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Organosilane with gemini-type structure as the mesoporogen for synthesis of hierarchical porous ZSM-5 zeolite

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ABSTRACT: A new kind of organosilane (1,6-bis(diethyl(3-trimethoxysilylpropyl)ammonium) hexane bromide) with a gemini-type structure was prepared and used as a mesoporogen for the synthesis of hierarchical porous ZSM-5 zeolite. There are two quaternary ammonium centers along with double hydrolysable -RSi(OMe)3 fragments in the organosilane, which results in a strong interaction between this mesoporogen and silica-alumina gel. The organosilane can be easily incorporated into ZSM-5 zeolite structure during the crystallization process, and it was finally removed by calcination leading to secondary pores in ZSM-5. The synthesized ZSM-5 has been systematically studied by XRD, nitrogen adsorption, SEM, TEM, TG and solid-state one-dimensional (1D) and two-dimensional (2D) NMR, which reveals information on its detailed structure. It has a hierarchical porosity system, which combines the intrinsic micropores coming from the crystalline structure and irregular mesopores created by the organosilane template. Moreover, the mesoposity including pore size and volume within ZSM-5 can be systematically tuned by changing the organosilane/TEOS ratios, which confirms this organosilane has high flexibility of using as template for the synthesis of hierarchical porous zeolite.

Introduction

Zeolites are crystalline microporous aluminosilicate materials.1 They have an open framework structure with well-defined pore architecture, high surface area, strong acidity, and good thermal stability.2 These unique properties enable them to become useful materials for a variety of applications in the area of catalysis, adsorption, separation, ion-exchange and functional materials.3 In the field of catalysis, zeolite play a vital role in petrochemical process for oil refining, which accounts for about 70% of catalyst in this process.4 The super catalytic performance of zeolites is mainly ascribed to their crystalline structure and unique porosity.

Till now, more than 220 different types of zeolite framework topologies have been reported and registered in the database of International Zeolites Association.5 However, none of them has an open pore size of above 1.5 nm. In such a case, the further application of zeolite materials in the catalytic reaction is substantially limited by its pore size and channel dimension. The diffusion in zeolite takes place in the configurational diffusion regime, and the diffusion rate is strongly restricted by its micropore size.6,7 Moreover, large molecules are not accessible to the active site located inside the zeolite crystal for the catalytic transformation. To date, the direct synthesis of zeolite materials with crystallographic mesopore and macropore system still remains a big challenge, because the formation of large membered-ring in zeolite structure is not a thermodynamic favored process.

Fortunately, the problem mentioned above could be resolved by an indirect strategy.8–18 The “high-way” could be made inside the zeolite crystal by the introduction of irregular mesopores or macropores into zeolite particle. Several methods have been developed for the creation of such large size pathways in zeolite. The treatment of zeolite with acid or base under mild condition will selectively dissolve silicon or aluminum atoms from zeolite crystal, which results in vacancies as mesopores in zeolite.19–25 Hard template, such as carbon particle, carbon nanotube and CaCO3 could be encapsulated or incorporated into zeolite during its crystallization process to introduce secondary pore inside zeolite crystal.23–25 The soft templates including meso-scale polymer and organo-silicon surfactant could be trapped into zeolite framework during the zeolite synthesis, and subsequent removal of these templates by a simple calcination will generate a large amount of mesopores in zeolite structure.26–32 Among these methods, the organosilane template developed by Ryoo et al. has shown high flexibility and versatility in the synthesis of mesoporous zeolite.33–38 Herein, we design a new kind of organosilane (1,6-bis(diethyl(3-trimethoxysilylpropyl)ammonium) hexane) with a gemini-type structure for the synthesis of mesoporous zeolite. This template can be easily prepared from the ordinary precursor by a simple synthesis route, and it has been used as an effective mesoporegen for the synthesis of hierarchical porous ZSM-5 zeolite.

Experimental section

1,6-dibromohexane (BrC6H12Br, 96%, Aldrich), diethyl(3-trimethoxysilylpropyl)amine (98%, Aldrich) and acetonitrile (CH3CN, Aldrich), tetraethoxysilane (TEOS, 98%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 40%, Alfa), aluminum nitrate (Al(NO3)3.9H2O, 98%, Aldrich), and distilled water were used as starting materials for the synthesis of organosilane template and ZSM-5 zeolite.

Synthesis

The preparation of organosilane (1,6-bis(diethyl(3-trimethoxysilylpropyl)ammonium) hexane bromide) with bi-quaternary ammonium head groups was prepared followed a typical quaternary ammonium synthesis procedure.39 1,6-dibromohexane (6.0 g, 23.7 mmol) and diethyl(3-trimethoxysilylpropyl)amine (11.7 g, 48.8 mmol) were mixed in 250 ml of acetonitrile containing a trace amount of KI as catalyst. The mixture was refluxed under an N2 atmosphere at 95 °C for 24 hours. After cooling to room temperature, the
products are labeled as ZSM55(1), ZSM55(2), ZSM55(3), ZSM55(4), and ZSM55(5), which corresponds to the product synthesized with BDSA/TEOS molar varying from 0.006 to 0.030. The following synthesis is a representative procedure for the preparation of conventional ZSM-5 zeolite solutions was prepared with the following molar composition: 1 Al₂O₃:60 SiO₂:15TPAOH:1800 H₂O. For the synthesis of hierarchical porous ZSM-5 zeolite, the BDSA was added into the synthesis with the BDSA/TEOS molar varying from 0.006 to 0.030. The following synthesis is a representative procedure for the preparation of hierarchical porous ZSM-5 zeolite with BDSA as the mesopore template. 0.29 g of Al(NO)₃ · 9 H₂O, 2.9 g of TPAOH and 11.1 g of deionized water were mixed together and stirred for 30 minutes to form a transparent solution. Then 4.8 of TEOS and 0.102 g of BDSA were added into the solution to yield a nominal molar composition of 0.36 BDSA: 1 Al₂O₃: 60 SiO₂: 15TPAOH: 1800 H₂O. The resulting mixture was stirred for additional 4 hours to form a homogeneous gel. Thereafter, the gel was transferred directly into a Teflon-lined autoclave for a hydrothermally synthesis at 170 °C for 7 days. After the completion of crystallization, the autoclave was cooled down, and the solid product was recovered by filtration, washed several times with deionized water, dried overnight at 120 °C, and followed by calcinations at 550 °C for 4 h in the flow of air. For clarity purposes, the zeolite products were labeled as ZSM-5(1), ZSM-5(2), ZSM-5(3), ZSM-5(4) and ZSM-5(5), which corresponds to the product synthesized with BDSA/SiO₂ ratios of 0.006, 0.012, 0.018, 0.024 and 0.030, respectively.

**Characterization**

X-ray diffraction (XRD) patterns of all samples were collected using a Bruker D8 Advanced A25 diffractometer (Cu K radiation, λ=1.5406 Å), operated at 40 kV and 40 mA. The data sets were acquired in step-scan mode over the 2θ range 10-90°, using a step interval of 0.05° and a counting time of 1s per step.

Nitrogen adsorption-desorption isotherms at 77 K were performed in a Micromeritics ASAP 2010 instrument. The analyses were carried out after outgassing the samples at 300 °C under vacuum overnight. The BET surface was evaluated from the relative pressure range of 0.05-0.35 in the nitrogen adsorption isotherm as range of linearity (using a molecular cross-sectional area for N₂ of 0.162 nm²). The pore size distribution was calculated from the desorption branch by DFT and BJH model.

The morphologies of the selected zeolites were recorded on an FEI Quanta 600 FEG environmental scanning electron microscope (ESEM). The sample was sputter-coated with gold prior to the measurement.

Transmission electron microscopy (TEM) images were obtained with a JEOL 2000 electron microscope operating at 200 kV.

Thermogravimetric analyses of the as-synthesized zeolites were performed on a Mettler-Toledo thermobalance. The samples were heated from 50 to 900 °C with a rate of 10°C/min in a flow of air (10 mL/min).

One-dimensional ¹H MAS, ¹³C and ²⁹Si CP/MAS as well as Two-dimensional double-quantum (DQ) solid state NMR spectra were performed on Bruker AVANCE III spectrometers operating at 600 MHz with a conventional double-resonance 3.2 mm CP/MAS probe. The 2D ¹H-¹³C heteronuclear correlation (HETCOR) solid state NMR spectroscopy experiments were recorded on a Bruker AVANCE III spectrometer using a 3.2 mm MAS probe. Detail of the NMR experimental procedure is provided in the supporting information.

**Result and discussion**

![Scheme 1. Structure of diethyl(3-trimethoxysilylpropyl)amine.](image1)

![Scheme 2. Structure of 1,6-bis(diethyl(3-trimethoxysilylpropyl)ammonium) hexane synthesized with 1,6-dibromohexane.](image2)

At the beginning, we attempted to introduce the diethyl(3-trimethoxysilylpropyl)amine (Scheme 1) into zeolite synthesis gel as the mesopore template for the preparation of hierarchical ZSM-5. However, the zeolite synthesis in the presence of this organosilane coupling agent did not produce the mesoporous zeolite. The diethyl(3-trimethoxysilylpropyl)amine is a typical silane coupling agent, which is a commercial available product with a wide applications in surface treatment. The diethyl(3-trimethoxysilylpropyl)amine can easily hydrolyze in the basic solution, and the silanol group will be formed in its structure. The silanol group can chemically bind to the SiO₂ gel, and thus an organo-inorganic silica hybrid composite will be formed. This uniform silica gel was submitted to the hydrothermal synthesis at 170 °C, and however two evident layers of product were always observed in the autoclave after the synthesis. The upper layer was a gel like product with low density; whereas the product at bottom was white crystal powder. These two layers of product were easily isolated with a spatula, and the separated products were first identified by...
XRD characterization. It was found that the upper layer product was amorphous silica and the lower layer was ZSM-5 crystal. This ZSM-5 product was further studied by nitrogen adsorption, showing that there was only an adsorption at relative low pressure (below P/P_{0}=0.1) and no evident adsorption was observable at high pressure. Therefore, it is a typical nitrogen adsorption behavior of microporous material, which is identical to that of conventional ZSM-5 reference. Based on these experimental observations, we believe that a phase separation between the organosilane and silica-alumina gel took place during the zeolite crystallization process. The formed Si-O-Si-R linker between the organosilane and SiO_{2} was not stable in the hydrothermal treatment at high temperature, and this Si-O-Si-R fragment seemed to be broken leading to a phase separation of organosilane and silica-alumina gel. Because of the incompatibility between silica and the organosilane, this organosilane was not incorporated into the ZSM-5 structure.

The interaction between diethyl(3-trimethoxysilyl)propyl)amine and silica-alumina is not strong enough to “encapsulate” the organosilane into the formed ZSM-5. The quaternization of tertiary amine moiety in diethyl(3-trimethoxysilyl)propyl)amine was thus proposed in order to increase the interaction between the organosilane and silica-alumina. This structure modification was achieved by a one-step simple synthesis between diethyl(3-trimethoxysilyl)propyl)amine and 1,6-dibromohexane. The modified product 1,6-bis(diethyl(3-trimethoxysilyl)propyl)ammonium) hexane (Scheme 2) has a gemini-type structure with long carbon chain, which possesses two quaternary ammonium cation centers and double trimethoxysilylpropyl groups. The presence of quaternary ammonium cation can significantly enhance the interaction between BDSA template and the silica-alumina gel due to the electrostatic interaction between positively charged quaternary ammonium and negatively charged silicate. Moreover, the BDSA has a larger size in comparison to diethyl(3-trimethoxysilyl)propyl)amine, which is beneficial for increasing its capability to create mesopores in zeolite. Further synthesis was carried out by adding this BDSA into the ZSM-5 synthesis precursor gel, and fortunately this new BDSA can act as mesoporogen template for the formation of hierarchical porous ZSM-5 zeolite. In this new synthesis, only one phase of solid product was found in the autoclave. Actually, the presence of BDSA in ZSM-5 synthesis decreases the crystallization rate. In contrast to conventional ZSM-5 synthesis, it took longer time to form crystalline mesoporous ZSM-5 product. The crystallization of conventional ZSM-5 with the tetrapropylammonium hydroxide as the structure-directing agent normally requires two days synthesis. However, the synthesis of ZSM-5 in the presence of BDSA requires 7 days to produce mesoporous ZSM-5 crystal. The lower crystallization rate of mesoporous ZSM-5 suggests that there is a strong interaction between BDSA and silica-alumina gel, which disturbs the zeolite crystallization process and slows down the growth of zeolite crystal. On the other hand this interaction would be finally helpful to incorporate BDSA into ZSM-5 structure.

A systematic investigation was carried out in this study on the synthesis of mesoporous ZSM-5 with the BDSA as the mesoporogen template. The ratios of BDSA/TEOS were varied from 0.006 to 0.030 in order to know the effect of this template on the structure and porosity of ZSM-5. In each synthesis, an overall zeolite yield of 70-80% was obtained. The XRD patterns of the synthesized samples are shown in Figure 1. All the zeolites exhibit the feature diffraction peaks located at 2θ of 7.9°, 8.8°, 21.1°, 23.9°, and 24.4°, which are exclusively ascribed to the ZSM-5 zeolite structure of a MFI topology. A zoom of 2θ diffraction range of 20-30° (Figure S3) of these samples shows there is no evident amorphous phase in the synthesized ZSM-5 zeolites. The intensity of these diffraction peaks decreases with the increase of BDSA/TEOS ratios, which indicates that more BDSA in the synthesis slightly decreases the crystallinity of ZSM-5.

The specific surface area and porosity of these zeolite samples were evaluated from the nitrogen adsorption characterization. The nitrogen adsorption isotherms of all the samples are shown in Figure 2, and the corresponding textural parameters for each sample are summarized in Table S1. Obviously, the conventional ZSM-5 zeolite exhibits a classic type I isotherm. A sharp increase of nitrogen uptake at a relative low pressure is observable in this sample, which is ascribed to the nitrogen filling within the micropore. There is no evident adsorption in p/p_{0} > 0.1 range, indicating there is no mesopore and macropore in conventional ZSM-5 sample. In the case of the zeolites synthesized with BDSA, the nitrogen adsorption behavior is totally different from that of conventional ZSM-5. In fact, the adsorption isotherms of these five samples exhibit both characters of Type I and IV isotherms along with a large H1-type hysteresis. Besides a micropore adsorption at the low pressure, a significant uptake in the p/p_{0} range of 0.7 to 1 is also measurable. This uptake along with a feature of H1-type hysteresis strongly suggests that there are mesopores in these samples. The pore size distribution of these mesopore
was calculated by a DFT model from the adsorption branch. The presence of mesoporosity in these samples is clearly evidenced from the pore size distribution from 10 to 30 nm with the peak at around 20 nm. The pore size distribution was also estimated by BJH model from the desorption branch (Figure S4), and it is consistent with the result from DFT model. The mesopore volume can be systematically controlled by the variation of BDSA/SiO$_2$ ratios. The mesopore volume increases from 0.19 cm$^3$/g to 0.68 cm$^3$/g, when the BDSA/SiO$_2$ ratios are changed from 0.006 to 0.030. Regarding the micropore volume, the sample synthesized with BDSA/SiO$_2$ ratio below 0.030 has quite similar micropore volume (around 0.11 cm$^3$/g), which is quite close to that in conventional ZSM-5 (0.12 cm$^3$/g). A small micropore volume (0.06 cm$^3$/g) is found in the sample synthesized with BDSA/SiO$_2$ ratio of 0.030. The small micro-porosity is due to a low crystallinity in this sample, which is also confirmed from the XRD characterization. With respect to the BET surface areas, they slightly increase with the BDSA/SiO$_2$ ratios, which is due to more mesopores in samples with high BDSA/SiO$_2$ ratios.

The evolution of the morphology of ZSM-5 synthesized with different BDSA content is clearly demonstrated from the SEM images (Figure 3). The conventional ZSM-5 synthesized in the absence of BDSA exhibits a well-defined shape and the particle has smooth surface. A coffin-like shape with a particle size of around 500 nm is observed in most particles of conventional ZSM-5. The introduction of BDSA into the synthesis indeed has an obvious effect on the morphology of ZSM-5, which suggests the presence of BDSA affects the crystal growth process. When a small amount of BDSA (BDSA/SiO$_2$=0.006) is used in the synthesis, the original shape of ZSM-5 (Figure 3b) is almost kept. With the increase of organosilane/SiO$_2$ to 0.012, the shape of ZSM-5 (Figure 3c) starts to turn into round and its surface becomes rough, which is a typical feature of the mesoporous zeolite synthesized by soft template. High organosilane/SiO$_2$ ratio of 0.024 yields the mesoporous ZSM-5 product (Figure 3d) without showing any regular morphology. It is therefore believed that the BDSA should have strong interaction with the silica-alumina gel, which affects the zeolite crystal growth process.

![Figure 2](image)  
**Figure 2.** Nitrogen adsorption (a) and corresponding pore size distribution (b) of conventional ZSM-5 and mesoporous ZSM-5 synthesized with different BDSA/SiO$_2$ ratios.

![Figure 3](image)  
**Figure 3.** SEM of conventional ZSM-5 and mesoporous ZSM-5 synthesized with different BDSA/SiO$_2$ ratios.
Figure 4. TEM of conventional ZSM-5 and mesoporous ZSM-5 synthesized with different BDSA/SiO$_2$ ratios.

The presence of the mesopores in the synthesized ZSM-5 zeolite is directly identified from the TEM investigation (Figure 4). The conventional ZSM-5 (Figure 4a, b) prepared without BDSA is a typical well-crystalline material, which shows regular shape and uniform size. No evident mesopore can be seen from this sample in the high magnification of TEM. Low BDSA/SiO$_2$ ratio (0.006) in the synthesis does not change the original morphology of ZSM-5 (Figure 4c, d). However, the big particle observed in low magnification is actually consisted of small unit, but they are packed together tightly to form big particle. In such a case, the mesopores between each small unit can be seen. When the synthesis of mesoporous ZSM-5 zeolite was perform at a high BDSA/SiO$_2$ ratio of 0.012, the ZSM-5 particle totally assembe from small units and it completely losses its well-defined morphology (Figure 4e, f). A large amount of mesopores can be clearly observed in this sample.

Figure 5. TG analysis on the as-synthesized conventional ZSM-5 and mesoporous ZSM-5 synthesized with different BDSA/SiO$_2$ ratios.

The TG analysis was performed on the as-synthesized zeolite samples to quantify the TPA$^+$ and BDSA template remaining in the structure (Figure 5). For the ZSM-5 synthesized without BDSA, the weight loss can be roughly assigned into two main stages. It is evident that no weight loss is detected below 360 °C. The first step of weight loss from 360 to 490 °C is ascribed to the oxidative decomposition of TPA$^+$ cation, which is trapped inside channels having strong interaction with the zeolite framework. The second weight loss starting from 490 °C is due to a complete elimination of organic residual decomposed from first step. Estimated from the TG analysis curve, the TPA$^+$ template represents about 8% in the as-synthesized conventional ZSM-5. In comparison to conventional ZSM-5, the as-synthesized hierarchical ZSM-5 exhibits multiple steps of weight loss, and the weight loss could be approximately assigned into four stages. Two steps of weight losses are observable below 360 °C. The weight loss below 200 °C mainly comes from the desorption of physically adsorbed molecules, such as water, amine inside zeolite pores. Obviously, the weight loss in this stage systematically increases with the increase of organosilane content used in the synthesis. This could be due to the fact that ZSM-5 prepared from high organosilane/SiO$_2$ ratios has larger total pore volume for the accommodation of much adsorbed molecules. The second weight loss begins from 200 °C, and extends to around 360 °C. It is should be noted that the TPA$^+$ structure directing agent cannot decompose at such low temperature, and we therefore assigned this weigh loss to the thermal pyrolysis of BDSA. The lower thermal decomposition temperature of this mesopore template is due to its longer hydrocarbyl chain in the structure, which makes it easy to degrade into small fragment in the presence of air. The last two steps of weight loss are ascribable to TPA$^+$ cations decomposition and the combustion of organic fragment from the degradation of TPA$^+$ and organosilane, respectively. The total weight loss in the as-synthesized mesoporous ZSM-5 is higher than that in conversion ZSM-5, and it systematically increases with the BDSA/SiO$_2$ ratios. The conventional as-synthesized ZSM-5 was used as a reference to estimate the amount of BDSA in the
as-synthesized mesoporous ZSM-5, and it is found that the BDSA content in ZSM-5 varies from 1% to 8.5%. From TG analysis, it can be concluded that a certain amount BDSA has been occluded into the ZSM-5 structure for the creation of secondary pores in zeolite.

Figure 6. Solid-state $^1$H MAS NMR spectra of conventional ZSM-5 and mesoporous ZSM-5.

Solid-state one-dimensional (1D) and two-dimensional (2D) nuclear magnetic resonance spectroscopy solid-state technique measurements were further applied to know the exact state of TPA$^+$ and BDSA templates in ZSM-5 zeolite. $^1$H MAS NMR spectra are shown in Figure 6 for the conventional ZSM-5 and hierarchical porous ZSM-5 zeolites. For the conventional ZSM-5, three typical peaks located at 0.9, 1.5 and 3.0 ppm, respectively can be ascribed to the protons in CH$_3$CH$_2$CH$_2$ of the TPA$^+$ molecules. Apart from these three peaks, additional resonances which are assigned to the adsorbed water molecules (at 4.3) and hydrogen-bonded protons (at 11.0 and 11.9 ppm) are also detected in the $^1$H MAS NMR spectra.$^{47}$ Moreover, all the proton signals in CH$_3$CH$_2$CH$_2$ group also exhibits auto-correlation peaks in the indirect dimension of the double-quantum (DQ) correlation spectrum (Figure S5), which indicates these protons are in methyl or methylene group. In the case of $^1$H MAS NMR spectra of hierarchical porous ZSM-5, the protons relative to different carbon are not well distinguished due to an overlap of the proton signals in BDSA structure. Approximately, the peaks at 0.9, 1.5, 3.0 and 3.2 are ascribable to the alkyl proton in both TPA$^+$ and BDSA. Also, the resonances from water molecules and hydrogen-bonded protons are detected in hierarchical ZSM-5.

Figure 7. Solid-state $^{13}$C MAS NMR spectra of conventional ZSM-5 and mesoporous ZSM-5.

The detailed structural information of template in zeolite can be elucidated from solid-state $^{13}$C cross-polarization magic-angle-spinning (CP-MAS) NMR spectra (Figure 7). The signals at 10.0 and 11.0 ppm (−CH$_3$), 16 ppm (−CH$_2$), and 63 ppm (N−CH$_3$) in conventional ZSM-5 are attributed to the carbon moieties related to the TPA$^+$ propyl chains. The narrow doublet of methyl signal is due to the TPA$^+$ structure directing agent located at the cross-sections between the zigzag and straight channels in MFI zeolite.$^{47,48}$ These signals are also detectable in the $^{13}$C CP-MAS spectra of the mesoporous ZSM-5 zeolite synthesized with BDSA template. Meanwhile, additional resonances emerging at 7, 8, 22, 26, 54, 57 and 59 ppm are resolved from the carbons in BDSA template. The details of the assignment of these peaks are shown in the Figure 7.
Solid-state two-dimensional (2D) nuclear magnetic resonance (NMR) spectroscopy is a more powerful technique to provide high resolution for the identification of local structure of the structure-directing TPA⁺ species and organosilane mesopore template trapped in zeolite structure. The 2D $^{13}$C-{$^1$H} HETCOR spectrum of conventional ZSM-5 is shown in Figure 8. Four strong correlation between proton and carbon signals ($\delta(^1H)/\delta(^{13}C)$) was observed in this spectra: both 0.9/10 and 0.9/11 are assigned to the methyl in propyl fragment; 1.5/16 and 3.0/63 are assigned to different methylene in propyl fragment. These correlations also exists in the 2D $^{13}$C-{$^1$H} HETCOR spectrum of hierarchical porous ZSM-5, suggesting the presence TPA⁺ species in this zeolite (Figure 8). Apart from these correlations, strong correlated signals are also observed at 3.0 ppm in the $^1$H dimension and at 54, 57, and 59 ppm in the $^{13}$C dimension, corresponding to three methylene moieties linked directly to quaternary ammonium center. The correlation between $^1$H dimension and $^{13}$C dimension at 1.5/22, 1.5/22 as well as 1.1/26 are ascribed to other three methylene groups. The methylene bonded to silicon atom in BDSA is evidenced from the correlation between 0.9 ppm in proton and 7 ppm in carbon signal. The only methyl group in BDSA could be resolved from the correlation between 0.9 ppm in proton and 8 ppm in carbon resonance. The solid-state nuclear magnetic resonance again unambiguously confirms the presence of BDSA in the hierarchical porous ZSM-5.

Solid-state single-pulse $^{29}$Si MAS NMR spectra were performed to further identify the BDSA in hierarchical porous ZSM-5. As shown in Figure 9, only the peaks from Q type of $^{29}$Si sites are found in conventional ZSM-5 zeolite, which are located at -105 for Q$^3$ species and -112 ppm for Q$^4$ species, respectively (Q$^n$ represents Si(OSi)$_n$(OH)$_{4-n}$). Apart from these Q$^n$Si sites signal, a T$^3$ $^{29}$Si signal (T$^n$ represents RSi(OSi)$_n$ structure) located at 63 ppm is distinguishable in the hierarchical porous ZSM-5. This signal clearly proves that the organosilane fragment has been bonded into zeolite framework.

The discussion above undoubtedly proves that hierarchical porous ZSM-5 zeolite could be synthesized with tetrapropylammonium as a structure-directing agent and BDSA as a mesoporogen. The tetrapropylammonium is known for directing the crystallization of zeolitic framework in the synthesis.
The double quaternary ammonium centers along with two hydrolysable \(-\text{RSi(Ome)}_2\) fragments in BDSA enable it to have strong interaction with silica-alumina gel, which results in its encapsulation into zeolite structure for creating mesopores. The synergetic cooperation between tetrapropylammonium and BDSA ultimately leads to the formation mesoporous zeolite.

Conclusions
In summary, a new kind of organosilane (1,6-bis (diethyl(3-trimethoxyxilpropyl)ammonium) hexane bromide) with a gemini-type structure was prepared from a simple synthesis route, and it was successfully used as a mesoporogen for the preparation of hierarchical porous ZSM-5 zeolite. The synthesized ZSM-5 zeolites were fully characterized by XRD, nitrogen adsorption, SEM, TEM, TG and Solid-state one-dimensional (1D) and two-dimensional (2D) nuclear magnetic resonance spectroscopy techniques. These hierarchical porous ZSM-5 zeolites possess two level of porosity: the microporosity arising from the crystalline structure, and the mesoporosity created by organosilane template. The micropore volume in hierarchical porous ZSM-5 is around 0.11 cm\(^3\)/g, which is close to that in conventional ZSM-5 zeolite. The mesopore size distribution is in the range of 10 to 30 nm, and the mesopore volume could be tuned from 0.06 to 0.60 cm\(^3\)/g by changing the organosilane/SiO\(_2\) ratios. The incorporation of organosilane into the ZSM-5 structure which finally leads to the mesoporosity within the zeolite particles was confirmed by the solid-state NMR characterization. This effective mesopore template has shown high flexibility in the synthesis of hierarchical porous ZSM-5 zeolite, which could be applied for the preparation of other types of mesoporous zeolites.

ASSOCIATED CONTENT
Supporting Information. \(^1\)H NMR, \(^13\)C NMR, XRD and DQ solid state NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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- Hydrothermal synthesis
- Structure-directing agent
- Mesopore gen
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