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SYNTHESIS, CHARACTERIZATION, AND CATALYTIC APPLICATION OF STRONGLY ACIDIC MESOPOROUS ALUMINOSILICATE MATERIALS

By

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A DISSERTATION

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ABSTRACT

SYNTHESIS, CHARACTERIZATION, AND CATALYTIC APPLICATION OF STRONGLY ACIDIC MESOPOROUS ALUMINOSILICATE MATERIALS

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Aluminosilicate materials are utilized in many industrial applications, including adsorbents, ion-exchange agents, catalysts, and catalyst supports.¹ In catalytic applications, those aluminosilicates with large surface area and well-defined pore structure are especially useful because such materials can provide excellent catalytic performance and shape-selectivity that are not available from conventional catalysts.

Mesostructured aluminosilicates templated from supramolecular assembly of surfactant molecules have the above two desired properties.² However, the weak acidity and low hydrothermal stability cast a shadow over their prospect as acidic catalysts. On the other hand, small pore sizes greatly limited the application of zeolites, crystalline and strongly acidic aluminosilicates.

The present work describes the synthesis of mesoporous aluminosilicates with strong acidity. First, a family of mesostructured aluminosilicates was prepared from the zeolite precursor hydrolyzed in the presence of surfactants, which interact and stabilize the zeolitic subunits. The resultant mesostructures, MSU-Z, showed an unprecedented 74% conversion in catalytic cumene cracking reaction compared to 11% conversion for the conventional MCM-41 material.³ Secondary, zeolite nano-crystals as small as 30 nm with high crystallinity and yield were prepared in the presence of organosilanes, which served as a surface modifier to control the crystal size. The resultant nano-sized zeolites showed uniform particle size, and constructed uniform intercrystal mesopores. Finally, organosilane modifier polymers were used as mesoporogen in the synthesis of zeolites.⁴ Zeolite products with small and uniform intracrystal mesopores tunable in the range of 2 to 10 nm can be prepared. Compared to conventional zeolites, 6-fold and 16-fold increase in external surface and mesoporosity can be achieved. Such materials exhibited superior catalytic performance in cumene cracking reaction.

References

- 1 Corma, A. Chem. Rev. 1997, 97(6), 2373.
- 2 Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. *J. Am. Chem. Soc.* **1992**, *114(27)*, 10834.
- 3 Wang, H.; Liu, Y.; Pinnavaia, T. J. J. Phys. Chem. B 2006, 110(10), 4524.
- 4 Wang, H.; Pinnavaia, T. J. Angew. Chem. Int. Ed. 2006, 45, 7603.

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LIST OF ABBREVIATIONS

- APTES 3-Aminopropyltriethoxysilane
- BEA Framework code for zeolite Beta
- BET Brunauer-Emmett-Teller
- BJH Barrett-Joyner-Halenda
- CIC Colloid-imprinted carbon
- CTAB Cetyltrimethylammonium Bromide, C₁₆H₃₃N(CH₃)₃Br
- EtOH Ethanol
- FAU Framework code for Faujasite
- FCC Fluid Catalytic Cracking
- FTIR Fourier Transform Infrared spectroscopy
- GOPTMS Glycidoxypropyltrimethoxysilane
- HDPE High-density polyethylene
- HTMS Hexadecyltrimethoxysilane
- LTA Framework code for Linde type A zeolite
- M41S Mobil family of Mesostructured silicas
- MCF Mesostructured Cellular Foams
- MCM-41 Mobil Composition of Matter 41, hexagonal mesophase
- MFI Framework code for ZSM-5 zeolite
- MSU-A Mesoporous zeolite A prepared from silylated polymer as mesoporogen
- MSU-J Large-pore wormhole mesostructured silica assembled using Jeffamine D series surfactants
- MSU-MFI Mesoporous ZSM-5 zeolite prepared from silylated polymer

- MSU-S Ultra stable and strongly acidic mesostructured aluminosilicates assembled from protozeolitic seeds precursor
- MSU-Y Mesoporous zeolite Y prepared from silylated polymer
- MSU-Z Mesostructured aluminosilicates prepared from zeolitic fragment
- MTES Methyltriethoxysilane
- NMR Nuclear Magnetic Resonance
- OTMS Octyltrimethoxysilane
- P123 Pluronic 123, triblock polymer, (EO)₂₀(PO)₇₀(EO)₂₀
- PEI Polyethylenimine
- PEO Polyethylene oxide
- PHAPTMS Phenylaminopropyltrimethoxysilane
- PP Polypropylene
- PPO Polypropylene oxide
- P/Po Relative Pressure, P= pressure, Po = saturation pressure
- ppm Part per million
- PS Polystyrene
- PTMS Phenyltrimethoxysilane
- Q² Incompletely condensed silica sites, SiO₂(OSi)₂
- Q³ Incompletely condensed silica sites, SiO(OSi)₃
- Q⁴ Completely condensed silica sites, Si(OSi)₄
- SAPO Silicoaluminophosphate, a family of crystalline microporous materials with zeolite-like structures
- SBA-15 Large pore hexagonal mesostructured silicas assembled

under low pH conditions with P123 surfactant

- S_{BET} Specific surface area in m²/g obtained from the linear part of the adsorption isotherm using BET equation
- SEM Scanning electron microscopy
- Si-L Organosilane
- STP Standard temperature and pressure
- T Tetrahedral sites, including Si and Al
- T² Incompletely condensed silica sites, SiO(OSi)₂R
- T³ Completely condensed silica sites, Si(OSi)₃R
- TEM Transmission electron microscopy
- TEOS Tetraethylorthosilicate
- TMAOH Tetramethylammonium hydroxide
- TPAOH Tetrapropylammonium hydroxide
- TTeA Tallow tetramine
- USY Ultrastable Y zeolite
- XRD X-ray diffraction

Chapter 1 Introduction

1.1 Background

Materials with well-defined porous frameworks like zeolites,^{1, 2} also noted as molecular sieve, attract much attention due to their great potential in the field of catalysis,^{3, 4} separation,⁵ and other areas.⁶ The typical pore diameter of zeolite materials is less than 1.2 nm.⁷ Because of the limitation of the pore diameter, only small molecules can be processed effectively. In 1992, Mobil Oil Corporation successfully synthesized a family of silica-based mesostructured materials, denoted M41S,^{8,9} whose pore diameter ranges from 2.0 to 10.0 nm, which exceeds the limitation of zeolite materials and allows bulky molecules to diffuse into the pore channel. For instance, MCM-41 materials have been used to absorb protein and other bulky biomolecules for use as a smart delivery system.^{10, 11} Compared to other materials, mesostructures showed higher absorbing capability with desired releasing properties.¹²⁻¹⁴ The uniform mesopore size and high surface area of mesostructures are also highly desirable for many catalytic processes like FCC (fluid catalytic cracking), which is one of the most important processes in the chemical industry.

MCM-41 silica was synthesized through a micelle-induced supramolecular assembly pathway. Figure 1.1 illustrates the mechanism proposed by Mobil scientists. Surfactant molecules, which are amphiphilic,

form micelles first. Then, an inorganic matrix precursor introduced which interacts with the micelles to form mesostructures. Depending on the nature of



Figure 1.1 Possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal phase initiated and (2) silicate anion initiated.⁸

the interaction, the mechanism can be categorized into four most common pathways. The S⁺I⁻ pathway is where the cationic surfactant (S⁺) interacts with an anionic inorganic reagent I⁻ through electrostatic forces.⁸ Conversely, there is an S⁻I⁺ pathway, where anionic surfactants like carboxylic acids are used.^{15,} ¹⁶ Also, nonionic surfactants can be used either through an S⁰H⁺-X⁻I⁺ pathway¹⁷⁻¹⁹ or a hydrogen-bonding S⁰I^o pathway under neutral conditions.²⁰⁻²² Recently, mechanisms involving other interactions including covalent bonding were developed.²³ It should be pointed out that mesostructured silicas synthesized through the hydrogen-bonding pathway usually have higher cross-linking or Q⁴/Q³ ratio²⁰ because no charge balance is required for surface silicon sites. However, the ordering is generally lower for a mesostructure made through the S⁰I^o pathway due to the weaker H-bonding interactions compared to electrostatic Coulomb forces. Moreover, different

mesostructures including hexagonal,⁹ cubic,⁸ wormhole,²¹ foam¹⁷ and lamellar ²⁰ structures can be assembled, depending on the reaction conditions and the choice of surfactant molecules.²⁴

Mesostructured aluminosilicates have been shown to have good acid catalytic activity due to the large pore diameter and high surface area. For instance, compared to microporous clay catalysts, mesostructured aluminosilicate catalysts showed higher activity and selectivity for the alkylation of diphenylamine with α -methylstyrene.²⁵ However, mesostructures have limited applications as refining catalysts, despite of the improvement in mass transportation rate. The main reason behind this is that the wall of mesostructured aluminosilicate is amorphous. Compared to zeolites, amorphous mesostructured aluminosilicates have much weaker acidity, which dramatically affect their performance in catalytic reactions such as FCC where strong acidity is required. Moreover, the amorphous walls are very unstable especially under hydrothermal conditions. The mesostructure easily collapses and forms a low surface area degradation product. The poor hydrothermal stability further undermines their catalytic applications because such catalysts cannot survive the hydrothermal conditions generated during catalyst regeneration.

The poor hydrothermal stability of mesostructured aluminosilicates also is partially due to the thin wall of these materials. The typical wall thickness for MCM-41 is $1\sim2$ nm. Mokaya et al.^{26, 27} used post-synthesis treatment to

thicken the wall of MCM-41 and subsequently improved the hydrothermal stability of the materials. The optimization of synthesis conditions can also modify the wall thickness. Wang and his co-workers²⁸ reported a two-step synthesis route to separate the hydrolysis and condensation reactions of silica, which in turn provided a thick-wall mesostructure with better hydrothermal stability. In 1998, Stucky and his coworkers synthesized an MCM-41 analog, denoted as SBA-15, using a polyethylene oxide (PEO) - polypropylene oxide (PPO) triblock copolymer as the surfactant.¹⁷ The SBA-15 structure has a larger pore diameter, which reaches to 10 nm, and has thicker walls compared to MCM-41 materials. It also was reported that when PPO-PEO block copolymers were used as mesoporogen, the wall thickness of the resultant mesostructure was controlled by the length of the hydrophilic PEO chain, which penetrated into the silica matrix during synthesis.²⁹ For instance, a FDU-1 mesostructured silica with walls thicker than 10 nm was synthesized using (EO)₃₉-(BO)₄₇-(EO)₃₉ surfactant as porogen, where BO is a butylene oxide unit.³⁰ Such materials retained majority of the mesopore volume and surface area after being boiled in water. The hydrothermal stability was further improved when the pore wall was modified with an organosilane to increase the hydrophobicity of the wall.

Cross-linking is another important factor that affects the structural stability of mesostructured materials. A high degree of cross-linking is desirable in the synthesis strategy. ²⁹Si NMR results showed that a significant amount of Si

atoms in the MCM-41 framework are Q³ sites, which means one of the four oxygens linked to Si is terminated by a proton. From the crosslinking perspective, a non-electrostatic pathway is the preferred driving force for the assembly of stable mesostructures. With non-ionic Gemini surfactant of the type $C_nH_{2n+1}NH(CH_2)_2NH_2$ as a structure-directing agent, Kim²⁰ synthesized MSU-G material with significantly reduced Q³/Q⁴ ratio than typical mesostructures. Moreover, without electrostatic interaction, non-ionic surfactants can be easily removed from the mesopores, as in the case of MSU-H and HMS silicas, through a simple solvent extraction.

Another important feature of mesostructured silicates is the intrinsic acidity.³¹ Oftentimes, mesostructures were prepared in a pure silica form. Although the ²⁹Si NMR spectrum revealed that substantial amounts of Q³ sites existed in the framework, the acidity associated with the surface silanol group is too weak to provide desired acid catalytic activity. Strong acidity is obtained when some of the silicon sites are isomorphically substituted by tetrahedrally coordinated aluminum atoms. The incorporation of tetrahedral Al makes the framework electron negative. Therefore a Bronsted acid site can be generated when the counter ion is exchanged to proton, as shown in Figure 1.2.

Figure 1. 2 Illustration of Brosted acid site in aluminosilicate materials.

In addition to introducing framework heteroatoms by direct synthesis.³² the introduction of heteroatoms also can be achieved through a post-synthesis method like grafting.²⁶ However, the amount of heteroatoms that can be incorporated into the wall of a mesostructure is guite limited. Moreover, mesostructures lose long range ordering after the post-synthesis treatment. Recently, Xiao et al.³³ demonstrated the synthesis of mesostructured aluminosilicate material with Si/Al close to 1. To achieve that ratio, a precursor with preformed Si-O-Al link such as aluminosilicate ester ((BuO)₂-Al-O-Si-(OEt)₃) (di-sec-butoxyaluminoxytriethoxysilane) was used as single source for both Si and Al. The resulting composition exhibited a well-defined mesostructure and a high surface area of 491 m^2/g .

However, as mentioned before, compared to commercial zeolite catalysts, the lack of atomic ordering in mesostructured aluminosilicate materials makes them less attractive as refining catalysts because of poor stability and, most importantly, weak acidity. The ideal way to solve the problem would be to synthesize aluminosilicate materials that have the large pore diameters and high surface areas characteristic of mesostructures, but also have crystalline walls to impart strong acidity and stability. In general, two different strategies have been taken. On one hand, one can start with a mesostructure, and try crystallizing the amorphous wall into a zeolite; or one can start with a zeolite, and build mesopores within the crystal phase.

1.2 Recent advances

1.2.1 Mesostructured aluminosilicates with zeolitic walls

Shortly after the weak acidity and poor stability of mesostructured aluminosilicates was realized, many attempts have been conducted to crystallize the amorphous wall into a zeolite. Van Bekkum³⁴ reported the crystallization of the amorphous walls of MCM-41 materials. The mesostructure was impregnated with tetrapropylammonium hydroxide, which is the structure-directing agent for an MFI zeolite. The crystallization was conducted in the solid state to minimize the mass transportation that causes the collapse of mesostructure. Partial crystallization was achieved. Products with improved acidity were obtained, as indicated by catalytic cumene cracking results. However, the wall-thickness of the MCM-41 mesostructure was $1 \sim 2$ nm, which is smaller than the 2.5 nm unit cell dimension of an MFI framework. The complete crystallization of the walls caused the collapse of the mesostructure, and formation of nano-sized zeolite crystals.³⁵ Kaliaguine and co-worker³⁶ applied a similar approach to MCF mesostructured aluminosilicate, which has a much thicker wall and a larger pore size. A product with a ZSM-5 crystallinity of 42% was formed after the crystallization. N₂ isotherm for the product confirmed the presence of mesopores and the microporosity derived from zeolite phase. Dark-field TEM image revealed the presence of zeolite nanocrystals around 5 nm in size. Compared to the parent mesostructure, the crystalline product, denoted UL-ZSM-5, showed stronger acidity. However,

TEM image also revealed the loss of mesostructure in the product.

In order to stabilize the mesostructure during recrystallization, Hu et al.³⁷ filled the mesopore of SBA-15 with carbon formed in-situ. The resultant material showed both low-angle and wide-angle X-ray diffraction peaks, confirming the preservation of long-range ordering. Such an ordered mesoporous zeolite showed much higher activity in catalytic alkylation of bulky 2-methylnaphthalene compared to conventional ZSM-5 catalyst.

Another attempted approach to achieving crystalline walls for a mesostructured aluminosilicate involved a one-step synthesis. Mokava³⁸ reported using mixed templates for both simultaneously forming a microporous zeolite framework and a mesostructure. However, when such a reaction mixture was heated at an elevated temperature, it failed to produce the targeted product. In a typical reaction, cetyltrimethylammonium bromide (CTAB), a cationic surfactant to template mesopores, was added to a reaction mixture for ZSM-5 synthesis. Due to the low structural stability of the surfactant micelles at high temperature, the reaction was conducted at a temperature lower than the one normally used for conventional ZSM-5 crystallization. The evolution of the product with time of reaction showed that an MCM-48 type mesostructure was formed first, without any sign of a zeolite phase. Such a mesostructure was then transformed into a zeolite as the reaction progressed. However, during the crystallization both the mesostructure and the mesopore volume were lost.

In general, the attempts to crystallize the amorphous walls of a mesostructure destroy the long-range ordering of the parent mesostructures. which results in the significant loss of pore volume and surface area. A major breakthrough was achieved in 2000 by the Pinnavaia group,³⁹ who used preformed protozeolitic nanoclusters as the precursor to assemble hexagonal mesostructures. In the first report, a synthesis gel for faujasite was aged at 100°C. Before the zeolite product was crystallized, the reaction was quenched by lowering the temperature. The resultant solution was then added to a surfactant solution as the silica-alumina precursor to a mesostructure. Later, seeds for other types of zeolite structures were also demonstrated to be suitable precursors. Through the use of protozeolitic seeds, zeolitic nanoclusters can be incorporated into mesostructured walls. In the case of MFI and BEA seeds,^{40,} the presence of zeolitic nanoclusters was verified by IR spectroscopy. The final mesostructured aluminosilicates, denoted MSU-S, showed a distinguishable absorbance band at 550 cm⁻¹. Such an absorbance was absent in the conventional mesostructured aluminosilicates such as MCM-41. The IR band can be assigned to the asymmetric stretching of Si-O-Si five-member ring, which is a subunit in the MFI and BEA zeolite frameworks. The incorporation of other zeolite subunits was also verified by ²⁷Al NMR that final MSU-S materials exhibited a similar chemical shift as the corresponding zeolite. The incorporation of zeolitic subunits greatly improved the acidity of mesostructured aluminosilicates. Catalytic cumene cracking results showed

that a regular MCM-41 aluminosilicate catalyst had a cumene conversion of 11%. With the same Si/Al composition, a MSU-S aluminosilicates showed a cumene conversion as high as 43%, a 4-fold increase.⁴¹ Moreover, the introduction of AI sites became much easier. Utilizing Faujasite seeds as precursor, up to 35% AI can be incorporated into the mesostructures. Unlike other direct synthesis methods, the resultant MSU-S retained high mesostructure ordering. NMR spectra revealed that the majority of AI sites are tetrahedrally coordinated, which is very important to achieving strong acidity. Using a high AI content MSU-S catalyst, the Pinnavaia group achieved unprecedented cumene conversion up to 57%.

In addition, the introduction of zeolite seeds in the framework walls greatly improved the hydrothermal stability of the resulting mesostructured aluminosilicates. MSU-S materials retained 80% and 90% of the original surface area and pore volume, respectively, after being steamed at 20% water vapor at 800°C for 2 hours. The steamed samples showed the presence of high quality mesostructures as confirmed by both XRD and N₂ isotherm results. Such strong acidity and hydrothermal stability makes this family of mesostructured aluminosilicates good candidates as refining catalysts.⁴²

Several studies further extended the scope of the zeolite seeds method for producing improved aluminosilicate mesostructures.⁴³⁻⁴⁵ Results have showed that the zeolitic subunits of MSU-S materials survived not only under basic conditions, but they also survived acidic environments. For example,

mesostructures such as large pore SBA-15 and MCF have been successfully prepared under strongly acidic condition using MFI and BEA seeds precursors. Results verified that five member ring subunits have been successfully incorporated into the MSU-S products. All these materials exhibited much improved hydrothermal stability and stronger acidity compared to mesostructures prepared from conventional precursors.

In 2002, Kaliaguine and co-worker developed a method to coat the walls of large pore mesostructures, such as SBA-15⁴⁶ and MCF⁴⁷ with a preformed seeds solution. The resulting materials were subjected to elevated temperature in a non-aqueous solvent to facilitate the crosslinking of the zeolite subunits to the mesostruture walls. The final materials retained the mesostructure, but the pore size, pore volume and surface area were reduced due to the zeolite seeds coating. NMR spectra showed that a distinguishable zeolitic phase co-existed with a regular mesostructured aluminosilicate phase. The zeolite coated mesoporous materials exhibited strong acidity. However, this approach is not applicable to small pore mesostructures such as MCM-41. Moreover, severe loss of mesoporosity and surface area was inevitable.

Recently, other methods have been developed to incorporate zeolite subunits into mesostructures. In 2002, Goto et al.⁴⁸ reported the use of base-hydrolyzed zeolite solutions as precursors for the preparation of mesostructure/zeolite composite mixtures with improved acidity and hydrothermal stability. To assemble a mesostructured aluminosilicates as a

pure phase, Inagaki et al.⁴⁹ only used the solution products of the hydrolyzed zeolite to form the mesostructure. Because only partial hydrolysis of the zeolite was achieved, the resulting mesostructure had a composition different from the source zeolite. Moreover, NaOH can easily destroy the zeolite structure completely. Thus, the resultant mesostructure showed no evidence for the presence of zeolite subunits. By adding cationic surfactants into the hydrolysis reaction, Wang et al.⁵⁰ were able to partially or completely convert zeolites into mesostructures. The resultant products exhibited catalytic activities that were not observed for either conventional mesostructures or zeolites. More importantly, this approach allowed the incorporation of subunits of certain zeolite structures that are not easily prepared directly, and provided a good supplement to seeds approach.

1.2.2 Mesoporous forms of zeolites

Small framework micropores limit the usefulness of zeolites for catalytic reactions and adsorption processes when the size of the guest molecule is larger than the pore size of the zeolite. Even when the guest molecule is smaller than the framework pore size of the zeolite, the diffusion rate of reactants and products into and out of the channels can be slow, thereby limiting catalytic activity and selectivity.

Open framework structures with pore sizes a few nanometers, ie., < 10

nm, in dimensions are expected to function as size or shape selective catalysts for the conversions of large molecules. For instance, using non-zeolitic mesostructured aluminosilicates for the catalytic cracking of polymeric macromolecules, Aguado et al.⁵¹ have shown that uniform mesopores a few nanometers in diameter provide higher yields of liquid fuels than are obtained using the same aluminosilicate composition with much larger and less uniform mesopore distributions. Thus, zeolites with uniform small mesopores or uniform large micropores can be expected to function as selective catalysts for the cracking of large petroleum molecules and other catalytic conversions of large molecules. However, zeolites with these desired pore size properties are unknown.

There are two types of mesopores for zeolites, namely *inter*-crystal and *intra*-crystal mesopores. *Inter*-crystal mesopores arise from the aggregation of zeolite nanoparticles. Typical zeolite crystals are micron size, which lead to inter-particle voids with a diameter of more than several hundred nanometers. To prepare zeolite crystals on a nanometer scale, several methods have been developed. Bein et al.⁵² prepared zeolite A by manipulating the crystallization condition. This method required the precise control of kinetic parameters such as reaction temperature, time, and concentration (stoichiometry). For instance, LTA nanoparticles of 10 ~ 30 nm can be synthesized at room temperature in a highly diluted reaction mixture. Similar methods have been applied to other types of zeolite structures.⁵³⁻⁵⁵ However, with kinetic control of the zeolite

crystallization process, the final zeolite products were always obtained in very low yields and with poor crystallinity. Upon the modification of the reaction process, Bein et al.⁵⁶ were able to recycle the un-reacted precursors to achieve higher yields. However, low crystallinity was still inevitable.

With the aid of hard templates, zeolite nanoparticles can be synthesized under conventional conditions. Jacobsen and co-workers^{57, 58} first demonstrated the concept of nano-zeolite synthesis in confined space provided by carbon black nanoparticles. ZSM-5 nano-crystals with a diameter of 5 ~ 50 nm can be prepared. After the removal of the carbon template and the TPA structure-directing agent, ZSM-5 zeolite with *inter*-crystal mesopores was obtained. However, due to the irregularity of carbon nanoparticle templates, the resultant nano-zeolites were not uniform in size and shape at all, which lead to non-uniform pore size distribution.

A much more uniform nano-sized ZSM-5 zeolite was prepared by Kim et al.⁵⁹ who used colloid-imprinted carbon (CIC) as a template (Figure 1.3). Uniform silica nanoparticles were used to template the mesopores within the CIC template, which were later used as nano-reactor to crystallize the zeolite crystals. The nano-sized zeolites prepared from CIC materials reflected the size of the initial colloidal silica templates and were very uniform in size based on TEM observation. Based on the use of different colloidal silica precursors, the particle sizes of the resultant ZSM-5 could be controlled within 8 \sim 90 nm. Moreover, an unprecedented pore volume as high as 1.7 cc/g could be

achieved. If the zeolite crystals were packed tetrahedrally, they possess inter-crystal mesopores of 2 \sim 20 nm. However, pore size distributions revealed that mesopore diameters far larger than expected were observed. The results suggested that the zeolite nanoparticles were not uniform in size. They were somehow inter-grown during crystallization or sintered during calcination.



Figure 1.3 Illustration for the preparation of nano-sized ZSM-5 zeolite using colloid-imprinted carbon (CIC) templates.⁵⁹

More recently, Aguado et al.⁶⁰ demonstrated the use of organosilanes to modify the morphology of zeolite crystals during crystallization. The purpose of organosilanes was to react with surface silanol groups of zeolite nanocrystals so that the crystal growth can be quenched through the reduction of the growing crystals. Nano-sized zeolites with very high external surface area and greatly improved mesoporosity were prepared. In a typical experiment, a reaction mixture for ZSM-5 zeolite was nucleated for a certain period to obtain zeolitic nanoclusters and to avoid zeolite formation before the addition of 5% phenylaminopropyltrimethoxysilane (PHAPTMS). Because of the bulkiness of the organosilane molecule, they could only react with the outmost surface of the zeolite crystals. From the TEM images, the final zeolite products consisted of aggregated nanoparticles that are not uniform in diameter. The catalytic cracking of polypropylene (PP) studies showed that, compared to conventional zeolite catalysts, the silane-modified nano-zeolites were more active due to the enhanced external surface area. A 4-fold increase of PP conversion was achieved.



Figure 1.4 Effect of crystal size on the accessible region of a zeolite catalyst.

The advantage of forming mesopores between nanoparticles lies primarily in speeding-up reaction rates through improved molecular diffusion and access to the framework pores of the crystals. For example, nanosized zeolites have been observed to show higher catalytic performance than
conventional monolithic zeolites due to the larger external surface areas and the more rapid diffusion of reactants and products through crystals that typically are smaller than a few hundred nanometers in size.⁶¹⁻⁶³ Figure 1.4 quantitatively illustrates how the size of zeolite crystal affects accessibility, and hence catalytic efficiency. Suppose that in a typical catalytic reaction, the average diffusion distance for reactant molecules into zeolite channel is 20 nm. Then, for a particle with 1 µm diameter, the accessible active sites account for 1/125000 of total active sites. If the particle size is reduced to 100 nm, 1/125 of the total active sites become accessible. Therefore the efficiency is improved by 1000 times. However, the mesopores generated through the aggregation of nano-particles generally are not uniform even though the fundamental particles are very uniform. More importantly, due to the irregular packing, the resultant inter-crystal mesopores are much larger than 10 nm, which is much bigger than typical molecular size to provide desirable shape-selectivity for the products. Finally, the processing of nano-particles requires centrifugation and sonification, which are very time-consuming. Therefore, for that perspective, zeolites with intra-crystal mesopore are preferable.

Intra-crystal mesopores usually are generated within zeolite crystals through a chemical leaching process, such as steaming or desilication through NaOH leaching.⁶⁴ Steaming processing is extensively used in industry to modify the properties of zeolite catalysts. For instance, zeolite Y is usually steamed at >600 °C. Steaming not only removes the Na+ ion trapped inside

the sodalite cages, but also removes significant amounts of framework aluminum sites and generates mesopores. The resultant Y zeolite, denoted as ultra-stable Y (USY), shows much higher hydrothermal stability and catalytic performance.⁶⁵ During the leaching process, silica and alumina are removed from the framework and recrystallize or form amorphous phases, and mesopores larger than 10 nm are generated (Figure 1.5).⁷⁷ But the resulting mesopores are not at all uniform. Moreover, the composition of the zeolites is changed by the treatment. For instance, steaming selectively removes alumina; while NaOH leaching is more effective for removing silica.



Figure 1.5 TEM images of steamed faujasite crystals.77

In another approach to the formation of intracrystal mesopores, attention had been focused on the incorporation of carbon nanoparticles into zeolite crystals as they crystallize. This approach is often referred as hard-templating. The subsequent removal of the occluded carbon particles by calcination results in intracrystal mesopores that replicate the size and shape of the hard templates. In particular, carbon black particles⁶⁶ have been used as a templating agent to form intracrystal mesopores in zeolites. Because carbon materials have a hydrophobic surface, which is not compatible with hydrophilic zeolite phase, specific measures have to be taken to ensure encapsulation of the carbon template in the zeolite crystals. For example, in order to incorporate carbon nanoparticle reliably, a mixture of zeolite synthesis solution and carbon template is evacuated to remove the majority of solvent. The solid residue is then subjected to elevated temperature to crystallize zeolites under solid state conditions. In the absence of solvent, the silica and alumina sources are less mobile, and the final products are more likely to have the carbon nanoparticles imbedded inside the zeolite crystals. In the presence of solvent, such a composite structure is collapsed and phase segregation occurs. In the latter circumstance, zeolite nano-particles were produced.^{57, 58} The intra-crystal mesopores templated through the embedding of carbon nanoparticles also are not uniform, and they usually are very large on average due to the nature of the mesopore templates. In a related approach, Schmidt⁶⁷ used carbon nanotubes to template intra-crystal mesopores in zeolites. TEM images (Figure 1.6) showed the incorporation of carbon nanotube inside the ZSM-5 crystal. However, such a process is very unlikely to be commercialized due to the high cost.



Figure 1.6 TEM image of mesoporous zeolite single crystal templated by carbon nanotube.⁶⁷

Tao and co-workers⁶⁸ used relatively an inexpensive carbon aerogel, which was formed from resorcinol and formaldehyde, as a mesopore template. The carbon aerogel had an average mesopore diameter of 23 nm. The mesopores were filled with a zeolite synthesis mixture to grow ZSM-5 crystals. After the removal of the carbon template by calcination, textual mesopores centered at 11 nm were formed with a width at half height of 3 nm. This is by far the smallest and narrowest textural mesoporosity yet reported for a crystalline zeolite through the hard-templating approach.

In 1999, Ryoo et al.⁶⁹ first reported the synthesis of a carbon replica of a mesostructured silica. Sucrose as well as other organics such as furfuryl alcohol⁷⁰ and aromatics⁷¹ were used as carbon sources. In the presence of

acid catalysts, these precursors lose water, and are further converted into carbon at high temperature. After the removal of silica, mesostructured carbon materials are obtained, which were widely used as templates for the synthesis of mesostructured metal oxides such as CuO.⁷² In 2004, Mokaya et al.⁷³ reported the use of mesostructured carbon CMK-3 as a template for mesoporous zeolite synthesis. The CMK-3 carbons were prepared from a MCM-48 template, and had a pore size of 2 ~ 4 nm. The pores of CMK-3 were then used as nano-reactors and filled with zeolite precursors. Although the mesopores of the template are continuous, after the crystallization of the zeolite only nano-crystals were found and the mesostructure was completely lost. Moreover, the observed zeolite crystal size was significantly larger than the mesopore size. The result implied that the crystallization of zeolite destroyed the mesostructure, hence, replication failed. Part of reason for failed templating is the thin wall thickness of the initial MCM-48 template. In 2006, Hu and co-work³⁷ reported the re-crystallization of SBA-15 walls into zeolite walls. Instead of filling the mesoporous carbon template with zeolite synthesis mixture, the authors directly utilized the SBA-15 silica/CMK-5 carbon composite to form the zeolite phase. The SBA-15/CMK-5 composite was impregnated with TPAOH and crystallized at high temperature in a water vapor-saturated environment. The product not only showed Bragg X-ray diffraction peaks characteristic of an MFI structure at wide scattering angle, it also exhibited the low angle diffraction peaks associated with the parent

SBA-15 template. The ordered mesoporous zeolite showed much higher activity for the catalytic alkylation of bulky 2-methylnaphthalene compared to conventional ZSM-5 catalyst.

In contrast to hard-templating, soft-templating is another approach that has been developed recently for the synthesis of mesoporous zeolites. Surfactant micelles have been shown to successfully template incredibly uniform mesopores in the range of 2 to 10 nm within an amorphous aluminosilica matrix as well as other metal oxides. However, the Van der Waals interaction between surfactant molecules is too weak, especially at high temperature, to balance the forces induced by zeolite crystallization. Therefore, once the mesostructured walls crystallize, the micelles collapse and fail to template uniform mesopores. Realizing that, Xiao et al. applied polymers as the mesoporogen.⁷⁴ The polymer has multiple quaternary ammonium sites that not only resemble zeolite structure-directing agents, but also make the polymer extremely water soluble. These properties allow the polymer to form a homogeneous mixture with zeolite synthesis precursors. Although the polymer retained its integrity throughout the zeolite synthesis, during crystallization phase-segregation again occurred and the resultant products were agglomerates of zeolite nanocrystals.

More recently, Ryoo and co-workers⁷⁵ modified the one-pot synthesis approach to zeolite synthesis using a specific organosilane as the soft template (Figure 1.7). The unique organosilane had a quaternary ammonium

section similar to tetrapropylammonium (TPA) ions that the authors believed could also serve as zeolite structure-directing agent. Also, the silane head group could form Si-O-Si bond with the zeolite phase, so that phase separation would not occur. Finally, the surfactant molecule had a structure very similar to the commonly used mesoporogen CTAB. Therefore, it is possible that the silvlated surfactant molecules could form micelles and subsequently direct the formation of ordered uniform mesopores within zeolite crystals. The evolution of the reaction product with time showed that a mesostructure was obtained initially. As the reaction continued, a new mesostructured zeolite phase emerged upon the consumption of the initial mesostructure. Based on X-ray diffraction results, the new structure had a much larger unit cell size that can accommodate several zeolitic unit cells. The resultant zeolite materials possessed very uniform mesopores comparable to those of MCM-41 materials. Mesoporous ZSM-5 prepared from this approach exhibited enhanced catalytic activity compared to both conventional ZSM-5 and classic mesostructured aluminosilicate catalysts. Other than the ZSM-5 structure, the authors also demonstrated that this soft-templating method was applicable to aluminum-rich zeolite types such as faujasite and zeolite A. More recently, the methodology was further extended to other crystalline microporous materials such as SAPO.⁷⁶ These works open the door for the development of novel materials that have promising applications in catalysis.



Figure 1.7 Mechanism for mesopores templated through the organosilane within zeolite crystals proposed by Ryoo et al.⁷⁶

1.3 Research objectives

There are three basic objectives that the current work tries to achieve. The first objective is to formulate a mechanism that can incorporate more zeolitic subunits into mesostructured aluminosilicate materials. The presence of zeolitic subunits in MSU-S materials showed significant acidity enhancement in comparison to convertional mesostructures. However, FTIR data revealed that compared to fully crystallized zeolites, the concentration of zeolitic subunits in MSU-S materials is very limited, which in turn affords catalytic activity that is not comparable with corresponding zeolite catalysts. Hence, a precursor with more zeolitic cross-linking is needed. The nano-clusters obtained from the hydrolytic fragmentation of preformed zeolite should fulfill that purpose. However, the basic hydrolysis of zeolites in NaOH results in precursors with complete loss of zeolitic character. In order to achieve the optimal conditions for zeolite hydrolyzation, both the type of zeolite structure and the stabilization of the resultant nano-clusters need to be taken into consideration.

The second objective is to develop a zeolite synthesis methodology that offers better control of the morphology of the final products on a nanometer scale, while at the same time providing high yields and crystallinity. The use of carbon templates greatly limited the versatility and controllability of the particle size. On the other hand, the formation of zeolite nano-particles is not a thermodynamically favored process because of Ostwald ripening. In order to

stabilize nano-particles in the absence of carbon templates, it is essential to deactivate the surface by planting inert species on the surface. In this way, control of the crystal size does not rely on kinetics, and the final products can be fully crystallized.

The third objective is to synthesize zeolites with uniform mesopores, both inter- and intra-crystal mesopores. There are two major disadvantages associated with the approaches described earlier for the formation of zeolites with textural mesoporous. The first one is that, with the exception of the zeolite formed by nanocasting in a carbon aerogel, the resulting mesopores, whether inter- or intra- particle mesopores, typically are widely distributed in size. The uniformity of the mesopores is dependent on the nanocrystals size or the carbon porogens, both of which tend to be irregular in both size and shape. Therefore, the resultant zeolites reflect the same broad distribution of mesopores, which is not suitable for shape or size selective catalytic conversions. Furthermore, little or no pore volume provided in the 1-2 nm large micropore range or in the 2-10 nm small mesopore domain, which is highly desired for shape- or size-selective catalytic conversions or separations of large molecules. Moreover, such mesoporosity is expected to show shape-selectivity in important catalytic industrial reactions such as petroleum cracking and refining.

1.4 References

- 1 Corma, A. Chem. Rev. 1997, 97(6), 2373.
- 2 On, D. T.; Kaliaguine, S. Series on Chemical Engineering 2004, 4, 47.
- 3 Davis, M. E. Micro. Meso. Mater. 1998, 21(4-6), 173.

4 Ding, Z.; Kloprogge, J. T.; Frost, R. L.; Lu, G. Q.; Zhu, H. Y. J. Porous Mater. 2001, 8(4), 273.

5 McLeary, E. E.; Jansen, J. C.; Kapteijn, F. *Micro. Meso. Mater.* 2006, 90(1-3), 198.

6 Corma, A.; Garcia, H. Chem. Comm. 2004, 13, 1443.

7 Corma, A.; Diaz-Cabanas, M. J.; Jorda, J.; Martinez, C.; Moliner, M. *Nature*, **2006**, *443*(7113), 842.

8 Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. *J. Am. Chem. Soc.* **1992**, *114*(*27*), 10834.

9 Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature*, **1992**, *359(6397)*, 710.

10 Katiyar, A.; Ji, L.; Smirniotis, P. G.; Pinto, N. G. *Micro. Meso. Mater.* 2005, *80(1-3)*, 311.

11 Slowing, I. I.; Trewyn, B. G.; Lin, V. S.-Y. J. Am. Chem. Soc. 2007, 129(28), 8845.

12 Zhu, Y.; Shi, J. Micro. Meso. Mater. 2007, 103(1-3), 243.

13 Slowing, I. I.; Trewyn, B. G.; Giri, S.; Lin, V. S.-Y. Adv. Funct. Mater. 2007, 17(8), 1225.

14 Hoffmann, F.; Cornelius, M.; Morell, J.; Froeba, M. Angew. Chem. Int. Ed. **2006**, *45*(20), 3216.

15 Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schueth, F.; Stucky, G. D. *Nature* **1994**, *368*(*6469*), 317.

16 Gao, C.; Qiu, H.; Zeng, W.; Sakamoto, Y.; Terasaki, O.; Sakamoto, K.;

Chen, Q.; Che, S. Chem. Mater. 2006, 18(16), 3904.

17 Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*(*5350*), *5*48.

18 Liu, X.; Tian, B.; Yu, C.; Gao, F.; Xie, S.; Tu, B.; Che, R.; Peng, L.; Zhao, D. *Angew. Chem. Int. Ed.* **2002**, *41*(*20*), 3876.

19 Kleitz, F.; Liu, D.; Anilkumar, G. M.; Park, I.; Solovyov, L. A.; Shmakov, A. N.; Ryoo, R. *J. Phys. Chem. B* **2003**, *107*(*51*), 14296.

20 Kim, S-S.; Zhang, W.; Pinnavaia, T. J. Science 1998, 282(5392), 1302.

21 Tanev, P. T.; Pinnavaia, T. J. Science 1995, 267(5199), 865.

- 22 Kim, S.; Pauly, T. R.; Pinnavaia, T. J. Chem. Comm. 2000, 17, 1661.
- 23 Shimojima, A.; Kuroda, K. Angew. Chem. Int. Ed. 2003, 42(34), 4057.
- 24 Wan, Y.; Zhao, D. Chem. Rev. 2007, ASAP.
- 25 Liu, Y.; Kim, S.; Pinnavaia, T. J. J. Catal. 2004, 225(2), 381.
- 26 Mokaya, R.; Jones, W. Chem. Comm. 1998, 17, 1839.
- 27 Mokaya, R.; Jones, W. J. Mater. Chem. 1999, 9(2), 555.
- 28 Jin, Z.; Wang, X.; Cui, X. J. Coll. Inter. Sci. 2007, 307, 158.
- 29 Flodstrom, K.; Alfredsson, V. Micro. Meso. Mater. 2003, 59(2-3), 167.
- 30 Kruk, M.; Celer, E. B.; Jaroniec, M. Chem. Mater. 2004, 16, 698.
- 31 Liu, Y.; Pinnavaia, T. J. J. Mater. Chem. 2002, 12(11), 3179.
- 32 Chen, L.Y.; Jaenicke, S.; Chuah, G.K. Micro. Mater. 1997, 12, 323.

33 Yang, X.; Vantomme, A.; Lemaire, A.; Xiao, F.; Su, B. Adv. Mater. 2006, 18(16), 2117.

34 Kloetstra, R. K.; Jansen J. C.; van Bekkum, H. Chem. Commun., 1997, 2281.

35 Verhoef, M. J.; Kooyman, P. J.; van der Waal, J. C.; Rigutto, M. S.; Peters,

J. A.; van Bekkum, H. Chem. Mater. 2001, 13(2), 683.

36 On, D.; Kaliaguine, S. Angew. Chem. Int. Ed. 2001, 40(17), 3248.

37 Fang, Y.; Hu, H. J. Am. Chem. Soc. 2006, 128, 10636.

38 Xia, Y.; Mokaya, R. J. Mater. Chem. 2004, 14, 863.

39 Liu, Y.; Zhang, W.; Pinnavaia, T. J. J. Am. Chem. Soc. 2000, 122, 8791.

40 Liu, Y.; Zhang, W.; Pinnavaia, T. J. Angew. Chem. Int. Ed. 2001, 40(7), 1255.

41 Liu, Y.; Pinnavaia, T. J. J. Mater. Chem. 2004, 14(7), 1099.

42 Liu, Y.; Pinnavaia, T. J. J. Mater. Chem. 2002, 12, 3179.

43 Liu, Y.; Pinnavaia, T. J. Chem. Mater. 2002, 14(1), 3.

44 Zhang, Z.; Han, Y.; Xiao, F.; Qiu, S.; Zhu, L.; Wang, R.; Yu, Y.; Zhang, Z.; Zou, B.; Wang, Y.; Sun, H.; Zhao, D.; Wei, Y. *J. Am. Chem. Soc.* **2001**, *123(21)*, 5014.

45 Zhang, Z. T.; Han, Y.; Zhu, L.; Wang, R. W.; Yu, Y.; Qiu, S. L.; Zhao, D. Y.; Xiao, F. S. *Angew. Chem. Int. Ed.* **2001**, *40*, 1258.

46 On, D. T.; Kaliaguine, S. Angew. Chem. Int. Ed. 2002, 41(6), 1036.

47 On, D. T.; Kaliaguine, S. J. Am. Chem. Soc. 2003, 125(3), 618.

48 Inagaki, S.; Ogura, M.; Inami, T.; Sasaki, Y.; Kikuchi, E.; Matsukata, M. *Micro. Meso. Mater.* **2004**, *74(1-3)*, 163.

49 Goto, Y.; Fukushima, Y.; Ratu, P.; Imada, Y.; Kubota, Y.; Sugi, Y.; Ogura, M.; Matsukara, M. *J. Porous. Mater.* **2002**, *9*, 43.

50 Wang, S.; Dou, T.; Li, Y.; Zhang, Y.; Li, X.; Yan, Z. J. Solid State Chem. 2004, 177(12), 4800.

51 Aguao, J.; Sotelo, J. L.; Serrano, D. P.; Calles, J. A.; Escola, J. M. *Energy* & *Fuels* **1997**, *11*, 1225.

52 Mintova, S.; Olson, N. H.; Valtchev, V.; Bein, T. Science 1999, 283, 958.

53 Majano, G.; Mintova, S.; Ovsitser, O.; Mihailova, B.; Bein, T. *Micro. Meso. Mater.* **2005**, *80*, 227.

54 Valtchev, V. P.; Bozhilov, K. N. J. Phys. Chem. B 2004, 108, 15587.

55 Aguado, J.; Serrano, D. P.; Escola, J. M.; Rodriguez, J. M. *Micro. Meso. Mater.* **2004**, *75*, 41.

56 Larlus, O.; Mintova, S.; Bein, T. Micro. Meso. Mater. 2006, 96(1-3), 405.

57 Schmidt, I.; Madsen, C.; Jacobsen, C. J. H. Inorg. Chem. 2000, 39, 2279.

58 Madsen, C.; Jacobsen, C. J. H. Chem. Commun. 1999, 673.

59 Kim, S-S.; Shah, J.; Pinnavaia, T. J. Chem. Mater. 2003, 15(8), 1664.

60 Serrano, D. P.; Aguado, J.; Escola, J. M.; Rodriguez, J. M.; Peral, A. Chem. *Mater.* **2006**, *18*, 2462.

61 Landau, M. V.; Vradman, L.; Valtchev, V.; Lezervant, J.; Liubich, E.; Talianker, M. *Ind. Eng. Chem. Res.* **2003**, *42*, 2773

62 Zhang, P.; Wang, X.; Guo, X.; Guo, H.; Zhao, L.; Hu, Y. *Catal. Lett.* **2004,** *92*, 63.

63 Vogel, B.; Schneider, C.; Klemm, E. Catal. Lett. 2002, 79, 107.

64 Groen, J. C.; Peffer, L. A. A.; Moulijn, J. A.; Perez-Ramirez, J. *Chem. Eur. J.* **2005**, *11(17)*, 4983.

65 Flanigen, E. M. Stud. Surf. Sci. Catal. 1991, 58, 13.

66 Janssen, A. H.; Schmidt, I.; Jacobsen, C. J. H.; Koster, A. J.; de Jong, K. P. *Micro. Meso. Mater.* **2003**, *65(1)*, 59.

67 Schmidt, I.; Boisen, A.; Gustavsson, E.; Stahl, K.; Pehrson, S.; Dahl, S.; Carlsson, A.; Jacobsen, C. J. H. *Chem. Mater.* **2001**, *13*, 4416.

68 Tao, Y.; Kanoh, H.; Kaneko, K. J. Am. Chem. Soc., 2003, 125(20), 6044.

69 Ryoo, R.; Joo, S.; Jun, S. J. Phys. Chem. B 1999, 103(37), 7743.

70 Che, S.; Garcia-Bennett, A. E.; Liu, X.; Hodgkins, R. P.; Wright, P. A.; Zhao, D.; Terasaki, O.; Tatsumi, T. *Angew. Chem. Int. Ed.* **2003**, *42(33)*, 3930.

71 Kim, C.; Lee, D.; Pinnavaia, T. J. Langmuir 2004, 20(13), 5157.

72 Lai, X.; Li, X.; Geng, W.; Tu, J.; Li, J.; Qiu, S. Angew. Chem. Int. Ed. 2007, 46(5), 738.

73 Yang, Z.; Xia, Y.; Mokaya, R. Adv. Mater. 2004, 16(8), 727.

74 Xiao, F., Wang, L.; Yin, C.; Lin, K.; Di, Y.; Li, J.; Xu, R.; Su, D. S.; Schlogl, R.; Yokoi, T.; Tatusmi, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 3090.

75 Choi, M.; Cho, H. S.; Srivastava, R.; Venkatesan, C.; Choi, D.-H.; Ryoo, R. *Nature Mater.* **2006**, *5*(9), 718.

76 Choi, M.; Srivastava, R.; Ryoo, R. Chem. Comm. 2006, 42, 4380.

77 Janssen, A. H.; Koster, A. J.; de Jong, K. P. *J. Phys. Chem. B* **2002**, *106*, 11905.

Chapter 2

Highly acidic mesostructured aluminosilicates assembled from surfactant-mediated zeolite hydrolysis products

2.1 Abstract

Mesostructured aluminosilicates with strong acidity were synthesized through a top-down approach using zeolite hydrolysis products as precursors. The hydrolysis of zeolites was conducted in the presence of surfactants, most preferably cetyltrimethylammonium ions, that helped to stabilize zeolitic subunits in solution. Commercial zeolites ZSM-5 (Si/AI = 40) and USY (Si/AI = 40) were successfully transformed completely into mesostructures. The resultant mesostructured aluminosilicates, denoted MSU-Z, showed high surface area (> 1000 m^2/g) and uniform mesopores (2.5 nm) comparable to MCM-41 silica prepared from conventional precursors. In the case of ZSM-5 zeolite as a precursor, the successful incorporation of zeolitic subunits into the resultant mesostructure was verified by IR spectroscopy. Compared to other methods, this top-down approach optimized the preservation of zeolitic subunits in solution for subsequent conversion to a mesostructure. The resultant MSU-Z aluminosilicates showed unprecedented high activity for catalytic cumene cracking.

Several factors affect the properties of MSU-Z materials assembled from

zeolite precursors. Low Si/Al zeolite Y with an initial Si/Al ratio of 6: 1 can only be partially transformed into a mesostructure even under severe hydrolysis conditions (OH⁻/T = 3, 100 °C). XRD data revealed that the residual zeolite has a lower Si/Al ratio than the starting zeolite, indicative of the preferred leaching of silica. Moreover, even in the presence of subunit-stabilizing surfactant, ZSM-5 zeolite can be over-hydrolyzed by reaction with excessive NaOH. Overhydrolyzed zeolite precursors afford a mesostructure equivalent in acidity and stability to conventional MCM-41. Several other surfactants including tallow tetramine and P123 were also used. Compared to cationic surfactant CTAB, these surfactants interact with zeolitic nanoclusters through H-bonding, and provide less stabilization of the subunits than a cationic surfactant.

2.2 Introduction

In 1992, Mobil researchers reported the synthesis of mesostructured MCM-41 silica through the supramolecular assembly of surfactant micelle templates.^{1, 2} These mesostructured materials showed very high surface area. typically above 1000 m^2/g , and uniform and controllable mesopore size from 2 to 50 nm. Such materials found many interesting applications in separation,^{3,4} adsorption,^{5, 6} electronic devices,⁷⁻⁹ and drug delivery.¹⁰⁻¹³ The high surface areas and large pore sizes of mesostructured aluminosilicates have been recognized as desirable properties for the catalytic processing of large molecules such as enzymes^{14, 15} and polymers.^{16, 17} The high surface area provides more surface-active sites, and the presence of uniform mesopores allows reactant and product molecules to diffuse easily in and out of the catalyst pore system. Moreover, the uniformity of the mesopore provide for the possibility of shape-selectivity that is not available for other catalytic materials.18-20

The cracking of hydrocarbons to produce lower molecular weight products is one of the most important reactions that allows the conversion of petroleum to lighter products such as transportation fuels.²¹ During the cracking reaction, a carbonium species is formed initially at strong acidic sites. Typical cracking catalysts consist of acidic aluminosilicates as main components. The discovery of strongly acidic zeolite catalysts greatly boosted the yield of transportation fuels due to their strong acidity.²² However, because

of the pore size limitation and poor diffusion through their micropores, the heavy fraction of petroleum is not easily processed over zeolites.²³ The pore sizes of most zeolites typically is limited to micropores of 0.3 ~ 1.2 nm.²⁴ Aluminosilicates with non-uniform mesopores act as supplemental components to zeolites for bulky molecule processing.²⁵ Due to their high surface area and uniform mesopores, mesostructured aluminosilicates have been considered as promising catalysts with a desirable selectivity.²⁶

Mesostructured aluminosilicates are not as stable hydrothermally as zeolites. The stability limitation of mesostructured aluminosilicates has been attributed in part to the thin and amorphous pore walls, typically 1 to 2 nm for MCM-41 material. However, later studies have shown that even thick-wall mesostructures such as SBA-15²⁷ and MCF²⁸ are not stable under hydrothermal conditions. More importantly, mesostructured aluminosilicates have very weak acidity, which limits their applications in acidic catalysis. The ultimate reason for the poor hydrothermal stability and acidity is that the mesostructured framework lacks atomic ordering in the walls.

In 2000, a novel approach to the preparation of mesostructured derivatives with improved hydrothermal stability and acidity was reported based on the incorporation of protozeolitic nanoclusters or "zeolite seeds" in the framework.^{29, 30} This was accomplished by quenching a zeolite synthesis gel prior to the onset of zeolite crystal formation and then transforming the quenched gel into a mesostructure. The generality of this approach and the

spectroscopic evidence supporting the presence of zeolitic subunits in the mesostructured framework has been substantiated by several subsequent studies.³¹⁻³⁴ This bottom-up approach greatly improved the catalytic activity of resultant mesostructured aluminosilicate materials in comparison to a conventional MCM-41 catalyst. However, their catalytic activities are still not comparable with commercial zeolite catalysts. This could be due to the limited amount of zeolite subunits incorporated into the mesostructures.

Several other approaches have been developed to improve the acidity of mesostructured aluminosilicates by introducing zeolitic subunits into the pore walls. The direct crystallization of amorphous walls of MCM-41 lead to the complete loss of mesostructure.³⁵ Even with very thick-wall materials like mesostructured cellular foam silicas, partial crystallization of the amorphous walls was achieved with the use of a non-aqueous solvent, accompanied by a significant loss of mesopores.³⁶ In a related approach, large pore silica mesostructures were coated with zeolitic seeds.^{37, 38} The incorporation of zeolite seeds was verified by the increase of acidity. However, through the re-construction of the mesostructure, great reduction of pore size, pore volume, and surface area was observed. Moreover, the coating approach is not applicable to small pore materials such as MCM-41.

In this study, we developed a new approach to the synthesis of highly acidic mesostructured aluminosilicates. Our top-down approach to improving the incorporation of zeolitic subunits into the framework walls is based on the

hydrolysis of a pre-formed zeolite in the presence of a cationic surfactant. The surfactant serves two purposes. The first purpose is to stabilize the zeolitic subunits through ion-pairing during the hydrolysis so that more zeolitic subunits can be preserved. After that, the surfactant also serves as a structure-directing porogen for the assembly of the mesostructure. The resultant mesostructured aluminosilicate materials, denoted MSU-Z, are characterized by N₂ isotherm, XRD, TEM and FT-IR.

2.3 Experimental section

2.3.1 Materials

ZSM-5 (CBV 8014), USY (CBV 780), and Y (CBV 712) zeolites with Si/Al atomic ratios of 40 were obtained from Zeolyst. Sodium hydroxide, cetyltrimethylammonium bromide (CTAB), and sulfuric acid (100%) were purchased from Aldrich. Tallow tetramine (TTeA, $C_{16}H_{33}(NH(C_3H_6))_{3}NH_2$) was obtained from Tomah as a gift. P123 ((EO)₂₀(PO)₇₀(EO)₂₀) surfactant was obtained from BASF.

2.3.2 Synthesis of mesostructured aluminosilicates from zeolite precursors

ZSM-5 zeolite (2.00 g, 33.3 mmol) was dispersed in a solution containing 55 mL of 0.45 M NaOH solution (OH'/T = 0.75, where T = Si + Al), to which 2.45 g (6.7 mmol) CTAB was added as mesoporogen. The mixture was stirred at room temperature for 1 hour, and transferred into a Teflon-lined autoclave, heated at 100 °C for 24 hours, and then cooled to room temperature. The pH of the solution was adjusted to 9.0 through the addition of sulfuric acid and the mixture was heated again at 100 °C for another 24 hours to form a hexagonal mesostructure. The product was filtered, washed, and calcined at 600 °C for 4 hours to remove the organic surfactant. The final product was denoted as MSU-Z. The protonated form of MSU-Z was obtained by duplicate ion-exchange reaction with 0.5 M NH₄NO₃ solution at 60 °C for 2 hours and

then calcining the product at 550 °C.

For the assembly of MSU-Z with a wormhole structure, ZSM-5 zeolite (2.00 g, 33.3 mmol) was dispersed in a solution containing 55 mL of 0.45 M NaOH solution (OH/T = 0.75, where T = Si + Al), to which 2.0 g TTeA was added as mesoporogen. The mixture was stirred at room temperature for 1 hour, and transferred into a Teflon-lined autoclave, heated at 100 °C for 24 hours, and then cooled to room temperature. Sulfuric acid (1.21 g, 12.3 mmol) was added and the mixture was heated again at 60 °C for another 24 hours in a shaking bath.

For the assembly of large pore hexagonal MSU-Z, ZSM-5 zeolite (2.00 g, 33.3 mmol) was dispersed in a solution containing 55 mL of 0.45 M NaOH solution (OH⁻/T = 0.75, where T = Si + Al), to which 2.4 g P123 was added as mesoporogen. The mixture was stirred at room temperature for 1 hour, and transferred into a Teflon-lined autoclave, heated at 100 °C for 24 hours, and then cooled to room temperature. The pH of the solution was adjusted to 4.5 with a diluted sulfuric solution. The reaction mixture was kept at 35 °C water bath for 24 hours and then 60 °C for another 24 hours.

The reaction stoichiometries for MSU-Z syntheses are listed in Table 2.1.

2.3.3 Characterization

The physical properties of MSU-Z materials were determined using X-ray diffraction (XRD), nitrogen adsorption/desorption isotherm, transmission

electron microscopy (TEM), ²⁷Al-NMR and FT-IR.

Powder XRD patterns were measured on a Rigaku Rotaflex Diffractometer equipped with an anode using Cu Ka radiation ($\lambda = 0.154$ nm). Scan consitions are 20 continuous reflective mode from 5° to 50° for wide angle or 1° to 10° for low angle at 2°/min and 0.05°/step. N₂ isotherms at -196 °C were obtained on a Micromeritics TriStar 3000. Samples were decassed at 150 °C and 10⁻¹ Torr for a minimum of 6 hours prior to analysis. The surface area was calculated using the BET equation. Pore size distributions were derived from the adsorption isotherms using the BJH model. TEM images were obtained on a JEOL 2200FS instrument operated at 200 kV. Samples were prepared by sonicating the ground sample in EtOH for 20 min, and then evaporating 2 drops of the suspension onto a carbon-coated holey film supported on a 300 mesh Cu grid. ²⁷AI MAS NMR spectra were recorded on a Varian VXR-400S spectrometer with zirconia rotors 4 mm in diameter and spun at 4 KHz. External $Al(H_2O)_6^{3+}$ was used as a chemical shift reference. FT-IR spectra were recorded on a Mattson Galaxy Series FTIR 3000. The adsorption band at 450 cm⁻¹ was selected as the internal reference. This band was present in all silica samples and was assigned to the Si-O-Si vibration.

2.3.4 Catalytic cumene cracking

Catalytic cumene cracking reactions at 300 °C were carried out in a 6 mm i.d. fixed bed quartz reactor (as shown in Figure 2.1) containing 200 mg of

catalyst. Prior to catalytic testing, the protonated catalysts were activated at 300° C under N₂ flow for a minimum of 2 hours. The cumene flow rate was 4.1 µmol/min in a 20 cm³/min carrier stream of N₂. Cumene conversions were reported after 1 hour on stream.

2.4 Results and discussion

Figure 2.2 provides the XRD patterns of MSU-Z aluminosilicates assembled from ZSM-5 and USY fragments. Both samples show four distinguishable Bragg diffraction peaks at low angle, indexed as 100, 110, 200, and 120 respectively, indicative of the formation of the same 1-D hexagonal mesostructure as of MCM-41. Moreover, no Bragg peaks at wide angle was found, which excluded the presence of a crystalline zeolite phase. The ²⁷Al MAS NMR chemical shifts of the as-made MSU-Z prepared from ZSM-5 hydrolysis product (Figure 2.3) indicate that all of the aluminium in the mesostructures is in tetrahedral coordination (51.2 ppm). The exclusively tetrahedral siting of aluminum is very desirable in providing strong acidity. Upon calcination, some octahedral aluminium is observed at ~3 ppm, but the majority of aluminum centers remain in tetrahedral coordination.

Diluted sodium hydroxide solution has been reported to leach out framework atoms from zeolites to generate intra-crystal mesopores.³⁹ The leached-out species can then be subsequently used as precursors to assemble mesostructures. Normally, the silica is more easily removed from a zeolite framework under basic conditions than alumina. Therefore, under partial hydrolysis conditions, the mesostructured aluminosilicates made from the hydrolysis products exhibited higher Si/Al ratio than that of parent zeolite.⁴⁰ Moreover, the incorporation of five-membered ring subunits in the framework walls of the mesostructure, as well as the cracking activity of the

mesostructure, is no better than what can be achieved through the direct assembly of aluminosilicate mesostructures from protozeolite seeds formed in the presence of a zeolite template. Under the surfactant-mediated hydrolysis conditions of the current study, however, all the zeolite starting materials are completely transformed into mesostructures, as confirmed by the absence of wide angle diffraction peaks in the final products. As listed in Table 2.2, no significant change in Si/Al ratio was observed for MSU-Z materials. The results suggested that all of the starting zeolite materials ended in the final mesostructured aluminosilicates. The new method offers the opportunity to easily control the Si/Al of resultant mesostructures.

As shown in Figure 2.4, the IR spectrum of MSU-Z formed from ZSM-5 fragments (curve C) exhibits an intense band near 550 cm⁻¹, indicative of five-membered ring subunits analogous to those subunits⁴¹ found for the pristine zeolite (curve D). This band is absent in the spectrum of MCM-41 prepared from conventional aluminosilicate precursors (curve A) and comparatively weak in the spectrum of MSU-S made from protozeolitic ZSM-5 seeds (curve B). As expected, this band is absent from the spectrum of MSU-Z made from hydrolyzed USY zeolite, as this zeolite does not contain five-ring subunits. On the basis of these FTIR results for MSU-Z made from hydrolyzed ZSM-5 fragments, it is clear that the "top-down" degradation of a zeolite in the presence of a fragment-stabilizing surfactant is superior to the earlier "bottom-up" approach to generating zeolite subunits from conventional

aluminosilicate precursors.

Figure 2.5 provides the nitrogen adsorption - desorption isotherms and framework pore size distributions for MSU-Z made from surfactant-mediated ZSM-5 and USY zeolite fragments (curves C and B, respectively) in comparison to conventional MCM-41 (curve A). All the samples showed typical type IV isotherm with a nitrogen capillary condensation at P/Po ~ 0.4, indicative of the presence of uniform cylindrical pores of 2~3 nm (Figure 2.6). The physical properties are listed in Table 2.2. In comparison to conventional mesostructured aluminosilicate MCM-41, MSU-Z materials exhibited similar BET surface area (> 1000 m²/g) and pore volume (0.86 cm³/g). Furthermore, the unit cell sizes derived from XRD patterns indicated an increase from 4.64 nm to 4.98 nm, while the pore size for MSU-Z remained the same as MCM-41. The results suggested that MSU-Z materials prepared from zeolite fragments have thicker walls than MCM-41, prepared from molecular precursors.

When the hydrolysis of ZSM-5 was carried out in the absence of surfactant and the pH adjusted to 9.0 (trial 10), a low surface area aluminosilicate gel was obtained that had no 550 cm⁻¹ IR band and virtually no activity for cumene cracking when exchanged with NH_4^+ ions and calcined. Thus, ion paring to the cationic cetyltrimethyl ammonium ion surfactant plays an essential role in stabilizing the anionic zeolitic fragments formed upon hydrolysis. We emphasize that it is possible to over-hydrolyze the zeolite precursor to the point where the concentration of zeolitic fragments available

for mesostructure formation is compromised despite the presence of a cationic surfactant (trial 4). Curve D in Figure 2.5 is the isotherm for a mesophase formed from ZSM-5 that was deliberately over-hydrolyzed by using an excessive concentration of sodium hydroxide. A unit cell size similar to MCM-41 was observed.

The hypothesis of ion-pairing between inorganic silica and organic surfactant was further investigated. Figure 2.7 provides the XRD patterns of hydrolyzed products of ZSM-5 in the presence of different amounts of CTAB. The broad diffraction peak near 23° is due to the Si-O bond on amorphous silica. It can be clearly seen that as the concentration of CTAB increased, the Bragg diffraction peaks characteristic of ZSM-5 zeolite showed up, as marked in Figure 2.6. It is conceivable that CTAB stabilizes zeolite structures during the hydrolyzation.

In order to test the acidity of MSU-Z mesostructures made from surfactant-mediated zeolite hydrolysis products, the cumene cracking was carried out as a probe reaction. Prior to catalysis the mesostructures were exchanged with NH₄NO₃ and calcined at 550 °C to afford the protonated form of the mesostructure. The results are listed in Table 2.2. For comparison, the cumene cracking also was carried out over an ammonium exchanged conventional MCM-41 with a Si/Al ratio of 50, which showed a cumene conversion of 11%, consistent with previous reported results.³² The MSU-Z mesostructure prepared from USY fragments showed a substantial 3.4-fold

increase in cumene conversion in comparison to MCM-41. This high cumene activity value is similar to the activity observed for MSU-S aluminosilicates assembled from faujasite zeolite seeds. The improved catalytic activity suggested that fragments of USY zeolite were incorporated into the mesostructured aluminosilicate. The 73% conversion found for MSU-Z made from the surfactant-mediated hydrolysis of ZSM-5 is 6.7-fold higher than observed for a conventional MCM-41. This level of cumene cracking activity is unprecedented among mesostructured aluminosilicates. The highest cumene conversion previously observed under analogous reaction conditions (57%) was for a MSU-S made from faujasite seeds at a Si/Al of 5.7.

The cumene cracking activity of MSU-Z made from surfactant-mediated ZSM-5 fragments approaches the 90 – 95% conversions observed for the pristine ZSM-5 at the same Si/AI ratio. This extremely high acidity cannot be attributed to the presence of residual ZSM-5 crystals in the mesostructured product, because the presence of such crystals is precluded by the absence of wide angle Bragg peaks in the XRD powder pattern. TEM image of MSU-Z sample exhibits a typical hexagonal ordering observed on MCM-41 mesostructures (Figure 2.8). Several composite compositions containing mixtures of zeolite and mesostructured aluminosilicate phases have been reported previously.^{42, 43} These mixtures show wide angle Bragg X-ray reflections characteristic of the zeolite phase. Also, the zeolite component of these mixtures typically exhibit lattice fringes in the bright field TEM mode and

dense nanocrystallite domains in dark field mode. None of these XRD or TEM features representative of a zeolite phase were observed for MSU-Z made from surfactant-mediated ZSM-5 fragments. Moreover, the absence of zeolitic microporosity was verified through t-plots of the nitrogen adsorption data, as expected for a framework that contains the secondary building units of a zeolite, but not zeolite cavities. A t-plot is a measurement that compares the sample with a standard surface. The deviation of the v-axis intercept from the origin indicates the presence of micropores. For a mixture of MCM-41 with 5% ZSM-5 (Figure 2.9, curve A), a positive deviation was observed, consistent with the presence of microporous zeolite phase. However, the t-plot of MSU-Z passed through origin (Figure 2.9, curve B). All the experimental results confirmed the absence of a zeolite phase in this highly acidic MSU-Z material. Therefore, the unprecedented high cracking activity is a result of the high concentration of zeolitic subunits incorporated into the mesostructure, as revealed by the FT-IR spectra.

It is noteworthy that much less NaOH is required to completely decompose USY than ZSM-5 zeolite. Compared to ZSM-5, which has 0.55 nm micropore size and 350 m²/g surface area, the larger pore diameter (0.74 nm) and higher surface area (800 m²/g) of USY enable the diffusion of NaOH more easily. Moreover, to produce USY, steaming and leaching treatments were applied to zeolite Y to remove framework atoms (especially Al) to generate irregular mesopores. The presence of mesopore greatly reduced the domain

size of zeolite so that it becomes more vulnerable to the basic hydrolysis. Compared to ZSM-5, which requires an OH/T of 0.75 to be completely hydrolyzed, pure mesostructured aluminosilicate can be prepared from USY with an OH/T value of 0.17. Such a low NaOH concentration can only partially decompose ZSM-5 structure. Therefore a mixture of zeolite and mesostructure was resulted. Figure 2.10 provides the XRD pattern of MSU-Z prepared from ZSM-5 hydrolyzed with insufficient NaOH. Bragg diffraction peaks corresponding to an MFI framework appear at wide angle, in addition to the low angle diffraction peaks of the mesostructure. The N₂ isotherm data showed a lower mesopore volume compared to MCM-41.

In addition to USY and ZSM-5, a similar methodology has also been applied to other zeolite structures such as mordenite.⁴⁴ As described above, for different zeolite frameworks, the NaOH concentration required to achieve complete hydrolyzation differs. In the case of zeolite Y, which has a Si/Al of 6 and same framework structure as of USY, the complete conversion into mesostructure was not accomplished in reasonable reaction conditions. For instance, a mixture of zeolite Y and mesostructured aluminosilicate was obtained at an OH⁻/T value of 2.25. XRD pattern of the final product revealed the presence of unconsumed zeolite Y. The reason for this observation could be two fold. First, although USY and Y share the same structure, the presence of mesopores within USY sample makes it more hydrolysable. In addition, zeolite Y has a much higher aluminum content. The higher degree of isotopic

substitution of Si by Al helps stabilize the zeolite structure under basic hydrolysis conditions. Moreover, a shift of d-space was observed in the wide angle X-ray diffraction patterns for the zeolite Y residues compared to the pristine zeolite. The d-spacing shift indicates a change in framework Si/Al ratio. As the framework is enriched in Al, an expansion of the unit cell was observed. We are able to determine the framework Si/Al of the residual Y zeolite using the following equation:⁴⁵

$$N(AI) = m (a_0 - X)$$
, where m = 115.2, X = 24.191

where N(AI) equals the framework aluminum sites per unit cell ($[T_{192}O_{384}]$ per unit cell for faujasite) and a_0 is the unit cell parameter in Å. After hydrolysis, a zeolite Y with Si/AI of 3 was observed, which suggested that silica was preferably leached out from the framework during basic hydrolyzation.

Surfactants other than cationic CTAB were also capable of stabilizing zeolite fragments and subsequently directing the formation of mesostructures. Figure 2.11 provides the N₂ isotherms and the corresponding pore size distributions for MSU-Z materials prepared from ZSM-5 and USY fragments in the presence of non-ionic surfactants P123 and TTeA. In both cases, high quality mesostructured aluminosilicate materials were produced. Physical properties are listed in Table 2.2. The resultant MSU-Z materials showed high surface area and uniform mesopores. The results are in agreement with the reported value for the large-pore hexagonal MSU-H and for the wormhole structure assembled from conventional precursors. XRD patterns (Figure 2.12)

showed that no zeolite phase was observed in the hydrolysis products. It is noteworthy that under the same hydrolysis condition (OH'/T ratio), wide angle Bragg peaks corresponding to the ZSM-5 zeolite (Figure 2.12, curve A) were found in the hydrolysis product using CTAB as structure-directing agent. Whereas the cationic CTAB surfactant can ion-pair with zeolite hydrolysis fragments in solution, the TTeA and P123 surfactants can interact with zeolitic nanoclusters only through hydrogen bonding. Apparently, the stronger electrostatic interaction provided by CTAB stabilizes the zeolitic subunits more efficiently than weaker H-bonding. Nevertheless, the results showed that the top-down approach to the incorporation of zeolitic subunits into the framework walls of a mesostructure is general and applicable to other zeolite precursors and surfactants.

2.5 Conclusion and perspective

Through the incorporation of zeolitic subunits into the walls, mesostructured aluminosilicates with strong acidity can be prepared. Two different pathways have been developed by our group to introduce zeolitic subunits, namely bottom-up (for MSU-S materials) and up-bottom approaches MSU-Z materials). MSU-Z materials are prepared with the (for surfactant-mediated hydrolysis product of preformed zeolites as precursors. Compared to bottom-up approach, mesostructured aluminosilicates prepared from up-bottom approach retained more zeolitic characteristics as judged by the absorbance intensity of five-member ring in IR spectra. The resultant MSU-Z materials are also much more acidic than conventional MCM-41 aluminosilicates and even MSU-S materials. For instance, in the catalytic cumene cracking reaction, 2%AI-MCM-41 aluminosilicate catalyst has a cumene conversion of 11%, at the same condition 2%AI-MSU-S materials provide a cumene conversion as high as 43%, which can be improved to 57% if the AI content of the mesostructure is increased to 15%. On the other hand, 2%AI-MSU-Z prepared from ZSM-5 precursor exhibits a cumene conversion of 74%, a 6-fold increase from 2%AI-MCM-41.

Other than ZSM-5, other types of zeolites such as USY can also be used as the precursors for MSU-Z. Due to the structural difference between ZSM-5 and USY, different hydrolysis conditions are used. Compared to ZSM-5, USY has larger framework pore diameter, larger surface area, and more textual porosity, and therefore is more vulnerable to hydrolyzation. An OH'/Si of 0.17 is enough to completely convert USY into a mesostructure, while at least OH'/Si of 0.75 is needed for ZSM-5. Moreover, the interaction between surfactant molecules and zeolite subunits is very important to preserve the zeolitic subunits during hydrolysis process. The hydrolysis product in the absence of surfactant shows no cumene cracking activity at all. In addition, several common types of surfactants have been successfully used to prepare MSU-Z materials. In general, the Coulomb force between cationic surfactant the hydrogen-bonding interaction between neutral surfactant and aluminosilicate cluster. Among the three surfactants, CTAB provides the best stabilization to the zeolitic subunits.

Assembled from small and uniform precursors with zeolitic cross-linking, MSU-S materials exhibited ultrahigh hydrothermal stability in comparison to conventional MCM-41 materials. Compared to bottom-up approach, the top-down approach produces precursors with substantial heterogeneity and probably larger size. Therefore, the structure of MSU-Z materials might not be as robust as MSU-S materials, although the former is more active in catalytic cumene cracking reaction. Future work should be focusing on the effect of zeolite Si/Al ratio. It is clear that framework Al stabilizes the crystal structure of zeolite during NaOH hydrolysis.⁴⁶ Therefore, the distribution of Al and the framework Si/Al ratio would greatly affect the properties of resultant zeolite
fragments, and subsequently affect the hydrothermal stability of final MSU-Z products.

Trial	Zeolite	Si/Al	NaOH/g	Surfactant	Surfactant/g
	source*				
1	ZSM-5	40	0.75	CTAB	2.45
2	ZSM-5	40	1.0	CTAB	2.45
3	ZSM-5	40	1.0	CTAB	3.45
4	ZSM-5	40	2.0	CTAB	2.45
5	ZSM-5	40	1.0	P123	2.4
6	USY	40	0.228	CTAB	2.45
7	USY	40	0.228	TTeA	2.0
8	Y	6	3.0	CTAB	2.45
9	ZSM-5	40	1.0	TTeA	2.0
10	ZSM-5	40	0.75		

 Table 2.1 Summary of reaction stoichiometry for the synthesis of MSU-Z

 materials from crystalline zeolites as the aluminosilicate source.

* For all the trials, the amount of zeolite is always 2.0 g.

Trial	Surface area, m²/g	Pore size, nm	Unit cell size a _o *, nm	Pore volume, cm ³ /g	Si/Al	Cumene conversioin, %
MCM-41	1135	2.4	4.64	0.87	50	11
2	1160	2.4	4.98	0.86	42	74
4	1114	2.2	4.75	0.73		17
5	804	7.2	11.7	0.93		
6	1051	2.5	4.98	0.86	43	37
7	650	4.5	5.92	0.71		
10	121	22.1		0.70		< 5

Table 2.2 Physical properties of different mesostructured aluminosilicatematerials.

* Hexagonal unit cell size was calculated from the d-100 spacing of XRD patterns. $a_0 = 2d/\sqrt{3}$.



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Figure 2.1 Reactor set-up for catalytic cumene cracking



Figure 2.2 X-ray diffraction patterns for (A), MCM-41 (Si/Al = 40) prepared from conventional precursors, and mesostructured aluminosilicates MSU-Z (Si/Al = 40) prepared from surfactant-mediated hydrolysis products of (B) ZSM-5 (trial 2) and (C) USY (trial 6) as precursors. Each curve is offset by 10,000 cps for clarity.



Figure 2.3 27 Al MAS NMR spectra of as-synthesized (solid line) and calcined (broken line) MSU-Z (Si/Al = 40) prepared from hydrolyzed ZSM-5 as precursor (trial 2).



Figure 2.4 FT-IR spectra for (A), conventional MCM-41 (Si/AI = 40); (B), MSU-S (Si/AI = 50) prepared from MFI seeds precursor; (C), MSU-Z prepared from zeolite fragment formed by hydrolysis of ZSM-5 (Si/AI = 40) in the presence of CTAB at a OH-/T ratio of 0.75 (trial 2); (D), commercial ZSM-5 (Si/AI = 40).



Figure 2.5 Nitrogen adsorption-desorption isotherms for (A), MCM-41 (Si/AI = 40) synthesized from conventional precursors; (B) MSU-Z (Si/AI = 40) made from zeolite fragments generated from USY in the presence of CTAB with OH⁻/T = 0.17 (trial 6); (C) MSU-Z (Si/AI = 40) assembled from CTAB surfactant-mediated ZSM-5 hydrolysis products (zeolite fragments) formed with OH⁻/T = 0.75 (trial 2); and (D), mesostructured aluminosilicate (Si/AI = 40) formed through over-hydrolysis of ZSM-5 with OH⁻/T = 1.50 (trial 4).



Figure 2.6 BJH pore size distributions obtained from adsorption isotherms for (A), MCM-41 (Si/AI = 40) synthesized from conventional precursors; (B) MSU-Z (Si/AI = 40) made from zeolite fragments generated from USY with OH⁻/T = 0.17 (trial 6); (C) MSU-Z (Si/AI = 40) assembled from surfactant-mediated ZSM-5 hydrolysis products (zeolite fragments) formed with OH⁻/T = 0.75 (trial 2); and (D), mesostructured aluminosilicate (Si/AI = 40) formed through over-hydrolysis of ZSM-5 with OH⁻/T = 1.50 (trial 4).



Figure 2.7 X-ray diffraction patterns of MSU-Z materials (Si/AI = 40) prepared from hydrolysis products of 2 g ZSM-5 in the presence of (A) 2.45 g (trial 2) and (B) 3.45 g (trial 3) of CTAB. The diffraction peaks indexed by arrows are attributed to the ZSM-5 residue.



Figure 2.8 TEM image of MSU-Z (Si/AI = 40) prepared from hydrolyzed ZSM-5 product (trial 2).



Figure 2.9 T-plots for (A), MSU-Z (Si/Al = 40) prepared from the hydrolysis product of ZSM-5 as precursor (trial 2); (B) a physical mixture of 5% ZSM-5 (Si/Al = 40) within conventional MCM-41 (Si/Al = 40).



Figure 2.10 X-ray diffraction pattern of MSU-Z (Si/AI = 40) prepared from incomplete hydrolyzed ZSM-5 precursor (trial 1).



Figure 2.11 N₂ adsorption-desorption isotherms and BJH pore size distributions for (A) wormhole MSU-Z (Si/AI = 40) prepared from the hydrolysis product of USY zeolite in the presence of TTeA (trial 7), and (B) large pore hexagonal MSU-Z (Si/AI = 40) prepared from the hydrolysis product of ZSM-5 in the presence of P123 surfactant (trial 5).



Figure 2.12 X-ray diffraction patterns for the hydrolysis products of ZSM-5 zeolite (Si/Al = 40) in the presence of (A) 2.45 g CTAB (trial 2); (B) 2.0 g TTeA (trial 9) (C) 2.4 g P123 (trial 5).

2.6 References

1 Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. *J. Am. Chem. Soc.* **1992**, *114*(27), 10834.

2 Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature*, **1992**, *359(6397)*, 710.

3 Martin, T.; Galarneau, A.; Di Renzo, F.; Brunel, D.; Fajula, F.; Heinisch, S.; Cretier, G.; Rocca, J. Chem. Mater. 2004, 16(9), 1725.

4 Mehraban, Z.; Farzaneh, F. Micro. Meso. Mater. 2006, 88(1-3), 84.

5 Katiyar, A.; Ji, L.; Smirniotis, P. G.; Pinto, N. G. *Micro. Meso. Mater.* **2005**, *80(1-3)*, 311.

6 McKimmy, E.; Dulebohn, J.; Shah, J.; Pinnavaia, T. J. *Chem. Comm.* **2005**, *29*, 3697.

7 Hatton, B. D.; Landskron, K.; Whitnall, W.; Perovic, D. D.; Ozin, G. A. *Adv. Funct. Mater.* **2005**, *15*(*5*), 823.

8 Alabi, C. A.; Davis, M. E. Chem. Mater. 2006, 18(24), 5634.

9 Marschall, R.; Bannat, I.; Caro, J.; Wark, M. *Micro. Meso. Mater.* 2007, 99(1-2), 190.

10 Lai, C-Y.; Trewyn, B. G.; Jeftinija, D. M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V. S.-Y. J. Am. Chem. Soc. **2003**, *125(15)*, 4451.

11 Munoz, B.; Ramila, A.; Perez-Pariente, J.; Diaz, I.; Vallet-Regi, M. Chem. *Mater.* **2003**, *15*(2), 500.

12 Slowing, I.; Trewyn, B. G.; Lin, V. S.-Y. J. Am. Chem. Soc. 2006, 128(46), 14792.

13 Balas, F.; Manzano, M.; Horcajada, P.; Vallet-Regi, M. J. Am. Chem. Soc. **2006**, *128(25)*, 8116.

14 Zhang, B. P.; Janicke, M. T.; Woodruff, W. H.; Bailey, J. A. J. Phys. Chem. B 2005, 109(42), 19547.

15 Goradia, D.; Cooney, J.; Hodnett, B. K.; Magner, E. J. Mol. Catal. B: Enzymatic 2005, 32(5-6), 231.

16 De Stefanis, A.; Kaciulis, S.; Pandolfi, L. *Micro. Meso. Mater.* **2007**, *99(1-2)*, 140.

17 Aguado, J.; Serrano, D. P.; San Miguel, G.; Escola, J. M.; Rodriguez, J. M.

J. Analy. Appl. Pyrolysis 2007, 78(1), 153.

18 Xu, B.; Hua, W.; Yue, Y.; Tang, Y.; Gao, Z. Catal. Lett. 2005, 100(1-2), 95.

19 Liu, Y.; Kim, S. S.; Pinnavaia, T. J. J. Catal. 2004, 225(2), 381.

20 Kim, S.-S.; Liu, Y.; Pinnavaia, T. J. Micro. Meso. Mater. 2001, 44-45, 489.

21 Masakatsu Nomura, editor, Parviz M. Rahimi, editor, Omer Refa Koseoglu, *Heavy hydrocarbon resources : characterization, upgrading, and utilization,* Washington, DC : American Chemical Society : Distributed by Oxford University Press, 2005.

22 Flanigen, E. M. Stud. Surf. Sci. Catal. 1991, 58, 13.

23 Corma, A. Chem. Rev. 1997, 97(6), 2373.

24 Meier, W. M.; Olsen, D. H. Atlas of Zeolite Structure Types, 1987, Butterworths.

25 Stocker, M. Micro. Meso. Mater. 2005, 82, 257.

26 Davis, M. E. Nature 2002, 417(6891), 813.

27 Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science*, **1998**, *279*(*5350*), *5*48.

28 Schmidt-Winkel, .; Lukens, W. W. Jr.; Zhao, D.; Yang, P.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1999**, *121(1)*, 254.

29 Liu, Y.; Zhang, W.; Pinnavaia, T. J. J. Am. Chem. Soc. 2000, 122(36), 8791.

30 Liu, Y.; Zhang, W.; Pinnavaia, T. J. Angew. Chem. Int. Ed. 2001, 40(7), 1255.

31 Liu, Y.; Pinnavaia, T. J. Chem. Mater. 2002, 14(1), 3.

32 Liu, Y.; Pinnavaia, T. J. J. Mater. Chem. 2004, 14(7), 1099.

33 Zhang, Z.; Han, Y.; Xiao, F.; Qiu, S.; Zhu, L.; Wang, R.; Yu, Y.; Zhang, Z.; Zou, B.; Wang, Y.; Sun, H.; Zhao, D.; Wei, Y. *J. Am. Chem. Soc.* **2001**, *123(21)*, 5014.

34 Zhang, Z. T.; Han, Y.; Zhu, L.; Wang, R. W.; Yu, Y.; Qiu, S. L.; Zhao, D. Y.; Xiao, F. S. *Angew. Chem. Int. Ed.* **2001**, *40*, 1258.

35 Mokaya, R. Chem. Comm. 2001, 633.

36 On, D. T.; Kaliaguine, S. Angew. Chem. Int. Ed. 2001, 40, 3248.

37 On, D. T.; Kaliaguine, S. Angew. Chem. Int. Ed. 2002, 41(6), 1036.

38 On, D. T.; Kaliaguine, S. J. Am. Chem. Soc. 2003, 125(3), 618.

39 Groen, J. C.; Peffer, L. A. A.; Moulijn, J. A.; Perez-Ramirez, J. Chem. Eur. J. 2005, 11(17), 4983.

40 Inagaki, S., Ogura, M., Inami, T., Sasaki, Y., Kikuchi, E., Matsukata, M. *Micro. Meso. Mater.* **2004**, *74*, 163.

41 Kirschhock, C. E. A.; Ravishankar, R.; Verspeurt, F.; Grob, P. J.; Jacobs, P. A.; Martens, J. A. *J. Phys. Chem. B* **1999**, *103*, 4965.

42 Karlsson, A.; Stocker, M.; Schmidt, R. Micro. Meso. Mater. 1999, 27, 181.

43 Goto, Y.; Fukushima, Y.; Ratu, P.; Imada, Y.; Kubota, Y.; Sugi, Y.; Ogura, M.; Matsukara, M. *J. Porous. Mater.* **2002**, *9*, 43.

44 Wang, S.; Dou, T.; Li, Y.; Zhang, Y.; Li, X.; Yan, Z. J. Solid State Chem. 2004, 177(12), 4800.

45 Szostak, R. Stud. Surf. Sci. Catal. 1991, 58, 153.

46 Groen, J. C.; Peffer, L. A. A.; Maulijn, J. A.; Perez-Ramirez, J. *Chem. Eur. J.* **2005**, *11*, 4983.

Chapter 3

Organosilane-assisted Synthesis of Zeolite Nano-crystals with High Crystallinity and Yield

3.1 Abstract

Nano-sized zeolites with controllable particle sizes were prepared from a reaction mixture containing an organosilane as a crystal growth modifier. The organosilanes not only mediate the crystal growth process, but also help to stabilize the nano-sized zeolites by reducing Ostwald ripening. Compared to other methods, this new approach allows for the use of conventional reaction conditions, allowing products with higher yield and crystallinity to be achieved. Two different pathways have been developed, which result in products with different properties. In general, the direct synthesis pathway, which combines the organosilane and silica and alumina sources at the start of the synthesis, produces irregular-shaped 30 ~ 150 nm particles in relatively low yields, typically less than 20% with 8% organo-trialkyoxysilane (organo groups include methyl, aminopropyl, octyl, and phenyl) as surface modifier. Alternatively, the post-nucleation pathway, wherein the precursors are nucleated prior to the addition of organosilane modifier, affords more uniform particles, typically 70 to 100 nm in size. Moreover, the organo functionality of the silane also plays a very important role that affects the morphology of the final product. Genally, inert organo group helps to increase the yield and crystallinity of final products. Nano-sized zeolite as small as 30 nm can be synthesized in substantial yields of 20~80% through the direct synthesis

pathway using methyltriethoxysilane as the surface modifier. On the other hand, yields greater than 80% and more uniform crystals can be achieved when the post-nucleation pathway is adopted. Moreover, the particle sizes can be more carefully controlled by regulating the amount of organosilane modifier and the nucleation time prior to silane addition. TEM results show that the new post-nucleation approach produces uniform and discrete nano-crystals. In the compacted powder state, these nano-sized zeolites of ~ 100 nm pack densely to form uniform inter-crystal mesopores of 22 ~ 60 nm, which are not provided by other methods for generating zeolite nanoparticles. Due to the reduction in crystal size, nano-sized zeolites show a much higher external surface area in comparison to conventional zeolites. Compared to 65 m²/g for bulky ZSM-5, m²/g was surface area 200 obtained with 4% external over methyltriethoxyliane in the post-nucleation pathway. In return, the presence of inter-crystal pores enhances the mass transportation. Cumene cracking results show that nano-sized zeolites exhibit more than 10% higher activity compared to conventional ZSM-5, perhaps due to improved access to both internal and external acid sites.

3.2 Introduction

Zeolites are a family of crystalline aluminosilicates that have uniform micropores that range from 0.3 nm to 1.2 nm in diameter. They are widely used in industry as catalysts,¹⁻³ adsorbents,^{4, 5} and ion-exchange reagents.^{6, 7} Normally, zeolites crystallize as micron size particles under hydrothermal conditions from gel compositions. Recently, numerous studies have been conducted to reduce the zeolite particle size from the micron scale to less than 100 nm.⁸⁻¹⁴ Nano-sized zeolite crystals hold promise for applications in sensor technology,¹⁵ electronics,¹⁶⁻¹⁹ and hierarchical structure assembly.²⁰⁻²² For instance, nano-sized ZSM-5 crystals have been coated on to polystyrene microspheres that were modified to carry positive charge to interact with negatively charged zeolite particles. After the removal of PS template, zeolitic hollow spheres or macroporous zeolites were produced depending on the experimental conditions. The presence of large pores (> 50 nm) allowed bulky molecules such as proteins to be processed over these materials.²³ Moreover, a decrease in particle size results in an increase of external surface area and pore volume. The resultant nano-sized zeolites exhibit significantly improved catalytic activity.

Nano-sized zeolites normally are prepared from clear solutions.²⁴ In order to obtain such solutions, inorganic cations such as Na⁺ are substituted by quaternary ammonium ions. The addition of quaternary ammonium facilitates zeolite nucleation while the elimination of inorganic cations slows down the crystal growth. The numerous nucleation sites in the super-saturated solution then evolute into nano-crystals. In practice, the manipulation of kinetic parameters is essential. Zeolite nanoparticles normally are prepared at

relatively low temperature, and low concentration, also the crystallization is quenched after a short reaction period. The resultant zeolites are usually recovered in very low yield and crystallinity through ultra-high centrifugations. For instance, Bein et al. prepared LTA-²⁵ and MFI-type²⁶ zeolite nanocrystals through kinetic control. The low yield caused the majority of the starting materials, including the costly structure-directing agent to be wasted, inducing environmental issues. Recently, the same group reported a multiple-step synthetic strategy that allowed reusing the non-reacted mother liquid.²⁷ The yield can be boosted significantly.

Another strategy for the preparation of nano-sized zeolites is nano-casting. Porous carbon materials were used as templates, which can be removed later by calcinations. In 2003. Pinnavaia and co-workers²⁸ described a method using colloid-imprinted carbons (CIC) as templates for the preparation of ZSM-5 nanoparticles. Uniform zeolite nano-crystals from 8 nm to 90 nm can be synthesized. Later, Mokaya et al.²⁹ used the mesostructured carbon CMK-3 as template to prepare zeolite nano-crystals within the mesopores. In a more general method, Jacobsen^{30, 31} reported the synthesis of nano-sized zeolites in a confined space provided by the aggregation of commercial carbon black nanoparticles. Typically, the nano-casting procedure required the filling of the mesopores with a zeolite synthesis mixture. The majority of solvent was then removed. Zeolite products were then crystallized in a solid state to minimize the immigration of inorganic phases so that a zeolite replica of the template can be prepared. However, due to the irregularity of templates, irregular zeolite nanoparticles were formed in most cases except for CIC templated ZSM-5. Moreover, although the fundamental

crystal sizes of the resulting nano-casted zeolite is very small, the aggregation of the nanocrystals, as well as the packing of the aggregates, is non-uniform and the resulting intercrystal pores are larger on average than the size of the fundamental particles themselves.

Various inorganic nanoparticles with uniform size distributions have been prepared using capping agents.³²⁻³⁷ For instance; gold nanoparticles less than 5 nm in diameter can be synthesized through the reduction of AuCl₃ solution in the presence of thiol molecules as a capping agent.³⁸ Due to the strong Au-S bond, nanoparticles can be prepared and stabilized. In the zeolite synthesis, organosilanes can serve as capping agents due to the stable Si-C bonds under severe conditions required for zeolite synthesis. Organosilanes have been found to modify the morphology of zeolite particles during crystallization.³⁹ Various zeolite structures with high external surface area and pore volume were synthesized. Such products showed much higher catalytic activity compared to conventional zeolite catalysts. Moreover, organosilanes can also bring desirable functionality to the resultant zeolite. Organo-functionalized aluminosilicates have found many applications in catalysis.^{40,41} heavy-metal trapping.⁴² proton-conductive membranes.⁴³ and drug delivery.^{44, 45} In addition, zeolites with organo-functionality also were used as building blocks for low dielectric constant thin films.⁴⁶ Compared to amorphous silica mesostructures, crystalline zeolite thin films exhibited superior mechanical strength. And the organo-functionality makes the thin films hydrophobic so that a low dielectric constant can be achieved even at high humidity.

In present study, we describe the use of organosilanes to prepare nano-sized ZSM-5 zeolites with controllable uniform particle size. This new

approach offers the possibility of synthesizing nano-sized zeolite products using a conventional sol-gel process in the absence of a template. The uniformity of the particles leads to uniform inter-crystal mesopores, which to our best knowledge has not been observed previously. Two different pathways have been investigated, which greatly affect the morphology and quality of the final products. One pathway, termed the direct synthesis pathway, combines the particle growth modifier, a silane of the type (RO)₃Si-L where L is an organo group, with the remaining reagents in a one-pot reaction mixture. In the other pathway, termed the post-nucleation pathway, a zeolite precursor mixture is nucleated prior to the addition of organosilane modifier.

3.3 Experimental section

3.3.1 Materials

Nanosized ZSM-5 zeolites were prepared from tetraethylorthosilicate (TEOS. Aldrich). aluminum tri-sec-butoxide (Aldrich). and tetrapropylammonium hydroxide solution (TPAOH, 1M solution, Aldrich), which serves as a structure-directing agent for MFI zeolite. A series of organosilanes (Si-L) were used as capping agents (or modifier), including 3-aminopropyltrimethoxysilane (APTMS, Aldrich), methyltriethoxysilane (MTES, Gelest). phenyltrimethoxysilane (PTMS. Aldrich). octyltrimethoxysilane (OTMS, Aldrich), and hexadecyltrimethoxysilane (HDTMS, Aldrich). Two different methods were used to introduce the modifiers, namely direct synthesis and post-nucleation pathway.

3.3.2 Synthesis of nano-sized ZSM-5 zeolite

3.3.2.1 Direct synthesis pathway

In the direct synthesis pathway, TEOS, aluminum tri-sec-butoxide, and a desired amount of organosilane were mixed in a polypropylene bottle. Then the TPAOH solution was added to the above solution with vigorous stirring to form a clear reaction mixture with a molar composition of $1 \text{ Al}_2\text{O}_3 : 100 \text{ SiO}_2 : x$ Si-L : 37 TPAOH : 2000 H₂O. In a typical synthesis, 0.10 g of Aluminum isobutoxide (0.42 mmol) was dissolved in a mixture of 4.4 g of TEOS (21.2 mmol) and 0.188 g MTES (1.06 mmol). To the resultant solution, 8.0 g of TPAOH (20 wt%) was added under stirring. After the completion of hydrolysis at room temperature, the reaction mixture was heated to 100 °C for 48 hours to form nanosized ZSM-5 zeolite. The final product was denoted as n-ZSM-5-DP.

The actual molar compositions are listed in Table 3.1.

3.3.2.2 Post-nucleation pathway

In the post-nucleation approach, silica and alumina precursors were mixed first. To the resultant solution, TPAOH was added under stirring. After the hydrolysis was completed, a milky solution was formed. The molar composition of the synthesis mixture was: 1Al₂O₃: 100 SiO₂: 37 TPAOH: 2000 H_2O . The reaction mixture was then digested under 100 °C for 0 to 12 hours to form protozeolitic nanoclusters or "zeolite seeds" in solution. To the above seeds solution, a desired amount of organosilane was added under stirring. After the hydrolysis was complete, the bottle was sealed again and heated to 100 °C for another 48 hours. The final molar composition was: 1Al₂O₃: 100 SiO₂: y Si-L: 37 TPAOH: 2000 H₂O. The product was denoted as n-ZSM-5-NP. The molar composition was listed in Table 3.1. In a typical synthesis, 0.10 g of Aluminum isobutoxide (0.42 mmol) was dissolved in 4.4 g of TEOS (21.2 mmol). To the resultant solution, 8.0 g of TPAOH (20 wt%) was added under stirring. After the completion of hydrolysis at room temperature, the reaction mixture was nucleated at 100 °C for 3 hours to form zeolitic nanoclusters. After the mixture was cooled to room temperature, 0.377 g MTES (2.12 mmol) was added. The resulting mixture was stirred at room temperature for 1 hour, and then heated to100 °C for another 48 hours

All the nano-sized ZSM-5 products were recovered by repeated centrifugation at 8,000 rpm followed by re-dispersion and washing with distilled water until the pH of the colloidal suspension reached 8~9. Air-dried samples were calcined at 600 °C for 4 hours to remove the organic modifier and

structure-directing agent.

3.3.3 Physical property characterizations

X-ray diffraction patterns were recorded on a Rigaku Rotaflex Diffractometer using CuK_a radiation (λ = 1.542 Å). Scan consitions are reflective mode from 5° to 50° 20 continuous at 2°/min and 0.05°/step.

 N_2 adsorption and desorption isotherms at -196 °C were determined on a Micromeritics ASAP 2000 sorptometer. The samples were degassed under 10^{-3} Torr at 250 °C for a minimum of 6 hours. The surface area was calculated from the BET equation. Pore size distributions were derived from the adsorption isotherms using the BJH model. The external surface area and micropore volume were derived from t-plot. The total pore volume (mesopore + micropore volume) was determined at P/Po of 0.95.

TEM images were taken on a Jeol 2200FS instrument operated at 200 kV. Samples were prepared by sonicating the colloidal products in EtOH for 20 min, and then evaporating 2 drops onto the carbon coated holey film supported on a 300 mesh Cu grid. SEM images were recorded on a JSM 6400 Electron Microscope at an acceleration voltage of 20 kV. The samples were sputter-coated with 7 nm of gold or carbon prior to imaging.

3.3.4 Catalytic cumene cracking

Catalytic cumene cracking reactions were performed in a 6 mm i.d. fixed bed quartz reactor with 200 mg catalyst at 250°C. Prior to catalytic testing, the catalysts were ion-exchanged twice with 0.5 M NH₄NO₃ solution followed by calcination at 550°C for 4 hours. The cumene flow rate was 4.1 µmol/min in a

20 cm³/min carrier stream of N_2 . Cumene conversions were plotted against time on stream after a 6-hour activation period at 250 °C in a pure N_2 atmosphere.

3.4 Results and Discussions

3.4.1 Direct synthesis pathway

In comparison to TEOS, a (RO)₃Si-L molecule has 3 hydrolysable Si-O bonds and one Si-C bond, which is stable under hydrolysis conditions. The inertness of the Si-C linkage toward hydrolysis has been demonstrated through the synthesis of organic zeolites and organo-functionalized zeolites. During zeolite syntheses, once an organosilane is anchored to the surface of the crystal, crystal growth at that specific site is hindered. Under ideal circumstances, the crystal becomes covered by the organic group and stops growing, as illustrated in Figure 3.1. The organosilane also stabilizes the nano-crystals by reducing Ostwald Ripening. Moreover, particle inter-growth is alleviated. Therefore, nano-sized zeolite particles could possibly be synthesized under more severe conditions, such as elevated temperature and higher concentration.



Figure 3.1 Illustration for the quenching of zeolite crystal growth using an organosilane as a capping agent.

Figure 3.2 provides SEM images of n-ZSM-5-DP samples synthesized in the presence of methyltriethoxysilane (MTES) as the modifier through the direct synthesis pathway. Conventional ZSM-5, prepared in the absence of MTES, adopts a rectangular crystal form with smooth surfaces and sharp edge (Figure 3.2A), which is typical for ZSM-5 zeolite. The average size of zeolite crystals is about 1 μ m. When 5 mol% MTES was added to the reaction mixture as a surface modifier, a dramatic drop in fundamental crystal size down to 150 ~ 200 nm is observed (Figure 3.2B). Some extra features, such as the dark lines across individual particle surface were observed, may indicate the presence of multiple domains within each crystal. A ZSM-5 zeolite with average particle size of 30 ~ 40 nm (Figure 3.2C) was obtained when 8 mol% MTES was added to the reaction mixture. It is evident that increasing the amount of organosilane decreases the fundamental particle size. However, there is a limit to how much organosilane can be added. When 10 mol% MTES was added, a clear solution was obtained after 2 days of reaction at 100 °C. The solid residue of the solution showed no crystalline phase.

Figure 3.3 provides the high-resolution TEM images of ZSM-5 nanocrystals formed by direct synthesis in the presence of MTES. The fundamental crystal domain sizes obtained with 5% and 8% MTES are 150 and 30 nm on average, respectively, which are consistent with the SEM observations. Lattice fringes are observed for both samples, indicative of the presence of a crystalline phase. The fringes for the n-ZSM-5-DP nanoparticle prepared with 5% MTES are aligned across the entire particle aggregate, suggesting that the aggregate is a single crystal made up of intergrown domain. Moreover, within this 150 nm crystal aggregate there are a few voids, which are revealed by the bright contrast in the TEM image. Such voids might also contribute to the dark features observed through SEM (Figure 3.2B). Due to the presence of intra-crystal voids, the actual domain size of this ZSM-5-NP sample would be well below 100 nm.

N₂ adsorption – desorption isotherm was used to measure the physical properties of the resultant nano-sized ZSM-5 products prepared by direct synthesis. The results are provided in Figure 3.4. A ZSM-5 zeolite sample synthesized through the conventional method was also included for comparison. All the ZSM-5 samples showed a steep nitrogen uptake at P/Po < 0.02, which is characteristic of a microporous zeolite. For the conventional ZSM-5, the adsorption curve levels out at high relative pressure. This typical type II isotherm behavior indicated the absence of mesoporosity and a lack of an appreciable external surface area for the sample. In comparison, the ZSM-5 products synthesized in the presence of MTES modifier showed distinguishable hysteresis loops above P/Po 0.8, indicative of the presence of mesopores. Interestingly, the position of hysteresis loop moved to higher P/Po when more MTES was added to the reaction mixture, indicative of larger average pore diameter (Figure 3.4, curve C). These hysteresis loops can be assigned to the textural pores arising from the aggregation of nano-sized crystals. Sample B shows an average inter-crystal pore size of 30 nm. Although smaller inter-particle pore size is expected from a smaller particle size. However, sample C exhibits an average pore size of 55 nm, which is larger than the fundamental particle size itself (Figure 3.4, inset). The larger pore size is probably due to the loose packing of irregular nanoparticles.

Figure 3.5 provides the XRD patterns of ZSM-5 samples prepared by the direct synthesis pathway under different conditions. All the ZSM-5-NP samples showed diffraction peaks characteristic of an MFI framework (Curve A), thereby confirming the presence of zeolitic phases. Moreover, it is also evident that the crystallinity of the resultant ZSM-5 samples is compromised as more

MTES is added to the synthesis gel, whereas the external surface area and mesopore volume increased substantially (Table 3.2). The decrease of diffraction intensity was proportional to the amount of MTES added.

Without the aid of templates, zeolite nanoparticles are usually prepared by a kinetic control approach. Low yields of product are inevitable under these reaction conditions that include low temperatures and concentrations. In the direct synthesis method reported here, the quenching of crystal growth was achieved by the surface silylation of the developing nano-particles, which also minimized Ostwald ripening. Therefore, normal reaction conditions can be utilized, which provide for higher yields of zeolites while retaining a nano-crystal morphology. For instance, with the addition of 8 mol% MTES, ZSM-5 with a 30 nm average particle size can be prepared at a yield of 18%.

In addition to MTES, other types of organosilanes can also be used as the surface modifier, which also offers the opportunity to incorporating desirable organic functionality into the zeolite nanoparticles. Figure 3.6 provides the isotherm of ZSM-5 prepared with 6 mol% APTMS as a surface modifier. A hysteresis loop at partial pressure of 0.9 was observed, suggesting the formation of nanoparticles. It is noted that at a silane level of 8 mol%, MTES still generated crystalline product with a reasonable yield, while APTMS failed to produce any crystals. Optical images of reaction products are provided in Figure 3.7. Colloidal ZSM-5 nanoparticles were obtained when 6 mol% APTMS was added to the reaction mixture. The colloidal suspension was stable even after several weeks, which suggests that the aggregation of nanoparticles was hindered. At higher APTMS contents, only clear solutions were obtained. The TEM image of the product obtained at 8 mol% APTMS

showed the presence of nanoparticles about 10 nm in diameter (Figure 3.8), but no indication of crystallinity. The reason could be attributed to the strong interaction between amino-group and silicon, which interrupted the crystallization of zeolites. Interestingly, hydrophobic organo-groups such as phenyl and octyl tend to boost the yield of nano-sized zeolites to up to 80%. It is probably because hydrophobic particles aggregate in the aqueous environment to form larger particles, therefore easier to collect by centrifugation.

Figure 3.9 illustrates the possible mechanism for the direct synthesis pathway. Because MTES molecules are present at the beginning, the protozeolitic nanoclusters initially formed have a surface partially covered by the organo group. If enough organosilane molecules are available during crystallization, zeolite nanocrystals completely covered by organo group will be formed as shown in Figure 3.9 (Path A). Otherwise, these partially covered nanoclusters will merge together to form a larger particle (Path B). Under this circumstance, the presence of organo group prevents the formation of a homogeneous phase. During nanoparticle coalescence, the hydrophobic organo groups tend to cluster on the surface to lower the surface energy. A crystal aggregate with voids will be generated (Path B).

It should be pointed out that the direct synthesis pathway usually produces nano-sized ZSM-5 products with relatively low yields compared to the conventional zeolite synthesis. A significant amount of raw materials including costly structure-directing agent TPAOH was wasted. This not only creates environmental issues, but also makes it difficult to predict the compositions of the final products. The reason most likely is related to the

interference of zeolite nucleation by the organosilane. Therefore, a more desired pathway was developed to boost the yield of nano-sized ZSM-5, denoted the post-nucleation pathway, as discussed below.

3.4.2 Post-nucleation pathway

In this new pathway, a composition for the conventional ZSM-5 synthesis was nucleated at the elevated temperature before the addition of a desired amount of organosilane to control crystal growth. At this point, no zeolite phase is present as confirmed by the X-ray diffraction pattern of the evaporated reaction mixture. Because the organosilane molecules are absent during the nucleation stage, zeolitic nanoclusters are produced without interference. Such protozeolitic seeds have been used as precurors to assemble mesostructured aluminosilicates with strong acidity and high hydrothermal stability.⁴⁷⁻⁵¹ The presence of zeolitic subunits has been confirmed by the IR absorbance band at 550 cm⁻¹, which is characteristic of five-member Si-O ring building blocks present in MFI and BEA zeolites. After the addition of an organosilane modifier, the preformed seeds facilitated the zeolite crystallization. Therefore, nanocrystals with higher crystallinity and yield can be produced, as judged by the Bragg peak intensity in the XRD patterns (Figure 3.10) and by the micropore volumes measured by N₂ isotherms.

In the post-nucleation pathway, a new parameter other than the percentage of organosilane is introduced, which is the nucleation time for the formation of zeolitic nanoclusters. Figure 3.11 provides the N_2 isotherm plots of n-ZSM-5-NP samples synthesized by the addition of 10 mol% MTES after different nucleation durations. In the direct synthesis pathway, the addition of

10 mol% MTES at the start of reaction doesn't give any solid product. However, after a nucleation for 24 hours at room temperature, a ZSM-5 product is obtained with slightly reduced crystallinity as suggested by the weak uptake of nitrogen in the nitrogen adsorption isotherm (Figure 3.11, curve F). When the nucleation is conducted at elevated temperature (100°C), high quality ZSM-5 products can be synthesized in more than 40% yield from 10 mol% MTES even after short nucleation step at this temperature (1h, Figure 3.11, curve E). Compared to ZSM-5 synthesized under conventional condition, all these samples show a hysteresis loop at P/Po > 0.8, indicative of high inter-particle porosity and small particle size.

Figure 3.12 illustrates the effect of organosilane content on the morphology of the final products. The evolution of the isotherms is very similar to the samples made by direct synthesis. However, a 3-hour nucleation step before the addition of the silane surface modifier greatly improves the crystallinity and yield of the final products, as judged by XRD peak intensity and micropore volume derived from N₂ adsorption-desorption isotherms. Whereas for direct synthesis pathway, a 10 mol% MTES gives no solid product, a 3-hour nucleation step produces a nano-sized ZSM-5 zeolite with high crystallinity. Such high crystallinity is compromised as more organosilane was added (Figure 3.12, curve E). In this case, smaller particles are produced, which might account for the decrease in crystallinity. Figure 3.13 provides the BJH pore size distributions of representative samples. We can see that at a fixed MTES content (10 mol%), extending the nucleation time from 3 hours to 12 hours increases the pore size from 22 nm to 50 nm. When the same nucleated precursor is used, reducing MTES amount to 4 mol% increases the

pore size to 35 nm. The variation in the inter-particle pore size reflects the change of the primary particle size.

Direct evidence for the formation of nanoparticles is obtained by TEM observation (Figure 3.14). The average fundamental particle size of n-ZSM-5-NP prepared by the addition of 4 mol% MTES after a 3-hour nucleation is under 100 nm (Figure 3.14A). Moreover, the particle size is very uniform. The high-resolution image shows zeolite fringes covering the whole particle, indicative of a single crystal with high crystallinity. Particles with average size of 60 ~ 70 nm are obtained when 15 mol% MTES was used (Figure 3.14B). It should be pointed out that the post-nucleation pathway not only produced high-crystallinity zeolites, it also greatly boosted the yields of products under the same condition. For example, a synthesis composition nucleated for 3 hours at 100 $^{\circ}$ C gives ZSM-5 nano-crystal with over 80% yield when less than 15 mol% MTES was added after the nucleation step.

The use of organosilane modifier during zeolite crystallization produced nano-sized zeolites. Based on TEM observations, the final products adopted a spherical morphology. These discrete spheres have an exceptionally uniform particle size distribution. During aggregation, uniform inter-crystal mesopored are formed, which have not been observed from nano-sized zeolite samples prepared from other methods. Moreover, an average mesopore size as small as 22 nm can be generated. The results further confirm the presence of uniform nano-crystalline zeolite particles that are packed orderly. When spheres with diameter of D are closest-packed as shown in Figure 3.15, two types of inter-particle voids emerged, namely tetrahedral and octahedral pores. The diameter (D_p) of resultant inter-particle voids is a function of D as shown in
the following relationship,



Figure 3.15 Nanoparticle packing schemes. Both tetrahedral and octahedral interparticle voids (pores) are expected for extensively compacted spheres.

 $D_p = 0.225D$ (for tetrahedral pores) or 0.414D (for octahedral pores)

Statistically, the ratio of tetrahedral to octahedral pores is 2 : 1 for extensively compacted spheres. However, the isotherm data showed that the mesopore size distribution is uniformly centered around an average value. For instance, mesopores with an average pore size of 35 nm was detected on ZSM-5 prepared with 4 mol% MTES after a 3-hour nucleation step. TEM image showed that this sample has an average particle size of 100 nm, which theoretically will result in uniform tetrahedral and octahedral inter-crystal mesopores of 22 and 42 nm, respectively. The observed pore size distribution results showed that the mathematical model gives a fair prediction. The results suggested that the zeolite spheres were packed relatively compacted. It is noteworthy that nano-sized ZSM-5 zeolite prepared by the direct synthesis

pathway exhibited much larger mesopores, which are larger than the diameter of fundamental particles sometimes. For example, 55 nm mesopores were observed for n-ZSM-5-DP prepared from 8 mol% MTES in a direct synthesis reaction.

Figure 3.16 illustrates the possible mechanism for the post-nucleation pathway. Because organosilane molecules are eliminated from the nucleation step, the resultant zeolitic nanoclusters are able to aggregate more densely to form larger particles, which subsequently are covered by organo groups upon the addition of the silane. A longer nucleation step produces larger nanoclusters, resulting in larger zeolite particles. Meanwhile, because the nucleation process is not interrupted by the organosilane, products with higher crystallinity and yield are observed. Two factors determine the final products. First, the conditions for nucleation step determine the number and size of zeolitic nanoclusters or seeds. On the other hand, after nucleation step, the number and size of larger zeolite particles formed are dependent on the amount of organosilane modifier added. Therefore, the zeolite particle size is controlled by a combination of both the nucleation step and the amount of silane modifier added after nucleation.

Table 3.2 summarized the physical properties of ZSM-5 samples prepared by both the direct synthesis and post-nucleation pathway under various conditions. Compared to the conventional ZSM-5, which has large particle size of 1 μ m and external surface of 50 m²/g, nano-sized ZSM-5 materials prepared from both direct synthesis and post-nucleation pathways exhibited a much higher external surface area. For instance, an external surface area of 211 m²/g was observed for the 100 nm ZSM-5 product

prepared with 4 mol% MTES after a 3-hour nucleation step. Based on micropore volumes, only little crystallinity was lost while a 4-fold increase on external surface area was achieved. Moreover, all the nano-sized ZSM-5 samples showed enhanced mesoporosity up to 0.56 cm³/g with uniform pore size distribution. Such a high mesopore volume should greatly improve the mass transportation rate by facilitating the diffusion of molecules inside the sample. In addition, the large external surface area will significantly increase the number of active sites that are easily accessible to reactant molecules, especially relatively large molecules such as cumene.

Figure 3.17 provides the cumene conversions over a nano-sized ZSM-5 catalyst prepared with 5 mol% MTES in a direct synthesis pathway. A conventional ZSM-5 catalyst was included for comparison. Both catalysts showed relatively low cumene conversions initially, which increased with the time-on-stream. This is probably due to the slow diffusion rate of cumene molecules in the small-pore MFI zeolites. Because of the presence of large external surface area and high mesoporosity, the n-ZSM-5-DP catalyst exhibited a somewhat higher cracking activity despite a slightly lower crystallinity.

3.5 Conclusion and perspective

Two different pathways have been developed using organosilanes as a surface modifier (capping agent) for the synthesis of zeolite nanocrystals. The direct synthesis pathway, wherein the silane is added as a reagent at the initial stages of synthesis, affords smaller crystals compared to the post-nucleation pathway, wherein the silane is added after zeolite nucleation has been initiated. For instance, an average particle size as small as 30 nm can be achieved with 8% MTES as surface modifier in the direct synthesis pathway. However, due to the irregularity and loose packing of nano-particles, the resultant inter-crystal mesopores are quite large (even exceeding the size of fundamental particles). Moreover, the presence of organosilane considerably affects the zeolite nucleation process; therefore the direct synthesis pathway generally affords nano-crystals at a yield less than 80%. On the other hand, the organosilane-free nucleation step in the post-nucleation pathway significantly improves the yield and crystallinity of the zeolite while the particle size of the final product is retained at the nanometer scale. More importantly, the zeolitic nanocluster precursors formed in the pre-nucleation step results in products with a uniform particle size distribution (70 ~ 100 nm). Because the external surface is covered by organo groups, the intergrowth between particles is greatly reduced, which in turn results in discreet zeolite nanocrystals. These well separated and uniform nano-particles can be used to assemble uniform inter-crystal mesopores. In addition, the post-nucleation pathway allows the use of silanes containing reactive organic groups, such as amino groups, without sacrificing the crystallinity and the yield of zeolite nanocrystals. Therefore, the post-nucleation pathway provides the opportunity to introduce

additional desirable functionalities to the final products. In any case, both pathways produce zeolite nano-crystals with much improved inter-particle mesoporosity and external surface area, which in turn boosts the catalytic activity by reducing the diffusion path length.

Compared to Serrano's method, which produces aggregates of nanocrystalline zeolites, our post-nucleation approach produces ~ 100 nm ZSM-5 crystals with uniform and controllable particle size. Moreover, the resultant zeolite nanoparticles are well separated. Therefore, uniform inter-crystal mesopores in the range 22 to 55 nm can be assembled through close-packing of nanocrystals. It is clear that the nucleation conditions are very critical in determining the textural properties of the final product. The uniformity of nanocrystals is the result of uniform nucleation of protozeolitic nano-clusters formed in the nucleation step. Therefore, future work should be focusing on the optimizing of nucleation process. In the ZSM-5 synthesis, homogeneous nucleation can be realized by substituting mineral ions such as Na⁺ with quarternary ammonium ion TPA⁺, which is the structure-directing agent for MFI structure. By increasing the TPA/Si ratio in the nucleation step, a precursor containing smaller and more uniform zeolitic nanocrystals.

Sample No. Nucleation, h Organosilane Si-L, mol% Yield, % ZSM-5 N/A 0 >90 N/A 1 N/A 2 MTES >80 2 N/A MTES 5 80 3 N/A 8 MTES 18 4 N/A APTMS 2 >80 5 N/A **APTMS** 4 >60 6 N/A APTMS 6 25 7 N/A OTMS 6 83 8 N/A PTMS 6 72 9 N/A HDTMS 6 >80 10 RT, 24 hours MTES 10 <20 11 100°C, 1 h 40 MTES 10 12 100°C, 3 h MTES 10 >80 13 100°C, 6 h MTES 10 >80 14 100°C, 12 h MTES 10 >80 15 100°C, 3 h MTES 4 >80 100°C, 3 h 7 16 MTES >80 17 100°C, 3 h MTES 15 35 18 100°C, 3 h APTMS 10 >50 19 100°C, 6 h APTMS 10 >50 20 100°C, 12 h APTMS >50 10 21 100°C, 3 h **APTMS** 4 >50 22 100°C, 3 h APTMS 7 >50

Table 3.1 Yields of ZSM-5 (Si/AI = 50) obtained in the presence of various organosilane surface modifiers.

Samples 1-9 were prepared by the direct synthesis pathway wherein the silane modifier was added at the start of the reaction. Samples 10-22 were prepared by the post-nucleation pathway wherein the silane modifier was added to the reaction mixture after a nucleation step.

Sample No.	BET surface area, m²/g	Mesopore volume, cm³/g	External surface area, m²/g	Micropore volume, cm³/g
ZSM-5	389	0.04	65	0.14
1	423	0.29	138	0.13
2	389	0.35	215	0.08
3	249	0.65	162	0.04
4	540	0.26	143	0.18
5	477	0.27	123	0.16
6	549	0.30	128	0.19
7	506	0.27	177	0.15
8	497	0.45	171	0.15
9	504	0.48	177	0.15
10	179	0.55	104	0.03
11	407	0.47	144	0.12
12	414	0.55	169	0.11
13	443	0.52	155	0.13
14	433	0.49	162	0.12
15	458	0.51	212	0.11
16	466	0.46	144	0.15
17	221	0.55	146	0.04
18	156	0.40	75	0.04
19	414	0.53	180	0.11
20	451	0.56	167	0.13
21	481	0.50	152	0.15
22	456	0.52	140	0.14

Table 3.2 Physical	properties	of ZSM-5 sa	mples	(Si/Al = 50)).
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Samples 1-9 were prepared by the direct synthesis pathway wherein the silane modifier was added at the start of the reaction. Samples 10-22 were prepared by the post-nucleation pathway wherein the silane modifier was added to the reaction mixture after a nucleation step.



Figure 3.2 SEM images for ZSM-5 samples (Si/AI = 50) prepared through the direct synthesis pathway in the absence and presence of methyltriethoxysilane (MTES): (A), 0% MTES; (B), 5% MTES and (C), 8% MTES at 100° C for 48 hours.



Figure 3.3 TEM images for ZSM-5 samples (Si/AI = 50) prepared through the direct synthesis pathway in the presence of (A), 5% MTES; (B), 8% MTES at 100° C for 48 hours.



Figure 3.4 Nitrogen adsorption-desorption isotherms of ZSM-5 samples (Si/Al = 50) prepared through the direct synthesis pathway in the presence of A, 0% MTES; B, 5% MTES and C, 8% MTES at 100°C for 48 hours. Curves B and C are offset by 50 and 150 volume units for clarity. Inset: BJH adsorption pore size distributions.



Figure 3.5 X-ray diffraction patterns for calcined ZSM-5 (Si/AI = 50) samples prepared by (A) a conventional method in absence of MTES, and by direct synthesis in the presence of (B) 2 mol% MTES, (C) 5 mol% MTES, and (D) 8 mol% MTES at 100 °C for 48 hours. Curves are offset by 4,000 counts each for clarity. Each sample was calcined at 600 °C for 4 hours.



Figure 3.6 N₂ adsorption-desorption isotherms for (A) conventional ZSM-5 (Si/AI = 50) in absence of organosilane and (B) n-ZSM-5-DP (Si/AI = 50) prepared by the direct synthesis pathway in the presence of 6 mol% 3-aminopropyltrimethoxysilane (APTMS) at 100 °C for 48 hours. Curve B is offset by 150 volume units for clarity.



Figure 3.7 Optical images for the reaction products formed by direct synthesis in the presence of (A) 6 mol% APTMS, (B) 8 mol% APTMS, and (C) 10 mol% APTMS after reaction at 100 °C for 48 hours.



Figure 3.8 TEM image for the amorphous product prepared by direct synthesis

in the presence of 8 mol% APTMS at 100 °C for 48 hours.



Figure 3.9 Illustration for the formation of nano-crystals by a direct synthesis pathway in the presence of $(RO)_3Si-L$ surface modifier. The formation of single nanocrystals (path A) or aggregates of intergrown nanoparticles (path B) depends on the amount of $(RO)_3Si-L$ present in the reaction mixture.



Figure 3.10 X-ray powder diffraction patterns for calcined ZSM-5 samples (Si/AI = 50) synthesized by the post-nucleation pathway and the addition of (A), 4% MTES after 3 hours nucleation step; (B), 7% MTES after 3 hours nucleation step; (C), 10% MTES after 12 hours nucleation step at 100 °C. Each curve is offset by 4000 units for clarity.



Figure 3.11 N₂ adsorption/desorption isotherms for calcined ZSM-5 samples (Si/AI = 50) synthesized by (A), conventional method and by the post-nucleation pathway and the addition of 10% MTES after (B) 12 hours nucleation step; (C), 6 hours nucleation step; (D), 3 hours nucleation step; (E), 1 hours nucleation step at 100 °C; (F), 24 hours nucleation step at room temperature. Each isotherm is offset by 200 volume units for clarity.



Figure 3.12 N₂ adsorption/desorption isotherms for calcined ZSM-5 samples (Si/Al = 50) synthesized by (A), conventional method; and by the post-nucleation pathway and by the addition of (B), 4% MTES; (C), 7% MTES; (D), 10% MTES; (E), 15% MTES after a 3-hour nucleation step at 100 °C. Each isotherm is offset by 200 volume units for clarity.



Figure 3.13 BJH (adsorption) pore size distribution of n-ZSM-5-NP samples (Si/AI = 50) synthesized by the post-nucleation pathway and the addition of (A), 10% MTES after 3 hours nucleation step; (B), 4% MTES after 3 hours nucleation step; (C), 10% MTES after 12 hours nucleation step at 100 °C.



Figure 3.14 TEM images of n-ZSM-5-NP (Si/AI = 50) synthesized by the post-nucleation pathway by the addition of (A), 4% MTES after 3 hours nucleation step; (B), 15% MTES after 3 hours nucleation step. Insets are the corresponding high-resolution images.







Figure 3.17 Catalytic cumene cracking conversion vs. time for (A), a commercial ZSM-5 from Zeolyst (Si/AI = 40); (B), n-ZSM-5-DP (Si/AI = 50) prepared from 5 mol% MTES by a direct synthesis pathway.

3.6 References

- 1 Flanigen, E. M. Stud. Surf. Sci. Catal. 1991, 58, 13.
- 2 Corma, A. Chem. Rev. 1997, 97(6), 2373.
- 3 Stoecker, M. Micro. Meso. Mater. 2005, 82(3), 257.

4 Choi, J. H.; Kim, S. D.; Noh, S. H.; Oh, S. J.; Kim, W. J. *Micro. Meso. Mater.* **2006**, *87(3)*, 163.

5 Erdem, E.; Karapinar, N.; Donat, R. J. Coll. Inter. Sci. 2004, 280(2), 309.

6 Jorgensen, T. C.; Weatherley, L. R. Water Research 2003, 37(8), 1723.

7 Caputo, D.; De Gennaro, B.; Pansini, M.; Colella, C. Stud. Surf. Sci. Catal. 1999, 125, 723.

8 Holmberg, B. A.; Wang, H.; Norbeck, J. M.; Yan, Y. *Micro. Meso. Mater.* **2003**, *59*, 13.

9 Valtchev, V. P.; Bozhilov, K. N. J. Phys. Chem. B 2004, 108, 15587.

10 Zhan, B.; White, M. A.; Lumsden, M.; Mueller-Neuhaus, J.; Robertson, K. N.; Cameron, S. T.; Gharghouri, M. *Chem. Mater.* **2002**, *14*, 3636.

11 Li, Q.; Creaser, D.; Sterte, J. Chem. Mater. 2002, 14, 1319.

12 Majano, G.; Mintova, S.; Ovsitser, O.; Mihailova, B.; Bein, T. *Micro. Meso. Mater.* **2005**, *80*, 227.

13 Aguado, J.; Serrano, D. P.; Escola, J. M.; Rodriguez, J. M. Micro. Meso. Mater. 2004, 75, 41.

14 Song, W.; Justice, R. E.; Jones, C. A.; Grassian, V. H.; Larsen, S. C. Langmuir 2004, 20, 8301.

15 Wang, Z.; Larsson, M. L.; Grahn, M.; Holmgren, A.; Hedlund, J. *Chem. Commun.* **2004**, 2888.

16 Wang, Z.; Wang, H.; Mitra, A.; Huang, L.; Yan, Y. Adv. Mater. 2001, 13, 746.

17 Wang, Z.; Mitra, A.; Wang, H.; Huang, L.; Yan, Y. Adv. Mater. 2001, 13, 1463.

18 Li, S.; Li, Z.; Yan, Y. Adv. Mater. 2003, 15, 1528.

19 Li, Z.; Li, S.; Luo, H.; Yan, Y. Adv. Funct. Mater. 2004, 14, 1019.

20 Wang, X. D.; Yang, W. L.; Tang, Y.; Wang, Y. J.; Fu, S. K.; Gao, Z. *Chem. Commun.* **2000**, 2161.

21 Holland, B. T.; Abrams, L.; Stein, A. J. Am. Chem. Soc. 1999, 121, 4308.

22 Valtchev, V.; Mintova, S. Micro. Meso. Mater. 2001, 43, 41.

23 Wang, Y.; Caruso, F. AdV. Funct. Mater. 2004, 14, 1012.

24 Tosheva, L.; Valtchev, V. P. Chem. Mater. 2005, 17, 2494-2513

25 Mintova, S.; Mo, S.; Bein, T. Chem. Mater. 2001, 13, 901.

26 Mintova, S.; Schoeman, B. J.; Valtchev, V.; Sterte, J.; Mo, S.; Bein, T. Adv. Mater. **1997**, *9*, 585.

27 Larlus, O.; Mintova, S.; Bein, T. Micro. Meso. Mater. 2006, 96(1-3), 405.

28 Kim, S-S.; Shah, J.; Pinnavaia, T. J. Chem. Mater. 2003, 15(8), 1664.

29 Yang, Z.; Xia, Y.; Mokaya, R. Adv. Mater. 2004, 16(8), 727.

30 Schmidt, I.; Madsen, C.; Jacobsen, C. J. H. Inorg. Chem. 2000, 39, 2279.

31 Madsen, C.; Jacobsen, C. J. H. Chem. Commun. 1999, 673.

32 Jagannathan, R.; Poddar, P.; Prabhune, A. J. Phys. Chem. C 2007, 111(19), 6933.

33 Mott, D.; Galkowski, J.; Wang, L.; Luo, J.; Zhong, C. Langmuir 2007, 23(10), 5740.

34 Bakshi, M.; Kaur, G.; Thakur, P.; Banipal, T.; Possmayer, F.; Petersen, N. O. J. Phys. Chem. C 2007, 111(16), 5932.

35 Bakshi, M.; Possmayer, F.; Petersen, N. O. Chem. Mater. 2007, 19(6), 1257.

36 Niesz, K.; Grass, M.; Somorjai, G. A. Nano Lett. 2005, 5(11), 2238.

37 Perez, H.; Pradeau, J.-P.; Albouy, P.-A.; Perez-Omil, *J. Chem. Mater.* **1999**, *11(12)*, 3460.

38 Pengo, P.; Polizzi, S.; Battagliarin, M.; Pasquato, L.; Scrimin, P. J. Mater. Chem. 2003, 13(10), 2471.

39 Serrano, D. P.; Aguado, J.; Escola, J. M.; Rodriguez, J. M.; Peral, A. *Chem. Mater.* **2006**, *18*, 2462.

40 Mbaraka, Isa K.; Shanks, Brent H. J. Catal. 2006, 244(1), 78.

41 Chen, H.; Huh, S.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. J. Am. Chem. Soc. 2005, 127(38), 13305.

42 McKimmy, E.; Dulebohn, J.; Shah, J.; Pinnavaia, T. J. *Chem. Comm.* **2005**, *29*, 3697.

43 Holmberg, B. A.; Hwang, S.; Davis, M. E.; Yan, Y. *Micro. Meso. Mater.* **2005**, *80(1-3)*, 347.

44 Slowing, I. I.; Trewyn, B. G.; Giri, S.; Lin, V. S.-Y. Adv. Funct. Mater. 2007, 17(8), 1225.

45 Lai, C.; Trewyn, B. G.; Jeftinija, D. M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V. S.-Y. *J.Am. Chem. Soc.* **2003**, *125(15)*, 4451.

46 Li, S.; Li, Z.; Medina, D.; Lew, C.; Yan, Y. Chem. Mater. 2005, 17(7), 1851.

47 Liu, Y.; Zhang, W.; Pinnavaia, T. J. J. Am. Chem. Soc. 2000, 122(36), 8791.

48 Liu, Y.; Zhang, W.; Pinnavaia, T. J. Angew. Chem. Int. Ed. 2001, 40(7), 1255.

49 Liu, Y.; Pinnavaia, T. J. Chem. Mater. 2002, 14(1), 3.

50 Zhang, Z.; Han, Y.; Xiao, F.; Qiu, S.; Zhu, L.; Wang, R.; Yu, Y.; Zhang, Z.; Zou, B.; Wang, Y.; Sun, H.; Zhao, D.; Wei, Y. *J. Am. Chem. Soc.* **2001**, *123(21)*, 5014.

51 Zhang, Z. T.; Han, Y.; Zhu, L.; Wang, R. W.; Yu, Y.; Qiu, S. L.; Zhao, D. Y.; Xiao, F. S. *Angew. Chem. Int. Ed.* **2001**, *40*, 1258.

Chapter 4

Synthesis, Characterization, and Catalytic Application of Zeolites with Uniform Intracrystal Mesopores

4.1. Abstract

Zeolites with intra-crystal mesopores were prepared through a sol-gel process. In this approach the nucleation of the zeolite phase is carried out in the presence of a silvlated form of a polymer such as polyethylenimine and α , ω-diamine surfactant Jeffamine such D series as $H_2N(CH(CH_3)CH_2O)_nCH_2CH(CH_3)NH_2$. As the zeolite crystals grow, the incorporated polymer becomes phase-segregated from the zeolite matrix, forming an intracrystal polymer network that is covalently linked to the zeolite framework through covalent Si-O-Si linkages. The average pore size can be tuned from 2 nm to 8 nm depending on the properties of polymer porogen. In addition to mesoporous ZSM-5 (denoted as MSU-MFI), mesoporous forms of other common zeolite structures of commercial importance such as Linde type A and zeolite Y also were prepared. The presence of the mesopores resulted in little or no decease in micropore volume. However, the external surface area and mesopore volume increased significantly. For MSU-MFI prepared from silylated D4000, a mesopore volume of 0.65 cm³/g was observed, which is 16-fold increase compared to a conventional ZSM-5 sample. Moreover, stability tests showed that after various hydrothermal treatments, the majority

of mesopores were retained, indicating of the robustness of the structure. The high external surface area and large mesopore volume greatly improved the mass transportation rate of MSU-MFI samples, dramatically improving their catalytic performance. In the cumene cracking reaction, MSU-MFI catalysts showed significantly higher cumene conversion compared to commercial USY and ZSM-5 catalysts. Moreover, the presence of mesopores facilitated secondary reactions that changed the product distribution from a 1:1 mixture of benzene and propylene for the conventional zeolite to benzene and C_{6+} hydrocarbons for the mesoporous zeolite. This effect on product selectivity could be very useful in many reactions such as the methanol to gasoline process.

4.2. Introduction

Aluminosilicate materials have widely been used as acid catalysts in the refining industry for decades.¹⁻³ Among all the different types of aluminosilicates, zeolites are the most important composition because of their super strong acidity and uniform pore size,⁴ which in turn provides high petroleum conversion rates and desirable product distributions. For instance, the 0.56 nm pore size of ZSM-5 allows a much faster diffusion rate for para-xvlene orthometa-xylene. than and Therefore, toluene disproportionation with a para-selectivity over 90% can be achieved on a modified ZSM-5 catalyst to eliminate the isomerization reaction.⁵ In addition to product shape-selectivity,⁶⁻⁸ the small 0.3 to 1.2 nm micropores of zeolites also greatly reduces the diffusion rate of reactant molecules to active sites, therefore affecting their catalytic activities. Moreover, bulky molecules can only be processed on the external surfaces of zeolite catalysts, which typically only accounts for less than 1% of the total surface area for a micron-size crystal. The change of oil supply quality and the pursuit of higher yields of transportation fuels demand the development of novel cracking catalysts. Large pore zeolite (ITQ-33) catalysts have shown the ability to provide higher vields of diesel fuel in the cracking product.⁹ The 1.22 nm pore size was defined by an 18-member ring, which was constructed partially through 3-member rings. Fluorine ions were added to the reaction mixture to stabilize the 3-member ring. Nevertheless, synthesizing new zeolites with pore sizes larger than 1.2 nm still remains a challenge, and several other approaches to obtaining larger pore zeolites have been explored extensively.¹⁰⁻¹⁸

Mesostructured aluminosilicate materials¹⁹⁻²⁵ seem to be a promising solution to obtaining large pore catalysts due to their high surface areas and controllable pore sizes. Moreover, due to the uniform mesopore size, desired products in higher yield can be produced using mesostructured aluminosilicate catalysts.²⁶⁻²⁸ However, the weak acidity associated with the amorphous walls prevent mesostructured aluminosilicates from performing better than zeolite catalysts in petroleum reactions, even though many improvements in acidity have been achieved.²⁹⁻³² Significant improvements in acidity can be achieved through the incorporation of zeolitic subunits into the pore walls.³³⁻³⁹ However, the acidity of mesostructured aluminosilicate materials still is not comparable to zeolites.

Recently, zeolites with intra-crystal mesopores have been investigated intensively.¹⁵⁻¹⁸ Compared to inter-crystal mesopores generated through nano-particle aggregation,¹⁰⁻¹⁴ intra-crystal mesopores are more interesting because the resulting pores are intrinsically smaller and more uniform, which are the two most favorable features needed to achieve desirable selectivity.⁴⁰ Moreover, the time-consuming steps associated with nano-particle processing are avoided. The presence of mesopores not only increases the external surface area that is accessible to bulky reactant molecules; it also greatly reduces the diffusion path length through the crystal, which helps to boost the catalytic activity.

The traditional methods for generating intra-crystal mesopores within zeolites, such as steaming and chemical leaching, leads to uncontrollable pores 10 nm or larger.⁴¹ Moreover, the composition, as reflected in the Si/Al ratio, changes during the treatment. Carbon-based materials^{15, 16} have been

used to template intra-crystal mesopores within zeolite crystals with limited control of the resulting mesopores. Upon calcination to remove the carbon template, intra-crystal mesopores are formed that reflect the size of carbon templates. Because of the hydrophobicity and low density of the carbon templates, phase-segregation often occurs, which results in the formation of zeolite nano-crystals.¹⁴ In addition, the irregularity of carbon templates inevitably results in irregular pores with large diameters, which are not suitable for shape- or size-selective catalysis. In the best case, a mesopore size centered at 11 nm and a width at half height of 3 nm was achieved for ZSM-5 using a preformed carbon aerogel as the carbon template.¹⁸

Supramolecular assembly has proved to successfully template uniform mesopores within amorphous aluminosilicate materials. However, the relatively weak interactions within the micelle and between the micelle and the silica surface make the soft template vulnerable to deformation at the high temperatures that are needed for zeolite crystallization.^{42, 43} As a result, no uniform mesopores have been obtained when the mesostructured wall are fully crystallized. Kaliaguine and co-worker⁴⁴ partially crystallized the thick walls of large pore mesostructured aluminosilicate material MCF with a significant loss of pore structure. In 2006, Ryoo and co-workers⁴⁵ used a unique surfactant whose hydrophilic head group was functionalized with a silane group. In the synthesis, the covalent bonding between surfactant and zeolite phase helped stabilize the mesopore size as small as 2.1 nm.

In the current study, we investigate the use of silvlated polymers as molecular templates for the formation of intra-crystal zeolite mesopores. This

molecular templating approach assures the formation of small and uniform mesopores. The presence of the silyl group in the polymer is used to secure the mesoporogen inside the zeolite crystals. Both polyethylenimine and α , ω diamine-polypropylene oxides with different average molecular weights have been used as mesoporogen to template intra-crystal mesopores and control the pore size. Moreover, this new approach was applied to other types of zeolite structures such as LTA and FAU. Hydrothermal stability of the mesopores has been studied. Also, in order to investigate the effect of the mesopores on catalytic behavior, catalytic cumene cracking was conducted on mesoporous ZSM-5. Commercial ZSM-5 and USY catalysts were used for comparison purpose.

4.3 Experimental Section

4.3.1 Materials

Tetraethylorthosilicate (TEOS, 98%), colloidal silica (Ludox 30%), and aluminum tri-sec-butoxide (97%) were obtained from Aldrich as silica and alumina sources. Aluminum metal (Spectrum Chemical) was obtained in a form of 5-mesh powder. Tetrapropylammonium hydroxide (20 wt%, TPAOH) and tetramethylammonium hydroxide (35 wt%, TMAOH) were obtained from Aldrich as structure-directing agents for MFI-, FAU-, and LTA-type zeolites. Glycidoxypropyl-trimethoxysilane (GOPTMS) was obtained from Gelest. Polyethylenimines (PEI) (Alfa Aesar) with average molecular weights of 600, 1800, 10000, 25000 (Aldrich) and α , ω diamine-polypropylene oxides with molecular weights of about 2000, and 4000 (Huntsman) were used as polymer precursors for mesoporogens. The latter polymers are commercially available under the trade name Jeffamine D-2000, and D-4000.

4.3.2 Synthesis of Mesoporgen

The polymer and GOPTMS modifier were dissolved into ethanol, which is used as the solvent. The resulting solution was heated to elevated temperature to form C-N bonds between the modifier and polymer, as illustrated in Figure 4.1. The most effective molar ratio of N-H to GOPTMS was found to be 5 to 10 for PEI and 1 for Jeffamine surfactants. In a typical synthesis, 0.5 g GOPTMS (2.12 mmol) and 2.12 g D-4000 (0.53 mmol) were dissolved in 8 g ethanol. The solution was then heated to 80 ~ 100 °C in a sealed container for 24 hours. After that, the ethanol was removed by applying vacuum to the sample. The resultant modified polymer products were denoted as MP-D2000, MP-D4000,

MP-600(x), MP-1800(x), MP-10000(x), and MP-25000(x), whereas x presents

the N-H/silane molar ratio.



Figure 4.1 Reaction for mesoporogen preparation.

4.3.3 Preparation of Mesoporous Zeolites

4.3.3.1 Mesoporous ZSM-5

MP-25000(5) was dissolved in TPAOH first. To the resulting solution, TEOS and aluminum tri-sec-butoxide were pre-mixed and then added under vigorous stirring. The gel composition was as follow: 1 SiO₂: 0.01 Al₂O₃: 0.37 TPAOH: 20 H₂O: 4 EtOH (from hydrolysis): 0.1 MP, whereas the mole of MP is calculated on the basis of silane. The synthesis mixture was then transferred into a Teflon-lined autoclave and heated to 150 °C for 48 hours. In the case that MP-D2000 and MP-D4000 were used as porogen, the reaction mixture was heated to 100 °C for 96 hours. More specifically, extra ethanol (EtOH/SiO₂ = 4) was added to the synthesis mixture from MP-D4000 to improve the solubility of mesoporogen. The product was washed, dried, and calcined at 600 °C for 4 hours. The final product was denoted as MSU-MFI.

4.3.3.2 Mesoporous Faujasite

A 1.503-g quantity of MP-25000(5) and 0.324 g NaOH were dissolved in 17.536 g TMAOH (25 wt%) and 50 g water first. To the resulting solution, 0.414 g aluminum was added slowly under vigorous stirring. After the aluminum was dissolved, 6.667 g colloidal silica (30 wt%) was added. The gel composition was as follow: 1 SiO₂: $0.23 \text{ Al}_2\text{O}_3$: 1.44 TMAOH: 0.243 NaOH: 113 H₂O: 0.1 MP, where the mole fraction of MP is calculated on the basis of silane. The mixture was then transferred into a Teflon-lined autoclave and heated to 100 °C for 96 hours. The product was washed, dried, and calcined at 600 °C for 4 hours. The final product was denoted as MSU-Y.

4.3.3.3 Mesoporous Zeolite A

A 1.503-g quantity of MP-25000(5) was dissolved in 8.507 g TMAOH solution (25 wt%) together with 0.057 g sodium hydroxide and 1g distilled water. Then 1.389 g aluminum triisoproxide was added. Finally, 6.667 g colloidal silica (Ludox SM-30, 30 wt% SiO₂) was added. The resulting mixture was put in a shaking-bath until a homogeneous sol was formed. The molar composition was $1SiO_2$: 0.1 Al₂O₃: 0.02 Na₂O: 0.1 Silane: 0.22 (TMA)₂O: 20 H₂O. The reaction mixture was heated to 100 °C for 60 hours. The solid product was collected by centrifugation, and then washed with water. After air-drying, the product was calcined at 500 °C for 6 hours to obtain the Na⁺ form of MSU-LTA.

4.3.4 Zeolite characterization

X-ray diffraction patterns were recorded on a Rigaku Rotaflex Diffractometer using CuK_a radiation (λ =1.542Å). N₂ adsorption and desorption isotherms at -196°C were obtained on a Micromeritics ASAP 2000 sorptometer. The samples were degassed under 10⁻³ Torr at 250°C overnight prior to analysis. The surface area was calculated from the BET equation. Pore size distributions were derived from the adsorption isotherms using the BJH model.

TEM images were taken on a Jeol 2200FS instrument operated at 200 kV. To prepare thin-sectioned specimens, powdered samples were embedded into a thermo set resin LR White and then microtomed into 70 nm thick slices. SEM images were recorded on a JSM 6400 Electron Microscope at an acceleration voltage of 20 kV. The samples were carbon-coated prior to imaging.

4.3.5 Catalytic cumene cracking

Catalytic cumene cracking reactions were performed in a 6 mm i.d. fixed bed quartz reactor with 200 mg catalyst at 200°C. Prior to catalytic testing, the catalysts were ion-exchanged twice with 0.5 M NH₄NO₃ solution followed by calcination at 550°C for 4 hours to convert the zeolite to the protonated form. The cumene flow rate was 4.1 μ mol/min in a 20 cm³/min carrier stream of N₂. Cumene conversions were plotted against time on stream after a 6-hour activation period under N₂ flow at 200°C prior to the addition of cumene. The reaction products were analyzed using an HP 5890 GC equipped with a 30-meter SP-1 capillary column and a flame ionization detector.

4.4 Results and Discussions

4.4.1 Formation of mesopores

Figure 4.2 (curve B) provides the X-ray diffraction patterns of a typical calcined mesoporous MSU-MFI zeolite synthesized using MP-25000(5) as the porogen. For comparison, a ZSM-5 zeolite synthesized without porogen is also included (Figure 4.2, curve A). The MSU-MFI possesses all the characteristic peaks of an MFI framework, confirming that MSU-MFI has the same framework structure as conventional ZSM-5 zeolite. However, the peak intensity of MSU-MFI is slightly weaker in comparison to conventional ZSM-5. Moreover, the diffraction peaks are broader in the case of MSU-MFI, indicative of a smaller crystal domain size.

Figure 4.3 provides the ²⁹Si NMR spectrum of as-made MSU-MFI with porogen present in the mesopores. Three distinguishable resonances were observed at 115, 105, and 70 ppm, which can be assigned to Q⁴, Q³, and T³ sites respectively. The deconvolution analysis shows that the T/Q value (0.13) in the MSU-MFI product is in agreement with the initial synthesis composition (0.10), thus confirming the complete incorporation of the porogen into the zeolite crystals. Moreover, no T² sites are found in the sample, which indicates that the organosilanes in the mesoporogen are linked to the zeolite crystal surface through 3 Si-O bonds. Such strong covalent bonding of multiple silane centers in a single polymer chain prevents the mesoporogen from being ejected out of zeolite crystals during crystallization. In a related experiment, a non-silyated polymer in place of the silylated polymer was added to a zeolite synthesis mixture.⁴⁶ No intra-crystal mesopores were found in the resulting zeolite product. In stead, aggregates of nanocrystals were observed. After
calcination, these silicon centers of the silylated porogen presumably form amorphous silica, which also may contribute to the decrease in the XRD intensity (Figure 4.2, curve B).

Figure 4.4 provides the nitrogen adsorption-desorption isotherms for mesoporous MSU-MFI zeolites made from silvlated PEI porogens. Included for comparison is the conventional ZSM-5 synthesized without porogen under equivalent conditions. In addition to the almost vertical N₂ uptake at P/Po below 0.05, which is characteristic of micropore filling for all samples, nitrogen uptake at P/Po between 0.1 and 0.6 is observed for the mesoporous MSU-MFI samples prepared from silvlated mesoporogen at a NH/Si of 5 (Figure 4.4, curve D). The nitrogen uptake in this region is indicative of the presence of small mesopores. A BJH analysis of the nitrogen adsorption curve indicated the average mesopore size to be 3.0 nm with the width of the pore distribution being 1.5 nm. Such features are not observed for conventional ZSM-5 (Figure 4.4, curve A). Direct evidence for the presence of intra-crystal mesopores is provided by the TEM images shown in Figure 4.5 for whole particle and thin-sectioned specimens. Each particle is permeated by randomly oriented small mesopores of nearly the same size. Higher resolution images (Figure 4.5 A) reveal lattice fringes that extend over the entire particle, indicating that each particle is a single crystal and not an aggregate of nanocrystals.

In addition to the *intra*crystal mesopores, MSU-MFI also possesses textual porosity as indicated by the hysteresis at P/Po > 0.9. Such porosity also is found for the ZSM-5 samples prepared from fully silylated PEI polymer (Figure 4.4, curve B and C), and can be assigned to either surface defects or inter-particle voids. However, when fully silylated PEI was used, no *intra*crystal

mesoporosity was found for the final products.

Regarding the formation of mesopores, we hypothesize that the PEI polymer binds to proto-zeolitic nanoclusters through SiO₃ units and becomes phase-segregated from the zeolite matrix as the crystal grows (Figure 4.6). However, when the PEI was fully silvlated, the large number of SiO³⁻ units present after hydrolysis prevents phase segregation, and causes the polymer to bind as a single strand to the zeolite surface or to be expelled altogether from the crystal, resulting in either case in a loss of mesoporosity. Figure 4.7 shows the SEM image of ZSM-5 samples prepared from fully silvlated PEI porogen. It can be clearly seen that not only is the zeolite crystal size reduced greatly, but also that the surface of each particle is full of defects (Figure 4.7 B). It is conceivable that the fully silvlated PEI polymer is mainly bonded to the external surface of the zeolite particle and therefore limits zeolite crystal growth to the sub-micrometer size domain, giving rise to zeolite with inter-crystal pores as indicated by the hysterisis at P/Po = 0.9. Moreover, such textual porosity is dependent on the amount of fully silvlated PEI added. For instance, the addition of more silylated PEI, further decreases the crystal size (Figure 4.7 B) and further increases the textual porosity (Figure 4.4, curve C).

4.4.2 Polymer effects on mesopore size

Figure 4.8 provides the mesopore size distributions and corresponding mesopore volumes for MSU-MFI zeolites prepared in the presence of PEI polymers with initial molecular weights of 600, 1,800, 10,000 and 25,000. Each porogen was prepared at a NH/Si ratio of 5.0. For each derivative, the pore size distribution is confined to values below 8 nm and the distribution of pores

is centered between 2.0 and 3.0 nm with a width at half-maximum < 1.5 nm. Moreover, the resulting mesopore size is in agreement with the order of molecular weight. These mesopore size distributions, which are in the range anticipated for selective polymer cracking, are unprecedented among all previously reported mesoporous forms of ZSM-5 or any other zeolite structure type. Also, the corresponding mesopore volumes for these new ZSM-5 derivatives $(0.07 - 0.11 \text{ cm}^3/\text{g})$ compare favorably with the micropore volume of the zeolite framework $(0.12 \text{ cm}^3/\text{g})$.

The 50% increase in average mesopore size observed upon increasing the polyethylenimine molecular weight from 600 to 25,000 is substantially lower than the ~3.4-fold increase expected for a 40-fold increase in polymer molecular weight. This latter observation indicates the zeolite matrix greatly alters the solvation and conformation of the phase-segregated polymer embedded in the crystal. Further evidence for confinement effects on the polymer is provided by a comparison of the hydrodynamic radius of the free polymer in comparison to the templated pore sizes. For instance, the hydrodynamic radius of polyethylenimine with MW = 25,000 is ~ 6.6 nm,⁴⁷ whereas the average radius of the mesopores templated by the silylated form of this polymer is ~ 1.5 nm.

Besides polyethylenimines, other N-H containing polymers such as Jeffamine surfactants also can be used as mesoporogens for MSU-MFI synthesis. The structure of Jeffamine D surfactants is illustrated in Figure 4.9. Because of the low density of N-H bonds, the Jeffamine D surfactants were fully silylated (N-H/Si = 1) to optimize the interaction between the mesoporogen and the zeolite phase through as many Si-O-Si linkage as

possible. Moreover, in the case of D-4000, additional ethanol was added to the reaction mixture to increase the solubility of the mesoporogen. Figure 4.10 provides the N₂ adsorption-desorption isotherms of MSU-MFI materials prepared in the presence of silylated Jeffamine D surfactants. Compared to conventional ZSM-5, both MSU-MFI samples exhibit distinguishable hysteresis loops between partial pressure of 0.5 and 0.8. The corresponding pore size distribution plots (Figure 4.10, inset) show uniform pore diameters centered at 3.0 nm and 5.4 nm, which are slightly larger than the pores templated by silylated polyethylenimine. The resultant mesopore diameter correlates with the molecular weight of the original polymer that was used as mesoporogen.



Figure 4.9 Structure of Jeffamine D surfactant

x = 33.2 for D2000, and 67.7 for D4000

The light contrast areas in the TEM image of a thin-sectioned sample (Figure 4.11) confirms the presence of uniform intracrystal mesopores that are distributed evenly within the crystal. In the magnified image of Figure 4.11, (inset), lattice fringes can be clearly seen, indicative of the crystalline phase. X-ray diffraction patterns (Figure 4.12) reveal that both MSU-MFI samples possess all the characteristic peaks of conventional ZSM-5. No other crystalline phase is found. It is safe to claim that MSU-MFI materials are mesoporous aluminosilicates with zeolite walls. The presence of uniform mesopores greatly reduces the domain size of the zeolite crystals, resulting in weaker and broader diffraction peaks. Compared with conventional ZSM-5, MSU-MFI samples have reduced diffraction intensity. This trend becomes

more evident when the mesopores get bigger.

4.4.3 Effect of reaction temperature

In addition to being dependent on the molecular weight of the mesoporogen, the templated mesopore size is also very dependent on the crystallization conditions. As shown in Figure 4.13, the same silvlated D4000 can provide different mesopore diameters depending on the temperature. At 100 °C, the average mesopore size is 5.4 nm, whereas at 125 °C, the pore size is expanded to 8 nm (Figure 4.13, curve B). In the case of silvlated D2000 as the mesoporogen, the average mesopore size can be expanded from 3.0 nm at 100 °C to 4.5 nm if the crystallization is conducted at 125 °C (Figure 4.13, curve A). For both mesoporogens, no uniform mesopores were formed if the reaction temperature was higher than 150°C. It is hypothesized that at the higher temperature, Jeffamine surfactant is not sufficiently stable to template intracrystal mesopores. But even at lower synthesis temperatures where uniform mesopores are obtained, no low angle X-ray diffraction peaks typical of MSU-J mesostructures with amorphous framework walls were found.⁴⁸ This latter result rules out the possibility that a mixture of mesostructure and zeolite was formed.

4.4.4 Other types of zeolite

Besides MFI zeolite, mesoporous forms of other zeolite structures can also be prepared though this polymer templating approach. Zeolite Y (FAU) and Linde type A (LTA) are two common zeolites that have found many applications in industry. Zeolite Y has been widely used as the main

composition in refining and cracking catalysts in petroleum industry. A mesoporous form of zeolite Y based cracking catalyst could meet the demand for high yields of transportation fuels and the challenge accompanying a change in crude oil quality. Zeolite A is well recognized as a good ion-exchanger and absorbent. Moreover, calcium-exchanged LTA was used to promote blood clotting.⁴⁹ The mesoporous form of zeolite A may be expected to perform more efficiently because the presence of mesopore allows bulky protein molecules to diffuse and bind more easily to the zeolite surface.

Figure 4.14 provides the N₂ adsorption-desorption isotherm of MSU-Y prepared from MP-25000(5). Compared to conventional zeolite Y (Figure 4.14, curve A), the mesoporous MSU-Y sample showed a distinguishable hysteresis loop at partial pressure of 0.4 (Figure 4.14, curve B), indicative of the presence of 3 nm mesopores. In addition to the enhanced mesoporosity, no loss of microporosity was observed for MSU-Y compared to conventional Y.

Figure 4.15 provides the N_2 isotherm of MSU-A. A hysteresis loop at higher partial pressure was observed, suggestive of larger mesopore. X-ray diffraction pattern confirmed the presence of LTA type framework (Figure 4.15, inset). These results suggested that this approach is applicable to other zeolite structures other than MFI.

4.4.5 Hydrothermal stability

Since zeolites have extraordinary hydrothermal stability compared to amorphous aluminosilicates, it is conceivable that mesoporous zeolite MSU-MFI with fully crystalline zeolite walls would exhibit much improved stability under hydrothermal conditions. Figure 4.16 provides the N_2

adsorption-desorption isotherms of MSU-MFI sample treated under different hydrothermal conditions. Compared to pristine MSU-MFI, hydrothermally treated MSU-MFI samples show expanded pore sizes. For instance, after being steamed with 20% water vapor at 800 °C for 2 hours, the mesopore diameter increased from 5.4 to 6 nm (Figure 4.16, curve B); while after being boiled in water at 100 °C for 7 days, an average mesopore size of 9 nm was obtained (Figure 4.16, curve C). In both cases, the mesopores remained relatively uniform, and most of the mesopore volume was retained after hydrothermal treatment. The results suggest that the mesopores templated by the silylated polymer are very stable under hydrothermal condition because of the crystalline walls.

4.4.6 Catalytic activity

Table 1 summarizes the physical properties of MSU-MFI samples. Compared to conventional ZSM-5, which only possesses a small external surface area and essentially no mesopore volume, all MSU-MFI samples templated by silylated Jeffamine D surfactants exhibit greatly increased external surface area. For instance, MSU-MFI prepared from silylated D2000 mesoporogen shows an external surface of 438 m²/g, a 6.7-fold increase compared to conventional ZSM-5. Moreover, the mesopore volume was significantly improved at the expense of a reasonable amount of micropore volume or crystallinity. For example, MSU-MFI templated with silylated D4000 offers a 0.65 cm³/g mesopore volume, a 16-fold increase in comparison to the conventional zeolite. When used as a catalyst, a zeolite with such a high mesoporosity should greatly reduce the diffusion path length, and therefore,

significantly enhance the catalytic performance. It is also noteworthy that after hydrothermal treatment, the external surface area of the zeolites decreased significantly. It is conceived that a lot of surface roughness was generated during mesopore templating. Under hydrothermal conditions, the surface is restructured without destroying the mesopores. Therefore, a significant loss of external surface area was observed with increase in mesopore size.

Cumene cracking was selected as a probe reaction to investigate the catalytic activity of mesoporous aluminosilicates. In this study, the reaction temperature was lowered from 300 °C to 200 °C so that commercial ZSM-5 shows a low cumene conversion. Figure 4.17 provides the activity versus time-on-stream results. Commercial USY and ZSM-5 zeolites with a Si/Al ratio of 40 were used as references. USY provided a very high initial cumene conversion of 50% (Figure 4.17, curve A), which decreased quickly to 20% after 6 hours on stream. The fast deactivation can be assigned to the larger pore size of faujasite, which is very vulnerable to coking. On the contrary, the commercial ZSM-5 showed steady increase of activity and reached maximum cumene conversion at 25% after 6 hours on stream (Figure 4.17, curve B). This increase in reactivity may be caused by a thermal stresses that cause the zeolite crystals to crack, exposing more external surface area with time on stream. After that, the catalyst started deactivating. The slow increase of activity might indicate the slow diffusion rate of reactant molecules into the catalyst. When mesoporous MSU-MFI materials were used as catalysts, not only was higher cumene conversion achieved, but also the maximum activity was reached almost instantly, indicative of the elimination of diffusion obstacle. For instance, a 65% cumene conversion was achieved on MSU-MFI prepared

from MP-25000(5) (Figure 4.17, curve C). MSU-MFI with larger uniform mesopores had an initial cumene conversion of 50% (Figure 4.17, curve D). This relatively lower activity of MSU-MFI prepared from MP-D4000 might be attributed to the lower crystallinity as judged by XRD peak intensity. After 24 hours on stream, both MSU-MFI catalysts showed a cumene conversion above 38%, which is almost a two-fold increase over conventional ZSM-5. We noted from TGA data that all spent catalysts have no more than 2wt% carbon residue after 24 hours on stream. Therefore, the deactivation due to coking is not a major concern. The unprecedented higher activity of MSU-MFI materials can be contributed to enhanced mesoporosity and much higher external surface area. Due to the presence of uniform mesopores and a high external surface area, more active sites can be accessed by reactant molecules more easily. Therefore, the catalytic activity was dramatically improved.

It is noteworthy that for MSU-MFI catalyst, a benzene to propylene molar ratio of 3:1 was observed in the product distribution. For a commercial ZSM-5 catalyst, the benzene to propylene ratio was found to be 1:1, which is the consistent with the expected reaction stoichiometry. As illustrated in Figure 4.18, for a commercial zeolite catalyst, the majority of the accessible active sites are located on the outer surface of crystal, where product molecules can easily escape. However, for a mesoporous zeolite catalyst, the majority of reaction can occur inside the mesopores due to the improved diffusion property. Not only is the catalytic performance greatly improved, but also the mesopores provide a constricted space. Before the product molecules can escape from the mesopore, they are likely to undergo secondary reaction to form heavier hydrocarbons. Since propylene is more reactive than benzene,

more propylene is consumed and a benzene to propylene ratio higher than 1:1 is observed. The ability to induce secondary reaction makes these materials good candidate catalysts for reactions such as methanol to gasoline ⁵⁰ where secondary reaction is preferred.

4.5 Conclusions and perspectives

The use of silylated templates in zeolite synthesis results in small and uniform intracrystal mesopores that are also controllable in diameter within zeolite crystals. These mesoporous zeolites have large external surface and mesoporosity, which in turn greatly improves their mass transportation properties. Therefore, higher catalytic activity can be achieved. Moreover, the presence of mesopores also increases the possibility of reactants contacting active sites on the walls, therefore, facilitates secondary reactions. In the cumene cracking reaction, the yield of propylene is greatly reduced on mesoporous zeolite catalysts.

Future work should be focusing on the application of mesoporous zeolites to other catalytic processes such as methanol to olefins conversion. In preliminary experiments, products obtained from MSU-MFI catalysts showed much higher propylene/ethylene ratio than the one from conventional ZSM-5 catalyst. The results are plotted in Figure 4.19. For instance, at 350 °C, mesoporous ZSM-5 prepared from silylated PEI and D4000 showed P/E ratio of 4.7 and 4.4 respectively, in contrast to 2.4 from conventional ZSM-5 catalyst. The reason is because the presence of mesopores and large external surface area greatly increases the reaction rate and helps to reach equilibrium state faster. In this reaction, medium pore ZSM-5 favors the formation of propylene over ethylene. Since in industry ethylene is more valuable than propylene, the commercial MTO catalyst uses small pore SAPO-34 as catalyst, which favors the formation of ethylene. Therefore, it will be worthwhile to synthesize mesoporous form of SAPO-34 and use it as MTO catalyst to investigate the effect of uniform mesopores on the product distribution.

In addition, as shown in Figure 4.20, in the polymer degradation reaction, the addition of commercial ZSM-5 products significantly lowers the degradation temperature of HDPE from 440 °C to 310 °C. Moreover, the presence of mesopores in ZSM-5 catalysts further lowers the degradation temperature to 290 °C. It is conceivable that MSU-MFI materials allow the diffusion of bulky molecules such as HDPE inside the zeolite crystals, where more active sites are accessible. In addition, from the results for bulky ZSM-5 catalysts, the framework Si/AI has significant influence on the degradation temperature. First, the degradation temperature decreases along with decreasing Si/Al, indicative of the strong correction between catalytic activity and acidic sites. The activity of ZSM-5 starts decreasing when the Si/AI ratio is lower than 20. This is probably due to the decreasing of acidic strength when the population of Al increases. It is well known that the framework Si/Al ratio of zeolite catalysts also affects the product distribution in reactions such as cracking. Therefore, the future work should be focused on the analysis of HDPE degradation products and investigating the effect of Si/AI on product distribution. Furthermore, mesoporogens other than the PEI and Jeffamine should also be explored to expand the scope of the current project.

Catalyst*	Polymer	BET	External	Micropore	Mesopore
	source	Surface	surface	Volum o ,	Volume,
		area, m²/g	area, m²/g	cm³/g	cm³/g
ZSM-5	N/A	389	65	0.14	0.04
MSU-MFI	MP-25000(1)	467	161	0.14	0.24
MSU-MFI	MP-25000(5)	451	255	0.09	0.27
MSU-MFI	MP-D2000	668	438	0.10	0.44
MSU-MFI	MP-D4000	613	405	0.09	0.65
MSU-MFI**	MP-D4000	517	327	0.08	0.49
MSU-MFI***	MP-D4000	494	306	0.08	0.60

Table 4.1 Physical properties of MSU-MFI materials

* Catalysts have a Si/Al ratio of 50.

** Sample was steamed at 800 °C, 20% water vapor for 2 hours.

*** Sample was boiled in water under 100 °C for 7 days.



Figure 4.2 X-ray diffraction patterns of (A), calcined conventional ZSM-5 (Si/Al = 50); (B), calcined MSU-MFI (Si/AI = 50) prepared from silylated PEI mesoporogen with an initial NH/Si ratio of 5: 1. Curve B is offset by 5000 counts.



Figure 4.3 ²⁹Si MASNMR spectrum of as-synthesized MSU-MFI (Si/AI = 50) prepared from 10% silane modified PEI porogen.



Figure 4.4 N₂ adsorption/desorption isotherms of ZSM-5 (Si/Al = 50) synthesized in the presence of A, no MP-25000; B, 5 mol% organosilane as MP-25000(1); C, 10 mol% organosilane as MP-25000(1); D, 10% organosilane as MP-25000(5). Each curve is offset by 50 cc/g.



Figure 4.5 TEM images of the MSU-MFI zeolite (Si/AI = 50) prepared in the presence of silylated polyethleneimine with an initial molecular weight of 25,000: A) whole particle specimen; B) thin-sectioned sample. The light contrast areas are intracrystal mesopores.









MP-25000(1); and C, 5% MP-25000(1).



Pore diameter, nm

Figure 4.8 BJH adsorption pore size distributions for MSU-MFI samples (Si/Al = 50) prepared from the following silylated PEI polymers: A, MP-600(5); B, MP-1800(5); C, MP-10000(5); D, MP-25000(5).



Figure 4.10 N₂ adsorption/desorption isotherms of MSU-MFI samples (Si/AI = 50) synthesized in the presence of A, MP-D2000; B, MP-D4000. Inset: BJH pore size distributions from adsorption isotherms.



Figure 4.11 TEM image of thin-sectioned MSU-MFI sample (Si/AI = 50) prepared from silylated D4000 as mesoporogen. Inset: high-resolution image of selected area.



Figure 4.12 X-ray diffraction patterns for (A) conventional ZSM-5 (Si/AI = 50); (B) MSU-MFI (Si/AI = 50) prepared from silylated D2000 as mesoporogen; (C) MSU-MFI (Si/AI = 50) prepared from silylated D4000 as mesoporogen.



Figure 4.13 N₂ adsorption-desorption isotherms for MSU-MFI samples (Si/AI = 50) prepared at 125 $^{\circ}$ C from (A) silylated D2000 as the mesoporogen and (B) silylated D4000 as the mesoporogen. The curve B is offset by 200 for clarity. Inset: BJH pore size distributions obtained from adsorption isotherms.



Figure 4.14 N₂ adsorption/desorption isotherms of zeolite Y (Si/Al = 2.2) synthesized A, in the absence of a mesoporogen; B, in the presence of MP-25000(5) as a mesoporogen.



Figure 4.15 N₂ adsorption/desorption isotherm of MSU-A (Si/AI = 5) synthesized with MP-25000(5). Inset: X-ray diffraction pattern.



Figure 4.16 N₂ adsorption-desorption isotherms for MSU-MFI sample (Si/AI = 50) prepared from silylated D4000. (A) pristine MSU-MFI; (B) steamed with 20% water vapor at 800 $^{\circ}$ C for 2 hours; (C) treated with boiling water for 7 days. The curves B and C are offset by 300 and 600 for clarity. Inset: BJH pore size distributions obtained from adsorption isotherms.



Figure 4.17 Catalytic cumene cracking conversion vs. time for A, commercial USY from Zeolyst (Si/AI = 40); B, commercial ZSM-5 from Zeolyst (Si/AI = 40); C, MSU-MFI (Si/AI = 50) prepared from MP-25000(5); D, MSU-MFI (Si/AI = 50) prepared from MP-D4000.



Figure 4.18 Illustration of catalytic cumene cracking on bulky and mesoporous zeolite catalysts.







Figure 4.20 HDPE degradation catalyzed by A, no catalyst; B, commercial ZSM-5 (Si/AI = 280); C, commercial ZSM-5 (Si/AI = 80); D, commercial ZSM-5 (Si/AI = 50); E, commercial ZSM-5 (Si/AI = 23); F, MSU-MFI (Si/AI = 40) prepared from MP-25000(5); and G, MSU-MFI (Si/AI = 40) prepared from D4000. HDPE/Catalyst = 4: 1.

4.6 References

- 1 Flanigen, E. M. Stud. Surf. Sci. Catal. 1991, 58, 13.
- 2 Corma, A. Chem. Rev. 1997, 97(6), 2373.
- 3 Stoecker, M. Micro. Meso. Mater. 2005, 82(3), 257.
- 4 Corma, A.; Martinez, A. Adv. Mater. 1995, 7(2), 137.

5 Kaeding, W. W.; Chu, C.; Young, L. B.; Butter, S. A. *J. Catal.* **1981**, *69(2)*, 392.

6 Dubbeldam, D.; Calero, S.; Maesen, T. L. M.; Smit, B. Angew. Chem. Int. Ed. 2003, 42(31), 3624.

7 Benazzi, E.; Leite, L.; Marchal-George, N.; Toulhoat, H.; Raybaud, P. J. Catal. 2003, 217(2), 376.

8 Chen, C. S. H.; Bridger, R. F. J. Catal. 1996, 161(2), 687.

9 Corma, A.; Diaz-Cabanas, M. J.; Jorda, J. L.; Martinez, C.; Moliner, M. *Nature* **2006**, *443*(7113), 842.

10 Mintova, S.; Olson, N. H.; Senker, J.; Bein, T. Angew. Chem. Int. Ed. 2002, 41(14), 2558.

11 Schmidt, I.; Madsen, C.; Jacobsen, C. J. H. Inorg. Chem. 2000, 39(11), 2279.

12 Kim, S. S.; Shah, J.; Pinnavaia, T. J. Chem. Mater. 2003, 15, 1664.

13 Serrano, D. P.; Aguado, J.; Escola, J. M.; Rodriguez, J. M.; Peral, A. *Chem. Mater.* **2006**, *18*, 2462.

14 Reding, G.; Maurer, T.; Kraushaar-Czarnetzki, B. *Micro. Meso. Mater.* 2003, *57*, 83.

15 Janssen, A. H.; Schmidt, I.; Jacobsen, C. J. H.; Koster, A. J.; de Jong, K. P. *Micro. Meso. Mater.* **2003**, *65(1)*, 59.

16 Schmidt, I.; Boisen, A.; Gustavsson, E.; Stahl, K.; Pehrson, S.; Dahl, S.; Carlsson, A.; Jacobsen, C. J. H. *Chem. Mater.* **2001**, *13*, 4416.

17 Jacobsen, C. J. H.; Madsen, C.; Houzvicka, J.; Schmidt, I.; Carlsson, A. J. Am. Chem. Soc. 2000, 12, 7116.

18 Tao, Y.; Kanoh, H.; Kaneko, K. J. Am. Chem. Soc., 2003, 125(20), 6044.

19 Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.;

Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. J. Am. Chem. Soc. 1992, 114(27), 10834.

20 Tanev, P. T.; Pinnavaia, T. J. Science, 1996, 271(5253), 1267.

21 Kim, S. S.; Zhang, W.; Pinnavaia, T. J. Science, 1998, 282(5392), 1302.

22 Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature*, **1998**, *396*(*6707*), 152.

23 Schmidt-Winkel, P.; Lukens, W. W. Jr.; Zhao, D.; Yang, P.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1999**, *121(1)*, 254.

24 Tanev, P. T.; Pinnavaia, T. J. Science, 1995, 267(5199), 865.

25 Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature*, **1992**, *359(6397)*, 710.

26 Xu, B.; Hua, W.; Yue, Y.; Tang, Y.; Gao, Z. Catal. Lett. 2005, 100(1-2), 95.

27 Liu, Y.; Kim, S. S.; Pinnavaia, T. J. J. Catal. 2004, 225(2), 381.

28 Kim, S.-S.; Liu, Y.; Pinnavaia, T. J. Micro. Meso. Mater. 2001, 44-45, 489.

29 Mokaya, R. Chem. Comm. 1997, 2185.

30 Mokaya, R. Angew. Chem. Int. Ed. 1999, 38, 2930.

31 Huang, L.; Guo, W.; Deng, P.; Xue, Z.; Li, Q. J. Phys. Chem. B 2000, 104, 2817.

32 Mokaya, R. Chem. Comm. 2001, 633.

33 Liu, Y.; Zhang, W.; Pinnavaia, T. J. J. Am. Chem. Soc. 2000, 122(36), 8791.

34 Liu, Y.; Zhang, W.; Pinnavaia, T. J. Angew. Chem. Int. Ed. 2001, 40(7), 1255.

35 Liu, Y.; Pinnavaia, T. J. Chem. Mater. 2002, 14(1), 3.

36 Liu, Y.; Pinnavaia, T. J. J. Mater. Chem. 2004, 14(7), 1099.

37 Wang, H.; Liu, Y.; Pinnavaia, T. J. J. Phys. Chem. B 2006, 110(10), 4524.

38 Zhang, Z.; Han, Y.; Xiao, F.; Qiu, S.; Zhu, L.; Wang, R.; Yu, Y.; Zhang, Z.; Zou, B.; Wang, Y.; Sun, H.; Zhao, D.; Wei, Y. *J. Am. Chem. Soc.* **2001**, *123(21)*, 5014.

39 Zhang, Z. T.; Han, Y.; Zhu, L.; Wang, R. W.; Yu, Y.; Qiu, S. L.; Zhao, D. Y.;

Xiao, F. S. Angew. Chem. Int. Ed. 2001, 40, 1258.

40 Aguao, J.; Sotelo, J. L.; Serrano, D. P.; Calles, J. A.; Escola, J. M. *Energy* & Fuels 1997, 11, 1225.

41 Groen, J. C.; Peffer, L. A. A.; Moulijn, J. A.; Perez-Ramirez, J. *Chem. Eur. J.* **2005**, *11(17)*, 4983.

42 Karlsson, A.; Stocker, M.; Schmidt, R. Micro. Meso. Mater. 1999, 27, 181.

43 Xia, Y.; Mokaya, R. J. Mater. Chem. 2004, 14, 863.

44 On, D. T.; Kaliaguine, S. Angew. Chem. Int. Ed. 2001, 40, 3248.

45 Choi, M.; Cho, H. S.; Srivastava, R.; Venkatesan, C.; Choi, D.-H.; Ryoo, R. *Nature Mater.* **2006**, *5(9)*, 718.

46 Xiao, F., Wang, L.; Yin, C.; Lin, K.; Di, Y.; Li, J.; Xu, R.; Su, D. S.; Schlogl, R.; Yokoi, T.; Tatusmi, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 3090.

47 Andersson, M. M.; Hatti-Kaul, R.; Brown, W. J. Phys. Chem. B. 2000, 104, 3660.

48 Park, I.; Wang, Z.; Pinnavaia, T. J. Chem. Mater. 2005, 17(2), 383.

49 Ostomel, T. A.; Stoimenov, P. K.; Holden, P. A.; Alam, H. B.; Stucky, G. D. J. Thrombosis and Thrombolysis **2006**, *22(1)*, 55.

50 Keil, F. J. Micro. Meso. Mater. 1999, 29(1-2), 49.

