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Synthesis of core-shell ZSM-5@meso-SAPO-34 composite and its application in methanol to aromatics

Ling Zhang, Zhong-Xiang Jiang, Yue Yu, Chong-Shuai Sun, Yu-Jia Wang, Hai-Yan Wang

A core/shell-structured ZSM-5@meso-SAPO-34 composite catalyst was hydrothermally synthesized through overgrowing SAPO-34 molecular sieve on the external surface of ZSM-5. The catalyst was thoroughly characterized with regards to their crystallinity, morphology, elemental composition, surface area and pore volume, acidity. The catalytic performance of the as-obtained ZSM-5@meso-SAPO-34 was tested by the conversion of methanol to aromatics reaction. ZSM-5@meso-SAPO-34 exhibited higher aromatics selectivity relative to that of pristine ZSM-5 and its physical mixture with SAPO-34. ZSM-5@meso-SAPO-34’s unique catalytic synergistic behaviors were ascribed to having an effective enhancement of aromatization as a result of the acid sites on the external surface covered by SAPO-34 shell.

1. Introduction

Currently, processes like the production of aromatics, including benzene, toluene, and xylene (BTX) are of great significance in the petrochemical industry. Classically, the production of aromatics mainly relies on the catalytic reforming of naphtha. Other alternate processes, such as methanol-to-aromatics (MTA) as replacement for the fossil-based processes have grown to be a new focus for the production of aromatics, owing to the rapid diminishing of fossil resources. Recent studies have demonstrated that methanol can be selectively converted to aromatics by using zeolite-based materials.

Aluminosilicate ZSM-5 zeolite, as a shape selective catalyst, has been extensively applied in the fields of petrochemical industry, and the fine chemical industry involving the MTA process. Furthermore, it possesses MFI-type topology connected by two types of 10-membered ring channels, desirable catalytic properties, e.g., high surface area, thermal stability and acidity, as well as adjustable pore size comparable to the molecular dimension of BTX. Accordingly, ZSM-5 zeolite exhibits both higher catalytic activity and remarkable selectivity to aromatics in the process of aromatization. However, the catalytic activity and selectivity for aromatics formation are usually alleviated significantly by deactivation and formation of coke associated with carbon deposition, which may lead to the covering of the active sites on the external surface. Additionally, acid sites on the external surface of ZSM-5 can enhance effectively the BTX-selectivity as well as side reactions, which inevitably influence the catalyst BTX-selectivity. Therefore, it is highly desirable to develop suitable catalysts for the production of aromatics. In order to obtain higher catalytic properties, various strategies have been attempted to reduce contributions from external surface acid sites via introduction of mesopores. Nevertheless, it may still result in partial destruction and species deposition in the pore structure, consequently influencing zeolite molecular transport properties.

Recent progress has demonstrated that fabrication of core-shell composite materials have paid particular attention to the fields of catalysis due to their acidic properties of the external surface of zeolites and diffusion efficiency can be altered in a desired way. Besides, it is noteworthy that core-shell composite materials show their synergetic effects and the multifunctional properties, e.g., nanoarchitectures, alterable compositions and sizes in catalytic reactions. Generally, the synthesis of uniform core-shell materials contains various synthetic approaches such as polytypism and epitaxy or overgrowth. Particularly, overgrowth on different materials can combine their different intrinsic properties based on structure and acidity. For instance, ZSM-5/SAPO-11 composites were synthesized by the in situ overgrowth, composed of an acidic H-ZSM-5 zeolite core covered with a SAPO-11 shell. It has been reported previously that the core-shell type composites have desirable acidity, which is favourable to enhance the synergism effect between Brønsted and Lewis acids. In addition, binary structure ZSM-5/SAPO-5 composite zeolites synthesized by overgrowing SAPO-5 over the crystal surface of ZSM-5 have shown a higher propylene yield and conversion of heavy oil, and a striking decrease in the number of surface active sites. More recently, ZSM-5/SAPO-34 composites with binary structures have been successfully fabricated employing pre-heated ZSM-5 suspension followed by secondary growth of SAPO-34 layer, which represented excellent catalytic performance and synergetic effect between ZSM-5 and SAPO-34 in propane dehydrogenation reaction. Despite the above described references, reports on the synthesis and application of ZSM-5/SAPO-34 core-shell structure composites are restricted. To the best of our knowledge, the fabrication of this kind of composite zeolites applying overgrowth strategy and its application in the MTA have never been reported before.
methanol-to-olefin (MTO) reactions owing to its characteristic CHA topology and small 8-ring pore (3.8 Å × 3.8 Å) opening, as well as mild acidity. However, the diffusion of bulky molecules such as aromatics in the catalytic reaction severely is hindered by the microporous channels of the SAPO-34 zeolites, probably a result of the presence of the small pores. This limitation could be overcome if the channels of the mesopore SAPO-34 system is increased in the configuration of the core–shell ZSM-5@SAPO-34.

In this work, we demonstrate a facile two-step hydrothermal synthesis strategy to prepare a series of core–shell heterostructures ZSM-5@meso-SAPO-34 formed by the growth of SAPO-34 crystalline overlays on ZSM-5 nanocrystals, and mesoporous SAPO-34 layer synthesized using diethylamine (DEA) and tetrapropylammonium hydroxide (TPAOH) as co-templates. The crystallization process of the ZSM-5@meso-SAPO-34 co-crystalline zeolite was systematically investigated via the XRD, SEM, TEM, and nitrogen adsorption characterizations. As a hierarchical-structured composite catalyst, ZSM-5@meso-SAPO-34 exhibits enhanced catalytic properties in the methanol to aromatics with high selectivity for BTX opposed to the mechanical mixing.

2. Experimental

2.1. Material preparation

2.1.1. Synthesis of ZSM-5 and mesoporous SAPO-34.
Zeolite ZSM-5: ZSM-5 crystals with a Si/Al ratio of 25 were synthesized by hydrothermal method. For the typical procedure, colloidal silica sol (30%) was mixed with sodium aluminate and deionized water, and the mixture was stirred for 2 h before tetrapropylammonium hydroxide (TPAOH, >25%) was added. The molar ratio of the reactants in this synthesis was set as 1.0SiO₂:0.035Al₂O₃:0.07Na₂O:0.2TPAOH:3H₂O. The mixture was vigorously stirred for 4 h before it was transferred into a 100 ml Teflon-line autoclave, which was preheated to 40 °C for 12 h. Zeolite ZSM-5 was then obtained by hydrothermal treatment at 453 K for 48 h under autogenous pressure, after which the products were washed with distilled water and dried at 383 K. The final products were obtained after calcination at 823 K for 5 h to remove any organic substances.

Mesoporous SAPO-34: Mesoporous SAPO-34 was prepared hydrothermally using DEA and TPAOH as the co-templates with the molar composition of 1.0Al₂O₃:1.0P₂O₅:0.6SiO₂:2.0DEA:0.2TEAOH:0.03CTAB:60H₂O. TPAOH and DEA was employed as structure directing agent and co-template. Typically, 2.9 g pseudoboehmite (70% Al₂O₃ mixed with the required amount of deionized water was added to 2.7 ml tetraethylorthosilicate (TEOS) under room temperature. After successive stirring for 2 h, 2.7 ml phosphoric acid (85%) was dispersed drop into the above solution with continuous stirring for a further 2 h. Subsequently, 3.2 ml TPAOH and 4.2 ml diethylamine (DEA) was added to the mixture, and the mixture was stirred for 5 h. Next, the solution was mixed with an aqueous (80 g of water) solution of CTAB (0.21 g) and stirred for 4 h. Final mixture was transferred into autoclave and aged at 313 K overnight, and then the resulting gel was heated at 453 K for 48 h. After the resulting solid were thoroughly washed with deionized water, filtrated, and dried 12 h at 383 K. The organic template were eliminated by calcination at 823 K for 6 h.

2.1.2. Synthesis of core-shell ZSM-5@meso-SAPO-34. Core-shell ZSM-5@meso-SAPO-34 materials were synthesized by adding amount of premade ZSM-5 precursor into the gel mentioned in SAPO-34 in the absence of TPAOH and DEA. Next, TPAOH and DEA was subsequently added dropwise into the resultant solution under room temperature, then the mixture was dispersed in an aqueous solution of CTAB, continuous stirring until dispersed in a uniformed suspension. After aged at 313 K overnight, the gel was crystallized at 453 K for 1-3 days. Finally, the product was filtrated, washed thoroughly with deionized water, and then dried overnight at 383 K. The organic template were eliminated by calcination at 823 K for 4 h. The final samples were designated CZS (n), where n represents the weight ratio of ZSM-5 precursor and SAPO-34 suspension gel.

2.1.3. Synthesis of mechanical mixture of HZSM-5 and SAPO-34. For control experiment, a mechanical mixture of ZSM-5 and SAPO-34 was prepared by mixing ZSM-5 as-synthesized and amount of mesoporous SAPO-34 as-synthesized with a weight ratio of 2:1. The composite zeolites were calcined at 873 K for 4 h and crushed into 20-40 meshes, and was denoted as HZS.

2.2. Catalyst characterizations

X-ray diffraction (XRD) patterns were performed to determine the phase structures of the samples using D/max –RB diffractometer with Cu-Kα radiation (40 kV, 50 mA). The morphology and size of the crystal materials were measured by scanning electron microscopy (SEM) on a HITACHI SU-8010 microscope equipped with an energy-dispersive X-ray spectrometer (EDS), and operated at 10-15 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) of the samples were performed on a JEOL JEM-2100F with an acceleration voltage of 200 kV.

Infrared absorption spectra were recorded on a WQF-510 Fourier transform infrared (FT-IR) with the resolution of 4 cm⁻¹. The sample powder and KBr were extruded into the self-supported wafer with the mass ratio of 1:300, and the spectra were recorded in the range of 4000~4000 cm⁻¹. The adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2405 analyzer at -196 °C. Prior to the measurement, each sample (100mg) was degassed at 300 °C for 10 h. The specific surface areas were calculated according to the BET method. The surface area, pore volume of the samples was calculated by BET, t-plot and BJH methods, respectively.

The acidic properties of the samples were determined by NH₃-TPD with a Micromeritics AutoChem II 2920 in the range of 150 ~ 600°C at a ramp rate of 20 °C min⁻¹, and the desorbed ammonia was monitored by a gas chromatograph with a TCD detector.

2.3. Catalytic activity measurement

MTA reaction was carried out in a continuous-flow fixed-bed reactor with inner diameter of 10 mm. The catalyst (5 mL) was loaded into the reactor. Methanol was pumped into the reactor after the catalyst was pretreated in nitrogen flow at 748 k for 3 h. The reaction was conducted under pressure (0.5 MPa), weight hourly space velocity (WHSV =1.2 h⁻¹), and the desorbed ammonia was monitored by a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector and a capillary column.

3. Results and discussion

3.1. Preparation and characterization of core-shell ZSM-5@meso-SAPO-34

3.1.1 XRD
ZSM-5@meso-SAPO-34 is prepared with a hydrothermal method by adding an amount of premade ZSM-5 precursor into the gel of SAPO-34. As displayed in Fig.1, the X-ray diffraction patterns of a composite comprising ZSM-5 and SAPO-34 treated for 48 h with the weight ratio of ZSM-5 precursor and SAPO-34 suspension gel varying from 1 to 2. The samples both show well-resolved diffraction peaks at 2θ=7.9°, 8.8°, 22-25°, and 9.5°, which are assigned to the MFI and CHA phases, respectively. The XRD results indicate that the presence of both ZSM-5 and SAPO-34 in the intergrowth zeolites. In addition, it appears that the crystallinity and intensity of CZS-2 are higher than those of CZS-1. In contrast, the reflections of the ZSM-5@meso-SAPO-34 core-shell are very comparable to the weight ratio of ZSM-5 precursor and SAPO-34 suspension gel continuously increased, the crystallinity and intensity of CHA in the ZSM-5@meso-SAPO-34 was relatively weaker than that of pure of SAPO-34 crystal, also the intensity of MFI gradually increased. It is observed that the intensity of MFI is higher than that of CHA in Fig.2e. This can be explained as follows: On the one hand, the growth rate of the ZSM-5 phase is fast enough to surpass that of the SAPO-34 phase when crystallization time extended, the former will protrude out of the latter, as shown in Fig.3e. Therefore, the intensity of MFI is observed higher than CHA. On the other hand, because the weight ratio of ZSM-5 precursor and SAPO-34 suspension gel is 2, which may lead to peaks of ZSM-5 are higher than that of SAPO-34 phase during the secondary crystallization process.

### 3.1.2 SEM and TEM

To further demonstrate the targeted core-shell structure in ZSM-5@meso-SAPO-34, the scanning electron microscope (SEM) was used to characterize the morphology of the as-synthesized. As displayed in Fig.3a, the sample of ZSM-5 as-synthesized possesses very uniform spherical-like morphology with particle sizes ranging from 1 to 2 µm, and consisting of hexagonal columnar monocrystals. Similar morphologies are observed in ZSM-5@meso-SAPO-34 core-shell (Fig.3c-f), and the size of the crystal particle is in agreement with the above. It is attributed to the aggregation of ZSM-5 crystals under the action of Gibbs free energy. In addition, the morphology did not suffer any influence from the gel system of secondary crystallization.

Additionally, Fig.3 mainly displays the morphology of ZSM-5@meso-porous SAPO-34 synthesized during the different crystallization time. Initially, only uniform cubic-like morphology SAPO-34 phase with smooth crystal-face and particle sizes of ca.10µm in diameter was observed in the composite structure after 24 h crystallization (Fig.3b), which is typical morphology of CHA crystalline zeolite. Furthermore, no trace of ZSM-5 crystal was detected on the surface of ZSM-5@meso-SAPO-34 other than SAPO-34 phase. It was assumed that a layer densely shell of the SAPO-34 formation begins to occur on the surface of ZSM-5 and ZSM-5 further grew into core phase until entirely covered by SAPO-34 shell. However, it did not ensure the core-shell structure only relied on the results. When crystallization time was prolonged to 48 h (Fig.3c-d), spherical ZSM-5 particles began to appear on the surface of ZSM-5@meso-SAPO-34 and part of particle embedded into the composite structure, which changed the surface of skeletons from smoothness to coarseness. With the crystallization time increased to 72 h (Fig.3e-f), the amount of spherical ZSM-5 particles increased continuously and scattered on the surface of SAPO-34 shell. It suggests that ZSM-5 precursors gradually form in the original silicoaluminophosphate gel of SAPO-34 and further fabricates core-shell composite structure with an increase of crystallization time. Thus, appropriate synthesis time is a critical factor in the synthetic procedure for the forming of self-assembled core-shell structure.
and few spherical ZSM-5 particles, which in good agreement with SEM results (Fig.3d). Moreover, the lattice fringes between core and shell can be better observed in the enlarged image (Fig.5B). The results indicate that SAPO-34 was grown on the surface of ZSM-5 crystallites successfully and fabricated a core-shell structure composite.

![Fig.3](image3.png)

**Fig.3.** SEM images of ZSM-5 as-synthesized (a), hierarchically mesoporous SAPO-34 (b), core-shell ZSM-5@meso-SAPO-34 (CZS-2) synthesized at different crystallization time: 48 h; high-magnification (c) and corresponding low-magnification (d), 60 h (e), 72 h (f).

![Fig.4](image4.png)

**Fig.4.** SEM-EDS line scanning of ZSM-5@meso-SAPO-34 core-shell (CZS-2).

Fig.5. TEM images of core-shell ZSM-5@meso-SAPO-34 (CZS-2) synthesized from crystallization time at 48 h: Low-magnification (A), High-magnification (B), and 72 h Low-magnification (C), High-magnification (D).

3.1.3 FT-IR

FT-IR spectroscopy assists in identifying surface species of shell formed during the crystallization. Fig.6 displays FT-IR spectra of as-synthesized samples of ZSM-5, SAPO-34, ZSM-5@meso-SAPO-34 core-shell (CZS-2) and mechanical mixture (HZS). Framework vibrations at 455, 793 and 1094 cm\(^{-1}\) are observed in CZS-2, which corresponds to the Si–O bending mode vibration of tetrahedron inner links of T–O–T similar to those of ZSM-5 zeolites. In addition, two bands at 546 cm\(^{-1}\) and 640 cm\(^{-1}\) for CZS-2 and HZS are assigned to the asymmetric vibration of the five-membered rings of T–O–T (T=Si or Al) in the MFI frameworks and the bend of double 6-ring, respectively. These results indicate that the core-shell composite sample contains the primary units of CHA zeolites besides MFI-type zeolites, which further proved the forming of shell phase around core phase during the second crystallization.

It's worth noting that distinct absorptions appear at about 1221 cm\(^{-1}\). The peak for CZS-2 slightly shifts to 1218 cm\(^{-1}\) and the intensity is lower than those in HZS and pure ZSM-5. This phenomenon can be ascribed to a particular conjunction form of tetrahedrons and a special skeleton structure at the interface between core and shell zeolites. Because the 1221 cm\(^{-1}\) IR band is sensitive to change in the zeolite structure, the decrease in intensity proves it maybe includes the presence of CHA structure besides MFI phase. In case of CZS-2 and HZS, all bands exhibit a lower intensity corresponding to pure ZSM-5 and SAPO-34. It is inferred that the introduction of SAPO-34 (shell) decreases the crystallinity of synthesized core-shell zeolite, which is in accordance with the result of XRD.
3.1.4 \( \text{N}_2 \) adsorption-desorption characterization

\( \text{N}_2 \) adsorption-desorption isotherms and pore size distributions were used to estimate the porosity features of samples shown in Fig. 7. The initial part of all samples exhibit the type I isotherm curves with a sharp uptake at relative pressure \( \frac{P}{P_0} \) below 0.1, indicating a characteristic micropore framework. The ZSM-5@meso-SAPO-34 sample displays type IV isotherm with a hysteresis loop at a relative pressure \( \frac{P}{P_0} \) of 0.45-0.95, as a result of the presence of mesopores, which is associated with capillary condensation. Comparatively, the isotherm curves of ZSM-5@meso-SAPO-34 core-shell and mechanical mixture are more or less similar to those of pristine ZSM-5 zeolite combined micropores and mesopores. Whereas, typical hysteresis loops of them obviously show differently. Compared with the latter, the isotherm curve of the core-shell composite sample appears a relatively flat curve with a type H4 hysteresis loop. The phenomenon is associated with narrow slit-like pores in accordance with the IUPAC,\(^35\) which is attributed to the presence of a large number of mesopores in the structured composite. In contrast, the sharp uptake in the adsorption-desorption isotherms of the HZS sample can be observed at higher relative pressure \( \frac{P}{P_0} > 0.9 \). Perhaps it arises from the formation of an agglomerate of particles from ZSM-5 and SAPO-34.

The textural properties of samples are listed in Table 1, in which the specific BET surface area and total pore volume of pristine ZSM-5 as-synthesized are 398 m\(^2\)g\(^{-1}\) and 0.21 cm\(^3\)g\(^{-1}\) respectively, with lower contribution to mesopores from intrinsic ZSM-5, only 81 m\(^2\)g\(^{-1}\)and 0.13 cm\(^3\)g\(^{-1}\), respectively. In contrast, the ZSM-5@meso-SAPO-34 composites possess a lower micropore volumes but more mesopores. The micropore volumes and total pore volumes of ZSM-5@meso-SAPO-34 core-shell are higher than the mechanical mixture, with about 0.16 cm\(^3\)g\(^{-1}\) and 0.23 cm\(^3\)g\(^{-1}\), respectively. It is in accordance with the result of Fig. 7.

Table 1 Textual properties of the zeolites samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{meso}} ) (m(^2)g(^{-1}))</th>
<th>( S_{\text{micro}} ) (m(^2)g(^{-1}))</th>
<th>( S_\text{BET} ) (m(^2)g(^{-1}))</th>
<th>( V_{\text{meso}} ) (cm(^3)g(^{-1}))</th>
<th>( V_{\text{micro}} ) (cm(^3)g(^{-1}))</th>
<th>( V_{\text{total}} ) (cm(^3)g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>81</td>
<td>317</td>
<td>398</td>
<td>0.08</td>
<td>0.13</td>
<td>0.21</td>
</tr>
<tr>
<td>CZS-2</td>
<td>68</td>
<td>309</td>
<td>377</td>
<td>0.16</td>
<td>0.07</td>
<td>0.23</td>
</tr>
<tr>
<td>HZS</td>
<td>57</td>
<td>299</td>
<td>356</td>
<td>0.14</td>
<td>0.08</td>
<td>0.22</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>52</td>
<td>270</td>
<td>322</td>
<td>0.09</td>
<td>0.16</td>
<td>0.25</td>
</tr>
</tbody>
</table>

\(^a, b\) surface area covered by mesopores and micropores calculated from t-plot, respectively. \(^c\) total surface area calculated using BET equation in a range of relative pressure from 0.05 to 0.3. \(^d, e\) pore volume covered by mesopores and micropores calculated from t-plot; \(^f\) Single point pore volume at \( \frac{P}{P_0} = 0.99 \).
Table 2 Product distributions of methanol transformation over the investigated catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product distribution (wt. %)</th>
<th>Y_{BTX} (%)</th>
<th>S_{BTX} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_{1-5}</td>
<td>B</td>
<td>T</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>64.5</td>
<td>2.1</td>
<td>9.8</td>
</tr>
<tr>
<td>HZS</td>
<td>62.3</td>
<td>2.9</td>
<td>12.1</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>97.0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>CZS-1</td>
<td>50.1</td>
<td>3.4</td>
<td>10.5</td>
</tr>
<tr>
<td>CZS-1.5</td>
<td>45.8</td>
<td>4.1</td>
<td>11.2</td>
</tr>
<tr>
<td>CZS-2</td>
<td>42.9</td>
<td>4.2</td>
<td>13.4</td>
</tr>
<tr>
<td>CZS-2.5</td>
<td>43.8</td>
<td>4.3</td>
<td>13.1</td>
</tr>
</tbody>
</table>

*Reaction conditions: 0.5 MPa, 460 °C, WHSV=1.2 h\(^{-1}\), time-on-stream = 4 h. \(C_{1-5}\) alkenes, \(B\) Benzen, \(T\) Toluene, \(o-X\) ortho-Xylene, \(m-X\) meta-Xylene, \(p-X\) para-Xylene, \(C_{9}\) and \(C_{9}+\) aromatics.

3.2 The acidity of ZSM-5@meso-SAPO-34 core–shell catalysts

The surface acidities of the as-synthesized samples were determined by the temperature programmed desorption of ammonia (NH\(_3\)-TPD). As illustrated in Fig.8, the spectrums of the ZSM-5@meso-SAPO-34 display two distinct desorption peaks, the high-temperature peak at ca. 440 °C and low-temperature peak centered ca. 183 °C, which mainly arise from the strong and weak acid sites, respectively. It can be seen that the area of the high-temperature peak shows an obvious decrease, and simultaneously slightly shifts towards lower temperature relative to that of pristine ZSM-5. It can be deduced that a portion of the strong acid sites of ZSM-5 or the surface of ZSM-5 core may be covered and replaced by the weaker acidity of SAPO-34 shell after the incorporation of SAPO-34, which is in agreement with our previous results. In addition, the mechanical mixture shows lower temperature and smaller acidity relative to that of core-shell ZSM-5@meso-SAPO-34.

3.3 Catalytic performance

Methanol-to-aromatics (MTA) conversion as a typical shape-selective reaction was used to evaluate the catalytic performance of the ZSM-5@mesoporuous SAPO-34 catalysts. Its catalytic properties were compared with those of ZSM-5 and physical mixing ZSM-5/SAPO-34 catalysts. As shown in Table 2, SAPO-34 showed an extremely low yield of aromatics (2.5 %) on account of weak acidity as characterized by NH\(_3\)-TPD. The yields to aromatics are around 30.1 wt % on parent ZSM-5 zeolites with the Si/Al ratio = 25. However, ZSM-5 exhibits a slightly higher yield of 84.7 wt % to BTX. Compared with the purely acidic ZSM-5, ZSM-5/SAPO-34 (HZS) prepared by physical mixing improves the aromatics yield to 37.7 wt % and gives obviously higher selectivity for BTX (85.5 wt %). In contrast, ZSM-5@meso-SAPO-34 catalyst exhibited high catalytically activity. It is worth noting that the yield to aromatics is obviously enhanced with the increase in ZSM-5/SAPO-34 weight ratio. The selectivity to BTX and yields to aromatics at reaction temperature 460 °C and WHSV=1.2 h\(^{-1}\) reach 81.5%, 85.1% and 40.2%, 48.6%, respectively. This result should be related to the increased acidity and acid amount in ZSM-5, which caused the enhancement of aromatics formation. Moreover, the addition of suitable amounts of SAPO-34 in the core-shell structure can be beneficial to aromatics. The direct connection between cores and shells lead to the fabrication of hierarchical porous structure and enhance the accessibility to active sites.

Fig. 9 shows the methanol conversion and selectivity of benzene, toluene, and xylene with time on over ZSM-5@meso-SAPO-34. As presented in the figure, the selectivity of BTX rises with time and can reach the maximum of 85.1% under approaching 100% methanol conversion. Whereas, selectivity levels decrease with time. The change of BTX selectivity could be related to the coking effect, which reduced the pore size of SAPO-34 shell in ZSM-5@meso-SAPO-34.
Fig. 9. Conversion and selectivity of BTX with time on stream over ZSM-5@meso-SAPO-34. B: benzene, T: toluene, X: xylene.

4. Conclusions
The hierarchical pore system with core-shell structured ZSM-5@meso-SAPO-34 is successfully prepared by the hydrothermal method via introducing mesoporous SAPO-34 system. The characterization of SEM, BET, XRD, FTIR, TEM, EDS and NH\textsubscript{3}-TPD indicated that the cetyltrimethylammonium bromide (CTAB) and TPAOH aided prepared ZSM-5@mesoporous SAPO-34 core-shell composites had large surface area, and high catalytic activity for the MTA. These excellent physicochemical properties for ZSM-5@mesoporous SAPO-34 come from the synergistic effects of ZSM-5 and mesoporous SAPO-34, which shorten diffusion path length within the composites zeolites. Under optimal conditions, the methanol to aromatics on the ZSM-5@mesoporous SAPO-34 achieved a power conversion efficiency of approximately 100% and higher yield of aromatics, which is comparable with the performance of the ZSM-5 and mixture of ZSM-5 and SAPO-34. These results indicate that the ZSM-5@mesoporous SAPO-34 is a promising composite material and provides a novel way for the production of high-value aromatics.

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