

Article

Effects of Silicalite-1 Coating on the *p*-Xylene Selectivity and Catalytic Stability of HZSM-5 in Toluene Methylation with Methanol

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Abstract: The methanol–toluene alkylation process over zeolites catalysts offers a promising route for the production of *p*-xylene from low-cost feedstocks. Herein, we present a catalyst by preparing a core-shell aluminosilicate zeolite with an epitaxial silicalite-1 shell that passivates acid sites on the exterior surfaces. The *para*-selectivity was obviously increased due to the inhibition of the unselective isomerization of *p*-xylene over the external acid sites, and the open porous structure of the silicalite-1 shell ensured the mass transfer of reactants and products. Meanwhile, the carbon deposition was suppressed over HZSM-5@silicalite-1 catalysts, as a result of the decreased external acid sites. Furthermore, pulse chromatographic experiments revealed that the silicalite-1 coating could also improve the separation efficiency of *p*-xylene over *o*-xylene and *m*-xylene, due to the steric hindrance and extended diffusion path, resulting in a higher selectivity for *p*-xylene compared to that of the parent HZSM-5. The HZSM-5@4%S-1 catalyst showed the highest *p*-xylene selectivity (>80%) and methanol efficiency (66%), with good catalytic stability throughout the 170 h reaction time.

Keywords: heterogeneous catalysis; methanol toluene alkylation; HZSM-5; silicalite-1; *para*-xylene



Citation: Pan, X.; Huang, X.; Wang, R.; Zhang, H.; Wei, H.; Chen, J.; Liu, S.; Sun, L.; Xu, D.; Liu, Y. Effects of Silicalite-1 Coating on the *p*-Xylene Selectivity and Catalytic Stability of HZSM-5 in Toluene Methylation with Methanol. *Catalysts* **2022**, *12*, 1538. <https://doi.org/10.3390/catal12121538>

Academic Editor: Antonio Eduardo Palomares

Received: 7 November 2022

Accepted: 26 November 2022

Published: 29 November 2022

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1. Introduction

Para-Xylene (PX) is an important and highly desirable aromatic intermediate in the polyester, pharmaceutical, chemical fiber, and pesticide industries [1,2]. Currently, *p*-xylene is mainly produced from crude oil in a refinery, using an aromatic complex [3]. In addition, it can also be obtained from the processes of toluene disproportionation, C8 aromatic isomerization, and transalkylation of heavy aromatics [2,4]. However, these processes are typically accompanied by energy-intensive and high-cost separation technologies for mixed xylenes containing *para*- (*p*-), *meta*- (*m*-), and *ortho*- (*o*-) isomers, as the concentration of *p*-xylene in xylenes produced in these processes is close to the thermodynamic equilibrium composition (ca. 25%) [5,6]. In contrast, toluene methylation with methanol is a promising route for the production of *p*-xylene, based on shape-selective zeolite catalysts [6–8].

ZSM-5 has been widely used in the alkylation of toluene with methanol to produce *p*-xylene. ZSM-5 is a medium-pore zeolite with intersecting straight (0.54 nm × 0.56 nm) and sinusoidal or zigzag (0.51 nm × 0.54 nm) 10 membered ring channels [9], which are comparable to the size of *p*-xylene. However, the methylation of toluene on the parent HZSM-5 zeolite catalysts also yields a thermodynamic equilibrium mixture of xylene isomers [10], attributed to the isomerization of *p*-xylene to its isomers [6,11]. In order to obtain a higher selectivity toward *p*-xylene, an effective way to solve this problem is to modify HZSM-5 zeolite with addition of P [12], B [13], Mg [14], and Si [15], which

act as acid-site neutralizing agents and provide diffusion obstacles for *m*-xylene and *o*-xylene during the reaction. Although these modification techniques could increase the *para*-selectivity, the catalytic activity was inevitably inhibited, because of the decreased acidic sites in channels and the increased diffusion resistance of reactants and products, due to the narrowing of the pore-opening size [16]. Moreover, these modifiers are also susceptible to losses in the long run, giving a poor stability [2].

In addition, coating with an SiO₂ membrane over original HZSM-5 crystals has also proven to be effective for enhancing *p*-xylene selectivity [17–19], as this can cover strong acid sites on the external surface and sequentially inhibit the isomerization of *p*-xylene, which leaves the pores as well as the coke formation. Lercher et al. [17] reported novel mesoporous nano-sized ZSM-5 crystals covered with an external SiO₂ over-layer, which could promote the formation of *p*-xylene, without losing catalytic activity, compared to the parent zeolite. Li et al. [18] investigated the modification of ZSM-5 using chemical liquid deposition of silica (SiO₂-CLD), to obtain the highly shape-selective ZSM-5 catalyst through toluene disproportionation. They found that the acid amount of the modified ZSM-5 was less than that of parent ZSM-5, and a high selectivity of *p*-xylene of up to 96.2% was obtained over the modified ZSM-5 catalyst, compared to the 24.3% selectivity of *p*-xylene over the parent ZSM-5 catalyst. However, these catalysts coated with SiO₂ membranes are normally deactivated quickly due to the inhibition of reactants and the product mass transfer through the thick layer [19–21].

In contrast, epitaxial growing of a silicalite-1 layer over HZSM-5 crystal, to synthesize an HZSM-5@silicalite-1 catalyst, is a better technical alternative for solving the above problems [20,22]. Silicalite-1 has the same MFI crystal structure as the HZSM-5 substrate, resulting in the formation of a single-crystal-like zeolite catalyst. This contributes to the enhancement of catalyst stability. Meanwhile, the silicalite-1 shell can, not only passivate the external acid sites of ZSM-5, but is also expected to extend the diffusion path length of xylenes, without a blocking channel or narrowing of the pore opening size [23]. Longer diffusion pathways are favorable for high *para*-selectivity and shape selectivity, as this can promote the isomerization of *o*-xylene and *m*-xylene to *p*-xylene and then ensure the release of *p*-xylene as a primary product from the outside channels [2]. Nishiyama et al. [24] reported a single-crystal-like ZSM-5/Silicalite-1 composite catalyst, in which the thin layers of silicalite-1 were grown over the HZSM-5 crystal surface. This catalyst showed an excellent *para*-selectivity of 99% in the alkylation of toluene with methanol (toluene/methanol (mol/mol) = 1), although the total selectivity of xylene was as low as ~36%. Yin et al. [25] synthesized a core-shell HZSM-5@silicalite-1 composite by overgrowing silicalite-1 on the external surface of HZSM-5. The obtained catalyst exhibited a *para*-selectivity of up to 76%, with no evidence of deactivation during the time on stream of 3 h through toluene methylation with methyl bromide (toluene/CH₃Br (mol/mol) = 0.5).

Although many researchers have found the excellent *para*-selectivity of HZSM-5@silicalite-1 catalysts in the alkylation of toluene, the promotion function of the silicalite-1 shell on the MFI zeolite structure and reaction performance still need to be further studied and improved. Moreover, the effect of the silicalite-1 shell on the long-term catalytic stability in alkylation of toluene is poorly understood. Herein, a series of HZSM-5@Silicalite-1 zeolites were synthesized by hydrothermal crystallization strategy, using TPAOH as a template and TEOS as the silica source. The effects of the silicalite-1 shell on the acid properties, textural structure, and shape-selective function of HZSM-5 were investigated. In the toluene methanol alkylation reaction, the HZSM-5@Silicalite-1 core-shell catalyst showed a highest *p*-xylene selectivity of >80% with a toluene conversion of >10%, and it exhibited good resistance to coking and excellent durability in a 170 h service life test. The various catalysts were characterized by N₂ physisorption, SEM, XRD, XRF, XPS, ²⁷Al MAS NMR, FTIR spectra, pulse chromatography, and NH₃-TPD.

2. Results and Discussion

2.1. Catalysts Characterization

The as prepared XRD patterns of the parent HZSM-5 and HZSM-5@silicalite-1 samples are shown in Figure 1. All the samples had a good crystallinity and exhibited the typical diffraction peaks of MFI structure zeolites in $2\theta = 7.9^\circ, 8.8^\circ, 23.1^\circ, 23.3^\circ$, and 23.9° (JCPDS 44-0003) [20]. No characteristic signals of amorphous silica (in the region of $2\theta = 20\sim 30^\circ$) or other impurities could be observed in any samples, implying that the structure of HZSM-5 was not destroyed after silica coating and that a HZSM-5@silicalite-1 core-shell structure was synthesized successfully during this modification process [20,22]. This was further confirmed by SEM imaging. Figure 2 presents SEM images of the as-synthesized HZSM-5 and HZSM-5@silicalite-1 samples with different TEOS additions. The parent HZSM-5 crystal had a regular hexagonal prism shape with a smooth surface, and the particle size was ca. 2 μm . After silicalite-1 coating (Figure 2b–d), the HZSM-5@silicalite-1 core-shell samples retained their hexagonal prism morphology and a similar particle size, but with the surfaces roughened. It can clearly be observed that the silicalite-1 crystals were covered on the surface of HZSM-5, especially for the HZSM-5@2.5%S-1 and HZSM-5@4%S-1 samples. Meanwhile, we did find any amorphous silica species in the zeolites, indicating a relatively high crystallinity, which is consistent with the XRD results.

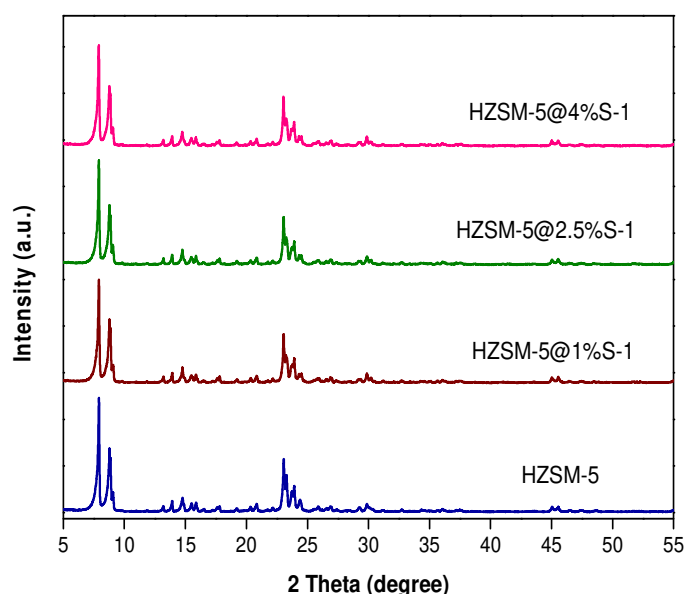


Figure 1. XRD patterns of the as prepared parent HZSM-5 and HZSM-5@silicalite-1 samples.

In order to investigate the effect of silicalite-1 coating on the textural structure of the HZSM-5@silicalite-1 catalysts, the as prepared parent HZSM-5 and HZSM-5@silicalite-1 samples were further characterized by low temperature N_2 adsorption–desorption experiment. As shown in Figure 3, all samples had typical type I nitrogen physical adsorption isotherms, indicating that all samples possessed a microporous structure [26]. At $p/p_0 = 0.1\text{--}0.2$, the adsorption isotherm appeared as a step-wise isotherm. This step-wise behavior can be explained by the fluid-to-crystalline-like phase transition of the adsorbed phase in the micropores and does not indicate any real porosity [27]. Moreover, as listed in Table 1, the BET surface area and total pore volume of the HZSM-5@2.5%S-1 and HZSM-5@4%S-1 samples were similar to those of the original parent HZSM-5, indicating the open porous structure of the silicalite-1 shell [25]. Hence, it was confirmed that the silica layer on the surface of HZSM-5 was crystalline silicalite-1 and that the shell formation did not result in appreciable pore blockage. However, for the HZSM-5@1%S-1 sample, it was found that the specific surface area ($297.2 \text{ m}^2/\text{g}$) was much lower than that of the original parent HZSM-5 ($352.6 \text{ m}^2/\text{g}$). Considering the SEM images in Figure 2b, we proposed that the lower TEOS

content in HZSM-5@1%S-1 sample was insufficient to form an epitaxial silicalite-1 shell on the external surface of HZSM-5, which led to the formation of new small silicalite crystals that blocked the pore openings of the parent HZSM-5. This was confirmed by the result that the micropore volume of the HZSM-5@1%S-1 sample ($0.07 \text{ cm}^3/\text{g}$) was obviously decreased compared with the parent HZSM-5 ($0.11 \text{ cm}^3/\text{g}$), according to the NL-DFT method. The corresponding pore size distribution showed that the average pore diameter of HZSM-5 and HZSM-5@silicalite-1 core-shell samples were ca. 0.5 nm. These results support that the pure siliceous silicalite-1 formed an epitaxial layer on the HZSM-5 crystals in this work, and the silicalite-1 coating did not affect the microporosity of the zeolites.

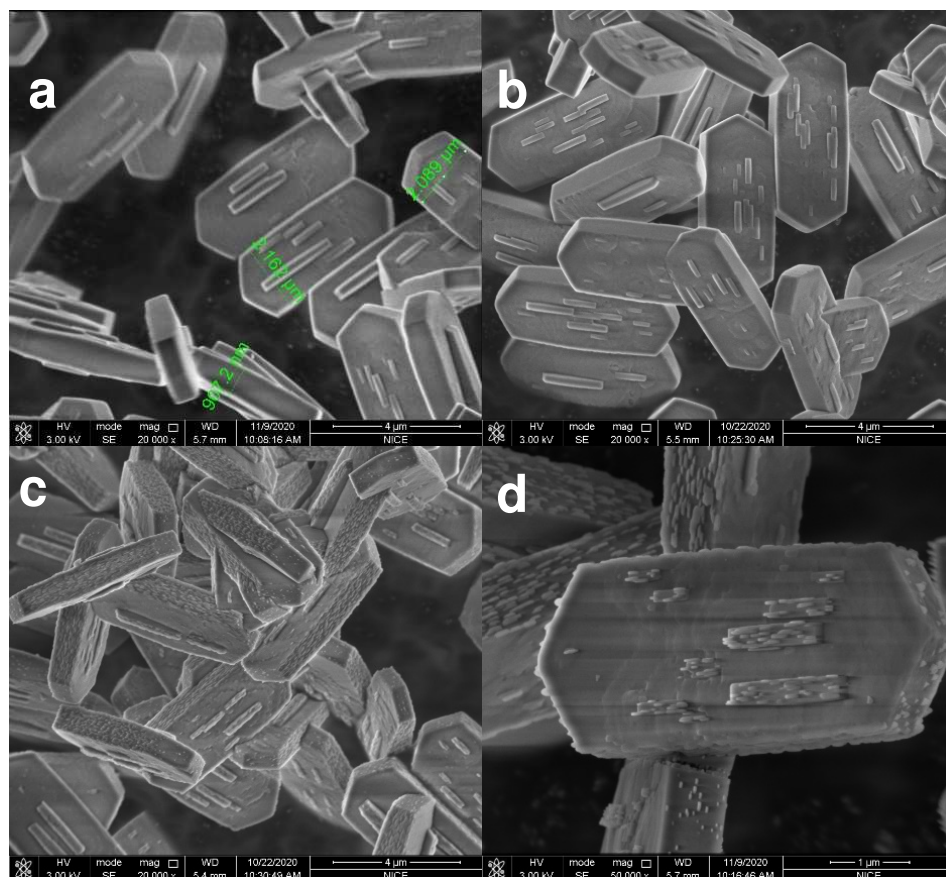


Figure 2. SEM images of (a) HZSM-5, (b) HZSM-5@1%S-1, (c) HZSM-5@2.5%S-1, and (d) HZSM-5@4%S-1 catalysts, as prepared.

Table 1. Textural properties of the as prepared parent HZSM-5 and HZSM-5@silicalite-1 catalysts.

Samples	S_{BET} m^2/g	S_{micro} m^2/g	S_{external} m^2/g	V_{total} cm^3/g	V_{micro} cm^3/g	V_{meso} cm^3/g	Si/Al Ratio	
							XRF	XPS
HZSM-5	352.6	269.3	83.3	0.19	0.11	0.08	186	72
HZSM-5@1%S-1	297.2	198.2	99.0	0.16	0.07	0.09	195	118
HZSM-5@2.5%S-1	348.7	253.5	95.2	0.19	0.10	0.09	196	128
HZSM-5@4%S-1	347.1	255.0	92.1	0.20	0.11	0.09	195	152

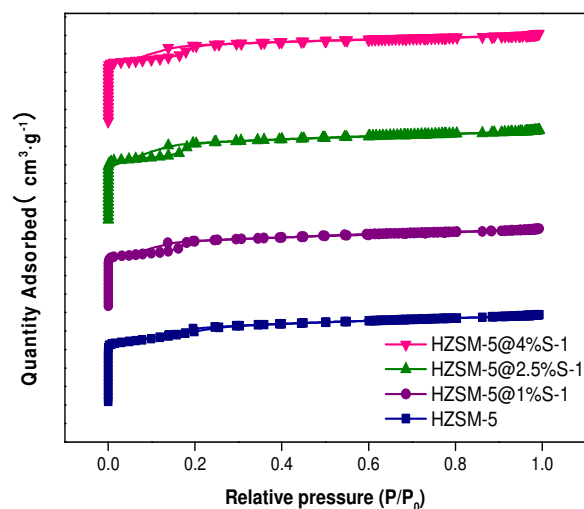


Figure 3. N_2 adsorption/desorption isotherms of the as prepared parent HZSM-5 and HZSM-5@silicalite-1 samples.

The structure of a thin silicalite-1 shell on the HZSM-5 crystals was further confirmed using a combination of XRF and XPS analytical techniques, as summarized in Table 1. The XRF results recorded the change in bulk Si/Al ratio of the zeolites samples, while the XPS results recorded the change in Si/Al ratio on the external surface of the zeolites samples. The XRF data show that the bulk Si/Al ratios of all HZSM-5@silicalite-1 samples were slightly higher than the parent HZSM-5, due to the formation of a thin silicalite-1 shell. Meanwhile, the XPS data indicate a significant increase in the surface Si/Al ratio after the epitaxial growth of the silicalite-1 shell, and the surface Si/Al ratio of HZSM-5@silicalite-1 samples increased with the increase of TEOS. The highest surface Si/Al ratio (152) was obtained for the HZSM-5@4%S-1 sample. In view of the short sampling depth of XPS (i.e., on the order of nanometers) [22], we proposed that the silicalite-1 shells formed for all HZSM-5@silicalite-1 samples were very thin. In addition, the lower Si/Al ratio in the XPS measurements suggests the potential for so-called “Al zoning”, a common phenomenon in ZSM-5 synthesis, wherein crystallization leads to a Si/Al gradient that decreases in magnitude from the particle interior to its exterior [28].

Figure 4 shows the ^{27}Al MAS NMR spectra of the parent HZSM-5 and HZSM-5@silicalite-1 samples. The chemical shift at around 56 ppm is attributed to the four coordinated Al species in the zeolite framework [29]. No apparent additional peak centered at 0 ppm was observed, which corresponds to the extra-framework aluminum in octahedral coordination [30]. These results indicate that all Al atoms in the HZSM-5@silicalite-1 samples were fully incorporated into the zeolite framework, even after the silica coating process. In addition, it is worth noting that the peak at 56.7 ppm corresponding to the framework of Al in HZSM-5 shifted downfield marginally to 55.9 ppm (HZSM-5@2.5%S-1) and 53.7 ppm (HZSM-5@4%S-1) after the silica coating treatment. This could have been due to the interactions between the silicalite-1 shell and external framework Al of the parent HZSM-5.

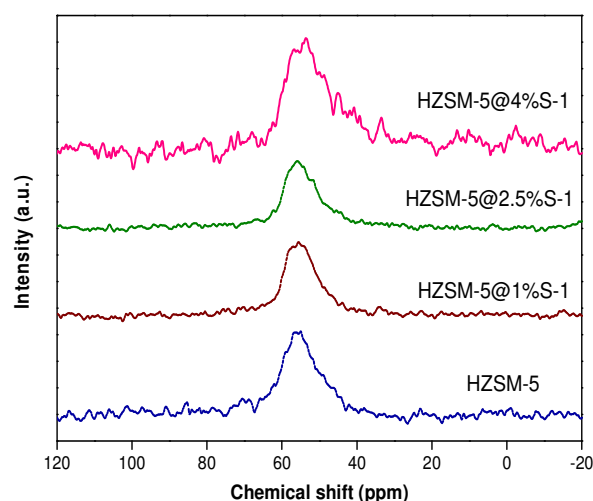


Figure 4. ^{27}Al MAS NMR spectrum of the as prepared parent HZSM-5 and HZSM-5@silicalite-1 samples.

The acidic properties of the parent HZSM-5 and HZSM-5@silicalite-1 samples were measured by temperature-programmed desorption of ammonia (NH_3 -TPD). As shown in Figure 5a, two distinct NH_3 desorption peaks could be observed in the temperature regions of 100–250 °C and 250–400 °C for all samples in the NH_3 -TPD profiles, corresponding to the weak and strong acid sites, respectively [25]. It was found that the concentrations of weak and strong acidic sites were obviously reduced after coating the silicalite-1 shell on the HZSM-5 crystals, which might have been related to the coverage of surface acidic sites on the HZSM-5 crystals by the pure-silica shell [31]. Moreover, compared with the parent HZSM-5, the strong acid desorption peak of the HZSM-5@silicalite-1 core-shell samples shifted to a low temperature, and the peak area decreased with the increase of TEOS, indicating that the introduction of a pure silicalite-1 shell reduced the acid strength of the zeolites. As reported, the acid sites required for toluene methylation are weaker than for the isomerization and disproportionation reactions [2]. Therefore, the decrease in acid strength for HZSM-5@silicalite-1 catalysts favored the main methylation reaction and suppressed the disproportionation and *para*-isomerization side reactions in this study. The amount of external Brønsted acid sites was further probed using the FTIR spectra of the adsorbed *tert*-butyl-pyridine (DTBPy) (Figure 5b), owing to its larger probe molecule, which cannot enter the internal pores of the ZSM-5 zeolite. The amount of external Brønsted acid sites that could be determined by the intensity of the characteristic band at 1616 cm^{-1} [32] decreased significantly after coating with the silicalite-1 shell. These results validated that the external Brønsted acid sites were successfully suppressed by coating with the silicalite-1 shell.

The diffusion of aromatic molecules in the zeolite catalysts plays a vital role in catalyst activity and product selectivity; particularly the reactants and desired products whose size is comparable to the catalyst pore size [2]. The pore size of the HZSM-5 crystal is almost comparable to the molecular size of *p*-xylene, but is smaller than the other two isomers (meta- and ortho-). It is proposed that these channels permit a quick diffusion of *p*-xylene molecules (minimum critical dimension of 0.53 nm), while restricting the meta- and ortho-isomers having a low diffusion coefficient. For verification and comparison, adsorption of the three pure xylene isomers (*p*-xylene, *m*-xylene, and *o*-xylene) over the parent HZSM-5 and HZSM-5@silicalite-1 samples was tested with a pulsed chromatography experiment at a lower temperature (220 °C) than the real reaction temperature (470 °C), as 250 °C is high enough to cause the isomerization reaction of xylene isomers [7]. During this experiment, larger molecules that cannot enter the zeolites pore elute first, because they have the least volume to move, leading to a shorter retention time. Correspondingly, the smaller molecules that can enter the pores of HZSM-5 elute last, with a longer retention time [7]. As shown in Figure 6a, *o*-xylene, the largest molecule among the three xylene

isomers, flowed out of the parent HZSM-5 sample packed column with the least retention. In contrast, the *m*-xylene molecule is relatively smaller and thus easier to diffuse into the micropores of the parent HZSM-5, which led to its slightly longer retention time in the column [33]. However, for all HZSM-5@silicalite-1 samples, there was no clear separation of *m*-xylene from *o*-xylene, indicating that the diffusion of *m*-xylene molecules from the external surface to the micropores of HZSM-5@silicalite-1 samples was also inhibited due to the higher internal barriers caused by the epitaxial growth of the silicate-1 layer. The very fast elution of *m*-xylene and *o*-xylene, together with the peak tailing in all samples, indicated that both *m*-xylene and *o*-xylene could not easily enter the pores of the coffin-shaped ZSM-5, although a small number of molecules could still diffuse into the pores, with slow intrapore diffusivity [33].

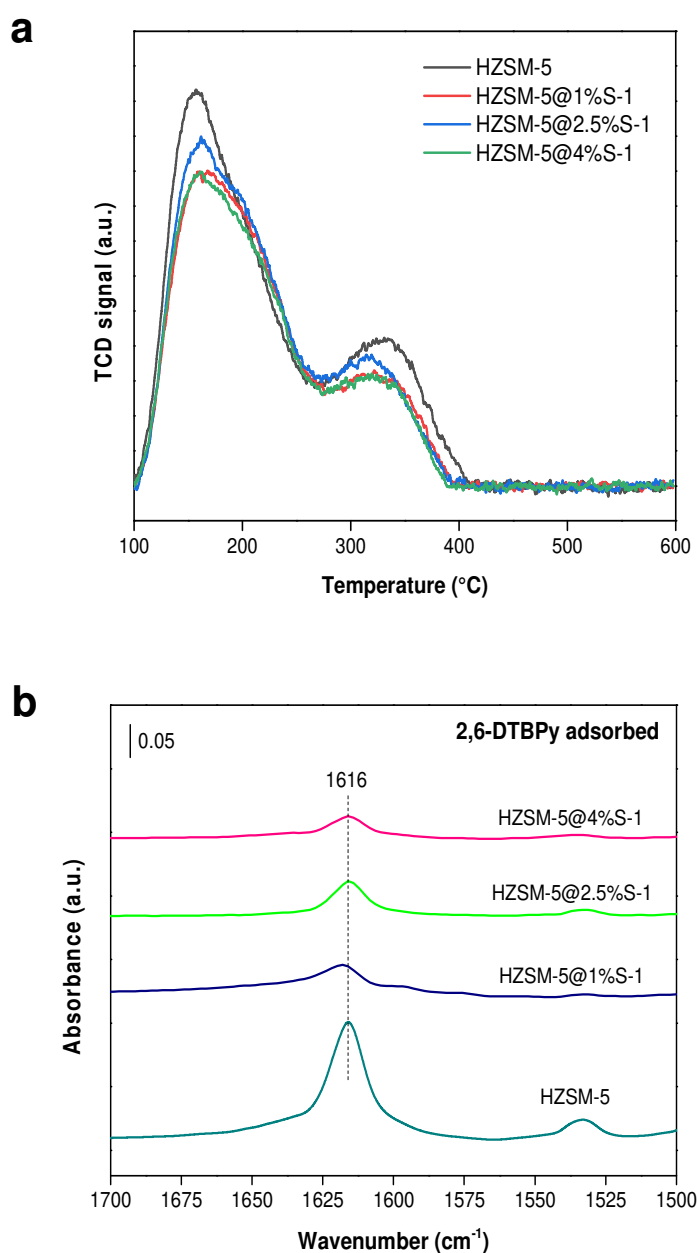


Figure 5. (a) NH₃-TPD curves of the parent HZSM-5 and HZSM-5@silicalite-1 samples; (b) 2,6-DTBPY adsorbed FT-IR spectra of the parent and modified HZSM-5@silicalite-1 samples.

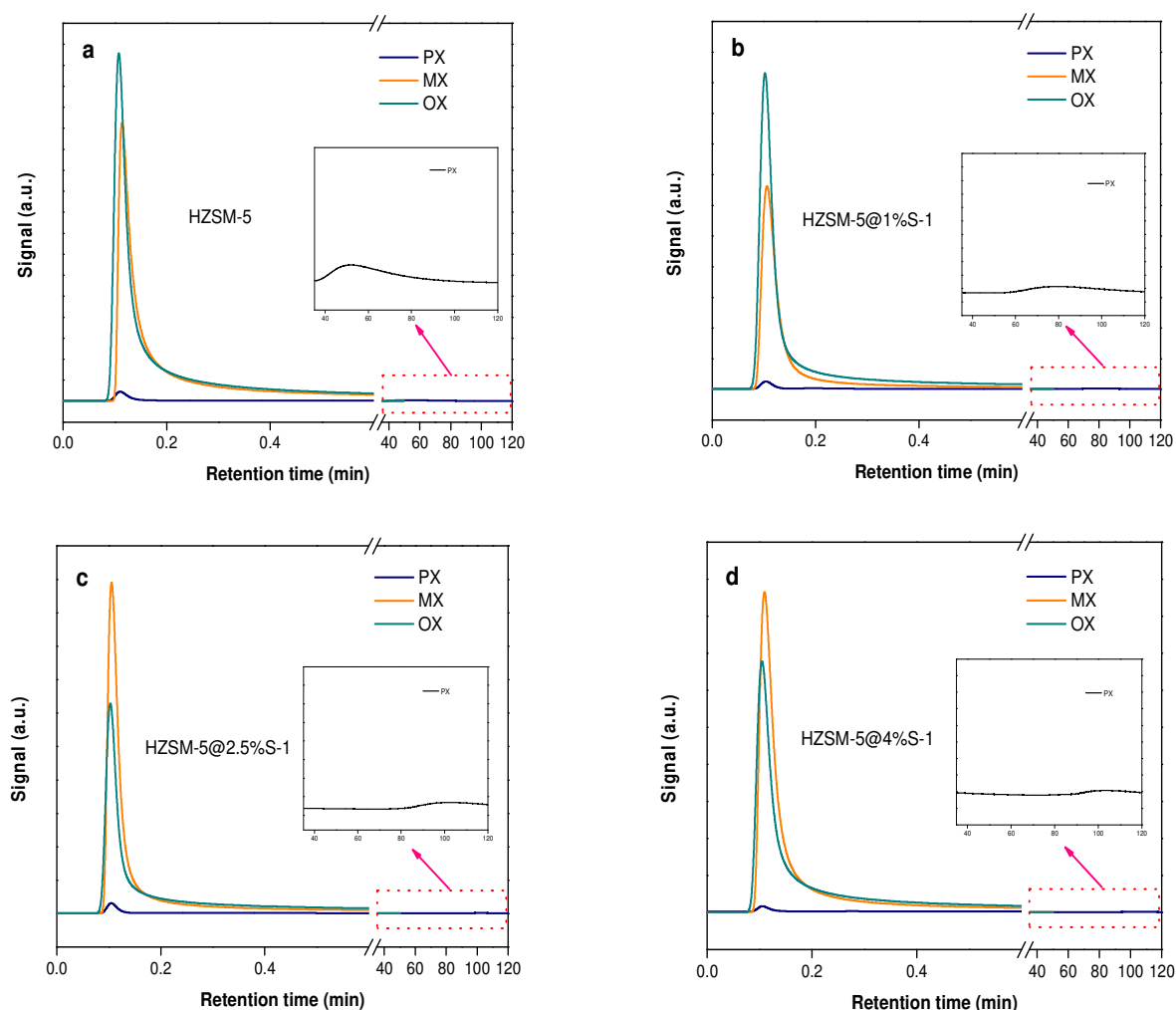


Figure 6. Pulse chromatography signal of xylene isomers (OX: *o*-xylene; MX: *m*-xylene; PX: *p*-xylene) passing through columns packed with as prepared (a) HZSM-5, (b) HZSM-5@1%S-1, (c) HZSM-5@2.5%S-1, and (d) HZSM-5@4%S-1 samples. The black solid lines illustrate a partial enlargement of the PX signal.

In addition, two weak peaks were found in the chromatogram of pure *p*-xylene for all samples over 120 min, as shown in Figure 6. The first small peak at the retention time of ~0.1 min can be ascribed to a very small part of the *p*-xylene molecules, without entering the ZSM-5 channel. Meanwhile, the second broad peak accompanied by obvious tailing at the retention time of 40–120 min could be explained by the *p*-xylene molecules, which entered the molecular sieve channel and flowed out throughout the 120 min. *p*-xylene is the smallest molecule among the three isomers and can be easily absorbed by the classic ZSM-5 micropores, and thus showed the longest retention time [7]. Meanwhile, it was found that the retention time of *p*-xylene in all silicalite-1 coated samples was much longer than for the parent HZSM-5, and the retention time of the HZSM-5@silicalite-1 samples increased with the increase of TEOS addition (Figure 6b–d). This was considered to be a result of the diffusion path of *p*-xylene molecules being extended in HZSM-5@silicalite-1 samples, due to the presence of an epitaxial silicalite-1 shell, which prolonged the pore length of the parent HZSM-5. This is in accordance with the results indicated by the N₂ physisorption, SEM, XRD, XRF, XPS, ²⁷Al MAS NMR, and NH₃-TPD. Hence, we proposed that this silicalite-1-coated HZSM-5 structure can enhance the pore shape-selective function, because of their steric hindrance, which led to the meta- and ortho-isomers eventually undergoing isomerization to *p*-xylene, to diffuse through the pores.

2.2. Catalytic Performance

The influence of the silicalite-1 coating on the *p*-xylene selectivity and catalytic stability of all zeolites catalysts in toluene methylation with methanol was investigated at 470 °C, 1 bar, and WHSV = 8 h^{−1}. As shown in Figure 7, the toluene conversion of the parent HZSM-5 and all HZSM-5@silicalite-1 samples was almost same, being ca. 11.0% under our reaction conditions. This result indicated that the epitaxial growth of the silicalite-1 layer on the external surface of the HZSM-5 crystal did not affect the intrinsic activity of the parent zeolites, since the textural structure and acidic sites in the channels of HZSM-5 were well maintained in all HZSM-5@silicalite-1 samples. It should be noted that the mole ratio of toluene to methanol was 6 in this study, which is much higher than in most other reports. Although this would lead to a relatively lower single-pass toluene conversion, the utilization efficiency of methanol for all catalysts in this reaction was improved to ca. 66%. The total xylene (*p*-xylene, *m*-xylene, and *o*-xylene) selectivity of all catalysts was higher than 95.4%, and the fractions of other aromatics (such as benzene, trimethyl benzenes, and ethyl toluenes) and light hydrocarbons were lower than 3.8% and 0.8%, respectively. In addition, compared with the parent HZSM-5, the *p*-xylene selectivity of HZSM-5@silicalite-1 samples gradually increased with the increase of TEOS (Figure 7). The HZSM-5@4%S-1 catalyst obtained the highest *p*-xylene selectivity of up to 78.4%. It is proposed that the silicalite-1 coated ZSM-5 could significantly passivate the external acid sites through the formation of a silicalite-1 layer that completely shielded the framework of Al on the external surface, and thus effectively avoided the occurrence of non-shape selective *p*-xylene isomerization on the external surface of the catalysts, resulting in a higher *p*-xylene selectivity [20,34]. In addition, the increase of *p*-xylene selectivity can be attributed to the extended diffusion path length of the xylenes in the HZSM-5@silicalite-1 samples, which enhanced the pore shape-selective function of the methanol toluene alkylation [23].

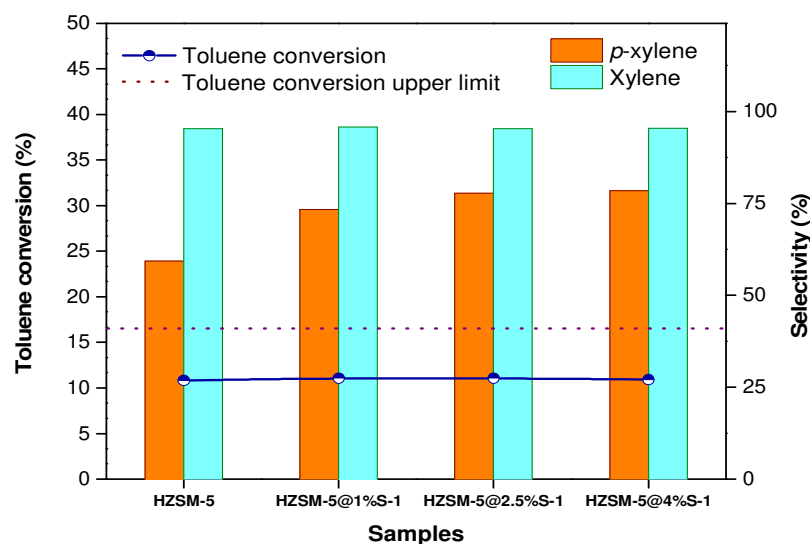


Figure 7. Catalytic performance of parent the HZSM-5 and HZSM-5@silicalite-1 catalysts in the methanol-toluene alkylation reaction. Reaction conditions: 0.2 g catalyst, 1 bar, 470 °C, WHSV = 8 h^{−1}, H₂ 55 mL/min. The data were taken at 3 h time on stream. Xylene selectivity signifies the total selectivity of *p*-xylene, *m*-xylene, and *o*-xylene.

Figure 8 shows the catalytic performance in alkylation of toluene with methanol over the parent HZSM-5 and HZSM-5@silicalite-1 catalysts, as a function of the reaction time. The parent HZSM-5 catalyst had a maximum *p*-xylene selectivity of 67.9% at TOS of 30 h, which was obviously lower than that (80.0~82.7%) of the HZSM-5@silicalite-1 catalysts at the TOS of 80~120 h. The initial toluene conversion of the parent HZSM-5 and HZSM-5@silicalite-1 catalysts were all ca. 11%; however, after reaction for 50 h, the toluene conversion of the parent HZSM-5 catalyst decreased to less than 9%, due to coke formation.

By contrast, the reduction in the toluene conversion to 9% over HZSM-5@1%S-1 took more than 130 h, since the coke formation was significantly hindered by the coverage of the surface acidic sites on the zeolites. Moreover, this deactivation time was progressively extended with the increase of amount of TEOS. The toluene conversion of HZSM-5@4%S-1 catalyst remained higher than 9%, even after a TOS of 170 h. These results indicate that the construction of HZSM-5@silicalite-1 catalysts, not only enhanced the *p*-xylene selectivity, but also prolonged the catalyst lifetime in the toluene methanol alkylation reaction. Meanwhile, it is interesting to note that a slow but continuous increase in the *p*-xylene selectivity had occurred before the first signs of deactivation, which is thought to be a result of the coke formation and its conversion to the geometry of the catalyst pore [20,35]. For the HZSM-5@4%S-1 catalyst, the long-term stability test showed that the toluene conversion remained stable at around 10%, and the selectivity of *p*-xylene remained at >80%, after a time-on-stream of 170 h. This suggests the potential of the present catalysts in industrial applications.

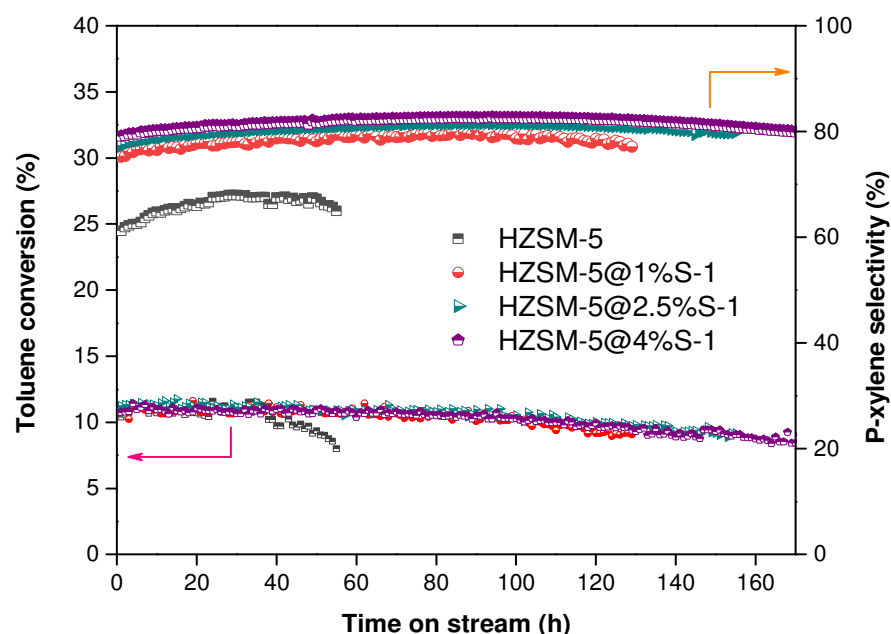


Figure 8. Long-term stability test of the parent HZSM-5 and HZSM-5@silicalite-1 catalysts. Reaction conditions: 0.2 g catalyst, 1 bar, 470 °C, WHSV = 8 h^{−1}, H₂ 55 mL/min. The pink arrow and orange arrow represent toluene conversion and *p*-xylene selectivity, respectively.

The TG analysis profiles (TGA) of all used catalysts after 20 h of reaction (Figure 9) revealed that the weight loss from the combustion of the retained coke species significantly decreased, from 14.3% on the parent HZSM-5 to only 3.5% on the HZSM-5@1%S-1 sample. This further decreased with the increase of TEOS. The HZSM-5@4%S-1 catalyst exhibited the lowest coke content (2.4%) among all catalysts, supporting that the coke formation was strongly suppressed in the core-shell structured HZSM-5@Silicalite-1 zeolite compared with the parent HZSM-5 catalyst. The results suggest that the epitaxial growth of the silicalite-1 shell on HZSM-5 passivated the surface acid sites and prevented the formation of coke species from aromatic molecules on the external surface of the HZSM-5@silicalite-1 catalyst [36], followed by improving the catalytic performance and the stability of the catalyst.

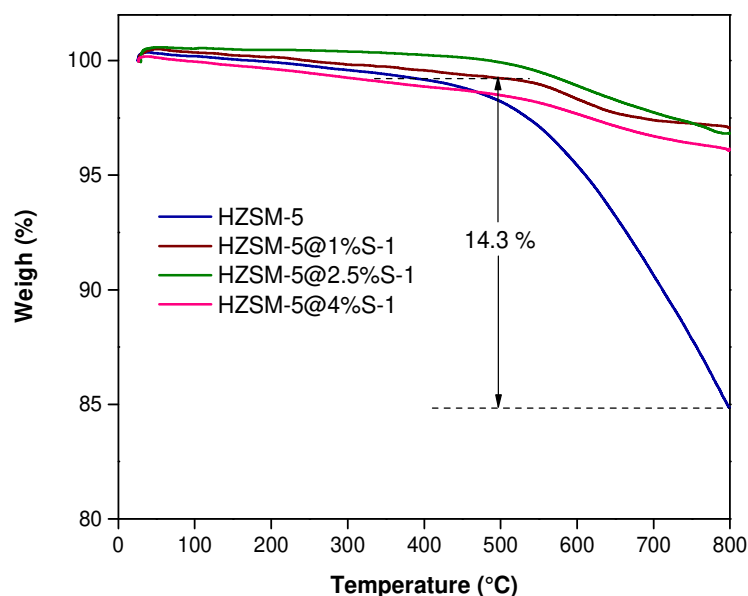


Figure 9. TGA curves of the parent HZSM-5 and HZSM-5@silicalite-1 catalysts after the toluene methanol methylation reaction for 20 h.

3. Materials and Methods

3.1. Preparation of Parent HZSM-5 ($\text{Si}/\text{Al} = 150$)

HZSM-5 was prepared using a seed-assisted hydrothermal synthesis method. Specifically, an NaAlO_2 aqueous solution (0.15 mol/L) was first mixed with TPABr aqueous solution (1.7 mol/L) to obtain the turbid sol, followed by sequential addition of silica gel and n-butylamine. Commercial HZSM-5 zeolite (0.01 g) with Si/Al ratios of 30 (purchased from Nankai University Catalyst Factory, Tianjin, China) was added to the above gel mixture as a seed crystal. The molar ratio of the obtained mixture was $300 \text{ SiO}_2:1 \text{ Al}_2\text{O}_3:1 \text{ Na}_2\text{O}:13.5 \text{ TPABr}:42 \text{ n-Butylamine}:1160 \text{ H}_2\text{O}$. Hydrothermal synthesis was performed in a Teflon-lined stainless-steel vessel at 180°C for 48 h. The obtained product was washed with deionized water several times, filtrated, and dried at 100°C for 24 h. The resulting white powder was calcined at 550°C for 6 h, to obtain the Na-ZSM-5, using a temperature increase of $2^\circ\text{C}/\text{min}$. After that, the Na-ZSM-5 was mixed with a 1.0 M ammonium nitrate solution to yield a 5 wt% suspension. This suspension was then heated at 80°C for 3 h, to allow the exchange of extra-framework Na^+ ions with NH_4^+ , and then calcined at 450°C for 5 h to obtain the proton-formed zeolite.

3.2. Preparation of HZSM-5@Silicalite-1 Catalysts

The HZSM-5@silicalite-1 catalysts were prepared following a procedure similar to that reported in [22]. The as prepared HZSM-5 crystal with a high Si/Al ratio of 150 was used as a parent zeolite, as the growth of silicalite-1 crystals on ZSM-5 zeolites with lower Si/Al ratios (<50) is more difficult [20]. First, tetraethyl orthosilicate (TEOS), tetra-propyl ammonium hydroxide (TPAOH), and deionized water were mixed, to form a gel with a molar ratio $\text{TEOS}:\text{TPAOH}:\text{H}_2\text{O} = 17:14:9500$. Then a certain amount of HZSM-5 powder was added to the gel, followed by stirring for 1 h. The above mixed aqueous solution was transferred to a Teflon-lined autoclave and hydrothermally treated at 170°C for 48 h. Afterwards, the suspension obtained by crystallization was centrifuged and washed with deionized water until neutral, dried at 120°C for 12 h, and calcined at 550°C for 6 h. The final HZSM-5@silicalite-1 core-shell material was obtained and marked as HZSM-5@X% S-1, where X represents w (SiO_2):w (HZSM-5).

3.3. Catalyst Characterization

Powder X-ray diffraction (XRD) patterns of all samples were determined at room temperature on a Bruker D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with Cu K α radiation ($\lambda = 0.1542$ nm) and a scanning rate of 8 min^{-1} , in the range of 2θ , from 5° to 55° . X-ray photoelectron spectroscopy (XPS) was carried out on a ThermoFisher ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), to characterize the chemical state of the surface species. A monochromatized Al K α source (1486.6 eV) was used as the X-ray source. The Si/Al ratio of the samples was analyzed using an X-ray fluorescence spectrometer (XRF, Bruker S8 tiger, Bruker). Scanning electron microscope (SEM) images of the as prepared samples were obtained on an FEI Nova Nano SEM 450 (Hillsboro, OR, USA). The N $_2$ static adsorption desorption curves of the HZSM-5 and HZSM-5@S-1 core-shell materials were measured using a micromeritics 3flex surface area analyzer at 77 K. Before adsorption measurements, the sample needs to be degassed at 350°C overnight. The BET method was used to calculate the specific surface area; the t-plot method was used to calculate the micropore surface area, surface area, and micropore volume; and the NLDFT model was used to calculate the pore size distribution of the sample. Temperature programmed ammonia desorption (NH $_3$ -TPD) was performed using a Micromeritics auto Chem II 2920 instrument (Norcross, GA, USA), employing helium as the carrier gas with a thermal conductivity detector (TCD). ^{27}Al MAS NMR was carried out on a Bruker AVANCE III 500 NMR instrument (Bruker), and the corresponding ^{27}Al spectrum was obtained, to study the existing state of aluminum in the catalyst. The resonance frequency of ^{27}Al was 104.2 MHz and the rotating speed was 7 KHz. Thermo-gravimetric analysis (TGA) was performed on the spent catalysts, to test coke amounts using a TG-DTA EXSTAR6000 instrument (Seiko Instruments Inc., Chiba, Japan). The samples were heated up at a rate of $10^\circ\text{C}/\text{min}$.

The acidity of the external surface of the zeolite was measured using IR spectroscopy, using the adsorption of 2,6-di-tert-butylpyridine (2,6-DTBP) on a Bruker Tensor 27 FT-IR spectrometer instrument (Bruker). First, the zeolite samples were pressed into a thin wafer. After pretreatment at 400°C and 10^{-2} Pa for 2 h, the sample was cooled to 150°C . The spectra of the degassed samples were collected as a background. Then the FTIR spectra were recorded after the samples were exposed to 2,6-DTBP at 150°C for 30 min.

Pulse chromatography was used to evaluate the pore opening shape selectivity of HZSM-5@S-1 core-shell samples. Approximately 150 mg of pristine powder HZSM-5 was packed in a 100 mm "1/8" stainless steel tube through vacuum suction, to form an adsorption column. The adsorption column was connected to an Agilent 7890B GC (Santa Clara, CA, USA) equipped with a flame ion detector (FID). The GC oven temperature was controlled at 220°C to ensure the least isomerization during the adsorption test.

3.4. Catalyst Evaluation Tests

The alkylation of toluene with methanol reaction was carried out at atmospheric pressure, using a fixed-bed tubular quartz reactor with an inner diameter of 8 mm and a length of 50 cm. The pristine zeolite powder was used directly, without granulation and tableting. Then, 0.20 g of the catalyst was loaded into the central zone of the reactor between two quartz wool layers. To increase the utilization efficiency of methanol as a methylation reagent, a T/M = 6 (molar ratio of toluene to methanol) ratio was used for the reaction. The toluene and methanol (0.03 mL/min) mixture was pumped into a reactor operating at 470°C for reaction (WHSV = 8 h^{-1}) and fed into the reactor with H $_2$ (55 mL/min). The products from the reactor were analyzed online using a 7890B gas chromatograph equipped with a flame ionization detector (FID) and an INNOWAX capillary column for product composition analysis. Toluene conversion and *p*-xylene selectivity were calculated according to the following formula:

$$C_T(\%) = \frac{\sum_{i=7}^{10} C_N H_{2N-6}}{1 + \sum_{i=7}^{10} C_N H_{2N-6}} \times 100\%$$

$$S_{PX}(\%) = \frac{N_{p\text{-xylene}}}{N_{\text{xylene}}} \times 100\%$$

where C_T is the conversion of toluene, S_{PX} is the selectivity of *p*-xylene in the xylene mixture, $C_{N H_{2N-6}}$ (carbon number from 7 to 10), $N_{p\text{-xylene}}$, and N_{xylene} is the number of aromatic moles detected by GC.

The methanol efficiency was calculated using the following formula:

$$\eta = \frac{C_T}{C_{\max}} \times 100\%$$

where η is the efficiency of methanol, C_T is the conversion of toluene, and $C_{\max}$ is the theoretical upper limit of toluene that can be reached with the specific toluene to methanol molar ratio, supposing that the methyl group in methanol was 100% transferred to toluene. For example, with a toluene to methanol molar ratio of 6, the $C_{\max}$ is 16.6%.

4. Conclusions

In summary, high-performance core-shell structured HZSM-5@silicalite-1 catalysts for toluene methylation with methanol could be obtained using a seed-assisted hydrothermal synthesis method. The epitaxial growth of silicalite-1 along the HZSM-5 crystal could better cover the external surface acidic sites of the parent zeolites, while basically reserving the pore structure of the parent zeolites, with an almost unchanged surface area and pore volume. As a result, the core-shell HZSM-5@silicalite-1 catalysts show an enhanced reaction lifetime and higher *p*-xylene selectivity compared with the conventional HZSM-5 catalyst. At atmospheric pressure, 470 °C, WHSV 8 h^{−1}, and toluene/methanol (mole/mole) = 6, the HZSM-5@4%S-1 catalyst exhibited the highest *p*-xylene selectivity (>80%), with a toluene conversion of ca. 10% and an exceptionally long stability (170 h).

Author Contributions: Conceptualization, X.P.; methodology, X.P.; formal analysis, X.P., H.W. and J.C.; investigation, X.P., S.L., R.W. and L.S.; resources, Y.L., X.H.; writing—original draft preparation, X.P.; writing—review and editing, Y.L.; visualization, Y.L.; supervision, Y.L., H.Z. and D.X.; project administration, Y.L., X.H.; funding acquisition, Y.L., H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of P. R. China (No. 22078006).

Conflicts of Interest: The authors declare no conflict of interest.

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