreover, CTABr and changing synthesis conditions create mesopore volume for boron containing ZSM-5 zeolites. As can be seen from Table 3.1, while mesopore volume increases with increasing boron content except mes2-[B]-ZSM-5, nanosized boron containing ZSM-5 zeolites have similar mesopore volume, which is around $0.110 \text{ cm}^3/\text{g}$.

Table 3.1 also gives elemental composition of the ZSM-5 zeolites. While boron content of the zeolites increases with increasing B content in the synthesis gel, Si/B ratios are much higher than those of the synthesis gel. This is due to the dissolution of boron species during crystallization [92].

Table 3.1 Elemental analysis and N₂ physisorption characteristic results for ZSM-5 zeolites

Sample	Si/Al ^(a)	Si/Al ^(b)	S _{BET} (m ² /g) ^(c)	S _{mic} (m ² /g) ^(d)	S _{EXT} (m ² /g) ^(e)	V _{total} (cm ³ /g) ^(f)	t-plot V _{micro} (cm ³ /g) ^(g)	V _{meso} (cm ³ /g) ^(h)
Conventional [Al]-ZSM-5	34	-	342	286	56	0.157	0.138	0.018
Mes-[Al]-ZSM-5 (1)	37	-	271	224	47	0.138	0.108	0.030
Mes-[Al]-ZSM-5 (2)	20±2	21	369	288	81	0.257	0.139	0.118
NS-[Al]-ZSM-5	35±8	-	372	253	119	0.285	0.123	0.162
NS-[Al]-[B]-ZSM-5	35±3	45	373	288	85	0.325	0.140	0.185
Mes-[Al]-[B]-ZSM-5	51±2	72*	353	181	172	0.173	0.092	0.081
Conventional H ⁺ -[B]-ZSM-5	-	1040	368	249	119	0.179	0.122	0.057
Mes1-[B]-ZSM-5	-	-	352	199	152	0.210	0.098	0.112
Mes2-[B]-ZSM-5	-	-	351	243	107	0.196	0.118	0.078
Mes3-[B]-ZSM-5	-	-	342	225	117	0.250	0.109	0.141
NS1-[B]-ZSM-5	-	-	380	289	91	0.256	0.140	0.116
NS2-[B]-ZSM-5	-	-	378	291	87	0.250	0.141	0.109
NS3-[B]-ZSM-5	-	-	386	305	81	0.255	0.148	0.107

a: Si/Al determined from EDX analysis

b: Si/Al and Si/B from ICP-OES

c: S_{BET}=BET surface area, which was calculated using Brunauer-Emmett-Teller (BET) method

d: S_{mic}= t-plot surface area, which was calculated using t-plot method

e: S_{EXT}= external surface area which was calculated from S_{BET}-S_{mic}

f: V_{total}=total volume determined from the adsorbed amount at P/P₀= 0.98

g: t-plot V_{micro} = Micropore volume calculated using t-plot method

h: V_{meso} = Mesopore volume, which was calculated from V_{total}- t-plot V_{micro}

*, results calculated from XRF

Texture properties of mes3-[B]-ZSM-5 obtained at the 7th, 10th and 14th day of the hydrothermal synthesis using N₂ adsorption isotherms are given in Table 3.2. The trends in the micropore-mesopore volume changes during the synthesis confirm a sequential mesostructure formation and crystallization of mesoporous structure to zeolite. According to the Table 3.2, The micropore formation was negligible (0.01 cm³/g) when compared to mesopore volume found by N₂ adsorption at -196 °C (0.54 cm³/g). The micropore volume obtained at the 10th day is 0.09 cm³/g while the mesopore volume value dropped to 0.30 cm³/g. Then, further crystallization under the effect of HDA gives more defined crystals at the 14th day (see Figure 3.9, c) resulting in a higher micropore volume (0.13 cm³/g) and a slightly lower mesopore volume (0.14 cm³/g). Furthermore, while the micropore volume and micropore surface area increase, the BET surface area decreases with increasing crystallization time.

Table 3.2 N₂ physisorption characteristic results of the mes3-[B]-ZSM-5 with respect to synthesis time.

Time (day)	S _{BET} (m ² /g) ^(a)	S _{mic} (m ² /g) ^(b)	S _{EXT} (m ² /g) ^(c)	V _{total} (cm ³ /g) ^(d)	t-plot V _{micro} (cm ³ /g) ^(e)	V _{meso} (cm ³ /g) ^(f)
7	508	18	490	0.55	0.01	0.54
10	448	189	259	0.39	0.09	0.30
14	395	268	127	0.27	0.13	0.14

a: S_{BET}=BET surface area, which was calculated using the BET method

b: S_{mic}=t-plot surface area, which was calculated using t-plot method

c: S_{EXT}= external surface area which was calculated from S_{BET}-S_{mic}

d: V_{total}= Total pore volume determined from the adsorbed amount at P/Po= 0.984

e: t-plot V_{micro}= Micropore volume calculated using t-plot method

f: V_{meso}= mesopore volume, which was calculated from V_{total}- t-plot V_{micro}

3.1.2 Characterization Results for SSZ-13 Zeolites

SSZ-13 zeolite has CHA topology. MTO reaction starts at lower temperature due to its higher acid strength so it can be an alternative for MTO reaction. However, small pore opening and higher acidity result in faster deactivation. Thus, mesoporous boron containing SSZ-13 zeolites were tried to be synthesized to decrease the coke formation and increase the methanol conversion. In literature, boron containing SSZ-13 have not

been studied yet so results obtained from boron incorporation for SSZ-13 are very important.

3.1.2.1 XRD

The XRD patterns of the synthesized SSZ-13 zeolites are shown in Figure 3.20. All samples have same peak positions and shapes as the conventional [Al]-SSZ-13, which represent the typical characteristic peaks of CHA with high crystallinity. Thus, mesoporosity and additional boron do not affect the crystallinity of SSZ-13 zeolites. Intensity of the first peak of conventional [B]-SSZ-13 have higher due to larger crystal size.

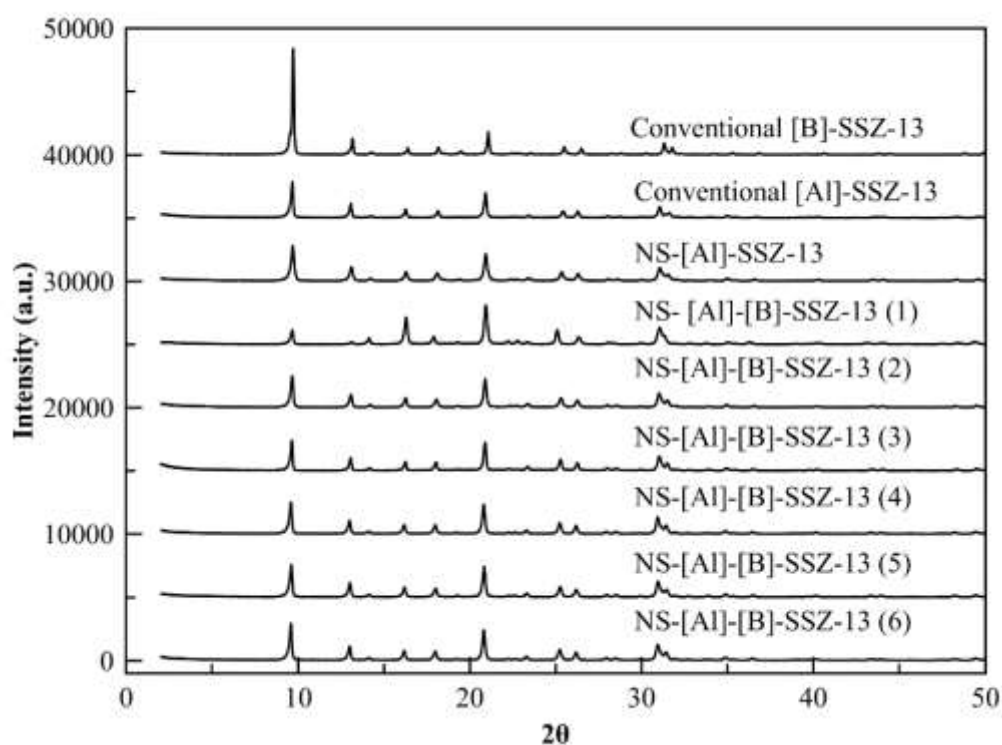


Figure 3.20. XRD patterns of SSZ-13 zeolites ($\lambda = 1.5418 \text{ \AA}$)

3.1.2.2 SEM Images

The SEM images of conventional [Al]-SSZ-13 and conventional [B]-SSZ-13 are shown in Figure 3.21. According to the Figure, both of them have regular crystals with an average size of 1 μm and 40 μm , respectively. Crystal size increases with boron incorporation.

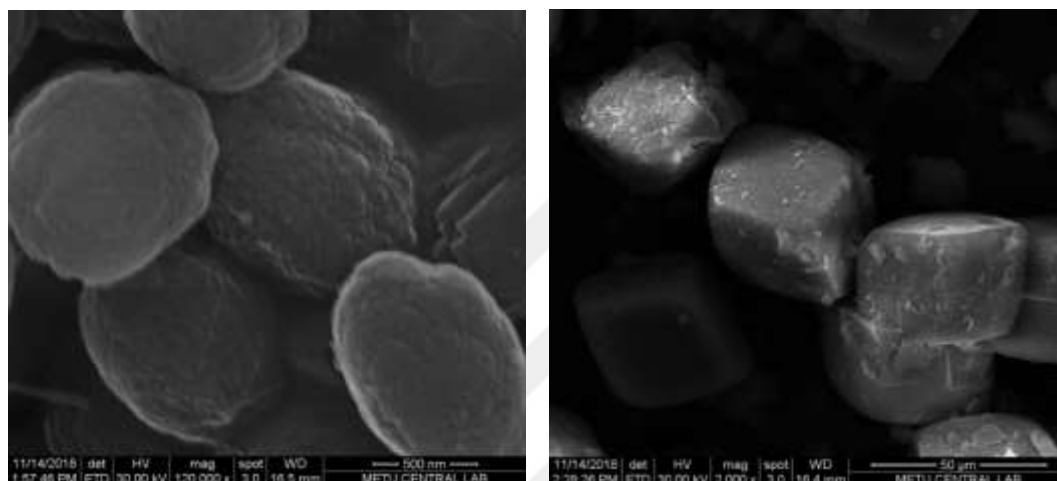


Figure 3.21. SEM images for conventional [Al]-SSZ-13 (a) and conventional [B]-SSZ-13 (b)

As can be seen in Figure 3.22 (a), NS-[Al]-SSZ-13 has different morphology from conventional SSZ-13. Micron-sized particles ranging from 3 to 5 μm form from aggregation of nanoparticles which are around 800 nm. According to Figure 3.22 (b), (c) and (d) boron incorporation of nanosized SSZ-13 also changes the morphology and crystal sizes. As Xue et al. reported, the size of the microsphere aggregates increases with increasing amount of CTABr [106]. In our cases, amount of CTABr also affects the crystal size, which increases with increasing CTABr content. While NS-[Al]-[B]-SSZ-13 (2), having larger CTABr content has larger crystals size in the range of 800 nm-1.8 μm , NS-[Al]-[B]-SSZ-13 (1) has crystals size in the range of 300-600 nm. The addition of CTAB at an early time of the nucleation does not affect the crystallinity and NS-[Al]-[B]-SSZ-13 (3) has crystals size in the range of 800 nm-1.5 μm .

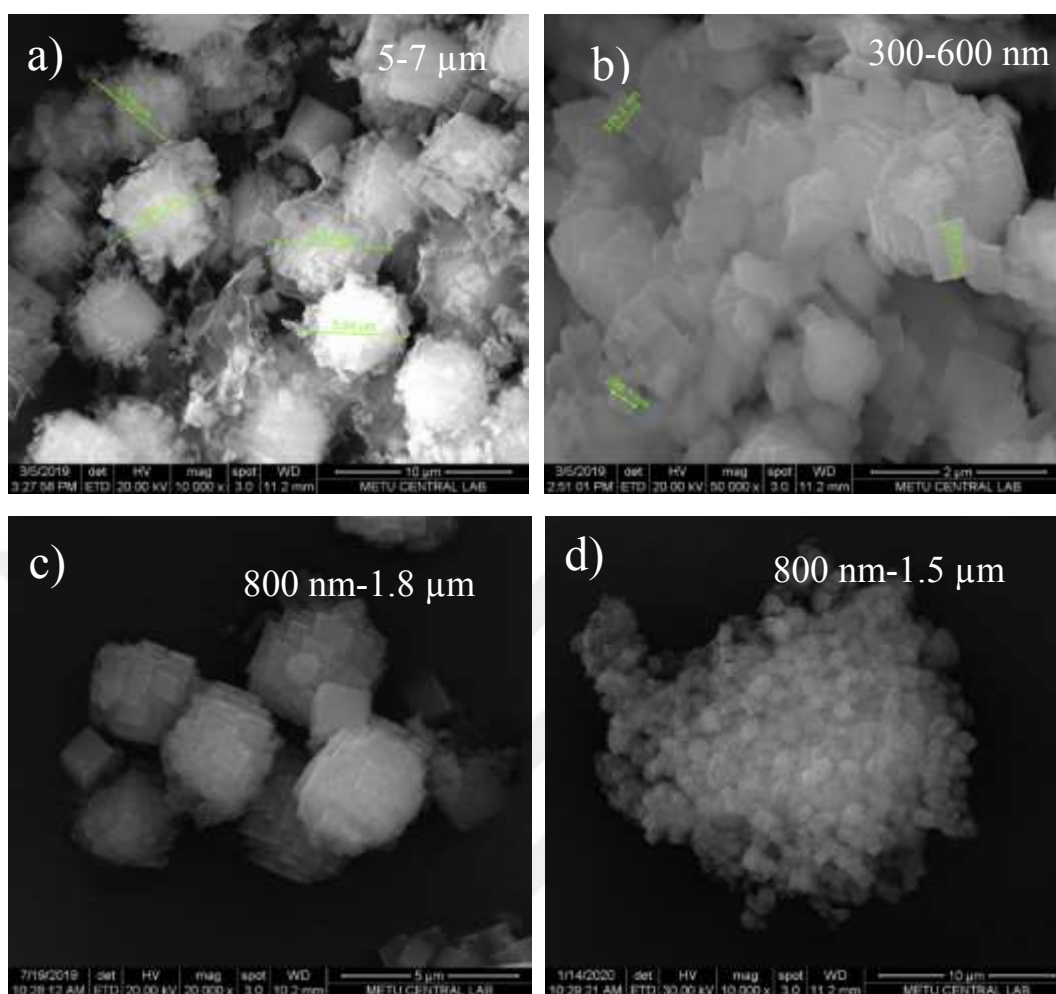


Figure 3.22. SEM images for NS-[Al]-SSZ-13 (a), NS-[Al]-[B]-SSZ-13 (1) (b), NS-[Al]-[B]-SSZ-13 (2) (c) and NS-[Al]-[B]-SSZ-13 (3) (d)

3.1.2.3 N₂ Physisorption Isotherms

Figure 3.23 represents N₂ adsorption-desorption isotherms for SSZ-13 zeolites. As can be seen in this figure, while conventional [Al]-SSZ-13 and conventional [B]-SSZ-13 have type I isotherm, NS-[Al]-SSZ-13 zeolites have type IV isotherm.

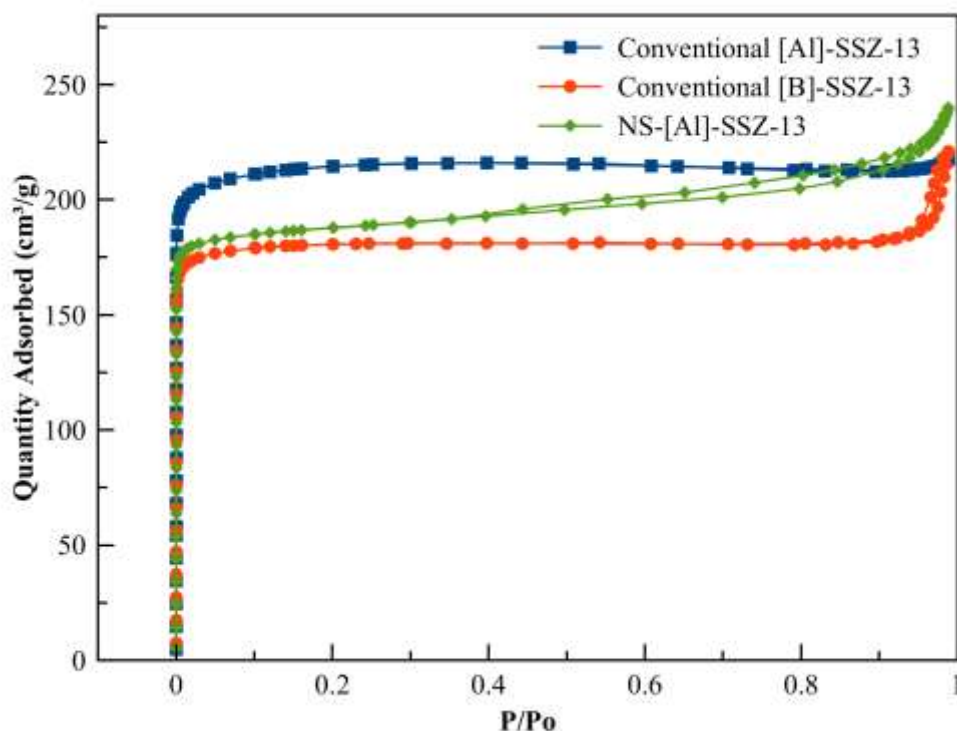


Figure 3.23. N₂ adsorption-desorption isotherms for conventional [Al]-SSZ-13 and [B]-SSZ-13 and NS-[Al]-SSZ-13 obtained at -196 °C

To synthesize nanosized [Al]-[B]-SSZ-13 samples, certain amount of CTABr is added when the zeolite precursors have already been formed. Firstly, small amount of CTABr was added. However, as you can see from Figure 3.24, it was not enough to produce mesoporosity. Increasing amount of CTABr results in higher adsorption quantity and hysteresis.

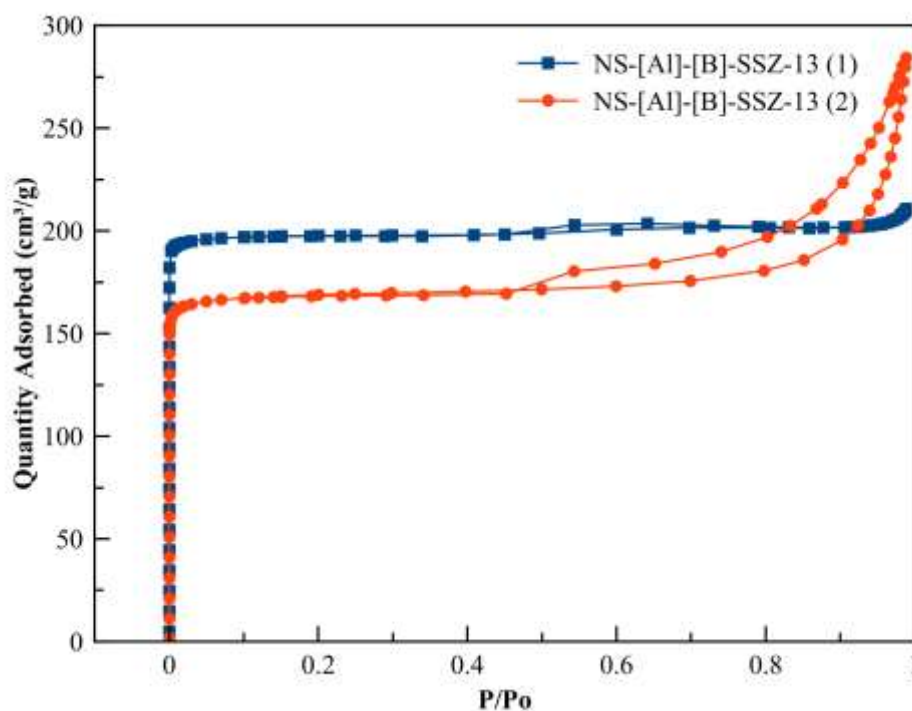


Figure 3.24. N₂ adsorption-desorption isotherms for NS-[Al]-[B]-SSZ-13 (1) and (2) obtained at -196 °C

The addition time of the mesoporegen; i. e., CTABr following the nucleation period of the zeolite synthesis was varied for different batches. The CTABr was added following 50 h of hydrothermal synthesis for NS-[Al]-[B]-SSZ-13 (3), it was 60 h and 69 h for NS-[Al]-[B]-SSZ-13 (2) and NS-[Al]-[B]-SSZ-13 (4), respectively. According to Figure 3.25, NS-[Al]-[B]-SSZ-13 (3) have the highest adsorption capacity and hysteresis. This may due to time used formation of the zeolite precursors.

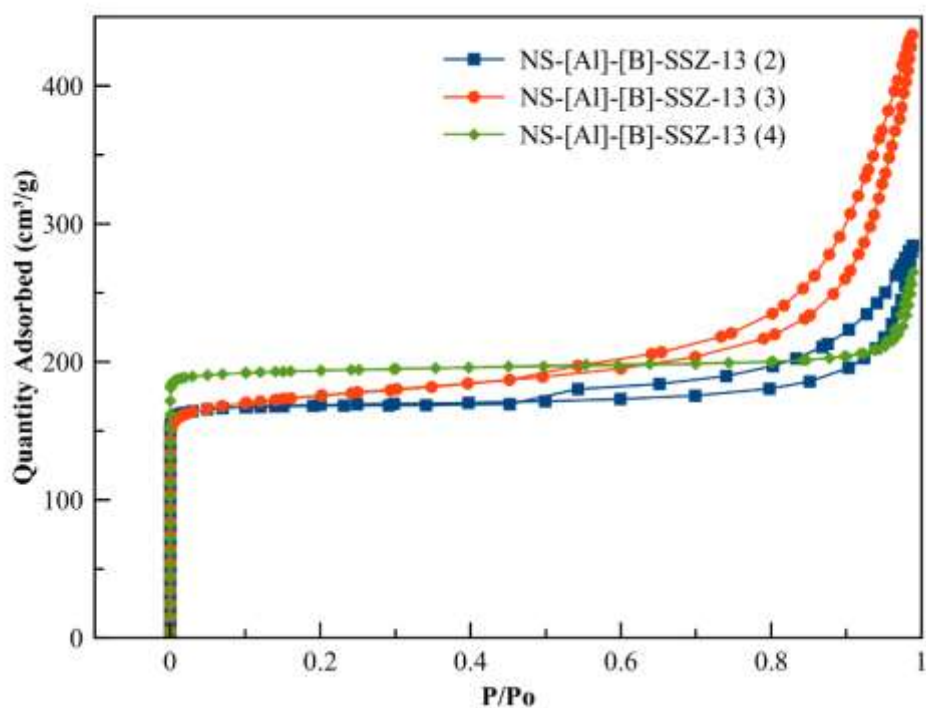


Figure 3.25. N₂ adsorption-desorption isotherms for NS-[Al]-[B]-SSZ-13 (2), (3) and (4) obtained at -196 °C

NS-[Al]-[B]-SSZ-13 (5) and NS-[Al]-[B]-SSZ-13 (6) were synthesized for consistency. They have same synthesis conditions with NS-[Al]-[B]-SSZ-13 (4). According to Figure 3.26, all have almost the same adsorption quantity except NS-[Al]-[B]-SSZ-13 (6) whose adsorption quantity is lower than others.

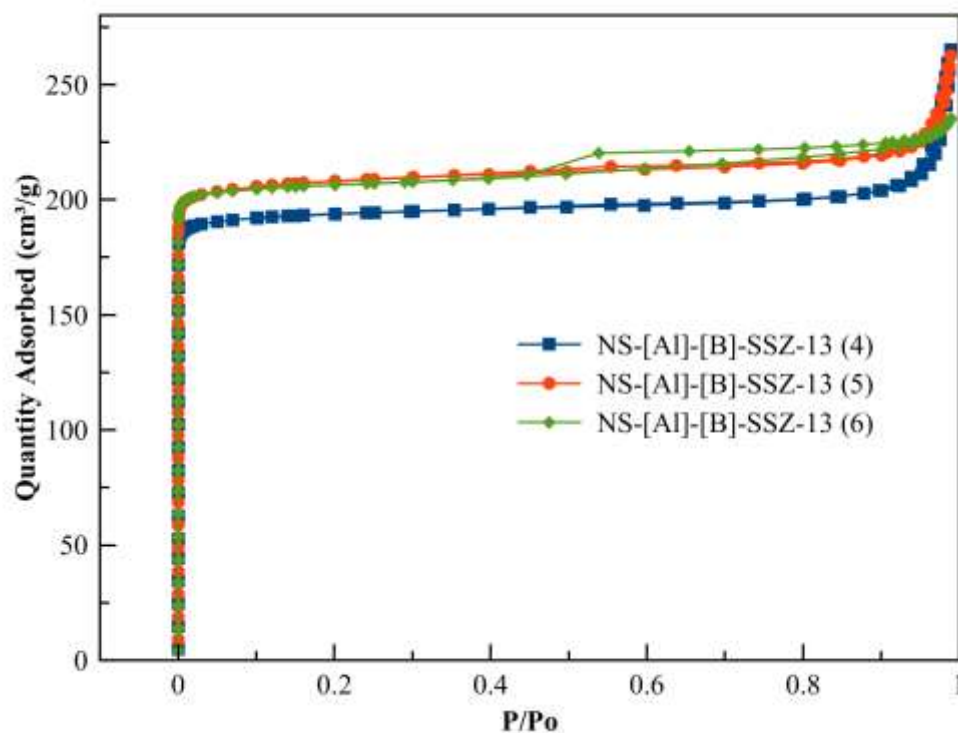


Figure 3.26. N₂ adsorption-desorption isotherms for NS-[Al]-[B]-SSZ-13 (4), (5) and (6) obtained at -196 °C

3.1.2.4 Pore Size Distributions

Figure 3.27 shows BJH pore size distributions for NS-[Al]-SSZ-13 and NS-[Al]-[B]-SSZ-13. According to the Figure, they have a broad range of the pore sizes and they have both mesopores and macropores. NS-[Al]-SSZ-13 has pores in the range of ~15 to 130 nm. On the other hand, NS-[Al]-[B]-SSZ-13 has pores in the range of ~30 to 150 nm.

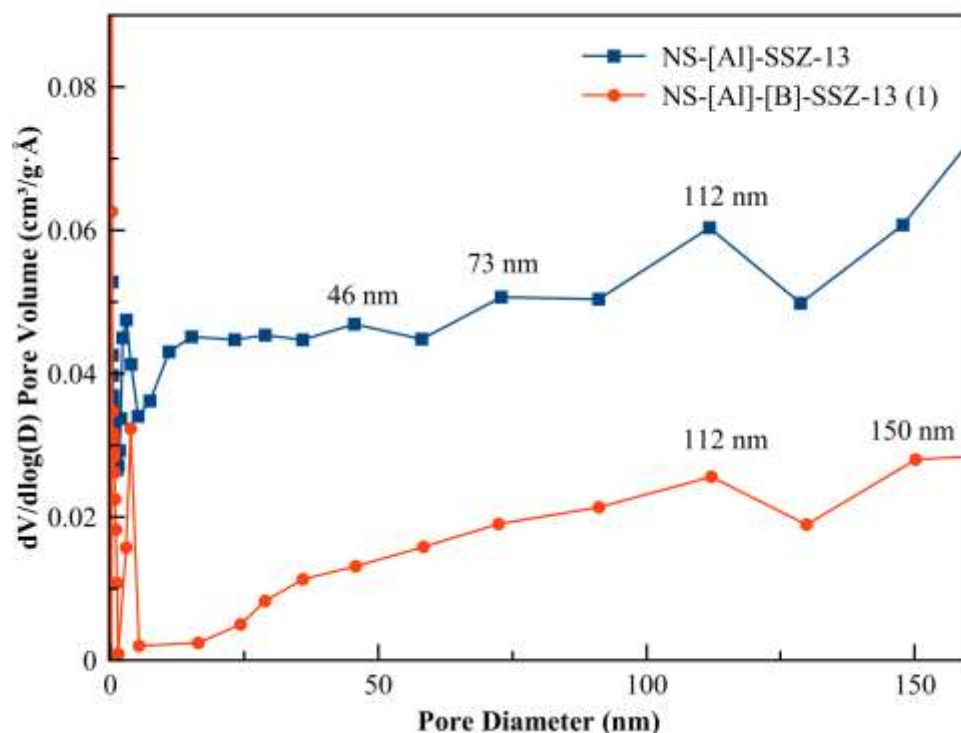


Figure 3.27. BJH adsorption branch pore size distribution of NS-[Al]-SSZ-13 and NS-[Al]-[B]-SSZ-13 (1)

BJH pore size distributions for NS-[Al]-[B]-SSZ-13 (2) and NS-[Al]-[B]-SSZ13 (3) are presented in Figure 3.28. According to the Figure, they also have a broad range of the pore sizes and they have both mesopores and macropores. NS-[Al]-SSZ-13 (2) has pores in the range of ~20 to 130 nm. On the other hand, NS-[Al]-[B]-SSZ-13 (3) has pores in the range of ~15 to 140 nm.

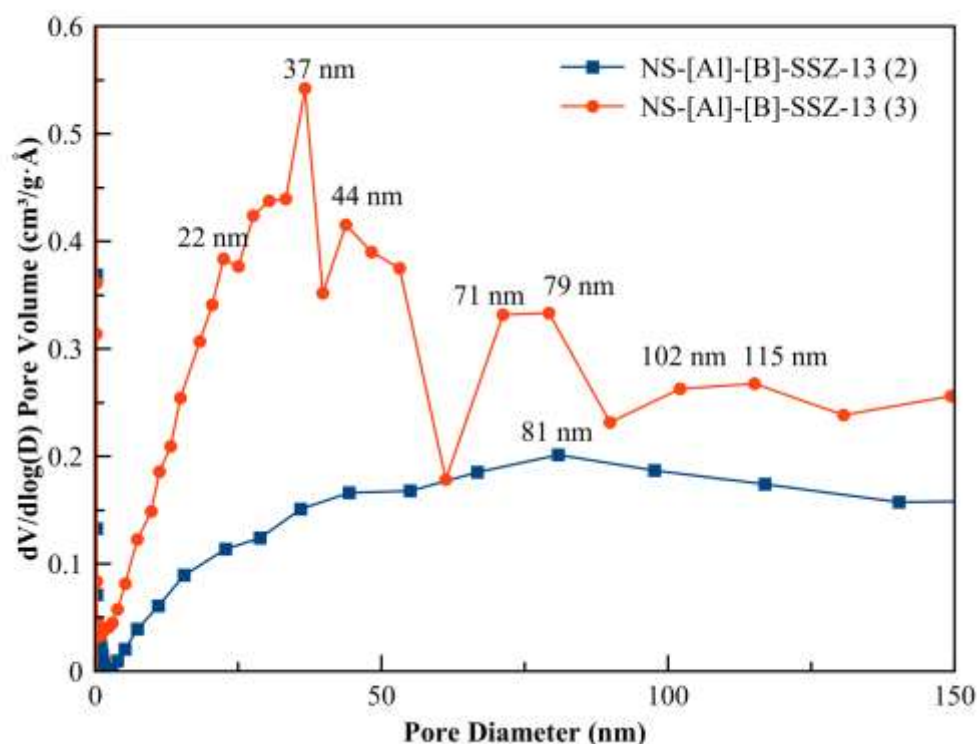


Figure 3.28. BJH adsorption branch pore size distribution of NS-[Al]-[B]-SSZ-13 (2) and NS-[Al]-[B]-SSZ-13 (3)

Figure 3.29 shows BJH pore size distributions for NS-[Al]-[B]-SSZ-13 (4), NS-[Al]-[B]-SSZ-13 (5) and NS-[Al]-[B]-SSZ-13 (6). According to the Figure, they have narrow pore sizes and they have macropores. While NS-[Al]-SSZ-13 (4) and NS-[Al]-SSZ-13 (5) have pores in the range of ~70 to 170 nm., NS-[Al]-[B]-SSZ-13 (6) has pores in the range of ~110 to 150 nm.

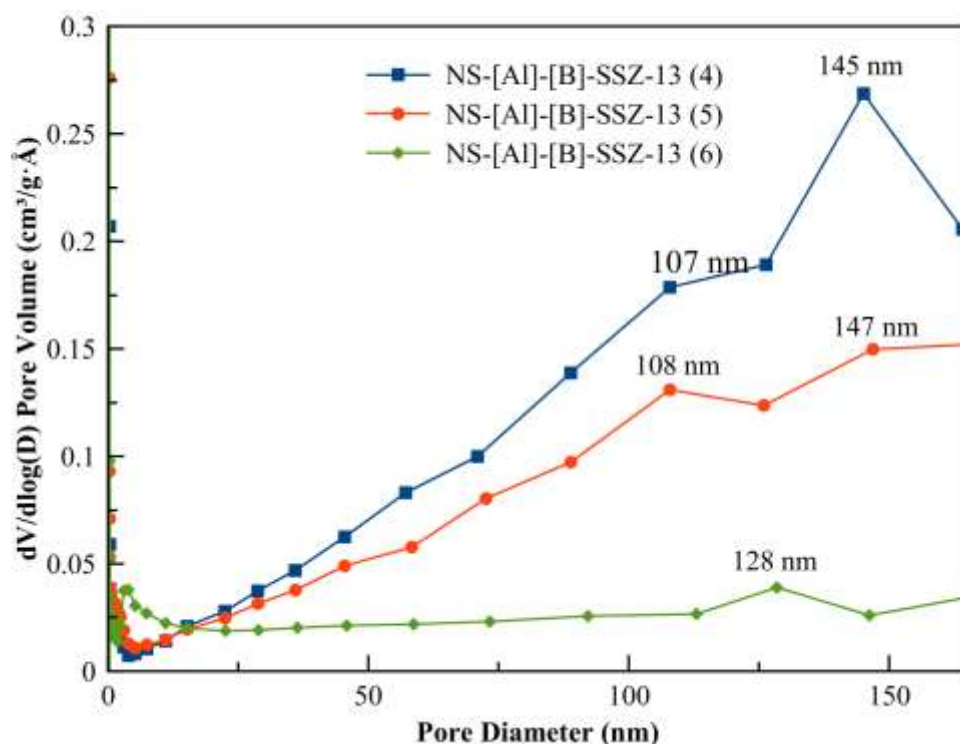


Figure 3.29. BJH adsorption branch pore size distribution of NS-[Al]-[B]-SSZ-13 (4), NS-[Al]-[B]-SSZ-13 (5) and NS-[Al]-[B]-SSZ-13 (6)

3.1.2.5 N₂ Physisorption Characteristic Results

Table 3.3 gives the texture properties of SSZ-13 zeolites using N₂ adsorption isotherms. As can be seen in this table, all SSZ-13 zeolites have similar microporous volume. However, addition of boron and decreasing crystal size decrease the Langmuir surface area of them. NS-[Al]-SSZ-13 have 0.1 cm³/g mesoporous volume so adding CTABr can create mesoporous volume. However, Li et al. [63] obtained 0.446 cm³/g mesopore volume using same procedure. Only difference between literature and our study is crystallization time. In our case, 9 days was not enough to formation SSZ-13 and it was heated for 13 days. While Li et al. synthesized smaller crystals in the range of 50-100 nm, our crystals have larger which are around 800 nm. Due to larger crystallization time, larger crystals were obtained. This can result in smaller mesopore volume. Moreover, mesopore formation was not observed for NS-

[Al]-[B]-SSZ-13 (1), which was the first trial of nanosized boron containing SSZ-13, due to addition of small amount of CTABr. Increasing amount of CTABr results in mesopore formation for other trials and NS-[Al]-[B]-SSZ-13 (2) have 0.161 cm³/g mesopore volume. The largest mesopore volume are obtained from NS-[Al]-[B]-SSZ-13 (3), which is 0.417 cm³/g. This can be due to the addition of CTAB at an early time of the nucleation, that could have resulted in better interaction of CTAB with the zeolite precursors.



Table 3.3 Elemental analysis and N₂ physisorption characteristic results

Sample	Si/Al ^(a)	Si/Al ^(b)	Si/B ^(b)	S _{BET} (m ² /g) ^(c)	S _{mic} (m ² /g) ^(d)	S _{EXT} (m ² /g) ^(e)	V _{total} (cm ³ /g) ^(f)	t-plot V _{micro} (cm ³ /g) ^(g)	V _{meso} (cm ³ /g) ^(h)
Conventional [Al]-SSZ-13	11±1	11	-	690	626	64	0.335	0.304	0.031
Conventional [B]-SSZ-13	-	-	88	583	558	25	0.325	0.267	0.058
NS-[Al]-SSZ-13	14±0.3	-	-	608	546	62	0.363	0.263	0.100
NS-[Al]-[B]-SSZ-13 (1)	9.6±0.6	10	276	630*	618*	12*	0.322*	0.300*	0.022*
NS-[Al]-[B]-SSZ-13 (2)	8.6±0.4	8.5**	120**	544	514	30	0.408	0.247	0.161
NS-[Al]-[B]-SSZ-13 (3)	10.4±0.9			571	452	119	0.636	0.219	0.417
NS-[Al]-[B]-SSZ-13 (4)				625	591	34	0.373	0.284	0.089
NS-[Al]-[B]-SSZ-13 (5)				670	621	49	0.382	0.300	0.082
NS-[Al]-[B]-SSZ-13 (6)				664	626	38	0.359	0.302	0.057

a: Si/Al determined from EDX analysis

b: Si/Al and Si/B from ICP-OES

c: S_{BET} = BET surface area, which was calculated using Brunauer-Emmett-Teller (BET) method

d: S_{mic} = t-plot surface area, which was calculated using t-plot method

e: S_{EXT} = external surface area which was calculated from S_{BET}-S_{mic}

f: V_{total} = Total volume determined from the adsorbed amount at P/Po = 0.98

g: t-plot V_{micro} = Micropore volume calculated using t-plot method

h: V_{meso} = Mesopore volume, which was calculated from V_{total} - t-plot V_{micro}

*: results were determined after ammonium exchange

**: results calculated from XRF

3.1.3 Characterization Results for SSZ-39 Zeolites

SSZ-39, which is a zeolite with AEI structure, has large cages connected by a three-dimensional small 8-ring pore system containing large cavities with D6R in its structure. SSZ-39 cage structure are similar to CHA cages. There are very few studies about SSZ-39 zeolite as a catalyst for MTO reaction [124], [125] and boron incorporation into the AEI framework [126]. Thus, boron containing SSZ-39 zeolites were tried to be synthesized.

3.1.3.1 XRD

Figure 3.30 shows that XRD patterns of SSZ-39 zeolites reveal the crystallization of the pure AEI structure. Additional boron does not affect the crystallinity. However, due to different crystal sizes for the samples, different diffraction intensities are observed.

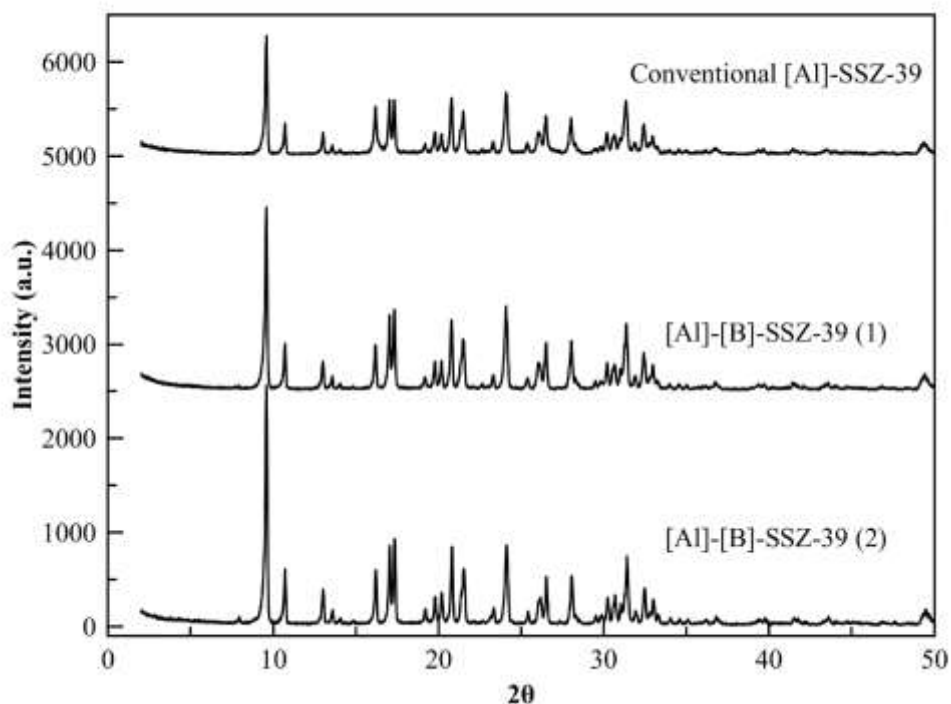


Figure 3.30. XRD patterns of SSZ-39 zeolites ($\lambda = 1.5418 \text{ \AA}$)

3.1.3.2 SEM Images

SEM images of [Al]-ZSM-5, [Al]-[B]-SSZ-39 (1) and [Al]-[B]-SSZ-39 (2) are shown in Figure 3.31. According to this figure, boron incorporation does not affect the morphology and crystal size for [Al]-[B]-SSZ-39. However, increasing amount of boron changes the morphology and increases the crystal size.

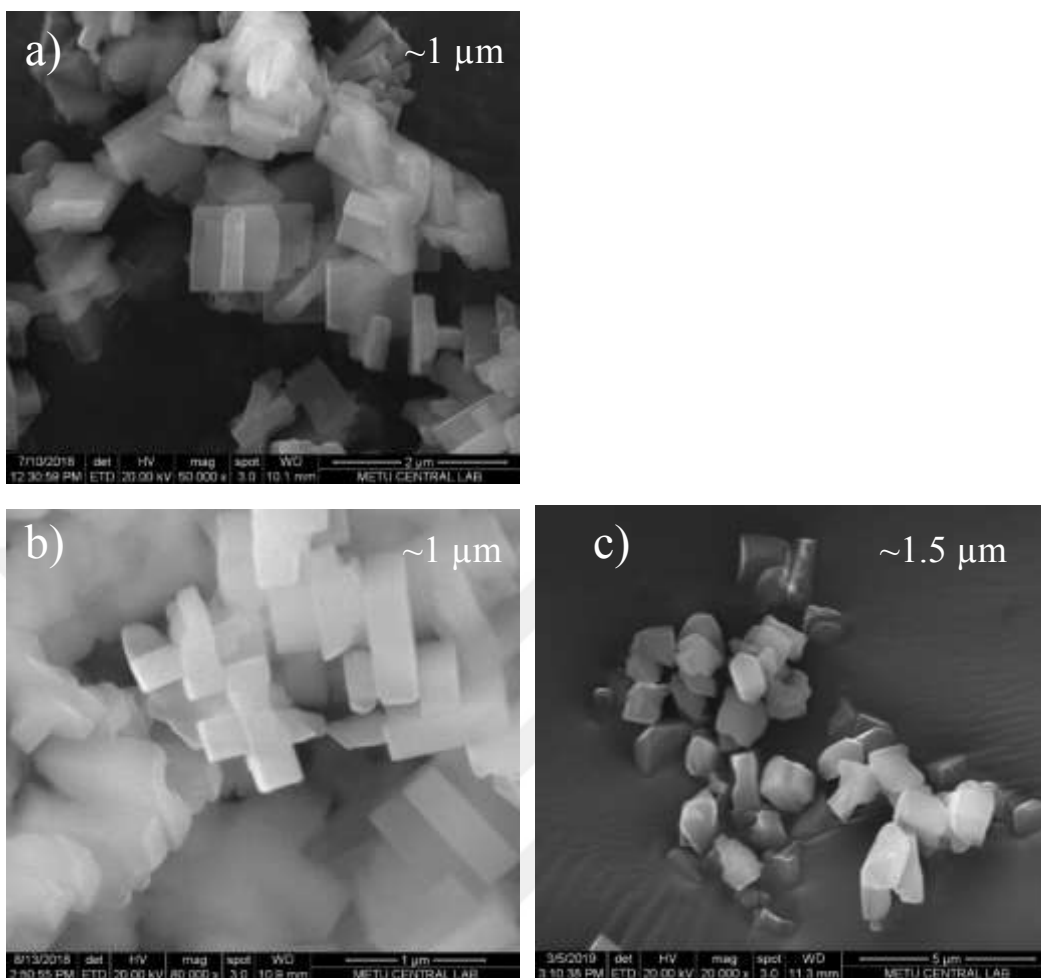


Figure 3.31. SEM images for [Al]-SSZ-39 (a), [Al]-[B]-SSZ-39 (1) (b) and H⁺-[Al]-[B]-SSZ-39 (2) (c)

3.1.3.3 N₂ Physisorption Isotherms

According to Figure 3.32 showing N₂ adsorption-desorption isotherms for SSZ-39, all samples have type I isotherm. Boron incorporation increases the adsorption capacity.

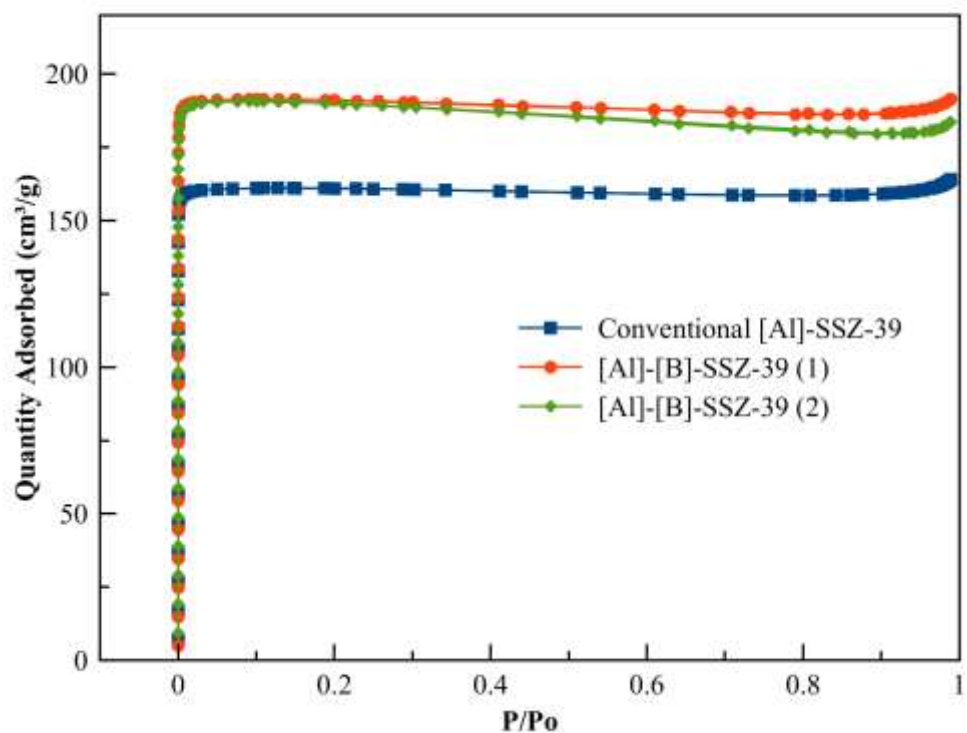


Figure 3.32. N₂ adsorption-desorption isotherms for SSZ-39 zeolites obtained at -196 °C.

3.1.3.4 N₂ Physisorption Characteristic Results

The texture properties of SSZ-39 zeolites are given in Table 3.4. Boron incorporation increases Langmuir surface area, total volume and micropore volume. Si/Al ratio and boron incorporation increase for [Al]-[B]-SSZ-39 (2) due to the use of dealuminated zeolite Y.

Table 3.4 Elemental analysis and N₂ physisorption characteristic results for SSZ-39 zeolites

Sample	Si/Al ^(a)	Si/Al ^(b)	Si/B ^(c)	S _{mic} (m ² /g) ^(d)	V _{total} (cm ³ /g) ^(e)	t-plot V _{micro} (cm ³ /g) ^(f)
Conventional [Al]-SSZ-39	6±2		-	517	0.252	0.250
[B]-[Al]-SSZ-39 (1)	10±0.3	10	731	619	0.295	0.299
H ⁺ - [B]-[Al]-SSZ-39 (2)	13±1	11	375	621	0.282	0.302

a: Si/Al determined from EDX analysis

b: Si/Al from ICP-OES

c: Si/B from ICP-OES

d: S_{mic}= t-plot surface area, which was calculated using t-plot method

e: V_{total}= Total volume determined from the adsorbed amount at P/P₀= 0.98

f: t-plot V_{micro} = Micropore volume calculated using t-plot method

3.2 Methanol to Olefins Reaction Results

The increasing demand for propylene motivated research for an alternative route to petrol: methanol-to-propylene via acidic zeolites, among which ZSM-5 is utilized for large scale production at atmospheric pressure and temperatures of 450–480 °C. The two most common problems encountered for ZSM-5 can be listed as catalyst deactivation and propylene selectivity, which is desired to be increased via lower Al content, mesopore formation, boron incorporation and selective Al distribution.

Here, we investigated the effect of mesopores and addition of B sites to decrease the acid content of the zeolites by comparing MTO results of NS-[Al]-[B]-ZSM-5 and Mes-[Al]-[B]-ZSM-5 to conventional [Al]-ZSM-5 and Mes-[Al]-ZSM-5 (2). Since Al content affects the acid concentration and product selectivity (as well as coke formation rates), the Al composition of the prepared zeolites are reminded to the reader in Table 3.5.

Table 3.5 Elemental analysis and N₂ physisorption results for zeolites used in MTO

Sample	Si/Al ^(a)	Si/Al ^(b)	Si/B ^(c)	S _{BET} (m ² /g) ^(d)	V _{total} (cm ³ /g) ^(e)	t-plot V _{micro} (cm ³ /g) ^(f)	V _{meso} (cm ³ /g) ^(g)
Conventional [Al]-ZSM-5	34	-	-	342	0.157	0.138	0.018
Mes-[Al]-ZSM-5 (2)	20±2	21	-	369	0.257	0.139	0.118
Mes-[Al]-[B]-ZSM-5	51±2		282*	353	0.173	0.092	0.081
NS-[Al]-[B]-ZSM-5	35±3	45	98	373	0.325	0.140	0.185

a: Si/Al determined from EDX analysis

b: Si/Al from ICP-OES

c: Si/B from ICP-OES

d: S_{BET}=BET surface area, which was calculated using Brunauer-Emmett-Teller (BET) method

e: V_{total}= Total volume determined from the adsorbed amount at P/Po= 0.98

f: t-plot V_{micro} = Micropore volume calculated using t-plot method

g: V_{meso} = Mesopore volume, which was calculated from V_{total}- t-plot V_{micro}

*: result calculated from XRF

Conventional [Al]-ZSM-5 showed micron sized coffin shaped crystals with negligible mesoporosity. Mes-[Al]-ZSM-5(2) showed agglomerated microspherical structure composed of cubic crystals of sizes around 100 nm (see Figure 3.7 a, b) that results in high mesopore volumes. NS-[Al]-[B]-ZSM-5 showed agglomerates of small crystals having sizes around 37 nm (see Figure 3.11, a), which resulted in larger mesopore (BET) areas coupled with high mesopore volumes. Mes-[Al]-[B]-ZSM-5; on the other hand, showed agglomeration of large ZSM-5 crystals of size 15*5 μm (see Figure 3.11, b) that showed high crystallinity.

The methanol to olefin activity versus time for the prepared H⁺-zeolites are given in Figure 3.33. According to the figure, conventional [Al]-ZSM-5 shows gradual loss of activity for methanol conversion from the beginning of the reaction, indicating loss of the active sites or blocking of the pores at the beginning. Mes-[Al]-ZSM-5(2) shows 100% methanol conversion for a longer time when compared to conventional [Al]-ZSM-5; however, Mes-[Al]-ZSM-5(2) loses methanol conversion activity with a steeper slope, resulting in a lower 50% activity time (880 min) when compared to conventional [Al]-ZSM-5 (t₅₀= 980 min, see Table 3.6).

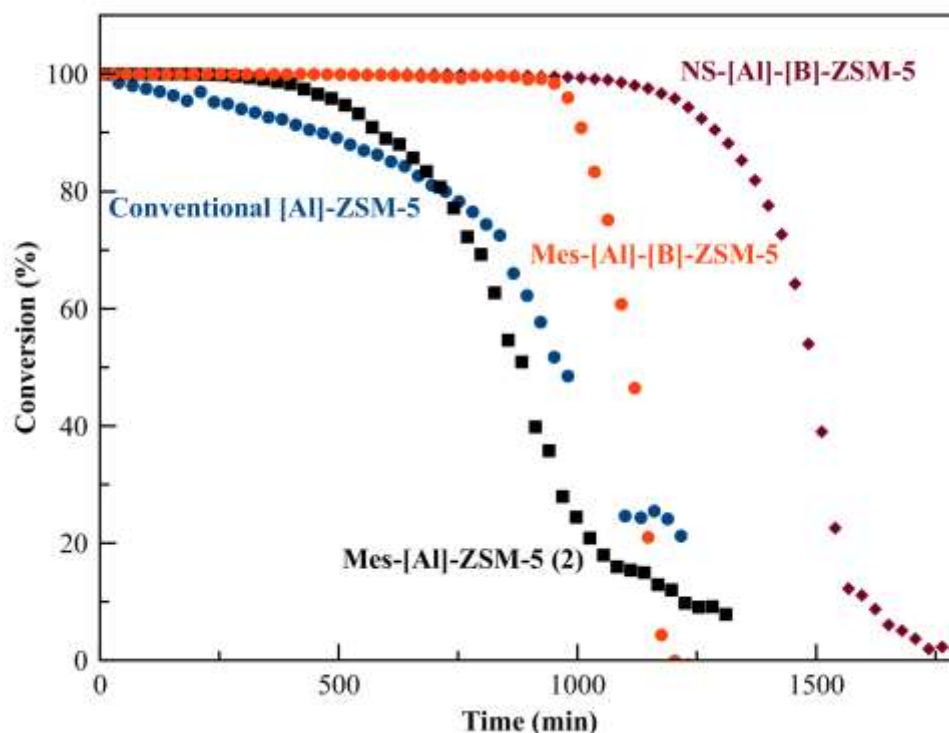


Figure 3.33. Methanol conversion vs. time for conventional [Al]-ZSM-5, Mes-[Al]-ZSM-5 (2), NS-[Al]-[B]-ZSM-5 and Mes-[Al]-[B]-ZSM-5 at 450 °C, 45 sccm He flow with 16.7 kPa CH₃OH partial pressure, WHSV = 5.5 h⁻¹

Mes-[Al]-[B]-ZSM-5 and NS-[Al]-[B]-ZSM-5 preserved their activity for longer times when compared to conventional [Al]-ZSM-5 and Mes-[Al]-ZSM-5 (2). The main parameters affecting the lifetime of the catalyst are the Al content and the mesopore volumes (or external surface areas). Considering the mesopore volumes both Mes-[Al]-ZSM-5 (2) and NS-[Al]-[B]-ZSM-5 should have shown similar long lifetimes. However, as can be seen from Figure 3.33, Mes-[Al]-ZSM-5 (2) deactivated much quicker due to its high acid content (higher Al concentration). Since the other three catalysts share the similar Al content, the lifetime changes are expected from the different mesopore volumes/ surface areas.

The highest lifetime is observed on NS-[Al]-[B]-ZSM-5, which also shows the highest mesopore volume and surface area due to the small particle sizes (~37 nm). The deactivation of the catalyst happens due to the coke formation and blocking of the

active sites. And it is shown to occur firstly on the outer surface areas of the zeolite crystals [127]. Considering this, high surface areas of NS-[Al]-[B]-ZSM-5 together with lower Al content could be accounted as the reason for the long lifetimes observed on it.

Table 3.6 Selectivity of MTO products and 50% catalyst lifetime for conventional ZSM-5, Mes-[Al]-ZSM-5, NS-[Al]-[B]-ZSM-5 and Mes-[Al]-[B]-ZSM-5 at 450 °C, WHSV = 5.5 h⁻¹

Samples	Selectivity %					HTI		
	C2=	C3=	C4=	C5=	C1-C4 Alkane	C3=/C2=	C4-/C4	t ₅₀ / min
ZSM-5	12	26	14	6	16	2.2	0.48	980
Mes-[Al]-ZSM-5	12	16	20	3	19	1.3	0.51	880
Mes-[Al]-[B]-ZSM-5	8	41	22	11	13	5.1	0.33	1120
NS-[Al]-[B]-ZSM-5	13	27	12	5	22	2.0	0.54	1490

Selectivity values are calculated using Eq. 2.2, for the observed products: CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₈, C₄H₁₀, C₅H₁₀, C₅H₁₂ (aromatics are also observed in small quantities but are not quantified here) and given in Table 3.6. According to the table, the desired highest selectivity for propylene is observed on Mes-[Al]-[B]-ZSM-5 with a C3=/C2= ratio of 5.1. Conventional [Al]-ZSM-5 showed a C3=/C2= ratio of 2.2, which is similar to expected C3=/C2= ratio of 1.8 observed on [Al]-ZSM-5 samples [128].

The formation mechanisms of ethylene and propylene are given by a dual-cycle concept by Olsbye et al.[102]. According to their proposal, ethylene is mainly produced from the aromatics-based hydrocarbon-pool cycle (including n-methylbenzenes); whereas propylene and higher olefins are produced from alkene methylations and interconversions (cracking) that occur simultaneously within the zeolite pores (see Figure 1.4).

According a recent study of Li et al., the aromatics-based hydrocarbon-pool cycle is happening at the intersection of the straight and sinusoidal channels of ZSM-5. During the synthesis of [Al]-[B]-ZSM-5, they showed that B ions are selectively located at the tetrahedral sites located near this intersection for a gel Si/Al ratio of 50 and Si/B

ratio of 50 and resulting Si/Al and Si/B ratios of 46 and 82 respectively. Following the deboronation of the sample, majority of the Al cations (or Bronsted acid sites) would be positioned at the straight 10 MR channels. This selective Al positioning is reported to result in an suppressed aromatics-based hydrocarbon-pool mechanism and therefore enhanced alkene mechanism that results in a higher propene selectivity (Propene yield increased from 25% to 40%) [94]. Moreover, it results in a long lifetime of 2250 h. In our case, mes-[Al]-[B]-ZSM-5 has a shorter lifetime of 1120 h.

During the synthesis of mes-[Al]-[B]-ZSM-5, we used a gel composition having a Si/Al ratio of 100 and Si/B ratio of 100 resulting in Si/Al ratio of 51 and Si/B ratio of 282 (following calcination). Hence, similar effect of selective introduction of Al sites at the straight channels of ZSM-5 could also be the case here that results in an enhanced alkene mechanism and increased propylene selectivity (see Figure 3.34).

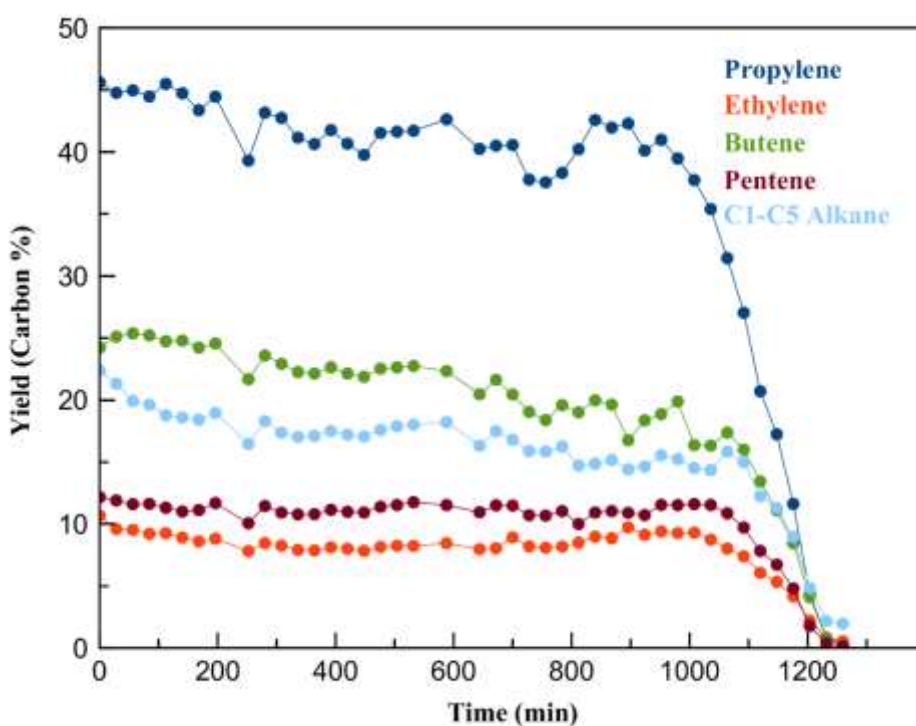


Figure 3.34. MTO product yields for mes-[Al]-[B]-ZSM-5 at 450 °C, 45 sccm He flow with 16.7 kPa CH₃OH partial pressure, WHSV = 5.5 h⁻¹

NS-[Al]-[B]-ZSM-5, having a Si/Al ratio of 45 and Si/B ratio of 98; on the other hand, did not show a higher C₃=/C₂= ratio when compared to conventional [Al]-ZSM-5. This observation questions the exclusive effect of B positioning at the intersection of ZSM-5 that favors propylene selectivity. Other factors should be also directing the enhancing propylene activity.

According to Sazama et al., presence of defect sites; i.e., the external silanols and extra-framework Al sites (acting as Lewis acid sites) are responsible for enhancement of aromatization (causing more ethylene formation) and hydrogen transfer reactions (causing alkane formation as well as coke formation) [129]. Hence, observed higher ethylene formation and alkane formation (C₁-C₄ selectivity of 22% found on NS-[Al]-[B]-ZSM-5 when compared to C₁-C₄ selectivity of 13% found on Mes-[Al]-[B]-ZSM-5) could be due to the higher concentration of defect sites on NS-[Al]-[B]-ZSM-5. The hydrogen transfer activity in MTO is measured with a hydrogen transfer index, which is defined as the ratio of C₄ alkanes to total C₄ concentration. When the HTI are compared, highest HTI is observed on NS-[Al]-[B]-ZSM-5; whereas lowest HTI is observed on Mes-[Al]-[B]-ZSM-5, again indicating lower alkane formation on Mes-[Al]-[B]-ZSM-5 due to lower defect sites.

To investigate one of the defect sites; i.e., the extra-framework Al sites, which are octahedrally coordinated, we performed ²⁷Al MAS-NMR experiment on Mes-[Al]-[B]-ZSM-5 and NS-[Al]-[B]-ZSM-5 (see Figure 3.35). According to the Figure 3.21, the peak at ca. 58 ppm is assigned to tetrahedral Al cations inside the framework; whereas, the peak at 2 ppm is assigned for octahedrally coordinated Al sites (extra-framework Al sites). Absence of the 2 ppm peak indicates Mes-[Al]-[B]-ZSM-5 to be free of extra-framework Al sites, therefore having a much lower defect concentration. This lower defect site explains both the higher C₃=/C₂= ratios and lower alkane formations on Mes-[Al]-[B]-ZSM-5.

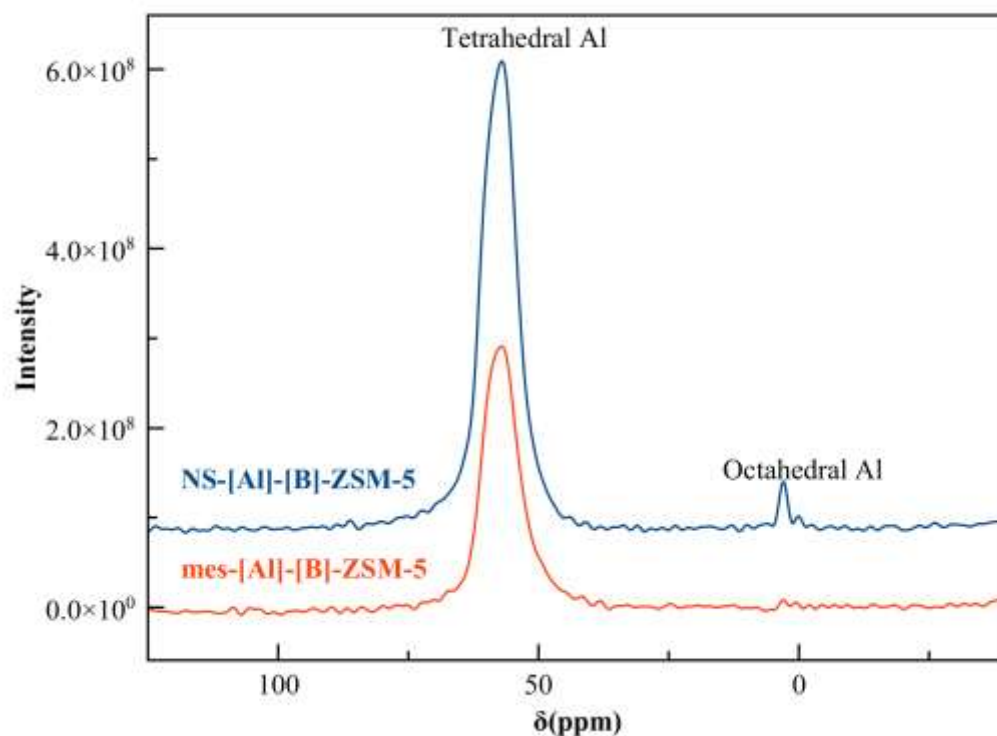


Figure 3.35. ^{27}Al MAS NMR spectra of NS-[Al]-[B]-ZSM-5 and mes-[Al]-[B]-ZSM-5

Another effect of defect site concentration on the MTO reaction is the coke formation rate. The thermogravimetric analysis (TGA) of the spent catalysis is shown in Figure 3.36. According to Figure 3.36, the highest amount of coke has formed on Mes-[Al]-ZSM-5 (2) and NS-[Al]-[B]-ZSM-5. When the coke formation rate is calculated using Eq. 3.1, it was also found that the highest coke formation rate was observed on mes-[Al]-ZSM-5 (2) and NS-[Al]-[B]-ZSM-5 that should have a higher concentration of defect sites.

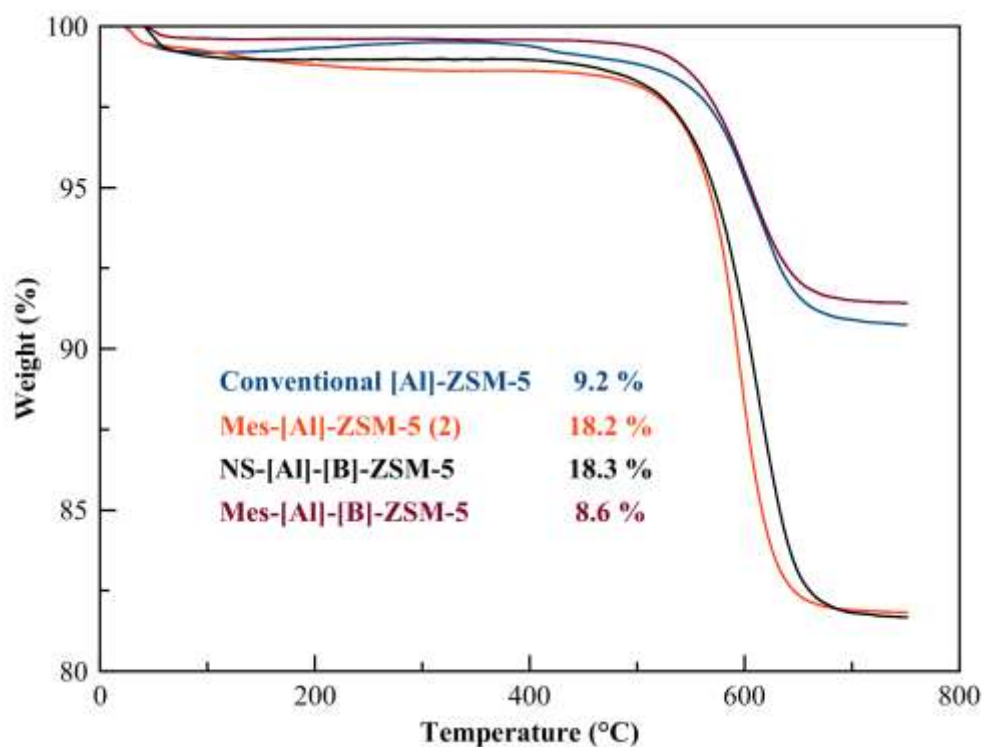


Figure 3.36. TGA analysis of spent conventional [Al]-ZSM-5, Mes-[Al]-ZSM-5 (2), NS-[Al]-[B]-ZSM-5 and Mes-[Al]-[B]-ZSM-5 following MTO reaction at 450 °C, 45 sccm He flow with 16.7 kPa CH₃OH partial pressure, WHSV = 5.5 h⁻¹

$$R_{coke}(mg\ g^{-1}h^{-1}) = \frac{M_{coke}(mg\ g^{-1})}{t_{cat\ 50\% \ lifetime}(h)} \quad \text{Eq.3.1.}$$

Table 3.7 Coke formation rate of used zeolites

Samples	$R_{coke}(mg\ g^{-1}h^{-1})$
Conventional [Al]-ZSM-5	5.6
Mes-[Al]-ZSM-5 (2)	12.4
Mes-[Al]-[B]-ZSM-5	4.6
NS-[Al]-[B]-ZSM-5	7.4

The defect-free synthesis of Mes-[Al]-[B]-ZSM-5 that results in sharp edges of ZSM-5 crystals (see Figure 3.11, b) and high XRD intensities can be due to the low NaOH concentration in the synthesis gel. OH⁻ ions in the gel are known to speed up the

nucleation and crystallization rate of zeolites by providing a better solubility to Si and Al sources. However, high OH concentrations are also known to result in defect sites on zeolites. At lower concentrations of NaOH (Si/Na₂O₃ ratio of 0.01), crystallization of the zeolite was not observed at 150 °C for 34 days. To accelerate the crystallization, we increased the synthesis temperature to 170 °C, at which after waiting approximately 3 weeks, highly crystalline and defect-free crystals are formed.

According to Losch et al., ZSM-5 synthesized in fluoride medium (absence of OH⁻ ions) resulted in defect-free highly crystalline catalysts that show more than 3 times longer catalyst lifetime and a C₃=/C₂= ratio of 7.5 (Si/Al = 139). They explain this high C₃=/C₂= ratio with enhanced effective diffusion rates of C₃=, caused by the defect-free structure even in a large zeolite crystal [130], similar to our Mes-[Al]-[B]-ZSM-5 sample.

To summarize, we were able to increase the lifetime of ZSM-5 catalyst by 1.5 times using a sample that has a high surface area and high mesopore volume (NS-[Al]-[B]-ZSM-5). The propylene selectivity was increased from 26% to 42% (also increasing C₃=/C₂= ratio from 2.2 to 5.1) using a B containing defect-free ZSM-5 crystals (Mes-[Al]-[B]-ZSM-5).

CHAPTER 4

CONCLUSION

In this thesis, synthesis approaches for mesoporous ZSM-5, SSZ-13 and boron containing SSZ-39 were investigated. The synthesis part (first part) of this thesis included three types of zeolites. The first type is the aluminum containing mesoporous ZSM-5, which were obtained using bottom-up approaches. The second type, boron containing ZSM-5 were synthesized to be able to use as precursors for isomorphous substitution with other cations such as Ti(IV). The third type; i.e., boron and aluminum containing ZSM-5, SSZ-13 and SSZ-39 zeolites were synthesized successfully using bottom-up approaches to increase the lifetime and olefin selectivity observed on the conventional zeolite catalysts for methanol-to-olefin reaction.

In the synthesis of aluminum containing mesoporous ZSM-5 ([Al]-ZSM-5):

- Mesoporous ZSM samples obtained via hard templating, soft templating and non-templating methods showed pure phases with high crystallinity.
- While hard template (carbon) does not result in mesopore formation for mes-[Al]-ZSM-5 (1), soft templating and non templating methods create mesoporous volume of 0.118 cm³/g and 0.162 cm³/g for mes-[Al]-ZSM-5 (2) and NS-[Al]-ZSM-5, respectively. For carbon-templating, insufficient interaction of the zeolite precursors with carbon particles was observed.

In the synthesis of boron containing mesoporous ZSM-5 ([B]-ZSM-5):

- [B]-ZSM-5 samples synthesized using soft template (CTABr) have mesoposity within a mesopore pore volume range of (0.112-0.141 cm³/g). Samples having the highest boron amount (mes3-[B]-ZSM-5) have highest mesopore volume, which is 0.141 cm³/g. Increasing boron content resulted in nanosized crystal formation (~450 nm) aggregated to form micron sized spheres containing mesopores between the nanocrystals.

- Moreover, nanosized boron containing ZSM-5 zeolites can be synthesized without using any template, which results in mesopore formation with reported mesopore volumes of 0.116 cm³/g.

In the synthesis of aluminum and boron containing mesoporous ZSM-5 ([Al]-[B]-ZSM-5):

- [Al]-[B]-ZSM-5 zeolites are synthesized using soft template and without using any template. Mes-[Al]-[B]-ZSM-5 and NS-[Al]-[B]-ZSM-5 showed 0.081 cm³/g and 0.185 cm³/g mesopore volume, respectively. Thus better results are obtained from nanosized ZSM-5 samples.

In the synthesis of aluminum and boron containing mesoporous SSZ-13 ([Al]-[B]-SSZ-13):

- Nanosized SSZ-13 zeolites are synthesized by adding CTABr when the zeolite precursors have already been formed.
- They have typical CHA topology with high crystallinity.
- CTABr results in aggregation of nanoparticles and creates 0.100 cm³/g mesopore volume for NS-[Al]-SSZ-13.
- Increasing amount of CTABr results in mesopore formation for NS-[Al]-[B]-SSZ-13 (2), which is 0.161 cm³/g. The highest mesopore volume (0.417 cm³/g) is observed on NS-[Al]-[B]-SSZ-13 (3) due to the addition of CTABr at an early time of the nucleation, which results in better interaction of CTABr with zeolite precursors.

In the synthesis of aluminum and boron containing SSZ-39 ([Al]-[B]-SSZ-39):

- Boron containing SSZ-39 zeolites have typical AEI peaks with high crystallinity without any mesopore formation.
- Using dealuminated Zeolite Y in the synthesis, increases the amount of boron in the framework.

In the second part of the study, catalytic performance of NS-[Al]-[B]-ZSM-5, mes-[Al]-[B]-ZSM-5 and mes-[Al]-ZSM-5 (2) for MTO reaction is compared with that of the conventional ZSM-5.

- According to the results, NS-[Al]-[B]-ZSM-5 showed the longest lifetime (1490 min) due to high mesopore volume and high surface area that accommodates more coke on the pores. However, the same sample (NS-[Al]-[B]-ZSM-5) also showed the highest coke formation rate due to the defects on its structure such as extra-framework aluminum species.
- Mes-[Al]-[B]-ZSM-5, was shown to possess lower mesopore volume ($0.081 \text{ cm}^3/\text{g}$) compared to NS-[Al]-[B]-ZSM-5 ($0.185 \text{ cm}^3/\text{g}$); however, it showed lower coke formation rate and also much higher propylene selectivity (41%) with low ethylene and alkane formation.
- Selective introduction of Al sites at the straight channels due to B presence in the synthesis gel is believed to result in selective propylene formation due to suppressed hydrocarbon-pool mechanism and enhanced alkene mechanism.
- Defect-free structure of mes-[Al]-[B]-ZMS-5 is shown using ^{27}Al MAS NMR and related to the low hydrogen transfer reaction products such as alkanes and aromatics that results in coke formation.
- A longer catalytic lifetime is observed on mes-[Al]-ZSM-5 (1120 min) when compared to conventional [Al]-ZSM-5 (980 min) even though mes-[Al]-ZSM-5 had higher acid concentration. This result could be due to the effect of higher surface areas and mesopores for a higher coke tolerance of mes-[Al]-ZSM-5.

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APPENDICES

A. N₂ Adsorption Experimental Data

Table A.1 N₂ ads. data for conventional [Al]-ZSM-5

Conventional [Al]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure (P/Po)	Quantity Adsorbed (cm ³ /g STP)
1.31619E-05	10.35258076	0.973477264	101.4623712
1.3926E-05	21.00798077	0.976868255	101.4665516
1.39235E-05	31.1760115	0.990162716	102.1463149
2.472E-05	80.1557452	0.990162716	102.1463149
0.000314081	89.88543052	0.977788296	102.4703462
0.000560062	91.27463574	0.968322821	101.7105126
0.001026185	92.66060228	0.954484018	101.6036509
0.002552923	94.59264364	0.943459695	101.5924728
0.004911468	95.90434981	0.930335036	101.6456539
0.007769912	96.82690863	0.917167152	101.74515
0.010589142	97.44503648	0.894740928	101.968667
0.014764551	98.09930717	0.865605635	102.3344337
0.019733998	98.70031143	0.830960618	102.8167752
0.029919012	99.57951232	0.791209989	103.3949007
0.049536199	100.7740301	0.731608313	104.2961333
0.069749989	101.7052296	0.642352893	105.5813649
0.100654334	102.8977635	0.542400032	106.8078347
0.149797684	104.4495123	0.442661674	107.2239019
0.200475391	105.6763146	0.346333248	107.4054007
0.250704637	106.5680635	0.291348703	107.1263857
0.300390209	107.1290582	0.241340915	106.5709406
0.397315004	107.4314384	0.200774323	105.8819563
0.50713399	106.8776894	0.160678938	104.9935424
0.607384511	105.8956797	0.140159682	104.4575972
0.707205589	104.6761847	0.120253771	103.865344
0.806338437	103.2645627	0.100244245	103.2102839
0.857901024	102.5009855		
0.912623343	101.825783		
0.933951634	101.6016564		
0.949242601	101.4698518		
0.962409168	101.4324542		

Table A.2 N₂ ads. data for mes-[Al]-ZSM-5 (1)

Mes-[Al]-ZSM-5 (1)			
Relative Pressure (P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure (P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000118546	6.572309107	0.960650823	87.76209515
0.00013214	16.0816268	0.964325093	87.86050017
0.000138232	26.34054106	0.970437072	88.120
0.000147322	36.60738361	0.975997644	88.45809099
0.000148411	46.88172479	0.981245266	89.05094712
0.000161443	57.11529708	0.984167868	89.38415204
0.000217573	65.16616449	0.985367062	89.6607299
0.001069004	74.55021172	0.987547092	90.1136912
0.002698172	76.32138517	0.988399365	90.57238398
0.005127487	77.43853887	0.975997644	88.45809099
0.007580813	77.95904422	0.988399365	90.57238398
0.010478193	78.32711778	0.979626141	89.44299314
0.014822962	78.6731562	0.968220772	88.60468452
0.01983921	78.97769822	0.955026963	88.02152471
0.029956858	79.45799057	0.944052181	87.68908465
0.04988337	80.17468049	0.930447292	87.45486813
0.070046344	80.62903252	0.91563708	87.32702016
0.100863614	81.280858	0.895390523	87.41704833
0.149707843	82.24466648	0.86614226	87.59748095
0.199727911	83.22128105	0.83131002	87.7279941
0.24933767	84.31345339	0.791425004	87.97049414
0.299350124	85.48115638	0.732191459	88.33157773
0.396624224	87.31322937	0.643684774	88.84883996
0.497200055	88.17175005	0.543925549	89.098254
0.60571425	88.21880697	0.444498394	88.20169276
0.706134927	87.84068772	0.349476783	86.50023995
0.805668535	87.24310234	0.301920541	85.11501426
0.857593143	86.94479691	0.241994381	83.04141831
0.911830313	86.87696405	0.194589085	80.04370569
0.93365059	87.04209266	0.158528725	75.18618152
0.939797176	87.05489177		

Table A.3 N₂ ads. data for mes-[Al]-ZSM-5 (2)

Mes-[Al]-ZSM-5 (2)			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.00010934	6.85246609	0.96188745	152.39959
0.00011023	16.7686008	0.97028124	156.60478
0.00011894	26.6587089	0.97589595	160.186937
0.00015885	35.8786986	0.98066598	163.867028
0.00016568	45.8027994	0.98389977	166.276421
0.00018425	55.6887546	0.98566772	167.709752
0.00018176	65.5765637	0.98772247	169.435848
0.00019848	75.4564838	0.98851029	170.240503
0.00034518	85.1586321	0.98851029	170.240503
0.00049927	87.7736504	0.98110318	168.335564
0.00102839	91.3443497	0.97126114	165.001362
0.00244618	94.7947337	0.96483848	162.126977
0.00518804	97.5606511	0.96348581	161.437051
0.00765079	98.9670629	0.9561465	158.312129
0.01036613	100.070822	0.9350799	150.775741
0.01470583	101.34877	0.92623781	148.229646
0.01975114	102.445732	0.9071689	143.53612
0.02972086	104.001498	0.875394	139.143139
0.04948053	106.100211	0.83223501	135.521501
0.06935433	107.620973	0.79112673	133.11072
0.10179761	109.523434	0.74313173	131.081514
0.15047532	111.687612	0.65012546	128.650946
0.20105236	113.418153	0.55124573	126.916959
0.25138169	114.788332	0.45006738	118.131062
0.30085173	115.903474	0.3498657	116.232507
0.39733043	117.739446	0.29182343	115.245192
0.49636703	119.393704	0.24156229	114.186861
0.59914753	121.217189	0.20122915	113.165569
0.69906415	123.582735	0.16073921	111.925432
0.79805444	127.541891	0.14021988	111.192422
0.84688667	130.730721	0.12030066	110.38666
0.90438567	137.044109	0.10032863	109.467259
0.92415554	140.498364		
0.93880126	143.814524		
0.95132436	147.73115		

Table A.4 N₂ ads. data for NS-[Al]-ZSM-5

NS-[Al]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
2.86414E-05	9.078162931	0.969867792	168.3610918
3.39888E-05	18.91305144	0.975709725	173.6117069
3.56807E-05	28.79641221	0.981283158	180.3394749
4.39295E-05	38.65963706	0.983958616	184.428351
4.07475E-05	48.46571592	0.985643475	188.2444248
6.04087E-05	58.29552606	0.987909712	193.8025318
5.62798E-05	68.13339516	0.988108698	196.2680575
8.39543E-05	77.89260109	0.988108698	196.2680575
0.000405301	87.3110591	0.983096504	191.1292634
0.000516267	88.24762002	0.977999766	185.2038799
0.001062286	90.43677421	0.972514469	179.1749827
0.002533255	93.09666844	0.971508372	177.546893
0.005075828	95.21348674	0.964498022	170.3932716
0.007681717	96.51647904	0.953006281	162.724107
0.01048288	97.53474082	0.941918741	158.1373943
0.014749384	98.67143905	0.928521008	154.3609875
0.019684418	99.691287	0.90732403	150.5644795
0.029690008	101.2823717	0.878630782	146.652401
0.049915417	103.630477	0.840327455	141.0836932
0.069306319	105.4621342	0.801984204	135.7464014
0.101253	108.0376805	0.740611447	130.2601503
0.150411537	111.2916908	0.638648897	125.7565728
0.202015398	113.9049545	0.54353651	123.3173666
0.252587178	115.8885189	0.438574025	120.5517644
0.301812542	117.4442583	0.351962381	118.6053926
0.397549343	119.8163831	0.301643897	117.3930881
0.496671216	121.8585624	0.241619534	115.5897776
0.595925634	124.0141741	0.200707737	114.0426815
0.699820876	127.0967518	0.160937759	112.1718382
0.798431994	132.3855397	0.140208538	111.0080933
0.846925205	137.185837	0.120280991	109.7507214
0.902988056	146.83514	0.100363915	108.3468122
0.925289478	152.0863966		
0.939935242	155.6934537		
0.951864041	159.1848114		
0.962043293	163.6268412		

Table A.5 N₂ ads. data. for NS-[Al]-[B]-ZSM-5

NS-[Al]-[B]-ZSM-5					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000106865	2.135052777	0.964224127	167.0597673	0.140217063	111.5644011
0.00013067	12.10236033	0.969545999	175.8036183	0.120356064	110.7244856
0.000162756	22.00239609	0.973902802	184.3880707	0.101444612	109.8142331
0.000151191	31.91162262	0.976756846	194.4692976		
0.00020093	41.79725069	0.980117495	202.6842349		
0.000205628	51.71997525	0.982203396	209.7926655		
0.000204769	61.63462377	0.984317647	218.3279447		
0.000217698	71.49920025	0.986160115	226.812002		
0.000263566	81.36786532	0.987855731	235.4029857		
0.000675994	90.97141171	0.987855731	235.4029857		
0.001015372	92.71607227	0.985231549	231.1322248		
0.002503538	96.10223072	0.983139404	225.9596785		
0.005159408	98.58460628	0.981399954	220.624771		
0.007503761	99.8550576	0.980097831	216.9273324		
0.010256087	100.9611041	0.975606213	204.9992326		
0.014823706	102.2494679	0.972506412	197.307708		
0.019630815	103.2772752	0.967536211	186.8456533		
0.029783108	104.8485018	0.96445716	180.4702729		
0.049409381	106.9389508	0.957279599	168.7876444		
0.06926595	108.4833639	0.953678478	164.2601065		
0.10196938	110.4807514	0.942919665	152.5797231		
0.15059301	112.7380028	0.94185402	151.6680475		
0.201669399	114.5418286	0.927377456	142.8354986		
0.252011125	115.985385	0.907160569	136.0739759		
0.301156733	117.1740941	0.871124928	130.3076689		
0.397108279	119.1325611	0.836729158	127.4354497		
0.496344888	120.823733	0.791954789	125.2034702		
0.599466319	122.5499457	0.731121457	123.358958		
0.699125801	124.4249465	0.641393391	121.6720472		
0.798308888	127.3542089	0.540816918	120.3017275		
0.846834371	129.7398556	0.441247504	118.6529873		
0.903061375	135.4765043	0.353147915	117.015917		
0.923335482	139.7459594	0.29302167	115.8843556		
0.938335398	144.721918	0.241473709	114.7133749		
0.949807624	151.2757889	0.202367367	113.6696626		
0.959242749	160.6475504	0.161394976	112.3531027		

Table A.6 N₂ ads. data. for mes-[Al]-[B]-ZSM-5

mes-[Al]-[B]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
2.43352E-05	9.030531547	0.993486558	112.2197036
5.41232E-05	18.94244367	0.993486558	112.2197036
4.58512E-05	28.82454117	0.977119371	112.053281
4.46685E-05	38.69007181	0.964738964	112.0075995
4.96354E-05	48.55319164	0.951980209	112.0115179
4.8922E-05	58.40853393	0.92834288	112.071046
5.36471E-05	68.24824012	0.912891574	112.115941
7.86897E-05	78.05642279	0.893336551	112.1953685
0.00061863	87.42821339	0.863453731	112.318274
0.00103046	88.42066649	0.828809132	112.489808
0.002631048	90.10699286	0.788900636	112.6619848
0.005138078	91.30114381	0.729442046	112.9563647
0.007734845	92.03048492	0.640291073	113.3005953
0.010540787	92.57314815	0.540351478	113.575167
0.014752875	93.16613454	0.441073545	113.2120107
0.019841137	93.70351051	0.352050535	112.810526
0.029714128	94.49950136	0.301467101	112.3409742
0.049512159	95.76293839	0.241923965	111.2980759
0.069085151	97.02197817	0.201078712	110.0101659
0.098541663	99.33200708	0.162336229	107.8296742
0.148151234	105.4083855	0.140428157	105.8388395
0.202725832	109.4559935	0.120667671	103.3660744
0.258225103	111.2688452	0.100624644	100.5308645
0.308101793	112.1587109		
0.396966906	112.8937131		
0.509054218	113.1540203		
0.609431289	113.0185841		
0.709260888	112.7335027		
0.808700566	112.3888461		
0.860476468	112.2269758		
0.914918927	112.0881317		
0.936659799	112.0446456		
0.951772836	112.0638701		
0.953498823	112.0395787		
0.975300401	112.0488155		
0.977348385	112.0492426		

Table A.7 N₂ ads. data for conventional [B]-ZSM-5

Conventional [B]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000104957	7.028095218	0.980476263	116.2945773
0.000129194	16.98055589	0.982932255	116.3492537
0.000142496	26.8818948	0.983587521	116.332301
0.00015375	36.77401271	0.994934334	117.8632339
0.000166603	46.66880452	0.994934334	117.8632339
0.000181014	56.56693113	0.979505563	116.3133245
0.000195014	66.45477816	0.967065154	115.9159213
0.000204203	71.84414285	0.953404715	115.7397059
0.000242255	81.68887213	0.942029796	115.7181942
0.00059482	91.17009566	0.929432148	115.6649717
0.000986764	93.01721263	0.91428943	115.6799052
0.00251562	95.81789924	0.894665773	115.6118951
0.005195703	97.77898444	0.864999332	115.830828
0.007813624	98.83680312	0.830148402	116.109115
0.010606686	99.61511763	0.790227087	116.4663403
0.0147328	100.4474115	0.73093131	117.0250403
0.019882195	101.1954547	0.641597752	117.7474528
0.029699176	102.2505933	0.542129391	118.3218753
0.049814064	103.7576102	0.442388022	118.0278408
0.069473677	104.9922382	0.353085821	117.2461011
0.100796618	106.8411925	0.301614879	116.1856736
0.149533156	109.5877348	0.242059079	114.1901151
0.200945568	112.2334692	0.200667008	112.2958327
0.251080553	114.5810713	0.160345446	110.299797
0.301708593	116.2741276	0.140243585	109.2318788
0.39751402	118.0106571	0.120323999	108.1355992
0.496540473	118.4984036	0.100358421	107.0055239
0.607612072	118.3018732		
0.70795761	117.6886096		
0.807190264	116.8882482		
0.859441084	116.4316424		
0.914047127	116.0421401		
0.935499956	115.9303052		
0.950554977	115.8754293		
0.96392615	115.9642765		
0.964094889	115.9086338		

Table A.8 N₂ ads. data for mes1-[B]-ZSM-5

Mes1-[B]-ZSM-5			
Relative Pressure (P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure (P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000106818	3.615952531	0.976338502	135.1677314
0.000138595	13.50400544	0.981451165	135.6797777
0.000139478	23.39640939	0.983720666	136.0344837
0.000155236	33.26935674	0.985561219	136.4255662
0.000185492	43.15452641	0.987608661	136.8380864
0.000201343	53.0658987	0.989521663	137.2197056
0.000218123	62.92565917	0.989521663	137.2197056
0.000248824	72.7598805	0.979142699	136.1588358
0.000776906	82.21033272	0.967753828	135.1281731
0.001128206	83.70926255	0.955566835	134.3007553
0.002555503	86.43532674	0.943625845	133.6902944
0.004949291	88.4882721	0.940194718	133.5247345
0.007601518	89.7877407	0.925503479	133.0060826
0.010368793	90.71200622	0.906068365	132.4672579
0.014613841	91.75920456	0.877256526	131.9532276
0.019899523	92.70931845	0.842243771	131.5028705
0.029695659	94.00917283	0.802281114	131.1041412
0.049506253	95.89102995	0.743328772	130.6505731
0.069360294	97.38915208	0.650387807	129.9419807
0.101102124	99.57092964	0.550253509	129.0751639
0.149033395	103.0487346	0.457949682	117.4424121
0.201005293	106.6797638	0.448090336	116.8952183
0.252460565	109.5020509	0.34162057	113.1236116
0.303178811	111.7952374	0.292999204	111.3056932
0.397096952	115.1630638	0.241592538	109.0396472
0.496117126	117.9995936	0.201062195	106.9137748
0.59920401	120.6450877	0.1611265	104.4053684
0.699013435	123.4120541	0.140239373	102.8501888
0.799166381	126.6940302	0.120236703	101.3033462
0.847099405	128.6423854	0.100142657	99.83208494
0.90157289	130.9945537		
0.923561588	131.9553052		
0.938515422	132.6363056		
0.95202019	133.3220223		
0.962709876	134.0058833		
0.970561131	134.5942572		

Table A.9 N₂ ads. data for mes2-[B]-ZSM-5

Mes2-[B]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
3.4758E-05	9.352782168	0.970624816	126.0832605
4.80767E-05	19.26422751	0.976362166	126.3631042
5.52449E-05	29.16368313	0.981364154	126.738304
6.40389E-05	39.0600467	0.984042563	126.9673597
3.97269E-05	48.9755763	0.985463261	127.1474544
4.83421E-05	58.8510556	0.987632318	127.4130634
6.31123E-05	68.72017787	0.988933667	127.5597477
0.00010286	77.78661096	0.988933667	127.5597477
0.000231719	82.35132462	0.978944665	126.8334556
0.000529396	85.17614585	0.967687131	126.3645933
0.001041399	87.36881114	0.954748255	126.0401602
0.002556406	90.09434964	0.94354665	125.8239798
0.004890648	92.03544249	0.93993306	125.7730481
0.007469755	93.29015075	0.925834833	125.62339
0.010324923	94.23667858	0.906168073	125.5852743
0.014583812	95.2544198	0.866457251	125.5844082
0.019720914	96.15375105	0.831236888	125.7214084
0.029674961	97.39450556	0.791470506	125.8062687
0.049431653	99.08596962	0.731971529	126.0828167
0.069231834	100.3496895	0.643395524	126.4342064
0.100865101	102.0428696	0.543383017	126.5594163
0.149328362	104.4167727	0.456239671	114.9267566
0.200579934	106.8365784	0.448598802	114.5519649
0.250753884	109.0125311	0.342112735	111.6628341
0.301183428	110.8719715	0.293091203	110.1899868
0.397216424	113.5421093	0.241650993	108.2905136
0.499604649	115.552392	0.201451164	106.5696725
0.608683208	117.4145587	0.160818859	104.7149636
0.699103052	118.977068	0.140188252	103.7606053
0.7985793	121.2111429	0.120340633	102.8202912
0.847163538	122.5557007	0.100545551	101.865048
0.904144254	124.550684		
0.925212043	124.9781073		
0.948007726	125.4848993		
0.952401473	125.5483886		
0.96272466	125.806503		

Table A.10 N₂ ads. data for mes3-[B]-ZSM-5

Mes3-[B]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
9.21297E-05	9.125156303	0.981420488	160.6743025
0.000100427	18.98043583	0.983832053	161.8082012
0.000110213	28.88609366	0.985593212	162.781331
0.000127565	38.78093514	0.987223823	163.9095989
0.00013067	48.24689579	0.988869808	165.1343127
0.000135871	58.13497299	0.988869808	165.1343127
0.000186481	67.93966201	0.981674905	162.1500831
0.000211372	68.38565369	0.971732063	159.0797833
0.000556185	74.92844121	0.96268808	157.4825459
0.002942747	81.98341981	0.954288484	156.3702197
0.00502176	84.17594045	0.940798793	155.1597968
0.007460275	85.82846418	0.92662195	154.3019837
0.010427727	87.2422559	0.906099073	153.4033984
0.014628336	88.70916906	0.877162417	152.4735495
0.019778348	90.04603599	0.842742926	151.6908199
0.029753838	91.9081267	0.802595864	150.9476701
0.04941496	94.41607579	0.730362899	149.68335
0.069347214	96.25787967	0.650140139	147.9897233
0.101265849	98.56299817	0.552098002	142.6768388
0.150522084	101.3911698	0.473334028	122.3224476
0.201121564	103.911172	0.448007365	116.2004253
0.251414451	106.1806233	0.348297586	110.0162356
0.300794656	108.3242805	0.293615976	107.7699284
0.399424508	112.6656714	0.242584223	105.6513952
0.497412717	120.59685	0.200940738	103.824763
0.596493358	131.1877301	0.160739048	101.9087592
0.697738695	139.7096766	0.14020346	100.8586395
0.798535865	146.6315187	0.120248362	99.76731315
0.858435405	149.9161737	0.100274603	98.5777084
0.913702757	152.8511363		
0.924544996	153.4044636		
0.938826638	154.2997589		
0.951549027	155.3168877		
0.962829403	156.5123269		
0.969740595	157.6374864		
0.976392502	159.1471651		

Table A.11 N₂ ads. data for NS1-[B]-ZSM-5

NS1-[B]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
4.58792E-05	9.165502659	0.969278969	146.1156681
3.84653E-05	19.05182395	0.975282529	151.0182188
4.3193E-05	28.92471917	0.979654228	157.7665642
5.85971E-05	38.81798429	0.982317702	165.4437215
6.06384E-05	48.70359952	0.984324824	173.7174606
7.91169E-05	58.59030059	0.985773667	182.5415457
9.91905E-05	68.50406944	0.986500364	190.8208781
9.4367E-05	77.6287195	0.986500364	190.8208781
0.000140343	87.46968426	0.983984816	187.4072411
0.00073325	96.88834976	0.981323591	182.101207
0.00098754	97.98727822	0.978700512	175.6322554
0.002446639	100.7902569	0.974603215	163.7387689
0.00523	102.9905635	0.972804094	160.0337146
0.007586717	104.0647492	0.964609384	147.3171025
0.010371478	104.9222028	0.950042301	139.5349835
0.014602138	105.859364	0.935807702	136.3491496
0.019738103	106.7046081	0.919199099	134.2748723
0.029760201	107.8759602	0.907180817	133.3061298
0.04951838	109.4457004	0.87818343	131.6321244
0.069230821	110.6278472	0.84240173	130.3835605
0.101000438	112.1677144	0.793654908	129.2485593
0.149664986	114.2351311	0.743371526	128.3931568
0.200935643	116.2029846	0.650692201	127.1377777
0.250833258	118.1108316	0.55040715	125.7768716
0.300399035	119.9525	0.450248299	124.0406436
0.396605835	123.013307	0.350683092	121.6521268
0.496820803	125.3877033	0.30119076	120.0415843
0.599226607	127.1909345	0.241302084	117.7252737
0.699329384	128.7320636	0.200949159	116.1790432
0.799089815	130.4589687	0.160645006	114.674371
0.846827394	131.6261769	0.140404904	113.9024443
0.904488808	134.0997411	0.120262871	113.0932254
0.924649169	135.693424	0.100282169	112.2408235
0.938869137	137.3352259		
0.951436163	139.5774927		
0.962105911	142.6867913		

Table A.12 N₂ ads. data for NS2-[B]-ZSM-5

NS2-[B]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000120596	6.650561493	0.969380813	144.0524312
0.000127934	16.52498837	0.97482089	148.3881499
0.000133739	26.40945752	0.980033352	154.7825183
0.000157053	36.29373666	0.982304463	161.9097121
0.000184881	46.22604615	0.984595135	170.3517904
0.000176857	56.1592707	0.986046506	178.9284903
0.000193745	66.03108868	0.986686206	187.3026203
0.000207061	75.90377157	0.986686206	187.3026203
0.000256611	85.73025634	0.98386522	183.7353972
0.000782449	95.13514956	0.981586394	178.2423961
0.001012453	96.27279491	0.978535047	171.6726647
0.002476182	99.51916465	0.97479674	160.6697014
0.005204244	101.8830054	0.972822929	157.2778032
0.007540772	103.0561389	0.96689457	147.4654144
0.010339746	104.0203223	0.954553403	139.2851822
0.014559464	105.0748111	0.937823189	135.1698046
0.019773484	106.0138512	0.919410888	132.8536916
0.02964779	107.2836551	0.898398092	131.1729413
0.049510732	109.019877	0.877059669	130.0478617
0.069301331	110.2890799	0.8340341	128.6062259
0.101575933	111.9646798	0.792944431	127.6742727
0.150119411	114.0556098	0.73019587	126.5983749
0.201130089	115.9564351	0.650648186	125.4889598
0.251167355	117.6681023	0.550641577	124.1169686
0.300666857	119.2463332	0.45051925	122.4635024
0.396917735	121.8973369	0.350769096	120.2439807
0.496789198	124.066165	0.301920403	118.9102863
0.599516002	125.8354056	0.241270129	117.0432398
0.699524194	127.3787752	0.2012719	115.71866
0.79883499	129.1247997	0.160633325	114.3197783
0.846668576	130.3220084	0.140334518	113.5740259
0.904861412	132.8307463	0.120335104	112.7788444
0.923806348	134.3019179	0.100320469	111.8997729
0.939266507	136.0528254		
0.952146565	138.1839472		
0.962019473	140.8587365		

Table A.13 N₂ ads. data for NS3-[B]-ZSM-5

NS3-[B]-ZSM-5			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000113179	4.033870236	0.961814169	142.4079602
0.000125234	13.93750873	0.969659286	146.0867558
0.000138231	23.8330186	0.975353927	150.5054422
0.0001547	33.73720444	0.979404118	156.9631337
0.000158427	43.64642169	0.981917887	165.0987803
0.000164926	53.53359895	0.983610072	173.2179333
0.000180877	63.42144283	0.984831333	181.4936508
0.000203779	73.32517408	0.986155939	190.3323492
0.000226748	83.19601535	0.986155939	190.3323492
0.000433448	92.8496047	0.983412349	186.5285242
0.000521564	94.09284769	0.980895064	181.1151178
0.001020037	97.48253543	0.9773273	174.2694676
0.002554836	101.0700995	0.974244607	166.409801
0.004920366	103.3742263	0.969759271	154.8621373
0.00753991	104.8559345	0.965925518	148.9036773
0.010395131	105.9419673	0.954999255	140.5837184
0.015923666	107.4144344	0.938082932	135.905282
0.019629682	108.1274983	0.919775422	133.4060326
0.029533911	109.5782753	0.897941125	131.7048862
0.050069327	111.57526	0.877590822	130.5354164
0.071437907	113.0378272	0.834027381	128.9916057
0.101780722	114.6854835	0.793458051	128.0117947
0.150048039	116.7464139	0.730423123	127.0307908
0.201165609	118.4628381	0.640649595	125.8790521
0.251337574	119.9333479	0.550409471	124.8430904
0.300791082	121.1669644	0.450590439	123.5077762
0.397290363	123.2257368	0.353223211	121.7947603
0.496746966	124.9344429	0.301776771	120.7666772
0.599753647	126.4337407	0.241367572	119.3559469
0.699161125	127.9111346	0.201105101	118.2384228
0.799475795	129.694668	0.160633635	116.9842212
0.846716857	130.8778599	0.140253982	116.2547299
0.904852353	133.5005219	0.120262021	115.4713362
0.924047804	135.0783537	0.100308684	114.5810696
0.938500086	136.8509766		
0.950893212	139.1465559		

Table A.14 N₂ ads. data for conventional [Al]-SSZ-13

Conventional [Al]-SSZ-13					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.00010755	4.73774828	0.508527469	215.4393568	0.160715192	213.4926444
0.000158127	14.59673216	0.608197331	214.6781984	0.140123435	212.8370239
0.00016073	24.51046142	0.707711094	213.889347	0.120251241	212.0730925
0.000158424	34.40832337	0.806725024	213.234572	0.100354549	211.1215202
0.000172958	44.31576472	0.858613015	212.9548505		
0.000194213	54.20733237	0.912646674	212.9334247		
0.000212834	58.12823257	0.934901442	213.1484743		
0.000219514	68.10028282	0.940452311	213.2015271		
0.000212986	78.0090164	0.95206918	213.5249642		
0.000221012	87.92328422	0.963481261	214.0363075		
0.000236969	97.8127879	0.970292025	214.5680386		
0.000239398	107.7381799	0.976767364	215.2653473		
0.000264682	117.6099321	0.981358516	215.9461562		
0.000253307	126.8617984	0.983856954	216.4079326		
0.000265308	136.7691553	0.985940671	216.8736884		
0.000269948	146.63866	0.988009507	217.4264054		
0.000292927	156.4639905	0.988640099	217.7214412		
0.000338772	166.3433199	0.943366047	212.8837903		
0.000480581	176.0996615	0.93024897	212.5314503		
0.00050476	176.7369505	0.915069756	212.3276675		
0.000998748	184.4914484	0.89549994	212.2206119		
0.002816135	191.6245052	0.865709543	212.2540247		
0.004993426	194.9775785	0.830535878	212.4275364		
0.00751021	197.2260197	0.790691537	212.7652236		
0.01000881	198.7615823	0.731166509	213.3740657		
0.015626228	201.1408429	0.641666879	214.4421891		
0.021152207	202.7342404	0.541313206	215.6564432		
0.029309656	204.4493353	0.441914471	215.9356893		
0.049373472	207.2315413	0.347593314	215.7818135		
0.06911156	209.05472	0.301044107	215.6267015		
0.102429328	211.1956322	0.241689956	215.0811852		
0.151024865	213.2207736	0.200649082	214.4377565		
0.200928648	214.521386	0.160715192	213.4926444		
0.25148148	215.3136793	0.140123435	212.8370239		
0.301297304	215.7848616	0.120251241	212.0730925		
0.397769418	215.9601081	0.100354549	211.1215202		

Table A.15 N₂ ads. data for conventional [B]-SSZ-13

Conventional [B]-SSZ-13					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000112979	7.456824812	0.805275533	181.0244996	0.120164808	179.6114521
0.000127449	17.41094419	0.847635267	181.3931727	0.100299556	179.1749143
0.000136073	27.31867346	0.904725144	182.5857011		
0.000144574	37.22269153	0.923762824	183.4294295		
0.000163022	47.1294811	0.938532864	184.6272008		
0.000147908	56.21363561	0.951660993	186.3958791		
0.000163986	66.14943152	0.962189513	189.0173179		
0.000170496	76.02208689	0.969633698	192.2251331		
0.000174478	85.88799322	0.975054396	196.7594888		
0.000171984	95.77664859	0.979723165	203.3726001		
0.000179635	105.6965473	0.983166549	209.9145104		
0.000190674	115.5423416	0.985357866	214.9936941		
0.000199342	125.3835003	0.987681273	219.7590223		
0.000187359	134.4815966	0.988732062	220.935348		
0.000249407	144.2873669	0.988732062	220.935348		
0.00043156	153.9361988	0.981467958	218.1699862		
0.00050483	156.0163012	0.974226685	212.802497		
0.000990753	161.1097481	0.970182198	206.9621892		
0.002540064	165.9453501	0.965848394	201.1021763		
0.005068519	168.7448063	0.954892615	191.1878763		
0.007500881	170.1976973	0.938689502	185.5773122		
0.010266559	171.3040035	0.919201311	182.9860754		
0.014582123	172.5095608	0.896957536	181.6075804		
0.01971475	173.5227763	0.866680255	180.8126693		
0.029619409	174.9008907	0.831471791	180.4532195		
0.049598865	176.6665075	0.791041986	180.4003282		
0.069338457	177.7633791	0.731373921	180.4886211		
0.101946556	178.9769522	0.642470026	180.8785894		
0.150619093	179.9704548	0.542068407	181.3855567		
0.200844354	180.6239479	0.443175954	180.94641		
0.246668114	180.9221763	0.346211377	180.8639765		
0.296499931	181.1015346	0.289864383	180.8941848		
0.397555438	181.1085764	0.230139151	180.7967035		
0.508024233	180.9357906	0.200459788	180.632326		
0.607589902	180.776959	0.160797182	180.2391713		
0.706508302	180.7131009	0.140124795	179.9500332		

Table A.16 N₂ ads. data for NS-[Al]-SSZ-13

NS-[Al]-SSZ-13					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000122208	5.062489994	0.699351315	201.0626992	0.160603572	186.8040027
0.000126669	14.23976051	0.798179351	204.8324206	0.140315003	186.261074
0.000137993	24.11021483	0.846364201	207.7761901	0.120259661	185.6510098
0.000135136	34.03342652	0.905143931	213.1038785	0.1001988	184.9873932
0.000148767	43.91543045	0.924424282	215.6382452		
0.00015094	53.7858797	0.938771784	218.0317788		
0.000170218	63.64616652	0.951673275	220.7019241		
0.000182636	73.57038347	0.96241664	223.692965		
0.000191055	83.44493688	0.970400386	226.4337029		
0.000193512	93.31107545	0.976118733	229.230112		
0.000186605	103.1792	0.981367673	232.4646346		
0.000209735	113.05381	0.983705074	234.5651592		
0.000225887	122.9152641	0.986086658	236.6187975		
0.000218256	132.7789918	0.987571439	238.4113218		
0.000236538	142.6197766	0.98847333	239.8831866		
0.000270598	152.4150526	0.98847333	239.8831866		
0.000355172	161.5224508	0.982831496	236.7724934		
0.000523519	166.0946888	0.977520244	233.3599102		
0.001020224	170.0105563	0.971678415	230.2190174		
0.002503901	173.4230584	0.964672672	227.6214851		
0.005166525	175.7505918	0.957193874	225.402988		
0.007584619	176.9293475	0.953691026	224.5484008		
0.010360861	177.8569882	0.940421037	222.2121392		
0.014660385	178.8822563	0.926575023	220.3434143		
0.019776105	179.7640831	0.906934349	218.2068904		
0.029714142	180.9786981	0.877641991	215.6361933		
0.049656857	182.5707798	0.842951401	212.9897103		
0.069366558	183.6582039	0.802367812	210.5209641		
0.101360545	184.9862323	0.740469708	207.3433787		
0.150182644	186.5138361	0.651086412	203.0841806		
0.200801275	187.8305169	0.552220142	200.22247		
0.252246184	189.0600427	0.443673719	195.8920418		
0.298253119	190.1633272	0.352756932	191.5423144		
0.396120147	192.7778238	0.301517255	190.0904495		
0.497191869	195.5630304	0.242461811	188.7381732		
0.596218791	198.2255032	0.201196322	187.7761831		

Table A.17 N₂ ads. data for NS-[Al]-[B]-SSZ-13 (1)

NS-[Al]-[B]-SSZ-13 (1)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000119712	4.945154489	0.697715488	201.4992785	0.120146395	197.1122992
0.00013613	14.84705136	0.805901509	201.4507432	0.10025926	196.9244256
0.000140712	24.76090409	0.858576318	201.3389388		
0.000159687	34.66265614	0.912231692	201.7179923		
0.000151883	44.57325971	0.924516408	201.9316894		
0.000162236	54.49102594	0.939012655	202.3993896		
0.000176025	64.40001495	0.951894062	203.0958888		
0.000177893	74.32731141	0.96296427	203.9844532		
0.00018252	84.23550679	0.970115947	204.8627632		
0.000181092	94.13808168	0.976156864	205.9742178		
0.00017843	104.0523536	0.981384777	207.3461399		
0.000189523	113.9066241	0.983840552	208.2894045		
0.000181209	123.7791216	0.986242071	209.0867406		
0.000189395	133.6943096	0.987870918	210.0118052		
0.000198264	143.5784455	0.989006394	210.7550844		
0.00018381	152.5843212	0.989006394	210.7550844		
0.000201989	162.5392533	0.981508737	207.7931997		
0.000228272	172.372302	0.970338098	205.136308		
0.000341688	182.1297255	0.955959091	203.4586592		
0.002617103	190.1653051	0.943491782	202.7670902		
0.004947077	191.5734224	0.930213254	202.2661738		
0.007927354	192.5229201	0.914862508	201.9180002		
0.01025881	193.0212246	0.905802671	201.7912644		
0.014748466	193.7212839	0.877314139	201.6465139		
0.019945243	194.2820462	0.831012194	201.7386444		
0.02982686	195.0128412	0.79022833	202.0081512		
0.049822475	195.9064189	0.730838867	202.5482234		
0.069601923	196.4472576	0.641370458	203.5482463		
0.101189539	196.9954768	0.543711187	202.8395		
0.15058741	197.4451561	0.450188885	198.2696718		
0.200316609	197.6619155	0.339032813	197.4138682		
0.250016526	197.7538285	0.289556251	197.4388913		
0.299028678	197.774804	0.229560081	197.4655402		
0.408584606	197.9743071	0.189149147	197.4285434		
0.49627557	198.8015246	0.149174305	197.2987195		
0.60002379	200.6524124	0.140033903	197.2402738		

Table A.18 N₂ ads. data for NS-[Al]-[B]-SSZ-13 (2)

NS-[Al]-[B]-SSZ-13 (2)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000125031	1.821442761	0.797818737	180.5967858	0.150719796	167.8411796
0.000133084	11.12163828	0.851397715	185.8358861	0.140053216	167.723202
0.000142308	21.03434021	0.903179106	195.7392829	0.120213947	167.4543305
0.000151536	30.94804074	0.923717142	202.6591339	0.100542013	167.1329938
0.000160547	40.86730825	0.939414603	209.9441357		
0.00014945	50.79985898	0.950777412	217.8869028		
0.000180708	60.72374454	0.960827355	227.5128574		
0.000179484	70.63115844	0.967879215	236.023036		
0.000195094	80.54328147	0.973496062	245.1431257		
0.000200436	90.44664882	0.978287621	255.4651559		
0.000205561	100.3540149	0.981825167	264.0591299		
0.000202981	110.2597988	0.984984825	272.6992267		
0.000225615	120.1622723	0.987383897	279.8535984		
0.000230343	130.0485342	0.988661665	284.2938654		
0.000255506	139.9029484	0.988661665	284.2938654		
0.00040742	149.6485412	0.983311553	280.339912		
0.000489964	151.1476648	0.978888281	275.3956984		
0.001006346	154.6121032	0.974032335	270.3071937		
0.002488174	157.5736021	0.971035969	266.9426545		
0.005127583	159.6474723	0.965980496	262.8368546		
0.00781232	160.8191485	0.952032185	250.2882265		
0.010545037	161.6412873	0.940811268	242.6098214		
0.014790993	162.5261045	0.927130579	234.6802926		
0.019766898	163.2789524	0.903510465	223.4428711		
0.029866802	164.3361575	0.875356331	213.0001032		
0.049751748	165.625771	0.868218897	210.8273705		
0.0697175	166.4705101	0.833433161	202.4729764		
0.101732455	167.3780936	0.80248238	197.0255044		
0.150396884	168.2817818	0.740404339	189.8291404		
0.200215978	168.9045093	0.651500215	184.0645691		
0.249077375	169.3329668	0.5429479	180.3095263		
0.298236819	169.7202616	0.452133638	169.4295934		
0.397325283	170.4378075	0.340928626	168.6517853		
0.499449086	171.4846783	0.291124286	168.5379661		
0.599424555	173.0570514	0.231295828	168.3798091		
0.698974907	175.6272556	0.190733088	168.1628347		

Table A.19 N₂ ads. data for NS-[Al]-[B]-SSZ-13 (3)

NS-[Al]-[B]-SSZ-13 (3)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000111229	4.850850738	0.844507133	231.3319336	0.915940892	320.3433905
0.00011076	14.77870099	0.851744756	233.9680619	0.90552846	307.4498543
0.000110949	24.65484036	0.882931127	249.284678	0.891265289	290.685171
0.000142589	34.48474798	0.898512094	260.2665598	0.877395872	277.9676556
0.000143345	44.4149594	0.905290695	266.1309403	0.857844643	262.4524453
0.000140309	54.28316065	0.916533326	278.0919879	0.842537251	253.2646021
0.000154863	64.20607044	0.923680866	286.4447303	0.816991241	240.9337765
0.000161638	74.06796776	0.931770412	298.1507423	0.801728437	235.1081051
0.000151933	83.94646233	0.936884103	306.5632132	0.747139268	220.8585302
0.000169798	93.81257669	0.943550057	318.6878468	0.733429524	218.3246584
0.000184977	103.7014638	0.947747591	328.997797	0.654017026	207.102628
0.000175738	113.6037936	0.952237947	336.9068325	0.641006458	205.761143
0.000192107	123.434973	0.957179643	348.2244009	0.542877606	197.2930833
0.000200839	133.2840668	0.960681369	356.5639446	0.451851686	186.9697049
0.000333304	143.0440144	0.964961605	367.4333694	0.348190168	181.8047431
0.001601603	152.1151984	0.970997162	376.1404426	0.29321922	179.474041
0.002527464	153.9293654	0.973702752	384.4333328	0.241672812	177.3189173
0.005026003	156.5841347	0.976749906	394.9385097	0.201354955	175.546481
0.007739719	158.3173131	0.979693857	403.0336066	0.160738242	173.6231108
0.010205536	159.3860465	0.982004336	411.2462784	0.140242432	172.5652256
0.015727065	161.1193782	0.984077487	419.740769	0.12027766	171.4524317
0.019567062	162.0371704	0.986123438	428.2753872	0.10030466	170.2389995
0.029726936	163.8326097	0.987860221	437.2137084		
0.049560913	166.2651442	0.987860221	437.2137084		
0.069142123	168.0494812	0.984123973	433.1051533		
0.101753561	170.4212013	0.981421907	428.3027771		
0.150473046	173.2886062	0.977911535	421.8102366		
0.202032529	175.8696701	0.974534596	415.3049572		
0.249662455	178.0574281	0.968708521	403.9507614		
0.301732665	180.3475823	0.964353549	396.3876777		
0.396273907	184.4364837	0.956033552	382.1073448		
0.495994301	189.1029042	0.947500736	367.7984852		
0.599999726	195.1861284	0.943881449	362.0563077		
0.699125645	203.6218955	0.935902721	349.2023132		
0.789929426	216.8492292	0.929392228	339.3700934		
0.80475491	219.9559443	0.925307847	333.7794534		

Table A.20 N₂ ads. data for NS-[Al]-[B]-SSZ-13 (4)

NS-[Al]-[B]-SSZ-13 (4)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000122337	4.800553704	0.59667252	197.5157925	0.241189127	194.2953797
0.000149603	14.70564637	0.699620492	198.5251473	0.200720776	193.8089075
0.000156977	24.62927921	0.799597199	200.0576522	0.160515964	193.2736377
0.000181463	34.53094228	0.847406173	201.3145677	0.140247468	192.9470475
0.000195612	44.42025465	0.900692163	203.9420339	0.120205425	192.579443
0.000221019	52.75938277	0.923634929	206.0077527	0.100238125	192.1631138
0.000224711	62.68746979	0.938845081	208.2658062		
0.000222532	72.61596487	0.951696864	211.2254443		
0.000250986	82.51962329	0.962109486	215.220748		
0.000237724	92.44993272	0.969389392	219.8442587		
0.000257208	102.381873	0.975732768	225.892134		
0.000255316	112.3081844	0.980518361	233.8159699		
0.000264712	122.2170047	0.983345083	241.1023734		
0.000276828	132.1323461	0.985894839	249.3068421		
0.000281511	142.0579118	0.987242854	256.361961		
0.000289272	151.9726141	0.989138972	265.0334964		
0.000295918	161.8840056	0.989138972	265.0334964		
0.000332509	171.7313753	0.985066935	259.4810482		
0.000775281	181.2283412	0.982409921	253.3240213		
0.00104708	182.334264	0.980191711	247.580265		
0.002568727	184.6687098	0.976820611	242.1151319		
0.004932038	186.034125	0.972716885	234.4596013		
0.007813515	186.9246721	0.964220865	223.3117691		
0.010176233	187.4254009	0.953529088	215.3703997		
0.014841543	188.1408046	0.938283024	209.7299869		
0.019890341	188.678903	0.919552995	206.2717781		
0.029832335	189.4340349	0.897558713	204.0357179		
0.049925111	190.4534034	0.877863984	202.7450452		
0.069701506	191.1622104	0.842634293	201.2836545		
0.101514073	192.0060362	0.802745418	200.3081969		
0.150587447	192.9717385	0.743768854	199.3992893		
0.201029132	193.7207217	0.638613104	198.45591		
0.251625213	194.3321802	0.553803916	197.9923449		
0.297183419	194.8557692	0.450654457	196.6737345		
0.397600133	195.91197	0.353529222	195.5084247		
0.497355175	196.761381	0.301115119	194.9423646		

Table A.21 N₂ ads. data for NS-[Al]-[B]-SSZ-13 (5)

NS-[Al]-[B]-SSZ-13 (5)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
5.35872E-05	9.046096222	0.397780724	210.9843551	0.301069201	209.7929268
5.54192E-05	18.98171461	0.497291771	212.1348077	0.241365881	208.869721
4.50381E-05	28.89953971	0.597332139	213.113465	0.200660247	208.179325
4.29574E-05	38.82099672	0.699447144	214.1999506	0.160497877	207.404066
5.28822E-05	48.73455154	0.799392508	215.7624432	0.140227515	206.9426524
5.98162E-05	58.63582765	0.847476428	216.9635761	0.120183878	206.437195
7.75836E-05	68.53660535	0.900730793	219.2991265	0.100250873	205.8590699
4.75598E-05	77.79481064	0.923701921	221.0694674		
6.4619E-05	87.72082728	0.939140833	222.9660518		
5.49218E-05	97.62871162	0.951382876	225.2036147		
6.53009E-05	107.5412053	0.962584157	228.5494319		
6.52995E-05	117.4459442	0.970449173	232.1043838		
6.48288E-05	126.7042564	0.975694393	236.1763808		
6.92061E-05	136.6020531	0.980595565	241.8639851		
7.56418E-05	146.4265521	0.983232072	246.8294224		
5.85867E-05	156.3525963	0.985915834	252.4538217		
6.94104E-05	166.2593523	0.987593752	257.4212325		
8.28061E-05	176.1213177	0.989063695	262.4509471		
0.000153344	185.5594717	0.989063695	262.4509471		
0.000222448	187.7455041	0.984878456	257.1622671		
0.000533477	191.6217489	0.981547339	251.6039953		
0.000981585	193.6656343	0.976928503	244.6739238		
0.002530819	196.1897658	0.970505684	237.4115108		
0.005046595	197.9244496	0.964669544	233.0077074		
0.007759206	198.9796016	0.955634347	228.5700802		
0.010457723	199.7021446	0.942107433	224.8479898		
0.014720845	200.529022	0.928351722	222.6011791		
0.019826386	201.2559253	0.907843841	220.5818028		
0.029804657	202.2681307	0.877807762	218.7924375		
0.049711227	203.5995242	0.842755545	217.5759671		
0.06946154	204.541009	0.802943931	216.6759002		
0.101089384	205.659793	0.743700026	215.8088913		
0.150108392	206.9606907	0.637794324	214.8652699		
0.200876237	207.9903798	0.553775647	214.3680142		
0.25103414	208.8464467	0.450721331	212.3825521		
0.300260004	209.6198038	0.353331771	210.5981558		

Table A.22 N₂ ads. data for NS-[Al]-[B]-SSZ-13 (6)

NS-[Al]-[B]-SSZ-13 (6)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000121423	4.018464754	0.397255518	209.0757294	0.2008253	206.4445534
0.000132206	13.92303226	0.49646388	211.1706336	0.160545083	205.8522001
0.000146246	23.84287385	0.596842723	213.4616918	0.140225751	205.5058851
0.000155664	33.7667453	0.696293463	215.6822437	0.120195929	205.1202025
0.000156721	43.68394106	0.799266627	218.4085371	0.100247185	204.6730913
0.000168113	53.58749672	0.847489197	219.9235545		
0.000186129	63.43857502	0.901464319	222.0739965		
0.000199466	73.36425741	0.92366264	223.2782503		
0.00019761	82.53145298	0.939852093	224.4306006		
0.000204037	92.45126039	0.951824396	225.5708966		
0.000197583	102.3577953	0.962982267	226.997102		
0.000208041	112.2867064	0.970391616	228.2514407		
0.000218374	122.2008786	0.97650436	229.6308478		
0.000217556	132.1242925	0.98142653	231.1941273		
0.000203226	142.0376485	0.98408803	232.2672232		
0.000215742	151.960949	0.985508756	233.2166088		
0.000219313	161.8761245	0.988009663	234.5074683		
0.000233763	171.7662046	0.989148791	235.4650055		
0.000253933	181.6263439	0.989148791	235.4650055		
0.000441001	191.3023906	0.981181707	232.5359263		
0.000527738	192.3574208	0.969985662	229.8121749		
0.00106327	194.8313016	0.955957631	227.8112434		
0.002624422	197.0767122	0.943258399	226.6844962		
0.00491378	198.4130787	0.929649182	225.8349697		
0.007896674	199.3556843	0.914543409	225.1081381		
0.010127496	199.849451	0.905879681	224.7484278		
0.014758661	200.5799267	0.876597153	223.8674222		
0.019876445	201.1552164	0.842325445	223.1369274		
0.029827223	201.9438222	0.802072872	222.5137298		
0.049865427	202.9949063	0.742876475	221.8275901		
0.069608469	203.7217911	0.654411248	221.0879796		
0.100934008	204.5748643	0.538406742	220.2341953		
0.150383318	205.5887263	0.446144017	210.6975036		
0.200616887	206.3625144	0.351560811	208.4616648		
0.250978721	207.0355913	0.290192973	207.5893565		
0.300420403	207.6621057	0.241494685	206.9846884		

Table A.23 N₂ ads. data for conventional [Al]-SSZ-39

Conventional [Al]-SSZ-39			
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000118779	6.67432268	0.860125699	158.6970547
0.000120468	16.59431571	0.902416166	159.0479372
0.000134216	26.49828381	0.9238493	159.4271052
0.000142757	36.37387685	0.939277003	159.8362716
0.0001565	46.27230208	0.952143722	160.3563532
0.000180458	56.18676608	0.963291656	160.9478653
0.000167104	66.07646868	0.971051062	161.5045398
0.000177338	75.99263547	0.976590938	162.043513
0.000183186	85.85894714	0.981671513	162.6879306
0.000185453	95.76218345	0.984470365	163.1206552
0.000197569	105.6514427	0.985915208	163.4033917
0.000203913	113.0473166	0.988022812	163.8495363
0.000214239	122.9285719	0.989145158	164.0831483
0.000217079	132.7685599	0.989145158	164.0831483
0.00024869	142.5690114	0.978988209	162.4180101
0.000529522	152.1008275	0.96705211	161.3281025
0.001044531	154.9832866	0.953446088	160.5335479
0.00248216	157.2472702	0.941978387	160.0783111
0.004925471	158.458022	0.928427538	159.7142601
0.008037759	159.1320586	0.913709388	159.3870782
0.010372724	159.4245654	0.905479526	159.2543282
0.014707404	159.7776378	0.876737966	158.9164197
0.01989606	160.055874	0.841929646	158.6881617
0.02994564	160.3779911	0.789918911	158.5812099
0.049897027	160.7037883	0.729917216	158.677121
0.069784199	160.8645337	0.640386898	158.9663951
0.100913358	160.9883152	0.540036664	159.4487531
0.150057225	161.0241103	0.43940632	159.8839624
0.200239082	160.9404183	0.341941509	160.4176588
0.24972574	160.7924907	0.28778043	160.6792104
0.302391813	160.5720825	0.227721972	160.937899
0.411415948	160.0685289	0.187504236	161.0581043
0.511027962	159.5687372	0.147479261	161.1330298
0.61090291	159.0933292	0.127580825	161.145628
0.709454086	158.734239	0.109346856	161.1401826
0.80861096	158.5887475	0.100130729	161.1184441

Table A.24 N₂ ads. data for [Al]-[B]-SSZ-39 (1)

[Al]-[B]-SSZ-39 (1)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
0.000117593	4.920937285	0.609394876	187.8017806	0.12875905	191.3633833
0.000130577	14.78825626	0.707832541	187.046833	0.109343423	191.4063409
0.00014692	24.69315462	0.80714603	186.5207185	0.09125859	191.4081385
0.000159784	34.60662906	0.858522354	186.3702448		
0.000151708	44.52446612	0.912434741	186.8213385		
0.000157919	54.44909294	0.924914463	187.0538222		
0.00017442	64.35132072	0.938582829	187.44148		
0.000173884	74.27420158	0.952817642	187.9883096		
0.000176202	84.18399264	0.963157301	188.4884686		
0.000186066	94.08896137	0.969927804	188.9917142		
0.000182759	104.0024595	0.976440734	189.5744027		
0.000190586	113.9132245	0.981609132	190.2008285		
0.000192404	123.8190471	0.984235706	190.5222104		
0.000193576	133.7242731	0.986311515	190.8863752		
0.000200298	143.6197254	0.98834678	191.2928868		
0.000211317	153.5282653	0.989136975	191.4713468		
0.000225533	163.4090605	0.989136975	191.4713468		
0.000315652	173.1632741	0.980123545	189.8715271		
0.000511099	178.3301563	0.968489131	188.6780355		
0.000998205	182.7456964	0.954712117	187.8838995		
0.002478791	186.4422484	0.943020481	187.428135		
0.004990578	188.2883048	0.929518129	186.9939778		
0.007898247	189.1707299	0.915025433	186.6393351		
0.010256469	189.5883036	0.905605479	186.4707533		
0.014664737	190.0664654	0.877537196	186.1924121		
0.019826339	190.4206307	0.831583253	186.1168093		
0.029829422	190.7993259	0.790402843	186.2302279		
0.049734188	191.1514675	0.731325603	186.60189		
0.075950443	191.34827	0.641773225	187.3538646		
0.100582126	191.4058168	0.541235643	188.3519041		
0.150204826	191.3249052	0.44113304	188.8977722		
0.200002345	191.1176843	0.343298634	189.8150127		
0.256783811	190.7682892	0.288994378	190.3074767		
0.300681525	190.4201905	0.229011949	190.8041038		
0.410203522	189.5039088	0.188777264	191.0776622		
0.509797286	188.6417711	0.148726133	191.2895836		

Table A.25 N₂ ads. data for [Al]-[B]-SSZ-39 (2)

[Al]-[B]-SSZ-39 (2)					
Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)	Relative Pressure(P/Po)	Quantity Adsorbed (cm ³ /g STP)
1.85779E-05	9.308424765	0.610291721	184.0372626	0.128477961	190.5460124
2.11379E-05	19.20795382	0.708803856	182.4654086	0.109192944	190.6621734
2.53986E-05	29.0945423	0.808094853	180.9857693	0.091055106	190.7170009
2.81699E-05	39.01013012	0.859117679	180.3539176		
3.9036E-05	48.90224169	0.91350734	179.9792881		
2.55853E-05	58.79330097	0.935566348	180.0477797		
3.85911E-05	68.70464751	0.939811964	180.0520741		
3.90035E-05	78.60496747	0.962226695	180.6428444		
3.17392E-05	88.51181785	0.964078857	180.7177726		
2.55556E-05	98.42048026	0.970609106	181.0699141		
3.51257E-05	108.3228794	0.976622025	181.6000871		
4.53268E-05	118.2017587	0.981611074	182.2268608		
4.14952E-05	128.1114471	0.984105668	182.5891213		
4.38245E-05	137.9983718	0.985682429	182.9764248		
5.53063E-05	147.8625445	0.987601907	183.4279183		
6.05674E-05	157.6948674	0.988816288	183.6500902		
0.000121504	167.5007285	0.988816288	183.6500902		
0.000223507	172.2086399	0.979463549	182.0673504		
0.000516926	177.3567954	0.96821629	180.9086839		
0.001009288	180.9939149	0.954842994	180.2201132		
0.002465459	184.6375525	0.942637326	179.8754055		
0.004980826	186.817731	0.929436781	179.6869365		
0.007822066	187.89211	0.914310873	179.5826805		
0.010204509	188.419269	0.894649553	179.5602257		
0.016146577	189.2173926	0.865018747	179.7304589		
0.019641055	189.504746	0.830114271	180.0277342		
0.029726183	190.0051687	0.789866307	180.5334657		
0.049807433	190.4549018	0.730285645	181.4430584		
0.075964305	190.6262088	0.641136772	182.9780915		
0.100730953	190.6156135	0.540123848	184.7472752		
0.150230367	190.3379162	0.439793069	186.3859343		
0.211564387	189.7698171	0.344196098	187.9070065		
0.261448061	189.2030134	0.288629628	188.7335035		
0.304693812	188.6492125	0.228445913	189.5328139		
0.410895164	187.1731776	0.188489181	190.006143		
0.510473808	185.643094	0.148492784	190.3815014		

B. MTO Reaction Formulas

Calculation of the $WHSV = \frac{g_{MeOH}}{g_{zeolite} * h}$

$$\begin{aligned}
 WHSV (h^{-1}) &= \frac{y_{MeOH} \left(\frac{kPa}{kPa} \right) * P(Pa) * Q_{Total} \left(\frac{cm^3}{min} \right) * 10^{-6} \frac{m^3}{cm^3}}{8.314 \frac{Pa * m^3}{gmol * K} * T (K)} * 60 \frac{min}{h} \\
 &* MW_{MeOH} \left(\frac{g}{gmol} \right) * \frac{1}{m(g \text{ zeolite})} \\
 &= \frac{\frac{16.8}{101.325} * 101325 * 42 \left(\frac{cm^3}{min} \right) * 10^{-6} \frac{m^3}{cm^3}}{8.314 \frac{Pa * m^3}{gmol * K} * 298 (K)} * 60 \frac{min}{h} * 32 \left(\frac{g}{gmol} \right) \\
 &* \frac{1}{0.1 (g \text{ zeolite})} = 5.5 h^{-1}
 \end{aligned}$$

Calculation of the molar flow rates of the products:

Molar flow rate of $CH_4 (F_{CH_4})$

$$\begin{aligned}
 &= \text{Area of } CH_4 * RF \left(\frac{ppm}{area} \right) * \frac{P (Pa) * Q_{Total} \left(\frac{cm^3}{min} \right) * 10^{-6} \frac{m^3}{cm^3}}{8.314 \frac{Pa * m^3}{gmol * K} * T (K)} \\
 &= 100 * 9.82 \left(\frac{ppm}{area} \right) * \frac{101325 Pa * 40 \frac{cm^3}{min} * 10^{-6} \frac{m^3}{cm^3}}{8.314 \frac{Pa * m^3}{gmol * K} * 295 K} \\
 &= 1.6 * 10^{-6} \frac{mol}{min}
 \end{aligned}$$

Calculation of inlet methanol flow rate:

Molar flow rate of CH_3OH ($F_{MeOH,in}$)

$$= \frac{y_{MeOH} \left(\frac{\text{kPa MeOH}}{\text{kPa}} \right) * P \text{ (Pa)} * Q_{inlet} \left(\frac{\text{cm}^3}{\text{min}} \right) * 10^{-6} \frac{\text{m}^3}{\text{cm}^3}}{8.314 \frac{\text{Pa} * \text{m}^3}{\text{gmol} * \text{K}} * T \text{ (K)}}$$

$$= 3 * 10^{-4} \frac{\text{mol}}{\text{min}}$$

Calculation of MeOH conversion:

$$Conversion\% = \frac{F_{MeOH,in} - (F_{MeOH,out} + 2 * F_{DME,out})}{F_{MeOH,in}} * 100$$

$$F_{MeOH,out} = \text{Area of } CH_3OH * RF \left(\frac{\text{ppm}}{\text{area}} \right) * \frac{P \text{ (Pa)} * Q_{Total} \left(\frac{\text{cm}^3}{\text{min}} \right) * 10^{-6} \frac{\text{m}^3}{\text{cm}^3}}{8.314 \frac{\text{Pa} * \text{m}^3}{\text{gmol} * \text{K}} * T \text{ (K)}}$$

C. MTO Reaction Data

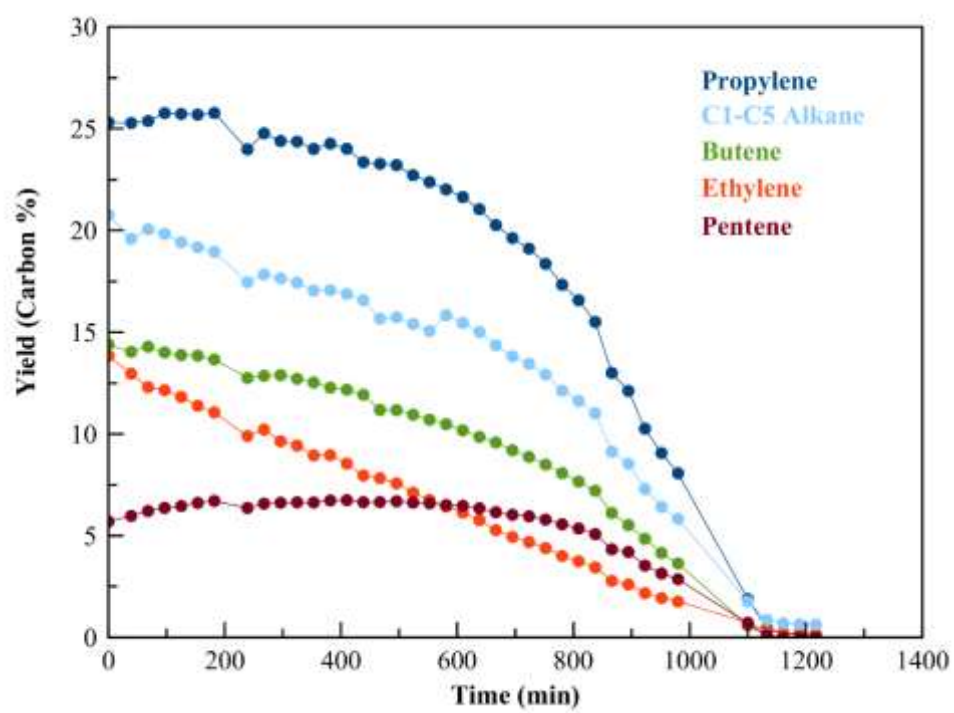


Figure C.1. Carbon yield versus time on conventional-[Al]-ZSM-5 at 450 °C, WHSV = 5.5 h⁻¹

Table C.1 GC FID areas of reactant and products for MTO reaction on conventional [Al]-ZSM-5 at 450 °C, WHSV = 5.5 h⁻¹

Time		Area													
min	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₄ H ₈	n-C ₄ H ₈	i-C ₃ H ₁₂	n-C ₃ H ₁₂	i-C ₃ H ₁₀	n-C ₃ H ₁₀	DME	MeOH
0	232.8	2824.4	61.6	4795.2	1258.9	1313.8	964	1177.8	431	504.1	150	292.7	617.2	55.4	1258.9
39	232.9	2644.4	55.9	4788.6	1103.5	1242.9	937.7	1186.3	430.2	464.3	163.4	309.7	643.8	95.3	135
68	230	2510.1	50.6	4806.9	1013	1233.1	977.1	1240.1	544.7	462.4	169.3	321.7	670.4	142.3	153.1
96.5	243.3	2478.8	48.9	4880.7	935.6	1165.3	970.6	1258.4	586.4	439.7	177.3	333.6	682.1	181.6	188.9
125	247.4	2412	46.4	4872.9	876.3	1143.2	962.9	1258.4	578.5	432.8	181.9	340.5	690.5	217.3	229.6
153.5	247.1	2323.6	43.2	4866.9	818.7	1131.7	959.6	1264.2	584.8	436.7	187	348.9	706.7	270.2	274.6
182	249.2	2257.2	40.7	4882.5	775	1116.5	946.2	1247.7	596.4	437.5	190.2	356	715.3	352.6	312.9
210.5	222	1839	36.6	3887.7	637.8	891.9	773.5	1048.6	492.5	338.7	145.1	276.2	551.6	189	285
239	237.8	2020.1	36	4542.9	684.4	1035.5	873.3	1171.5	548.9	418.2	177.8	334.2	681.6	346.7	367.7
267.5	264.8	2084.4	38	4692.6	664.8	1010.8	899.7	1214.1	580.9	405.1	188.6	348.5	701.5	379.9	374.4
296	253.9	1967.5	34.7	4621.2	626.7	1014.4	894.6	1217.2	582.8	421.4	187.9	351.2	705.3	439.7	444.9
324.5	258.5	1924.2	33.1	4615.5	591.6	992.9	887.8	1206.9	584.8	418	189.9	353.6	707	484.5	490.9
353	251.7	1825.5	30.6	4547.3	554.5	975	869.7	1193.4	573.8	423.2	189.1	353.4	705.7	543.9	553
381.5	271.2	1828.9	31.3	4595.7	526.9	941	878	1183.3	588.1	406.4	195.4	359.8	714.6	583.9	552.2
410	265.2	1743.1	28.9	4549.2	492.4	930	871.9	1177.3	591.4	412.7	195.6	361.6	715.1	654.9	621.7
438.5	251.7	1623.8	26.1	4423.6	454.1	902.2	849.5	1161.9	610.1	416.3	191.9	356.3	704.9	718.3	681.2
467	267.4	1596.6	26.5	4408.5	426.5	829.5	793.7	1105.5	550	395.4	195.4	358.4	704	754.4	736
495.5	273.2	1545.4	25.7	4397.2	400	817	820.1	1116.5	557.1	388.9	197.7	361.7	706.6	825.9	782.4
524	263.8	1452	23.7	4302.5	367.1	789	815.6	1105.3	549.2	385.8	195.8	357.2	700.7	899.7	881.6
552.5	261.1	1376.9	22.3	4239.2	339	769.3	797.7	1083.1	544.5	380.7	195.4	355.7	696.8	981.4	944.4
581	265.5	1312.6	21.8	4169.9	312.4	727.3	796.9	1086	705.7	364.9	194.7	352.7	686.6	1056.8	961.3
609.5	270.8	1253.1	21.3	4099.6	286.6	685.1	787.4	1076.3	689.5	348.9	194.6	350.9	681.8	1133	1068
638	268.9	1176.9	20.4	3986.1	260.4	648.7	768.4	1056.6	678.1	333.2	192.7	345.4	667.9	1200.3	1111.8
666.5	247.2	1075.3	17.7	3838.7	231.1	618.5	738.7	1039.8	658.3	327.4	185.4	333.3	649.6	1323.2	1234
695	246.2	1008	17.2	3717.3	207.7	578.3	715.9	1013.4	637.4	307.8	182.9	327.7	634.8	1427	1374

Table C.1 GC FID areas of reactant and products for MTO reaction on conventional [Al]-ZSM-5 at 450 °C, WHSV = 5.5 h⁻¹
(Continued)

723.5	253.8	956.4	17.2	3619.2	187.3	539	701.9	996.7	625.7	286.5	182.4	323.8	626.7	1529.4	1417
752	257.8	895.6	17.1	3477.5	166.6	499.5	679.7	970.8	605.7	262.2	179	315.8	608.5	1662.6	1529
780.5	245.5	817.2	15.7	3283.3	143.8	483.6	652.5	913.8	562	242.2	172.2	301.1	587	1839.8	1584.7
809	249.6	764.5	15.5	3138.4	127.5	431.1	623.3	894.6	549	220.6	166.4	290.4	564.4	1996.2	1749.5
837.5	249.2	702.1	15.3	2936.9	110	391.2	590.1	855.7	532.8	196.2	159.2	276.1	534.5	2162.6	1839.2
866	221.1	566.9	12.5	2462.1	68.6	311.9	494.4	746.9	447.5	154.9	135.8	235.5	456.2	2731	2176
894.5	241.8	530.5	14.2	2295.1	59.1	297.5	464.9	657.9	398.2	132.4	134.4	227.3	443.5	2940	2576
923	204.1	443.4	11	1943.2	43.4	251.8	396.4	586.9	353.2	111.7	112.8	190.6	373.2	3302	2869.4
951.5	200	395	10.7	1716.1	34.1	188.6	341.6	529.5	313.3	90.1	100.4	172	329.6	3680.2	3420.7
980	212.9	359.6	11.5	1527.8	27.1	149.9	303.7	479.3	278.4	71.5	93.2	158.1	298.2	4002	3523.9
1100	177.6	149.6	8.3	356.1	3.2	9.9	61.2	91.6	44.8	13.4	26.9	32.6	77.9	6247.8	4505.9
1133	143.4	66	6.2	82.7			12.8	14.8	6.5	6.5	3.5		14.7	6367.9	4362.6
1161	138.8	48	5.9	42.4				5.9	5.9					6259.1	4323.9
1189	132.2	39.4	5.4	26.3					3.8					6305.5	4509.5
1217	132.4	36.1	5.4	20.7										6493.2	4770.1

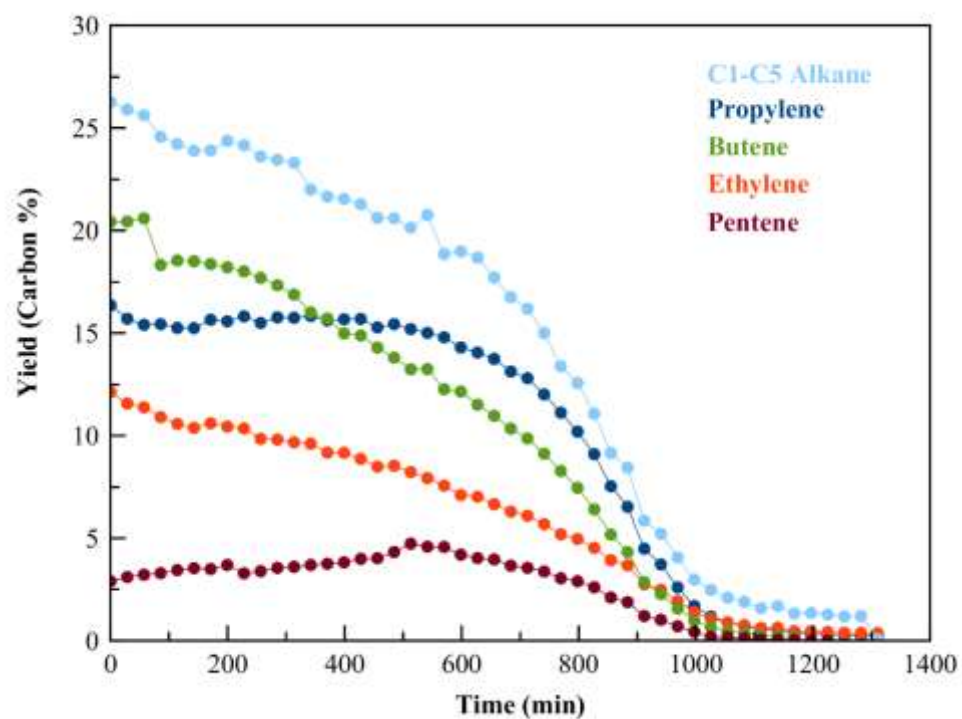


Figure C.2. Carbon yield versus time on Mes-[Al]-ZSM-5 (2) at 450 °C, WHSV = 5.5 h⁻¹

Table C.2 GC FID areas of reactant and products for MTO reaction on Mes-[Al]-ZSM-5 (2), at 450 °C, WHSV = 5.5 h⁻¹

Time min	Area		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₄ H ₈	n-C ₄ H ₈	i-C ₃ H ₁₂	n-C ₃ H ₁₂	i-C ₃ H ₁₀	n-C ₃ H ₁₀	DME	MeOH
0	303.7	2433.4	117.2	3047.3	2010.6	2595.5	945.9	881.2	258.5	972.1	50.4	116.4	339.2				
28.5	325.5	2321.5	101.5	2924.8	1870.2	2671	905.1	807.7	241.9	1082.1	50	143.8	343.7				
57	324.5	2283.7	94.5	2869.5	1784.3	2710.5	883.7	795.2	240.4	1136.8	50.5	155.8	349.4				
85.5	349.7	2188	74.8	2875.5	1512.2	2413.1	917.1	705.4	310.1	1099.3	54.1	160.1	357				
114	359.4	2121.6	68.6	2841.1	1428.8	2466.3	869.9	689.9	293.5	1165.7	58	170	370.6				
142.5	374.3	2082.8	63.8	2839.5	1350	2479.4	834.9	670.2	282.2	1212.9	61	172.7	382.8				
171	414.2	2127.8	64.3	2915.5	1317.6	2470.1	804.6	656.5	261.2	1258.1	63.4	157.1	391.8				
199.5	437.7	2096.1	62.1	2901.2	1251.5	2430.9	833.4	669.1	378	1246.3	54.7	143.3	436.4				8.4
228	453.5	2077.5	59.6	2946.3	1192.9	2424.1	814.3	642.1	367.6	1285.8	48.4	154.9	361.1				17.2
256.5	440.6	1976.2	52.9	2886.2	1105.5	2401.8	792.5	609.5	366.4	1305.6	51.7	161.9	370.4			4.7	30.5
285	458.4	1968.7	51.6	2937.3	1058.3	2355.1	781.4	595.2	366.7	1310.3	59	170.6	386.8			10.5	50.7
313.5	474.2	1941.3	50	2932.9	1018.1	2301.5	778.5	571.3	367.6	1309.1	62.6	174.7	391.2			28.8	72.1
342	499	1928.5	50	2950	974.5	2203.2	708.7	521.7	257.5	1284.1	66.6	179	400.9			52.2	94.3
370.5	473.4	1840.7	44.3	2908.6	905.4	2178	706.5	496.5	270.3	1299.7	69.3	181.2	407.9			69.3	140
399	510.3	1839	45	2919.6	876.5	2068.1	720.1	482.1	275.7	1258.6	72.1	183.8	416.2			94.4	168.8
427.5	492.4	1779.7	42.2	2923.4	816	2042.1	723.5	491.9	285	1265.9	77.5	186.7	440.2			161	230.2
456	485	1703.9	39.3	2846.1	765	1958.4	699.1	474.5	279.9	1236.9	80	180.9	450.8			231.8	280.4
484.5	527.1	1712.6	42.2	2875.6	749	1874.8	696.9	474.5	283.8	1204.3	88.9	185.2	493.5			288.6	326
513	525	1649.9	40.5	2830.7	698.3	1788.2	676	464.9	281.8	1177.7	108.8	197.7	545.5			388.2	384.7
541.5	518.5	1591.2	38.3	2796	650.3	1740.4	739.9	513.9	405.9	1152.2	105.5	195.5	524.1			512.2	460.3
570	501	1517.3	35.7	2755.7	589.9	1632.8	638.4	454.3	283.6	1121	109.4	196.8	521.2			739.4	534
598.5	474	1425.7	32.3	2663.9	528.7	1573.7	682.5	494.7	398.5	1079.1	97.2	184.7	474.1			906.5	623.8
627	518.5	1409.1	35.3	2617.3	511.9	1476.1	666.4	482.7	392.3	1034.8	94.4	182.3	450.5			1000.2	665.6
655.5	501.4	1336.3	32.7	2560.1	453.3	1398.3	636.1	468.3	376.5	986.6	95.7	181	441.6			1218.7	751.1

Table C.2 GC FID areas of reactant and products for MTO reaction on Mes-[Al]-ZSM-5 (2), at 450 °C, WHSV = 5.5 h⁻¹ (Continued)

684	492.5	1263	31.3	2444.8	407.6	1303.8	600.9	456.5	362.4	932.4	91.8	175.1	399.7	1434.1	845.9
712.5	505.3	1223.2	31.6	2384	372	1228.2	577.5	449.8	353	895	90.5	177.9	380	1675.8	957.7
741	487.8	1140.8	29.4	2236.9	312.5	1125.8	532	426.2	336.6	833	87.5	170.8	359.3	2016.2	1088.1
769.5	443.5	1041.1	25.3	2070.9	250	1010.2	473.6	398.4	309.6	751.5	80.4	160.2	317.9	2482.8	1267.6
798	477.2	995.1	27.3	1899	229.3	914.4	437.4	354.5	281.9	674.6	79	149.9	305.2	2785.6	1346.9
826.5	465.8	909.2	26.1	1694.6	185.4	777.1	380.7	313.3	248.9	574.8	73.2	132.4	276.8	3359.5	1665.2
855	424.9	787.9	22.3	1403.3	138.7	625.7	308.2	254.6	202.6	469.3	59.6	110.1	220.4	4158.6	1906.2
883.5	476.7	738	26.4	1216.3	124.5	518.1	266.1	217.8	169.9	402	54.7	99.9	195.6	4569	1948.5
912	375.8	551.8	18.9	835.5	75.5	347.5	176.4	138.4	121.4	260.5	35.1	61.8	127.5	5697.6	2224.2
940.5	414.5	498.8	22.1	692.7	66.2	273	139.4	114	80.2	215.2	31	52.7	107.3	6123.4	2304.5
969	374.9	388.1	19.8	485	47	190.2	97.5	75.7	55	152.4	20.8	35.4	74.8	6919.9	2500.7
997.5	316.1	281.2	16.2	315.6	31.6	122.2	60.9	45.2	32.5	103	12.6	21.9	46	7301.8	2546.9
1026	281.4	215.5	14	218.7	23.4	82	42.1	29.1	21.6	90.7	8.1		30.3	7657.9	2652
1054.5	267.4	178.4	13.4	166.1	18.7	59.9	30.9	20	15.2	69.1			27.5	7924	2772.1
1083	259.9	152.3	13.3	131.7	15.6	46.4	24.4	15.6	11.9	54.6			20.5	8097.5	2870.9
1111.5	240	126.3	12.2	101.4	12.5	35.3	18.1	11	9.3	32.8			9.3	8137.6	2918.3
1140	262.6	128.4	13.9	99	12.4	31.5	17.9	7.8	9	30.8			9.3	8197.2	2898.5
1168.5	212.6	95.2	10.7	68	9.1	21.9	12.1	5.5	6.2	23.8			5.3	8302.3	3124
1197	221.1	93.4	11.5	63.8	8.6	19.2	11.2		5.5	22.3				8372.9	3181.7
1225.5	215.1	85.6	11.1	56.4	7.5	16.1	9.7		5	17.8				8554.8	3313.7
1254	204.3	77.4	10.4	48.4	6.8	13.6	7.9		3.6	15.6				8596.8	3378.3
1282.5	210.5	76.4	11	46.7	6.3	11.6	7.5		3.7	14.1				8584.4	3383.7
1311	211.7	74.4	11.1	44	5.9	6.8			3.4	12				8700	3446.2

Table C.3 GC FID areas of reactant and products for MTO reaction on Mes-[Al]-[B]-ZSM-5, at 450 °C, WHSV = 5.5 h⁻¹ (Continued)

672	272	1757	15.3	7519.9	260.5	401.8	1346	2353	1025	205	322	542.3	1255	7.3	75.3
700	281.1	1733.9	15.2	7476.4	259.7	388.2	1347	2311.8	953	203	322	541	1251	9.9	77.7
728	282.3	1752.8	15	7628	264	415	1364	2310	1157	214	334	560	1292	15.2	101.7
756	309	1821	17.6	8008	229	315.6	1292	2245.6	1120	136	326	524	1155	43.4	80
784	349	1924	19	8478	241	259	1289	2286	1245	145.9	355	573	1260	2	66
812	370	1898	19	8355	235.5	286.6	1300	2217.9	1249	144	361	581	1272	4.5	78
840	453.8	2087	24	8421	239	229.8	1172	2091.2	884	120	372	585	1244	4.1	59.5
868	422.9	1957.9	23	7987	223	243.3	1241	2028	1211	112	374	585	1214	10.6	72
896	484.3	2016	25	8160	222	259.1	1297	2074	1254	116	406	634	1303	22	154
924	544.6	1986.6	26	7859	207	191.5	1280	2133	1370	109	410	638	1296	39	107
952	620	1995	29	7513	196	142.8	1151	1999	904	102	422	649	1299	91	177.9
980	618	1876	28	7046	180	133.4	1145	1996	898	103	422.9	647.2	1289.1	262	406
1008	610	1719	26	6259	154	340.9	1263.7	1888	1175	94	401	607	1215	675	783
1036	640	1586	27	5382.5	128	346	1171	1725	1096	79	362	545	1086	1340	1237
1064	615	1301	25	4122	93.4	233	955	1440	926	56	292	445	868	1910	1990
1092	623	1143	24	3431	71	274.9	824	1173	782	45.9	247.7	384.5	743	3506	2328
1120	637	892	22.8	2314.3	32.6	219	597	868	616	26	178.8	280.5	526	5087.8	2668
1148	517.9	469.7	15	855	7.1	122.9	270.1	414.6	330		62.3	109.9	188	8060	3015
1176	482.8	177.5	12.5	163				126	13.6		8.3	34	29	9869	3469
1204	433.5	116	10	70				18.1	5.6			14.3	9.6	10341	3606
1232	356	82.9	7.9	39.7										10447.6	3555
1260	322	69	6.7	31										10425	3928

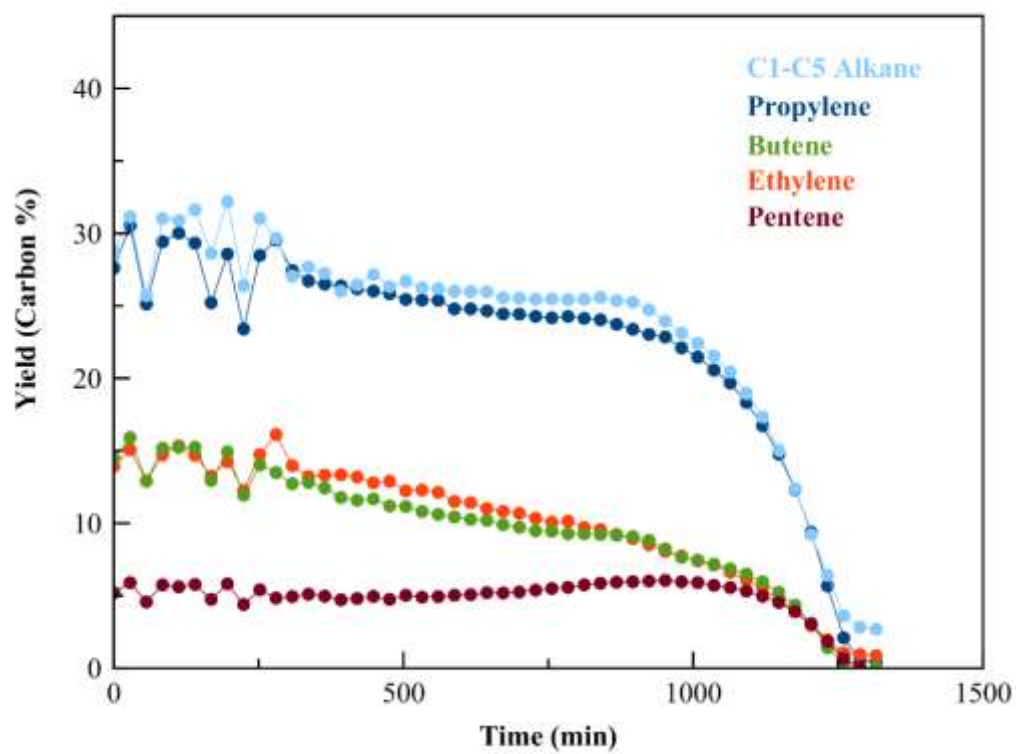


Figure C.3. Carbon yield versus time on NS-[Al]-[B]-ZSM-5 at 450 °C, WHSV = 5.5 h⁻¹

Table C.4 GC FID areas of reactant and products for MTO reaction on NS-[Al]-[B]-ZSM-5, at 450 °C, WHSV = 5.5 h⁻¹

Time	Area														DME	MeOH
min	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₄ H ₈	n-C ₄ H ₈	i-C ₃ H ₁₂	n-C ₃ H ₁₂	i-C ₃ H ₁₀	n-C ₃ H ₁₀			
0	100.2	2922.9	33.3	6505.8	1485.2	1220.4	1255.4	2274.4	681.6	476.1	857.5	216.6	209			
28	86.4	2345.3	28.7	5260.4	797.7	1174.9	1114.5	1983.5	744.4	533.8	142.2	295.1	657.4			
56	114.1	2778.4	36.9	5855.6	907.9	1257.9	1143.5	2066	653.5	561.6	136	292.4	647			
84	116.9	2598.1	36.8	5364.7	883.8	1244.4	1106.2	1931.1	713.4	548.6	124.1	268.4	594.9			
112	129.7	2601.5	39.4	5342.6	950.5	1368.4	1147.8	1968	717	607	129.9	282.6	624.7			
140	103.4	1855.1	30	3665	669.9	941.9	778.8	1316.3	520.6	409.8	82.5	182.7	404.7			
168	90	1435.6	26.2	2775.3	575.4	799.2	621.5	1006.3	384.9	348.2	62.9	143.6	316.7			
196	68.2	963.2	17.4	2005.5	378	540.6	379.6	641.8	216.6	233.6	37.2	89.6	198.6		5	
224	165.4	2209.7	42.9	4175.2	913.6	1288.8	918.2	1486.2	478	569.6	93.5	215	481.3			
252	200.3	2455.1	45.7	4685.2	935.6	1331.3	999.4	1639.6	569.1	602.6	105.5	237.9	529.8			
280	208.3	2289.2	47.3	4210.6	914.1	1269.5	920.3	1456.8	518.9	567.2	88.2	205.3	464			
308	237.3	2476.8	48.5	4653.9	948.4	1377.9	998.5	1608	561.8	633.2	101.1	233.4	524.8			
336	225.4	2120.7	44.7	3830.5	801.6	1122	816.8	1278.8	484.3	510.2	77	180.1	407.4			
364	263.2	2417.1	49.2	4486.7	928.9	1381.2	964.2	1529.2	541.3	647.4	99.4	228.9	509.9			
392	293.6	2519.9	53.1	4577.4	924.9	1353	960.8	1510.1	565.9	639.5	98.2	224.9	496.8			
420	287.7	2411.9	50.4	4472	920	1422.6	960.9	1520.7	557.2	679.6	100.1	232.7	510.4			
448	285.4	2179.5	51.4	3845.2	866.7	1290.8	835.4	1275.8	488.1	603	80.5	188.9	421.7			
476	297.2	2340.5	49.3	4357	904.4	1480.9	950	1487.5	547.8	715.3	100.4	232.8	514.8			
504	281	2014.2	46.7	3568.4	762.2	1197.7	769	1163.2	461.7	568.9	74.7	175.5	389.3			
532	340.6	2420.3	54.1	4342.7	878.8	1406.5	892.3	1393.9	518	685.1	94.5	218.1	476.8			
560	415.1	2648.4	62.1	4503.6	849.6	1288	853.5	1328.8	509.7	630.9	85	195.6	426.4			
588	354.7	2294.9	48.7	4184.3	714.5	1191.9	795.6	1259.1	475.3	604.8	88.3	200.5	434.9			
616	339.7	2171.9	45	4073.8	701.5	1256.8	798.7	1257.4	488.6	644.3	91.5	207.9	448.2			
644	364.6	2188.2	46.6	4040.6	683.9	1228.5	773.4	1209.1	483.5	636.6	89.3	205.1	434.3			

Table C.4 GC FID areas of reactant and products for MTO reaction on NS-[Al]-[B]-ZSM-5, at 450 °C, WHSV = 5.5 h⁻¹ (Continued)

672	394.6	2192.8	47.4	4021.9	642.6	1159.7	726.4	1151.5	451.7	605.2	85.2	195.2	411
700	408.2	2168.2	47.9	3990.1	638.7	1188.7	727.1	1138.7	439.7	624.8	88	199.5	418.6
728	400	2101.3	45.1	3966.6	630.3	1253.3	732.3	1143.8	446.4	664.8	89.4	207.1	429.7
756	436.8	2118.9	47.6	3938.8	601.8	1197.3	699.7	1087.3	436.6	640.6	87.2	200.2	410.1
784	414	2010.3	43.8	3879	584.1	1244.4	699.1	1088.5	430	674.3	92.9	211.5	434.8
812	446	2019.1	45.6	3873.2	564.3	1207.3	682.8	1050.7	421.4	659.8	91.1	207.6	422.4
840	457.4	1993.7	44.9	3870.1	545.1	1210.5	671.7	1026.5	418	667.9	92.1	209.5	425.5
868	440.3	1889.2	41.9	3780.1	517.6	1219.6	663.6	1005.2	414.7	679.8	94.3	213.7	433.9
896	459.1	1876.2	42.5	3780.5	503.9	1214.3	658	980.9	414.7	684.2	95.7	216.5	435.7
924	451.3	1810.7	40.1	3759.2	484.4	1225.3	652.7	970	416.8	697.4	98.9	222.7	446.7
952	465.7	1778.4	40.5	3726	464.1	1198.2	637.8	937.6	408.7	689.4	99.5	222.9	444
980	482.4	1755.3	40.4	3725	449	1192.9	634	917.7	404.3	694.3	101.1	225.8	449.5
1008	481.9	1700.5	39.3	3701	430.5	1186.4	637.2	880.7	406.7	700.1	105.4	232.6	459.6
1036	482.3	1655.4	38.3	3686.1	416	1188.8	638	867.9	415.1	709.9	108.4	237.7	469.1
1064	530.5	1667.3	41.5	3700.1	406.6	1155	641.7	838.3	420.2	698	112.4	242.3	474.4
1092	509.4	1593.8	38.2	3680	387.6	1169.2	643.1	833	423.4	716.3	115.9	250.4	489.3
1120	528.4	1572.8	39	3665.5	378.3	1162.9	650.1	819	431.2	719.8	120.7	255.9	497.2
1148	527.5	1516.7	37.8	3618.3	362	1147.5	648	807	434.7	720.6	123.3	260.1	502.3
1176	532	1467	37	3565.9	345	1136.7	651.3	792	436.7	722.6	125	261.9	505
1204	546.1	1425	37	3511.5	327.5	1099.8	647.2	783.9	437	712.9	128.4	264.5	508.3
1232	568.1	1399	38.1	3484.2	314.7	1063.1	604.2	756.7	376.3	708.3	131.6	267.2	511.2
1260	557.3	1323	36.1	3370.3	291.1	1021.3	575.1	740.1	317.1	692.2	130.4	263.9	502.1
1288	571.6	1271.3	36.4	3272.8	271	968.3	564	721.5	315.9	669.6	131.4	260.6	498.2
1316	590.2	1215.3	37.3	3137.4	248.2	907.3	545	697	304.8	635.6	129.7	253	482
1344	624.3	1168.1	39.1	2999.4	226.1	838.5	526.3	670.2	297	598	129.8	246.9	468.7
1372	637.4	1087.7	39.3	2795	196.2	756.1	498	634.3	285.4	542	126.9	235.4	448.4
													794.4

Table C.4 GC FID areas of reactant and products for MTO reaction on NS-[Al]-[B]-ZSM-5, at 450 °C, WHSV = 5.5 h⁻¹ (Continued)

1400	639.8	1000.1	39.4	2550.9	165.9	669.3	459.5	596.3	265.8	483.4	121.1	219.9	418.8	1599.3	919.9
1428	654.1	908.5	40.2	2251.4	128.2	570.7	410.6	543.4	237.8	410.3	114	201.8	381.3	2009.1	1025.6
1456	600.8	770.8	34.9	1880.1	91.2	468.8	343.6	471.9	204.6	326.8	100.3	173	328.4	2698.9	1222
1484	583.1	641.8	32.8	1431.5	59.7	328.5	262.6	384.5	153.7	230	80.7	136.3	255.2	3549.1	1442.8
1512	552.3	482.8	30.3	866.3	29.9	153.6	158.3	265.2	93.1	119.8	50.3	84.7	152	4862.3	1652.6
1540	557	322.7	31.3	318.8	10	53.9	56.2	95.9	30	34.2	17.2	32.3	51.9	6331.2	1833.3
1568	457.2	173.4	25.1	83.4			12	15.2	3.9				10.9	7237.7	1973.3
1596	461.8	155.9	26.9	62.3			8.1		4.7					7336.5	1992
1624	443.1	142	26.4	51.6			6.4		4.2					7526.8	2052.2
1652	449.8	140.1	27.6	48.3			5.5		3.3					7745.5	2117.6
1680	379.3	114.6	22.7	39.1			4.1							7795.9	2190.7
1708	351.4	104.2	21.1	35.1			3.7							7898.8	2241.4
1736	374.6	110.3	23.3	36.8			3.6							8055.5	2256.7
1764	389.6	113.2	24.9	37.7			3.7							8029	2247.2
1792	379.3	109.3	24.5	36.6										8059.3	2245.3
1820	348.2	99.2	22.3	33.4										7892.5	2234.5