BEA Nanosponge/Ultra-thin Lamellar MFI Prepared in One-Step: Integration of 3D and 2D Zeolites into Composite for Efficient Alkylation Reactions

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Abstract: The synthesis of hierarchical meso-/microporous zeolite materials with spatially controlled morphology, meso-/microporosity, and acidity is an expanding area of research interest for a wide range of applications. Here, we report a one-step dual template synthesis method for integration of 3-dimensional (3D) BEA nanosponge and ultra-thin 2D lamellar MFI into a new type of hierarchical meso-/microporous zeolite composite structures. Specifically, the 2D layered MFI nanosheets were laid over the surface of or interdigitated into the 3D BEA particles in the bulk BEA nanosponge-lamellar MFI (BBLM) zeolite structure, which generated a unique morphology of interconnected micropores and mesopores underneath the ‘skinning’ shell (~3-10 nm) of MFI nanosheets. The BBLM zeolites have higher mesoporosity than either bare BEA or lamellar MFI zeolites. The micropore size decreases with increasing lamellar MFI component in the composite. The fraction of external acid sites of BBLM zeolite composite, represented by the percentage of active sites accessible to bulky organic base molecules, decreases with increasing MFI component. Additionally, the types of acid sites are diversified in the BBLM composites compared to either bare BEA or lamellar MFI zeolites. The catalysis tests using conversion of benzyl alcohol in mesitylene showed that BBLM zeolites had significant higher activity and durability than single zeolites or their physical mixture. The BBLM composite zeolite provides a good model catalyst with integrated 2D-3D structures and meso-/microporosity for studying a series of important catalytic reactions in hierarchical zeolites. The one-step dual template synthesis method described herein is versatile and facile, which may prove to be a general platform for hierarchical composite zeolite design at the unit-cell scales of zeolites and with potentially broader applicability to other porous materials.

Keywords: Lamellar-bulk zeolite composites; Meso-/microporosity; Hierarchical structure; Dual template; Alkylation reaction.

1. Introduction

Zeolites are a class of crystalline aluminosilicates with uniform and ordered networks of micropores that provide size/shape selective molecular discrimination for adsorption, separation, and catalysis applications.[1-3] The single type of framework in conventional zeolite, however, hinders the practical application of zeolite in achieving simultaneous separation-adsorption or separation-catalysis for some industrial processes.[4-8] To achieve high separation, zeolites must have pore diameters close to those of species to be separated, but such zeolites often have low adsorption capacity.[4, 9, 10] Similarly, zeolites with high separation power usually show low catalytic activity due to intracrystalline diffusion constraints.[4, 7, 11] Therefore, zeolites with multiple level porosities are desired to achieve concurrently effective adsorption, separation, and catalysis.

Intensive research has been conducted to create hierarchical zeolites with multi-level porosity[12-14] or zeolite composites with multiple framework structures[6, 15-17] for above mentioned applications. The hierarchical meso-/microporous zeolites, coupling the structural feature of microporosity and the fast mass transport consequence of mesoporosity in a single material, are promising materials to overcome mass-transfer constraints in catalysis. Zeolite composites, combining different types of pore topologies, crystalline characteristics, and acid properties into single particles, result in multiple levels of microporosity and compensated acidity to enable excellent catalytic performances.[15, 18, 19] The integration of hierarchical meso-/microporosity into zeolite composites is expected to further advance their performance in combined adsorption, separation, and catalysis applications.

Zeolite composites has been synthesized mainly via epitaxial growth[15, 20-23] or overgrown[4, 7, 24-27] methods. In epitaxial growth, the pre-synthesized zeolite particles are

added into the precursor yielding another type of zeolite crystals. This synthesis method has been used for formation of core-shell[15, 20] or bi-phase[28-30] structured zeolite composites that have similar framework structures.

The overgrown method is generally used to create core-shell zeolite composites that have different framework structures. In this synthesis, the incompatibility between chemical compositions and crystallization conditions of the core and shell zeolite crystals is circumvented by the preliminary seeding of core crystals with shell nanoparticles to induce the growth of the shell. Table S1 in Supplementary Information of this paper summarizes the zeolite framework types and structural properties of composite zeolites synthesized via these methods. It should be noted that both epitaxial growth and overgrown methods require multiple synthesis steps to obtain the zeolite composites. Additionally, they have limited capability of creating the multi-level porosities in the zeolite composites. One-step synthesis of zeolite composites have been practiced in a fluoride growth media[31, 32]. The zeolite shell thickness typically exceeds 1 μm and with limitation of generating mesoporosity in the composites [33]. Our previous work reported the successful synthesis of meso-/microporous lamellar MFI on microporous MFI zeolite via a one-step dual template synthesis approach [34, 35]. To the best of our knowledge, synthesis of hierarchical meso-/microporous zeolite composites with dissimilar framework types in one-step, however, has not been previously reported.

Here, we report a facile one-step dual template synthesis strategy to construct hierarchical zeolite composites containing dissimilar framework structures and dual meso-/microporosity via synergistic integration of 2D layered ultra-thin MFI and 3D bulk BEA nanosponge zeolites. In contrast to previous epitaxial growth or overgrowth methods, both BEA and MFI zeolite phases in the bulk BEA-lamellar MFI (BBLM) composites were formed sequentially in one step

synthesis under the assistance of tetraethyl ammonium hydroxide (TEAOH) and diquatery ammonium surfactant ($[\text{C}_{22}\text{H}_{45}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}]\text{Br}_2$, (C_{22-6-6})) templates, respectively. TEAOH is the traditional molecular template to assist BEA zeolite synthesis[36]; while C_{22-6-6} leads to the coherent assembly of the zeolite layer and the surfactant to produce 2D lamellar MFI zeolite nanosheet structures[37]. The co-existence of C_{22-6-6} and TPAOH template in the synthesis led to the formation of 2D MFI nanosheet covering on the surface of or penetrating into the 3D BEA particles. A fractioning of bulk BEA into a nanosponge-like morphology that was comprised of randomly aggregated nanoparticles was simultaneously observed. The catalytic reactions of benzyl alcohol in mesitylene showed that the BBLM zeolite has an excellent activity and stability compared to single zeolites or their physical mixture.

2. Experimental

2.1. Materials

Tetraethylammonium hydroxide (TEAOH, 35 wt%) aqueous solution, aluminum isopropoxide (metal basis) ($\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$, 99.99+% purity), benzyl alcohol (99+%), and 2,6-Di-tert-butylpyridine (DTBP, 97+% purity) were purchased from Alfa Aesar. Ludox colloidal silica (30 wt%), sodium hydroxide (NaOH , $\geq 97.0\%$ purity), and ammonium nitrate (NH_4NO_3 , $\geq 99.0\%$) were bought from Sigma-Aldrich. Mesitylene was supplied by Acros Organics. Deionized (DI) water was used throughout the experiment. Diquaternary ammonium surfactant ($[\text{C}_{22}\text{H}_{45}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}]\text{Br}_2$, (C_{22-6-6})) was synthesized based on the method reported by Ryoo et al.[37] and the C_{22-6-6} synthesis method has also been described in our previous publications.[34, 38, 39]

2.2. Zeolite composite synthesis

The recipe used for dual template synthesis of the BBLM zeolite composite was as follows: $100\text{SiO}_2/1.4\text{Na}_2\text{O}/1\text{Al}_2\text{O}_3/x\text{C}_{22-6-6}/36\text{TEAOH}/1692\text{H}_2\text{O}$, where $x=0, 1, 3$, and 9 , respectively. Typically, the synthesis was performed by dissolving 0.0667 g NaOH into 8.7353 g TEAOH (35 wt %). Then, $11.5487\text{ g Ludox silica}$ (30 wt %) and $0.236\text{ g Al}[\text{OCH}(\text{CH}_3)_2]_3$ were added to the mixture and the mixture was sonicated at room temperature for 0.5 h until complete dissolution of $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$. Finally, this solution was mixed with a C_{22-6-6} solution that was prepared by dissolving the desired amount of C_{22-6-6} in 3.8462 g DI water at 333 K . After continuous mixing for 2 h at room temperature, the resultant gel was transferred into a Teflon-lined stainless-steel autoclave, followed by hydrothermal synthesis for 14 days by tumbling the autoclave vertically at 30 rpm in an oven heated at 423 K . After synthesis, the zeolite product was filtered, washed with DI water, and dried at 343 K overnight. The as-obtained sample was named BBLM- $x/36$ based on the molar ratio of C_{22-6-6} and TEAOH templates used in the synthesis recipe. Conventional microporous BEA zeolite was synthesized using the same recipe mentioned above without adding any C_{22-6-6} ($x=0$) as the template for comparison, and it was designated as BEA. Synthesis of lamellar MFI was listed in section S2 of the Supplementary Information of this paper.

All the as-synthesized zeolite samples were calcined in flowing air (100 mL min^{-1} , ultrapure, Airgas) by increasing the temperature from ambient temperature to 873 K at 1.45 K min^{-1} and holding the sample at 873 K for 6 h . The calcined samples were then ion-exchanged three times using $1\text{ M aqueous NH}_4\text{NO}_3$ (weight ratio of zeolite to NH_4NO_3 solution = $1:10$) at 353 K for 12 h , and subsequently, collected by centrifugation, washed with DI water three times, and dried at 343 K overnight. The second calcination in dry air (100 mL min^{-1} , ultrapure, Airgas)

was conducted by increasing the temperature from ambient temperature to 823 K at 1.45 K min⁻¹ and holding the sample at this condition for 4 h to thermally decompose NH₄⁺ to NH₃ and H⁺. Eventually, the zeolite samples in the H⁺-form were used for acidity characterization and catalytic reaction tests discussed below.

2.3. Materials characterization

Powder X-Ray diffraction (XRD) patterns were collected by a Bruker D8 Advance Lynx Powder Diffractometer (LynxEye PSD detector, sealed tube, *Cu K_α* radiation with *Ni β*-filter). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations of the samples were performed using a Hitachi SU-70 and a JEM 2100 LaB6 electron microscope, respectively. The argon (Ar) adsorption-desorption isotherms were measured using an Autosorb-iQ analyzer (Quantachrome Instruments) at 87 K. Prior to the measurement, samples were evacuated overnight at 623 K and 1 mm Hg. Si and Al contents of zeolite samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500 dual view). The magic angle spinning NMR (MAS NMR) spectra were recorded at a field of 7 T (Bruker DSX 300) and 9.4 T (Bruker Avance III 400) for ²⁹Si and ²⁷Al, respectively. ²⁹Si MAS NMR spectra were recorded at 59.63 MHz using 4 mm rotors at a spinning speed of 10 kHz, a dwell time of 19.95 μs, a $\pi/2$ pulse of 5.0 μs, and a recycle delay of 60 s. The spectra were referenced with respect to 3-(trimethylsilyl)-1-propanesulfonic acid salt. ²⁷Al MAS NMR spectra were recorded at 104.21 MHz using 4 mm rotors at 10 kHz spinning speed, a dwell time of 1.006 μs, a selective $\pi/10$ pulse of 3 μs, and a recycle delay of 2 s. An aqueous solution of aluminum nitrate (0.1 M) was used as the reference. The acidity of the zeolite was evaluated by ammonia temperature programmed desorption (NH₃-TPD) method using an Autosorb-iQ instrument

(Quantachrome, ASIQM0000-4) equipped with a thermal conductivity detector (TCD). In the measurement, 0.1 g catalyst sample was loaded into a quartz reactor and heated at a rate of 10 K min⁻¹ to 873 K under He (40 mL min⁻¹) and maintained at this temperature for 2 h. After being cooled to 373 K under He stream, the catalyst sample was exposed to NH₃ (30 mL min⁻¹, ultrapure, Airgas) stream for 0.5 h. Physisorbed NH₃ was then removed by flowing He gas (40 mL min⁻¹) for 2 h. Afterwards, the catalyst sample was ramped to 1023 K at a ramp rate of 10 K min⁻¹, and the NH₃-TPD profile was recorded during this step.

2.4. Determination of external and internal Brønsted acid sites

The total number of Brønsted acid sites, defined as total acid sites, was determined via dimethyl ether (DME) titration experiment given that the Brønsted acid sites participate in reactions of DME with H⁺ to form surface methyl groups, $\text{CH}_3\text{OCH}_3 + 2[\text{SiO}(\text{H})\text{Al}] = 2[\text{SiO}(\text{CH}_3)\text{Al}] + \text{H}_2\text{O}$. [39, 40] The number of active Brønsted acid sites on the external surface of zeolites, defined as external acid sites that comprise of acid sites on the geometrical external surface and in pore-mouth region of the catalysts, was measured by 2,6-di-tertbutyl-pyridine (DTBP) titration during methanol dehydration reactions since the bulky DTBP molecule has limited accessibility to acid sites located in micropores of the medium-pore zeolites [41, 42]. The experimental setup and reaction conditions for chemical titration of acid sites were same as those described in our previous publications. [35, 39, 43, 44] The Brønsted acid sites only accessible to DME titrant were defined as the internal acid sites. The fraction of external Brønsted acid sites was calculated by the ratio of the number of Brønsted acid sites accessible to DTBP titrant to the number of Brønsted acid sites accessible to DME titrant.

2.5. Catalytic conversion of benzyl alcohol in mesitylene

The liquid phase catalytic conversion of benzyl alcohol in mesitylene was conducted to examine the catalytic performance of the BBLM zeolite composites. The reaction setup consisted of a three-necked round bottom flask (100 mL) equipped with a reflux condenser and heated in a temperature controlled oil bath under atmospheric pressure and magnetic stirring (1" stirring bar, 500 rpm stirring speed) conditions. In a typical experiment, 15 mL of mesitylene was added to the desired amount (0.075 g) of zeolite catalyst. The reaction mixture was maintained for 0.5 h at the required reaction temperature (348 K) and stirring conditions (500 rpm) and then 0.25 mL of benzyl alcohol was added. This moment of adding benzyl alcohol to the reaction mixture was taken as the initial reaction time. Liquid samples were withdrawn at regular time intervals and analyzed by a gas chromatograph (Agilent 7890A) equipped with a methylsiloxane capillary column (HP-1, 50.0 m x 320 μ m x 0.52 μ m) connected to a flame ionization detector (FID) to calibrate and separate the reactants and products.

3. Results and discussion

3.1. BBLM structure formation assisted by dual templates

To examine the effect of dual templates on the formation of BBLM zeolite composites, the synthesis was comparatively carried out using the recipe comprised of TEAOH, C₂₂₋₆₋₆, as well as dual TEAOH and C₂₂₋₆₋₆ (molar ratio of C₂₂₋₆₋₆/TEAOH: 1/36, 3/36 and 9/36) templates, respectively. The usage of bare C₂₂₋₆₋₆ template in the synthesis led to amorphous product, while bare TEAOH or the combinational usage of TEAOH and C₂₂₋₆₋₆ templates resulted in crystalline zeolite products. Figure 1 shows the XRD patterns of the as-synthesized BEA and BBLM zeolite

composites. The co-existence of TEAOH and C₂₂₋₆₋₆ templates in the synthesis led to the crystallization of both BEA and MFI zeolites. An increase in concentration of C₂₂₋₆₋₆ in the recipe resulted in an increase in MFI zeolite quantity, as indicated by the increase in peak intensity of the MFI diffraction peaks in Figure 1. The emergence of the diffraction peak around $2\theta \sim 4^\circ$ in BBLM-9/36 suggests that a multi-lamellar MFI structure[45, 46] started to form in this synthesis recipe, while only disordered or one and half unit-cell thick MFI nanosheets formed in BBLM-1/36 and BBLM-3/36 composite zeolites.

The SEM and TEM observations were conducted to understand the morphological characteristics of the BBLM zeolite composites. Figure 2(A) shows that the BEA zeolite contains sphere-like particles with an average size of ~ 250 nm. When a small amount of C₂₂₋₆₋₆ was added into the BEA synthesis gel (C₂₂₋₆₋₆/TEAOH = 1/36, i.e., BBLM-1/36), the size of BEA particles was increased ~ 2 times and the very near surface seemed to be covered by a skin-like material (Figure 2(B)). BBLM-3/36 in Figure 2(C) shows that the particles have similar sizes to BEA particles, but a very rough surface comprised of interdigitated nanosheets was observed. A further increase in C₂₂₋₆₋₆ content in the synthesis, as shown by BBLM-9/36 (Figure 2(D)), led to aggregation of BEA particles which are covered by a 2D MFI “skin” layer. The SEM images demonstrate that the BEA and MFI zeolites in the BBLM-type zeolite composite are integrated into single particles, not a random physical mixture of both types of zeolite phases.

The integrity of the MFI and BEA zeolites in the BBLM zeolite composites was further examined by the TEM observation, as shown in Figure 3 and Figure S1 in the Supplementary Information. Figure 3(A)-(C) confirm the presence of single BEA zeolite particles with relatively smooth surfaces. Figure 3(D)-(F) show that BBLM-1/36 contains fractioned BEA particles with intraparticle voids (Figure 3(D)) and channeled surface (Figure 3(F)). The 2D MFI nanosheets

are observed in Figure 3(E), which lie in parallel with the BEA surface, contrast to the vertical epitaxial growth of 2D MFI nanosheets from MFI zeolite surface in our previous work[20, 35]. It should be mentioned that the number of 2D MFI nanosheets is not enough to fully cover the bulk BEA particle in BBLM-1/36 sample. BBLM-3/36 has a BEA/lamellar MFI composite structure (Figure 3(G)), in which a number of 2D MFI nanosheets aggregate and/or wrinkle together to form a ‘skin’ layer for bulk BEA zeolite particles. The bulk BEA was further fractioned into a nanosponge-like structure, which was verified by visualization of the center component in BBLM-3/36 (Figure 3(H)) after partially peeling off the ‘skin’-like MFI nanosheet shell by vigorous sonication. A closer look of the nanosponge-like structure (Figure 3(I)) illustrates that BEA particles with sizes of ~10-20 nm and internal voids with equivalent sizes co-exist uniformly through the center component. Some MFI nanosheets seem to penetrate into the nanosponge-like BEA zeolite, as shown in the inset image in Figure 3(H). The interface between MFI and BEA zeolites in the BBLM-3/36 sample shows MFI nanosheet stays closely on the surface of the BEA (Figure 3(I)). The intimate growth of some 2D lamellar MFI zeolite in the BEA zeolite body and more importantly the close contact between ultra-thin 2D MFI and BEA guarantees the communication between MFI and BEA components in the BBLM zeolite composites. Figure 3(J)-(L) demonstrate the structural features of the BBLM-9/36 sample, which contains nanosponge-like BEA in the center of the composite particle (Figure 3(K)) and 2D lamellar MFI on the surface, similar to BBLM-3/36. The thickness of the MFI component, i.e., the number of 2D MFI nanosheets, covered on the BEA surface, is increased (Figure 3(J) and (L)). The increase of C_{22-6-6} content in the synthesis recipe led to more 2D MFI in the BBLM zeolite composite. The SEM and TEM images show that the BBLM zeolite composites are not only a simple layout of one type of zeolite on the other, but also an interdigitated structure

extended to the bulk BEA component. Additionally, the bulk BEA is comprised of a hierarchical meso-/microporous structure. Therefore, it is expected that BBLM composite has intimate communication between micropores of two different types of zeolites, which was further studied by the catalytic reactions below.

3.2. Scheme for formation of BBLM zeolite composite

To understand the formation scheme of BBLM zeolite composite and the functionality of C₂₂₋₆₋₆ and TEAOH templates in the synthesis, the growth of the BBLM-3/36 as a function of the hydrothermal synthesis time (1, 3, 7 and 14 days, respectively) was examined. After 1 day of hydrothermal synthesis, the resultant sample mainly consisted of amorphous material, indicated by the featureless XRD pattern in Figure 4 and irregular particle shapes in Figure S2(A). When the hydrothermal synthesis was continued for 3 days, the BEA zeolite was formed, as indexed by the XRD diffraction peaks and the nearly spherical particles in Figure S2(B). The co-existence of ‘skin’-like material that stayed around the BEA particles was also observed in this sample. When the synthesis time was extended to 7 days, the XRD pattern in Figure 4 shows the appearance of MFI zeolite in the sample, and the as-obtained sample contains irregular small debris-like particles covered on the BEA zeolite (Figure S2(C)). The synthesis time of 14 days led to transformation of irregular small particles into lamellar nanosheet particles (Figure S2(D)) and the XRD diffraction pattern indicates that the as-crystallized material is MFI, besides the BEA component that has formed since 3 days of hydrothermal synthesis.

The Ar isotherms and non-local density functional theory (NLDFT) pore size distributions were further used to track the transformation of the materials in the BBLM-3/36 growth. Figure 5 illustrates that the BBLM-3/36 material has the type-IV isotherm with ~5 nm

mesopore after 1 day of hydrothermal synthesis, similar to aluminosilicate MCM-41 material[47]. After 3 days of synthesis, the isotherm of BBLM-3/36 exhibits both micro- and mesoporous features, with micropore size of ~ 0.61 nm and reduced mesoporosity compared to 1 day of synthesis. The appearance of the micropore size of ~ 0.61 nm confirms the crystallization of BEA zeolite in the synthesis. The decrease in mesoporosity and increase in microporosity (Table 1) as well as a left-shifting of micropore size (~ 0.58 nm, inset in Figure 5(B)) are observed after the synthesis time was extended to 7 and 14 days, respectively. The results suggest the growth of lamellar MFI on the BEA zeolite by consuming the amorphous materials existing in the sample. It should be noted that the textural properties of BBLM-3/36 after 7 days of synthesis remained similarly to that after 14 days, although the morphology was progressed into layered nanosheet structure.

Table 1. Textural properties of the BBLM-3/36 zeolite composite at different synthesis times determined from Ar isotherms.

Synthesis time	V_{micro}^a [cm ³ g ⁻¹]	S_{micro}^a [m ² g ⁻¹]	S_{ext}^a [m ² g ⁻¹]	V_t^b [cm ³ g ⁻¹]	V_{meso}^c [cm ³ g ⁻¹]	S_{BET}^d [m ² g ⁻¹]
1 day	0	0	781	1.005	1.005	781
3 days	0.033	119	538	0.875	0.842	658
7 days	0.110	224	328	0.976	0.866	552
14 days	0.118	239	331	1.012	0.894	570

^a Determined from t-plot method; ^b Determined by NLDFT method; ^c $V_{\text{meso}} = V_t - V_{\text{micro}}$; ^d Determined from Brunauer, Emmett, and Teller (BET) method.

The evolution of BBLM-3/36 structure with hydrothermal synthesis time suggests a possible growth scheme for the BBLM 2D-3D zeolite composite with the assistance of C₂₂₋₆₋₆ and TEAOH templates. In the initial stage of the synthesis, the zeolite synthetic gel formed

amorphous materials with ordered mesoporosity under the assistance of C₂₂₋₆₋₆ template. With the progression of the synthesis, the bulk BEA zeolite particles started to form with the assistance of TEOH template. The growth of bulk BEA zeolite was accompanied by the consumption of the amorphous ordered material. Upon extension of the synthesis time beyond 7 days, the crystallization of MFI zeolite directed by C₂₂₋₆₋₆ template occurred, and then the lamellar MFI structure evolved at the last stage of the synthesis (up to 14 days). The formation of the amorphous ordered phase followed by formation of the bulk BEA zeolite in the initial stage of the synthesis indicates the sequential functions of C₂₂₋₆₋₆ and TEOH, which was consistent with dual template synthesis using CTAB and TEOH templates[48]. In the later stage of the synthesis, a transformation of the amorphous material to crystalline lamellar MFI zeolite was realized under direction of C₂₂₋₆₋₆, and thus resulted in the formation of BBLM zeolite composite. A cooperative and sequential functioning between C₂₂₋₆₋₆ and TEOH is expected in the synthesis process because single C₂₂₋₆₋₆ or TEOH can only produce amorphous or bulk BEA particles, respectively, under the same synthesis conditions.

3.3. Textural properties of BBLM zeolite composites

Figure 6 shows the textural properties of the synthesized BBLM zeolite composites. For comparison purpose, lamellar MFI synthesized following the recipe reported by Ryoo et al.[37] was included in the analyses. Generally, BEA or BBLM composite samples have higher Ar uptake than the lamellar MFI (Figure 6(A)) because BEA has relatively large micropore sizes[49, 50]. At the relative pressure of $P/P_0 > 0.5$, the BBLM zeolite composites have higher Ar uptake than bare BEA zeolite due to the mesoporosity in the bulk BEA and lamellar MFI in the zeolite composite. The NLDFT pore size distribution data in Figure 6(B) reveals that the mesoporosity

increases from bare BEA, BBLM-1/36, BBLM-3/36 and then to BBLM-9/36 sample. All of these composite samples have higher mesoporosity than lamellar MFI zeolite, which is consistent with the morphologies determined from SEM and TEM observations above. A closer look on the micropore size distribution in the BBLM, BEA and lamellar MFI zeolite samples is shown in Figure 6(C). The bare BEA and lamellar MFI zeolites have the characteristic micropore sizes of 0.64 nm and 0.50 nm, respectively. The transition of the micropore pore sizes from BEA to MFI was achieved in the BBLM-1/36, BBLM-3/36, and BBLM-9/36, showing the micropore sizes center at 0.63 nm, 0.60 nm, and 0.55 nm, respectively. The cumulative pore volume versus the pore width of these samples (Figure 6(D)) further confirms the existence of both MFI and BEA zeolite frameworks in the BBLM zeolite composites.

The textural properties of the BBLM zeolite composites were also summarized in Table 2. The total pore volume (V_t), mesopore volume (V_{meso}), external surface area (S_{ext}), and Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of BBLM zeolite composite increase with increasing C_{22-6-6} concentration in the one-step dual template synthesis recipe. This is due to the facts of fractioning of bulk BEA into nanosponge-like structure and formation of mesoporous 2D lamellar MFI nanosheets directed by C_{22-6-6} template. The micropore volume (V_{micro}) and micropore surface area (S_{micro}) of these zeolite composites, however, decrease with an increase in C_{22-6-6} content due to the formation of more MFI zeolite that has smaller pore sizes. It should be noted that the measured micropore volumes of BBLM zeolite composites lie between the respective micropore volumes of the bare BEA ($0.184 \text{ cm}^3 \text{ g}^{-1}$) and lamellar MFI ($0.063 \text{ cm}^3 \text{ g}^{-1}$). Based on the micropore volumes in Table 2, the mass fraction of BEA in the BBLM composite particles can be calculated, showing that the mass fractions of BEA in BBLM-1/36, BBLM-3/36 and BBLM-9/36 are 89%, 45%, and 7%, respectively.

Table 2. Textural properties, acidity, and acid site distribution and fraction of BEA content in BBLM zeolite composites.

Catalyst	V_{micro}^a [cm ³ g ⁻¹]	S_{micro}^a [m ² g ⁻¹]	S_{ext}^a [m ² g ⁻¹]	V_t^b [cm ³ g ⁻¹]	V_{meso}^c [cm ³ g ⁻¹]	S_{BET}^d [m ² g ⁻¹]	Si/Al ^e	f_B^f (%)	f_{BEA}^g (%)	f_{BEA}^h (%)
BEA	0.184	349	145	0.506	0.559	493	22	85	100	100
BBLM-1/36	0.171	290	234	0.630	0.468	525	24	86	89	100
BBLM-3/36	0.118	239	331	1.012	0.894	570	27	79	45	90
BBLM-9/36	0.072	199	389	1.357	1.285	587	30	64	7	64
Lamellar MFI	0.063	141	169	0.462	0.399	310	49	27	0	0

^a Determined from t-plot method; ^b Determined by NLDFT method; ^c $V_{\text{meso}} = V_t - V_{\text{micro}}$; ^d Determined from Brunauer, Emmett, and Teller (BET) method. ^e Determined by ICP-OES analysis; ^f Fraction of external acid sites determined by DTBP titration; ^g Mass fraction of BEA determined based on the micropore volume extracted from Ar adsorption-desorption measurements. ^h Mass fraction of BEA determined based on the DTBP titration measurements.

3.4. Acidity of BBLM zeolite composites

In order to understand acidity and acid site accessibility in the BBLM zeolite composites, a combination of ICP-OES, DME and DTBP titrations, solid state NMR, and NH₃-TPD analyses were conducted. Table 2 shows that the Si/Al ratio is slightly increased from bare BEA to the BBLM-9/36 sample. The decrease in Al content with an increase in the lamellar MFI structure in the BBLM zeolite composites suggests that the acid site distribution may not be uniform in the BBLM zeolites. The accessibility of the acid sites was further explored by the DME and DTBP titrations, indicated by the fraction of acid sites (f_B) of each zeolite composite which represents the percentage of active sites that can be accessible by DTBP molecule. Table 2 shows that f_B decreases from 86% to 79% and then to 64% in the BBLM-1/36, BBLM-3/36, and BBLM-9/36 samples, respectively. The measured f_B in bare BEA and lamellar MFI are 85% and 27%, respectively. On the basis of DTBP molecule accessibility to active sites in bare BEA and

lamellar MFI samples, the mass fractions of BEA in each BBLM zeolite composite can be calculated to be 100%, 90%, and 64% for BBLM-1/36, BBLM-3/36, and BBLM-9/36, respectively. The higher mass fractions of BEA in BBLM composites estimated by this method compared to those calculated from micropore volumes of these zeolites suggests that the number of acid sites in the lamellar MFI is less than that in the BEA component in the BBLM zeolite composites.

Solid state NMR was employed to investigate the local bonding environment in the BBLM zeolite composites. Figure 7(A) shows the ^{29}Si single pulse (SP) NMR spectra of BEA and BBLM zeolites. Two resolved peaks (at -113 and -103 ppm) can be observed in the spectra, which correspond to crystallographically nonequivalent Q^4 tetrahedral sites (Q^n stands for $\text{X}_4\text{-nSi}[\text{OSi}]_n$) [51-54] and Q^3 sites arising from the silanol groups on the zeolite surface [55]. The slight increase in the Q^3 peak intensity from bare BEA to BBLM-9/36 suggests that more defects in the local bonding environment are formed which is caused by the formation of more 2D lamellar MFI in these BBLM zeolite composites. Figure 7(B) shows the ^{27}Al MAS NMR spectra of these zeolite samples. The peak at 55 ppm is assigned to the tetrahedrally coordinated framework aluminum (Al_F) [39, 54], while the peak at around 0 ppm is designated to an octahedral coordination of extra-framework Al (Al_EF). The fractions of the extra-framework Al in BBLM-1/36, BBLM-3/36 and BBLM-9/36 samples are calculated from the intensities of the peak around 0 ppm over the peak around 55 ppm in the ^{27}Al NMR spectra to be < 9%, suggesting that quite similar Al bonding environments exist in all the BBLM zeolite composite samples.

NH_3 -TPD profiles were measured to evaluate the strength of acid sites in the BBLM zeolite composites. Figure 8 shows two desorption peaks in the high temperature range of 450–

700 K and low temperature range of 350-450 K, respectively, in each BBLM composite, bare BEA and lamellar MFI samples. The high temperature desorption peak has been assigned to the adsorption of NH_3 by acid sites, while the low temperature desorption peak is ascribed to the physisorbed NH_3 in the catalysts.[56-59] When the sample is transited from BEA to BBLM and then to lamellar MFI zeolites in Figure 8, the high temperature and low temperature desorption peaks in the NH_3 -TPD profiles shift towards higher and lower temperatures, respectively. Concurrently, the peak intensities at both temperature ranges decrease. The broadening in peak width and decrease in peak height in Figure 8 indicate that the types and strengths of acid sites in BBLM zeolites are diversified, lying between bare BEA and lamellar MFI zeolites. Multiple types of acid sites with variant strengths have been identified to exist in lamellar MFI zeolites.[60-63] The integration of 2D lamellar MFI in the BBLM zeolite composites, spontaneously, leads to the diversification of the acidity in the resultant samples.

3.5. Catalytic performance of BBLM zeolite composites

The catalytic performance of the BBLM zeolite composites were tested in catalytic conversion of benzyl alcohol in mesitylene. Our previous studies[35, 38, 64] show that benzyl alcohol is simultaneously converted to 1,3,5-trimethyl-2-benzylbenzene and dibenzyl ether by mesitylene alkylation and benzyl alcohol self-etherification reactions, respectively (refer to the reaction scheme in Figure S2 of Supplementary Information). For comparison purpose, the same reaction was carried out over bare BEA and physical mixture of the BEA and lamellar MFI zeolites, respectively. The mass fraction of BEA in the physical mixture of BEA and lamellar MFI zeolites was controlled to be the same as that in BBLM-3/36 zeolite composite. Figure 9(A) shows that the conversion of benzyl alcohol at the reaction time of 7 h over the zeolite catalysts

follows the order of bare BEA < mixture of BEA and lamellar MFI < BBLM-1/36 < BBLM-9/36 < BBLM-3/36. A close look at the benzyl alcohol conversion in the initial stage of reaction (< 0.5 h, Figure 9(B)) indicates, however, the conversion of benzyl alcohol is in the order of bare BEA > BBLM-3/36 > BBLM-9/36 > mixture of BEA and lamellar MFI > BBLM-1/36. The discrepancy between the benzyl alcohol conversions over the catalysts at the initial and long-term reaction stages indicates the change in activity and stability of the catalysts through the course of the catalytic reactions. The highest benzyl alcohol conversion at reaction time less than 0.5 h and lowest conversion at reaction time of 7 h over bare BEA zeolite suggests that BEA has the highest activity and fast deactivation rate among all the tested catalysts. On the other hand, the BBLM zeolite composites have the relatively lower initial rates but much enhanced stability compared to bare BEA. Particularly, BBLM-3/36 has the comparable initial activity to bare BEA but with the highest stability in the tested zeolite samples. The physical mixture of BEA and lamellar MFI zeolite has only slightly better stability than BEA, although it has equivalent composition to BBLM-3/36 zeolite composite. The increase in 2D lamellar MFI content in the BBLM zeolite composites (from BEA to BBLM-1/36 and then to BBLM-3/36) led to an increase in both catalytic activity and stability in the catalytic benzyl alcohol reaction. A further increase (i.e., from BBLM-3/36 to BBLM-9/36), however, resulted in a reduction in the catalytic performances in this reaction.

The performance of BBLM zeolite composites in catalytic reactions depends on the acidity, pore structure, and crystallite size of both BEA and MFI zeolites.[65, 66] MFI zeolite consists of two interconnected 10-membered ring (10-MR) channel systems: one is straight running along the *b*-axis direction (0.53 x 0.56 nm) and the other is zigzag running parallel to the *a*-axis direction (0.51 x 0.55 nm). BEA zeolite structure consists of 12-MR straight channels of a

free aperture of 0.66 x 0.67 nm viewed along *a*-axis and 12-MR zigzag channels of 0.56 x 0.56 nm viewed along *c*-axis. The 3D pore systems and pores running along the *a*- and *b*-axes, respectively, in both BEA and MFI zeolites guarantee the ease of pore communication in the BBLM composites for any molecules smaller than micropore sizes of MFI. The ultra-thin lamellar MFI with straight channel normal to the BEA surface (visualized from TEM images in Figure 3) even intensify the communication between two zeolite structures.

The high initial reaction rates observed in Figure 9(A) across all the tested zeolite samples indicate that stronger acidity and larger micropore of BEA than 2D lamellar MFI are responsible for higher activity. This high activity also led to fast growth of alkylated aromatics, polyalkylaromatics, and even polycondensated carbonaceous products to deactivate the catalysts. Studies on Friedel-Crafts alkylation reactions over acidic zeolite catalysts have suggested that the high acidity, large zeolite micropore size, and larger zeolite crystallite sizes exacerbate the deactivation rates of the catalysts, which is due to the pore-mouth blockage or local poisoning of active sites by irreversible adsorption of carbonaceous residues.[67-72] Therefore, bare BEA zeolite in the present study had the fastest deactivation behavior. The BBLM zeolite composites contain 2D lamellar MFI zeolite nanosheet that has smaller micropore size than BEA, low acidity due to diversification of acid sites, together with small BEA crystallite sizes and mesoporosity due to fractioning of bulk BEA. All these characteristics contribute to the highly enhanced catalyst stability of BBLM zeolites. The decrease in the catalytic performance of BBLM-9/36 compared to BBLM-3/36 might be due to the thick coverage of the BEA zeolite surfaces by lamellar MFI (as shown by the TEM image in Figure 3 (J)-(L)), which prevents the facile mass transport. The ultra-thin (~3-10 nm) 2D MFI nanosheets functions as soft patches that conforms to the BEA nanosponge and lead to facile transport of reactant or products formed

in the center compartments in the BBLM-3/36 composite. The incomplete coverage of BEA in the BBLM-1/36 sample caused a slight increase in catalytic performance, but much lower than BBLM-3/36. Therefore, the unique structural scenario of BBLM-3/36 zeolite composite together with modulated acidity enabled the observed performances in the catalytic reactions of benzyl alcohol in mesitylene for BBLM zeolite composites.

4. Conclusions

The bulk BEA nanosponge-lamellar MFI (BBLM) zeolite composites were synthesized by a facile one-step dual template method. The TEOH and C₂₂₋₆₋₆ were employed as templates, which function sequentially and cooperatively in directing the bulk BEA and lamellar MFI formation and fractioning of BEA into nanosponge-like structure in the zeolite composites. The variation on the acidity, domain sizes of the 2D lamellar MFI and bulk BEA, and thus the textural properties of the BBLM zeolite samples were realized by simply modulating the content of the C₂₂₋₆₋₆ template in the synthesis. The concurrent occurrence of low acidity, small BEA crystallite sizes and mesoporosity in the BBLM zeolite composites enabled high catalytic activity and stability of BBLM zeolites in the reactions of benzyl alcohol with mesitylene. The conformation of ultra-thin 2D MFI nanosheets on BEA zeolite, in which straight micropore channels of MFI is normal to the BEA, allows a positive transmission way of reactant from the smaller micropore channel of MFI zeolite to the relatively larger one of BEA zeolite. The synthesis of BBLM bi-phase zeolite composites in single particles offers a pathway for tuning the physicochemical properties of zeolite materials, particularly beneficial for heterogeneous catalysis. The simple one-step dual template synthesis approach may prove to be a general

platform for hierarchical zeolite composite design at the unit-cell scales that could potentially be applicable to the other nanoporous materials when proper templates are selected.

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References

- [1] M. Moliner, C. Martínez, A. Corma, *Angew. Chem. Int. Ed.* 54 (2015) 3560-3579.
- [2] N. Rangnekar, N. Mittal, B. Elyassi, J. Caro, M. Tsapatsis, *Chem. Soc. Rev.* 44 (2015) 7128-7154.
- [3] E.T.C. Vogt, G.T. Whiting, A. Dutta Chowdhury, B.M. Weckhuysen, *Adv. Catal.* 58 (2015) 143-314.
- [4] Y. Bouizi, I. Diaz, L. Rouleau, V.P. Valtchev, *Adv. Funct. Mater.* 15 (2005) 1955-1960.
- [5] Y. Bouizi, G. Majano, S. Mintova, V. Valtchev, *J. Phys. Chem. C* 111 (2007) 4535-4542.
- [6] Y. Bouizi, L. Rouleau, V.P. Valtchev, *Chem. Mater.* 18 (2006) 4959-4966.
- [7] Y. Bouizi, L. Rouleau, V.P. Valtchev, *Microporous Mesoporous Mater.* 91 (2006) 70-77.
- [8] Z. Song, Y. Huang, L. Wang, S. Li, M. Yu, *Chem. Commun.* 51 (2015) 373-375.
- [9] C.L. Cavalcante, Jr., D.M. Ruthven, *Ind. Eng. Chem. Res.* 34 (1995) 185-191.

- [10] G.D. Pirngruber, C. Laroche, M. Maricar-Pichon, L. Rouleau, Y. Bouizi, V. Valtchev, *Microporous Mesoporous Mater.* 169 (2013) 212-217.
- [11] J. Čejka, S. Mintova, *Catal. Rev. Sci. Eng.* 49 (2007) 457-509.
- [12] J. Shi, Y. Wang, W. Yang, Y. Tang, Z. Xie, *Chem. Soc. Rev.* 44 (2015) 8877-8903.
- [13] Y. Wei, T.E. Parmentier, K.P. de Jong, J. Zecevic, *Chem. Soc. Rev.* 44 (2015) 7234-7261.
- [14] K. Zhang, M.L. Ostraat, *Catal. Today* 264 (2016) 3-15.
- [15] A. Ghorbanpour, A. Gumidyala, L.C. Grabow, S.P. Crossley, J.D. Rimer, *ACS Nano* 9 (2015) 4006-4016.
- [16] G. Wang, Y. Liu, J. Zheng, M. Pan, H. Zhang, B. Li, S. Yuan, Y. Yi, H. Tian, R. Li, *J. Mater. Res.* 30 (2015) 2434-2446.
- [17] Y. Zhang, N. Ren, Y. Tang, in: S. Mintova, M. Tsapatsis (Eds.) *Ordered Porous Solids*, Elsevier, Amsterdam, 2009, pp. 441-475.
- [18] S. Mintova, J. Čejka, *Stud. Surf. Sci. Catal.* 168 (2007) 301-326.
- [19] J. Zhang, W. Fan, Y. Liu, R. Li, *Appl. Catal. B: Environmental* 76 (2007) 174-184.
- [20] W.-g. Kim, X. Zhang, J.S. Lee, M. Tsapatsis, S. Nair, *ACS Nano* 6 (2012) 9978-9988.
- [21] S. Nair, M. Tsapatsis, L. A. Villaescusa, M. A. Camblor, *Chem. Commun.* (1999) 921-922.
- [22] T. Okubo, T. Wakihara, J. Plévert, S. Nair, M. Tsapatsis, Y. Ogawa, H. Komiyama, M. Yoshimura, M.E. Davis, *Angew. Chem. Int. Ed.* 40 (2001) 1069-1071.
- [23] Z. Wang, W. Wan, J. Sun, W. Carrillo-Cabrera, D. Gruner, X. Yin, S. Qiu, G. Zhu, X. Zou, *CrystEngComm* 14 (2012) 2204-2212.
- [24] Y.-Q. Deng, W.-F. Zhou, H.-M. Lv, Y.-Y. Zhang, C.-T. Au, S.-F. Yin, *RSC Adv.* 4 (2014) 37296-37301.

- [25] A.M. Goossens, B.H. Wouters, V. Buschmann, J.A. Martens, *Adv. Mater.* 11 (1999) 561-564.
- [26] D. Kong, J. Zheng, X. Yuan, Y. Wang, D. Fang, *Microporous Mesoporous Mater.* 119 (2009) 91-96.
- [27] M. Okamoto, Y. Osafune, *Microporous Mesoporous Mater.* 143 (2011) 413-418.
- [28] A.S. Kovo, E. Opuoma, S.C. Olu, M.O. Eloga, *JMEST* 2(2015) 1400-1407.
- [29] X. Qi, D. Kong, X. Yuan, Z. Xu, Y. Wang, J. Zheng, Z. Xie, *J. Mater. Sci.* 43 (2008) 5626-5633.
- [30] Z. Xie, Z. Liu, Y. Wang, Q. Yang, L. Xu, W. Ding, *Int. J. Mol. Sci.* 11 (2010) 2152.
- [31] E. de Vos Burchart, J.C. Jansen, H. van Bekkum, *Zeolites*, 9 (1989) 432-435.
- [32] J. Zheng, X. Zhang, Y. Wang, Y. Bai, W. Sun, R. Li, *J. Porous Mater.* 16 (2009) 731-736.
- [33] W. Schwieger, A.G. Machoke, T. Weissenberger, A. Inayat, T. Selvam, M. Klumpp, A. Inayat, *Chem. Soc. Rev.* 45 (2016) 3353-3376.
- [34] L. Emdadi, D. Liu, *J. Mater. Chem. A* 2 (2014) 13388-13397.
- [35] L. Emdadi, S.C. Oh, Y. Wu, S.N. Oliaee, Y. Diao, G. Zhu, D. Liu, *J. Catal.* 335 (2016) 165-174.
- [36] R.F. Lobo, S.I. Zones, M.E. Davis, *J. Inclus. Phenom. Mol.* 21 (1995) 47-78.
- [37] M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, *Nature* 461 (2009) 246-249.
- [38] L. Emdadi, Y. Wu, G. Zhu, C.-C. Chang, W. Fan, T. Pham, R.F. Lobo, D. Liu, *Chem. Mater.* 26 (2014) 1345-1355.
- [39] D. Liu, A. Bhan, M. Tsapatsis, S. Al Hashimi, *ACS Catal.* 1 (2011) 7-17.
- [40] P. Cheung, A. Bhan, G. Sunley, D. Law, E. Iglesia, *J. Catal.* 245 (2007) 110-123.
- [41] D. Fărcașiu, R. Leu, A. Corma, *J. Phys. Chem. B* 106 (2002) 928-932.

- [42] J. Macht, C.D. Baertsch, M. May-Lozano, S.L. Soled, Y. Wang, E. Iglesia, *J. Catal.* 227 (2004) 479-491.
- [43] Y. Wu, L. Emdadi, S.C. Oh, M. Sakbodin, D. Liu, *J. Catal.* 323 (2015) 100-111.
- [44] Y. Wu, L. Emdadi, Z. Wang, W. Fan, D. Liu, *Appl. Catal. A: General* 470 (2014) 344-354.
- [45] K. Na, M. Choi, W. Park, Y. Sakamoto, O. Terasaki, R. Ryoo, *J. Am. Chem. Soc.* 132 (2010) 4169-4177.
- [46] W. Park, D. Yu, K. Na, K.E. Jelfs, B. Slater, Y. Sakamoto, R. Ryoo, *Chem. Mater.* 23 (2011) 5131-5137.
- [47] Q. Lei, T. Zhao, F. Li, L. Zhang, Y. Wang, *Chem. Commun.* (2006) 1769-1771.
- [48] W. Guo, C. Xiong, L. Huang, Q. Li, *J. Mater. Chem.* 11 (2001) 1886-1890.
- [49] J.B. Higgins, R.B. LaPierre, J.L. Schlenker, A.C. Rohrman, J.D. Wood, G.T. Kerr, W.J. Rohrbaugh, *Zeolites* 8 (1988) 446-452.
- [50] J.M. Newsam, M.M.J. Treacy, W.T. Koetsier, C.B.D. Gruyter, *Proc. R. Soc. London A* 420 (1988) 375-405.
- [51] R. Aiello, F. Crea, F. Testa, G. Demortier, P. Lentz, M. Wiame, J.B. Nagy, *Microporous Mesoporous Mater.* 35-6 (2000) 585-595.
- [52] S.L. Burkett, M.E. Davis, *J. Phys. Chem.* 98 (1994) 4647-4653.
- [53] M.A. Camblor, A. Corma, M.J. Diaz-Cabanas, C. Baerlocher, *J. Phys. Chem. B* 102 (1998) 44-51.
- [54] W. Kolodziejski, C. Zicovichwilson, A. Corma, *J. Phys. Chem.* 99 (1995) 7002-7008.
- [55] S. Maheshwari, C. Martínez, M. Teresa Portilla, F.J. Llopis, A. Corma, M. Tsapatsis, *J. Catal.* 272 (2010) 298-308.
- [56] H. Liu, Y. Li, W. Shen, X. Bao, Y. Xu, *Catal. Today* 93-95 (2004) 65-73.

- [57] D. Ma, W. Zhang, Y. Shu, X. Liu, Y. Xu, X. Bao, *Catal. Lett.* 66 (2000) 155-160.
- [58] Y. Xu, J. Wang, Y. Suzuki, Z.-G. Zhang, *Appl. Catal. A: General* 409–410 (2011) 181-193.
- [59] Q. Zhao, W.-H. Chen, S.-J. Huang, Y.-C. Wu, H.-K. Lee, S.-B. Liu, *J. Phys. Chem. B* 106 (2002) 4462-4469.
- [60] C. Jo, R. Ryoo, N. Zilkova, D. Vitvarova, J. Cejka, *Catal. Sci. Technol.* 3 (2013) 2119-2129.
- [61] J. Jung, C. Jo, F.M. Mota, J. Cho, R. Ryoo, *Appl. Catal. A: General* 492 (2015) 68-75.
- [62] W. Kim, R. Ryoo, *Catal. Lett.* 144 (2014) 1164-1169.
- [63] Y. Seo, K. Cho, Y. Jung, R. Ryoo, *ACS Catal.* 3 (2013) 713-720.
- [64] Y. Wu, Z. Lu, L. Emdadi, S.C. Oh, J. Wang, Y. Lei, H. Chen, D.T. Tran, I.C. Lee, D. Liu, *J. Catal.* 337 (2016) 177-187.
- [65] S. Bhatia, J. Beltramini, D.D. Do, *Catal. Rev. Sci. Eng.* 31 (1989) 431-480.
- [66] P.C. Mihindou-Koumba, H.S. Cerqueira, P. Magnoux, M. Guisnet, *Ind. Eng. Chem. Res.* 40 (2001) 1042-1051.
- [67] S. Al-Khattaf, S.A. Ali, A.M. Aitani, N. Žilková, D. Kubička, J. Čejka, *Catal. Rev. Sci. Eng.* 56 (2014) 333-402.
- [68] J. Čejka, B. Wichterlová, *Catal. Rev. Sci. Eng.* 44 (2002) 375-421.
- [69] J.J. Chiu, D.J. Pine, S.T. Bishop, B.F. Chmelka, *J. Catal.* 221 (2004) 400-412.
- [70] A. Corma, F.J. Llopis, C. Martínez, G. Sastre, S. Valencia, *J. Catal.* 268 (2009) 9-17.
- [71] A. Feller, Reaction mechanism and deactivation pathways in zeolite catalysed: Isobutane/2-butene alkylation, PhD dissertation (Technischen Universität München), (2003).
- [72] C. Flego, G. Pazzuconi, E. Bencini, C. Perego, in: B. Delmon, G.F. Froment (Eds.) *Studies in Surface Science and Catalysis*, Elsevier, 1999, pp. 461-464.

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Figure 1. XRD patterns of BEA and BBLM zeolite composites after 14 days of hydrothermal synthesis. XRD pattern of lamellar MFI catalyst has been presented for comparison purpose.

Figure 2. SEM images of BEA (A), BBLM-1/36 (B), BBLM-3/36 (C), and BBLM-9/36 (D), respectively, after 14 days of hydrothermal synthesis.

Figure 3. TEM images of BEA (A), (B), and (C), BBLM-1/36 (D), (E), and (F), BBLM-3/36 (G), (H), and (I), and BBLM-9/36 (J), (K), and (L) zeolite composite catalysts with Si/Al=50 after 14 days of hydrothermal synthesis.

Figure 4. XRD patterns of BBLM-3/36 zeolite composite after 1 day, 3 days, 7 days, and 14 days hydrothermal synthesis, respectively.

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Figure 8. NH_3 -TPD profiles of the BEA, lamellar MFI and BBLM zeolite composites.

Figure 9. Conversion of benzyl alcohol in mesitylene versus reaction time of 7 h (A) and 2 h (B) over BBLM zeolite composite catalysts. BEA and physical mixture of BEA/lamellar MFI zeolites were included for comparison (0.075 g catalyst, 15 mL mesitylene, 0.25 mL benzyl alcohol, 348 K and stirring speed of 500 rpm).

Hierarchical 3D BEA nanosponge/2D ultra-thin MFI composite