Synthesis of micro-mesoporous molecular sieve ZSM-5/SBA-15: tuning aluminium content for tert-butylation of phenol

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Abstract. Micro-mesoporous ZSM-5/SBA-15 molecular sieve was derived from mesoporous molecular sieves SBA-15 by hydrothermal crystallization approach. The silica-alumina ratio significantly affects the structure and catalytic performance of ZSM-5/SBA-15. When the n_{Si}/n_{Al} is less than 25, the two-dimensional hexagonal pore structure of SBA-15 keeps intact with relatively low crystallinity of the pore wall. However, when the n_{Si}/n_{Al} is larger than 50, the SBA-15 pores are severely damaged. When n_{Si}/n_{Al} is 25, the catalyst ZSM-5/SBA-15 retains relatively good pore structure and shows excellent catalytic performance with 96.2% phenol conversion and 53.5% selectivity to 2,4-ditert-butyl phenol in the tert-butylation of phenol.

Keywords. SBA-15; ZSM-5; micro-mesoporous molecular sieve; phenol tert-butylation.

1. Introduction

Alkylation of phenol is considered to be an important reaction, as alkylated phenols are extensively used as crucial intermediates to manufacture antioxidants, polymerization inhibitors, ultraviolet absorbers, lube additives, phenolic resins, and heat stabilizers for polymeric materials.¹ Great efforts have been made for tert-butylation of phenols over various catalysts, including zeolites,²⁻⁴ hydrotalcites,⁵ clays,^{6,7} heteropolyacids,^{8,9} modified mesoporous aluminophosphates,¹⁰ modified mesoporous zirconias^{11,12} and mixed oxides.¹³ Generally, the use of homogeneous acid catalysts is not desired due to their non-renewability, corrosivity, and poor heat resistibility properties. Therefore, many investigations have focused on the potential applications of microporous zeolites and mesoporous materials due to their high thermal stability and recyclability.

Since Mobile Corporation developed the M41s series of mesoporous molecular sieves in 1992, great efforts have been widely made on an unprecedented fiery

situation in the field of mesoporous materials.¹⁴⁻¹⁸ The application of mesoporous molecular sieves in acid catalysis is seriously restricted due to the relatively low acidity and relatively poor hydrothermal stability. Hierarchically porous molecular sieves with partially crystallized mesoporous walls can take good advantages and further effectively combine micro-mesoporous structure to enhance catalytic reaction. Compared to the pure microporous molecular sieves, micro-mesoporous porous molecular sieves with a larger mesoporous pore size greatly accelerate the mass transferability. The partial crystallization of mesoporous molecular sieves with suitable acidity and good hydrothermal stability can boost their acid catalytic performance.¹⁹⁻²⁷

Relatively few reports focused on the preparation of micro-mesoporous molecular sieves by mesoporous wall crystallization, mainly due to the small pore wall thickness that is difficult to be completely crystallized. Huang *et al.*,²⁸ synthesized the ZSM-5/MCM-41 composite molecular sieve by partially crystallizing the amorphous pore wall of MCM-41 through a

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two-step crystallization process, in which the crystallization time was controlled at the second step. The catalytic cracking of dodecane over ZSM-5/MCM-41 composite molecular sieve (9.0%) was higher than that of mechanically mixed ZSM-5 and MCM-41, indicating that interconnection of micropores and mesopores were more favorable for the reaction. The molecules contacted the active center and improved the catalytic cracking performance. While the preparation process with two-step crystallization was relatively complicated. Kloetstra *et al.*,²⁹ introduced tetrapropyl ammonium ion (TPA^+) into the pore walls of synthetic mesoporous MCM-41 and HMS molecular sieves, followed by recrystallization to obtain microporous and mesoporous composite molecular sieves, namely PAN-1 and PAN-2. The catalytic conversion over two kinds of composite molecular sieves was increased by about 24.0%, relative to that of the corresponding MCM-41 and HMS. However, this method had strict requirements on the synthesis conditions. Verhoef *et al.*,³⁰ introduced TPA^+ into MCM-41 mesoporous molecular sieves *via* a hydrothermal treatment to partially crystallize the pore walls into a ZSM-5 structure. It was found that the mesoporous wall can be only crystallized under certain alkaline conditions ($\text{pH} > 9$), while the mesoporous structure severely collapsed under such high alkaline conditions.

Extensive studies have enabled the conversion of mesoporous structures with amorphous walls to crystalline zeolite frameworks. Dry gel conversion in the presence of an organic microporous SDA results in ordered mesoporous substances, such as SBA-15 and MCM-41, undergoing partial crystallization on their walls to give a zeolitic structure.^{31,32} This method leads to the intercrystalline mesopore formation. Clearly, the factors (including the morphology, topology and phase purity of the zeolite crystals) and parameters (typically refers to the distribution, location, size, shape, and interconnectivity of the mesopores) are closely related to the template type and good interaction with aluminosilicate species in the synthesis gels. Unfortunately, the zeolite and mesoporous substrates nucleate synchronously result in the formation of a physical mixture with these two components during conventional hydrothermal synthesis. Moreover, crystallization of mesopore walls to zeolites with different crystalline and amorphous phase densities leads to the breakage of the aluminosilicate framework, so that the partial collapse of the final mesostructured material occurs.³³ Herein, microporous template tetrapropyl ammonium hydroxide (TPAOH) and aluminum sulfate aqueous solution ($\text{Al}_2(\text{SO}_4)_3$) were used to prepare ZSM-5/SBA-15 composite through a hydrothermal method. Meanwhile, the

effect on the addition of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in the mesoporous pore wall crystallinity was investigated. The obtained ZSM-5/SBA-15 materials with different addition of aluminum were evaluated in the phenol tert-butylation reaction to discuss the relationship between the synthesis parameters and acid catalysis performance.

2. Experimental

2.1 Chemicals

All materials were used directly as received. Polyethylene oxide-polypropylene oxide-polyethylene oxide (P123) was purchased from Sigma company (America). NaOH were purchased from Da Mao Chemical Reagent Factory (Analytical purity, Tianjin, China), HCl was purchased from Da Mao Chemical Reagent Factory (Analytical purity, Tianjin, China), aluminum sulfate 18-hydrated and ammonium nitrate were purchased from Da Mao Chemical Reagent Factory (Analytical purity, Tianjin, China). Tetraethyl orthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) were obtained from the chemical reagent of national medicine group (Analytical purity, Shenyang, China).

2.2 Catalyst preparation

2.2a Preparation of SBA-15 molecular sieve: 4.0 g of polyethylene oxide-polypropylene oxide-polyethylene oxide (P123) solid was added into a beaker containing 105 mL of distilled water and 20 mL of concentrated hydrochloric acid mixed solution, which was stirred at a constant temperature of 40 °C for 3 h. Then 9.2 mL of tetraethyl orthosilicate was slowly added with a continued stirring for 4 h. The suspension was placed in a Teflon-lined reactor at 100 °C for 24 h. After suction filtration and subsequent washing and drying, it was calcined in a muffle furnace at 550 °C for 5 h to remove the template P123. Finally, a mesoporous molecular sieve SBA-15 was obtained.

2.2b Preparation of pore wall crystallization SBA-15 molecular sieve: Different dosages of aluminum sulfate 18-hydrated solids (0.55 g, 0.33 g, 0.17 g) were mixed with 1.5 g mesoporous SBA-15 molecular sieve, 0.13 g NaOH, 36 mL H_2O , and 1.5 mL tetrapropylammonium hydroxide (TPAOH) and stirred for 12 h in the reactor at 160 °C for 72 h. After thoroughly washing, drying, and calcining at 550 °C for 5 h in air, a white powder material was obtained. The sample was denoted according to the silica-alumina ratio, namely n-SBA-15 (n = 15, 25 and 50).

2.2c Preparation of H-type pore wall crystallization SBA-15 molecular sieve: 1.5 g of ion-exchanged molecular sieve, 24.0 g of ammonium nitrate and 100 mL of distilled water were mixed and stirred for 5 h in a water bath at 90 °C to complete the first ion exchange. After filtration and drying, the second ion exchange was carried out. The ZSM-5/SBA-15

molecular sieves were dried and ion-exchanged twice, placed in a muffle furnace and calcined at 500 °C for 5 h to obtain H-type ZSM-5/SBA-15 molecular sieves.

2.3 Catalysts characterization

X-ray diffraction was performed on a Bruker D8 (Bruker Company, Germany) with Ni-filtered Cu target K α -ray (operation at 30 kV, 40 mA, wavelength $\lambda = 0.15418$ nm). Nicolet-5700 Fourier Infrared Spectrometer (Nikoli, USA) and Hitachi S4800 Transmission Electron Microscope (Japan Hitachi) and JEM-2100F electron microscope (Japan, JEOL) at an accelerating voltage of 200 kV were used to analyze the samples.

N₂ adsorption/desorption isotherms were recorded at 77 K with an ASAP 2020 (Micromeritics, USA). Before measurements, samples were out-gassed at 573 K for 3 h. The specific surface area and pore volume of the sample were measured. The sample was degassed at 573 K for 3 h and absorbed at liquid nitrogen temperature before determination. BET specific surface area is calculated by the BET equation, and BJH square is used. The mesoporous distribution (PSD) of the samples was calculated from the adsorption branch of the isothermal curve, and the total pore volume was obtained at the relative pressure of about 0.974.

²⁷Al-MAS NMR spectra were determined on a 600 M spectrometer (Agilent, USA), operating at a magnetic field of $B_0 = 0.94$ T with NMR frequencies of 104 MHz, at a spin rate of 10 kHz. The chemical shifts were referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. NH₃-TPD spectra was measured using a fixed-bed reactor connected to a thermal conductivity detector (TCD). Sample (0.05 g) was activated at 773 K for 1 h in pure nitrogen flow, then cooled down to 373 K, and begin to adsorb ammonia for 0.5 h. Physically adsorbed ammonia was removed by pure nitrogen flow at 373 K. Ammonia desorption measurements were achieved in the range of 373–773 K to increase the temperature at 10 K min⁻¹.

2.4 Catalytic test

The product was analyzed by a fixed-bed reactor as a micro-quantitative reactor and a gas chromatograph. 0.5 g H-type ZSM-5/SBA-15 molecular sieve was used as a catalyst for the reaction. The molar ratio of reactant phenol to tert-butanol was 1:2.5. The injection volume was 2.2 mL h⁻¹ and the reaction temperature was 418 K. The reaction product was dissolved in absolute ethanol and the product was analyzed by a gas chromatograph. The area normalization method was used to obtain the conversion of phenol and the selectivity of each reaction product.

3. Results and Discussion

3.1 Analysis of XRD Results

Small-angle and wide-angle X-ray diffraction (XRD) spectra were conducted on mesoporous molecular sieves SBA-15 and n-SBA-15 (15, 25 and 50) in Figure 1. SBA-15 shows diffraction peaks at the (100), (110) and (200) planes of SBA-15 at 2θ of 0.8°, 1.6° and 1.8°, indicating that SBA-15 has a long-range order of two-dimensional hexagonal mesoporous structure (Figure 1a). With the addition of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and TPAOH alkaline solution into the SBA-15 molecular sieve, the diffraction peak intensity of SBA-15 clearly decreases, suggesting that the long-range ordered mesoporous structure of SBA-15 has been destroyed. With the higher amount of aluminum, the XRD spectra of 15-SBA-15 demonstrates that the (100), (110) and (200) crystal faces of SBA-15 are still observable. The weaker peak intensity indicates that the long-range order is slightly reduced but the 2-D hexagonal mesoporous structure still maintains. Further increasing the aluminum amount in the catalyst of 50-SBA-15, no

Figure 1. (a) Small-angle and (b) wide-angle XRD spectra of the samples: SBA-15 (black line) and n-SBA-15 (n = 15, red line; 25, green line and 50, blue line).

Figure 2. FT-IR spectra of the samples: SBA-15, black line; 15-SBA-15, red line; 25-SBA-15, green line and 50-SBA-15, blue line.

obvious diffraction peaks are detected, suggesting that the two-dimensional hexagonal mesoporous structure of SBA-15 seriously damaged in Figure 1a. It is noted that the wide-angle XRD of SBA-15 and n-SBA-15 ($n = 15, 25$ and 50) in Figure 1b exhibits that the pore wall of SBA-15 is amorphous or the size of pore walls is too thin. A characteristic diffraction peak can be attributed to the zeolite ZSM-5 appeared in the XRD spectrum. As a result, the increasing content of the aluminum slows down the crystallization rate of the zeolite. Therefore, the ZSM-5 zeolite crystal is preferentially formed in the system with low aluminum content and the SBA-15 mesopores channel is destroyed. In combination with the small-angle XRD pattern analysis of the sample in Figure 1a, the higher the aluminum content is, the lower the crystallinity of the pore wall is. Lowering the aluminum content, the mesoporous order of the sample is reduced, and the crystallinity of the pore wall is higher. It is easier to form ZSM-5 crystal with less addition of aluminum sulfate octahydrate. According to the literature, the higher ratio of silicon to aluminum is beneficial to form the MFI topology.²⁰

3.2 Characterization of FT-IR results

Figure 2 shows the FT-IR spectra of the samples. The infrared spectrum of SBA-15 displays typical peaks located at 3430 cm^{-1} and the 1630 cm^{-1} , which can be ascribed as the stretching vibration absorption peak of Si-OH, and the bending vibration absorption peak of Si-OH, respectively. The peaks centered at 1080 cm^{-1} can be ascribed as the vibration absorption peak produced by the anti-symmetrical stretching of Si-O-Si. The wide shoulder peak of Si-O ranging from 900

to 1450 cm^{-1} in the catalyst of 25-SBA-15 could be deconvoluted consistently into three distinctly separate peaks at around 1024 cm^{-1} , 1090 cm^{-1} and 1200 cm^{-1} in Figure S1, Supplementary Information. These observations could be supportive of at least two structural models of silicon dioxide disclaiming the generally accepted continuous random network arrangement. The symmetrical stretching vibration and bending vibration of Si-O-Si at 800 cm^{-1} and 460 cm^{-1} are generated. The absorption peak of the infrared spectrum of the sample after crystallization of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and TPAOH are not significantly different from that of SBA-15. The samples of 25-SBA-15 and 50-SBA-15 exhibits weaker infrared absorption at 550 cm^{-1} , indicating secondary structural units of ZSM-5 in the sample.

3.3 Analysis of N_2 adsorption-desorption results

Figure 3 shows the N_2 adsorption-desorption isotherms and the Barrett-Joyner-Halenda (BJH) pore size distribution of n-SBA-15 ($n = 15, 25$ and 50) and SBA-15. As shown in Figure 3a, there is a typical IV with a hysteresis loop for n-SBA-15 ($n = 15, 25$ and 50), indicating the appearance of a mesoporous structure in the SBA-15 molecular sieve crystallized by the pore walls. The isothermal curve of 15-SBA-15 with larger initial addition of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is similar to that of SBA-15, indicating that the higher content of aluminum results in lower crystallized mesoporous SBA-15. The N_2 adsorption-desorption isotherm curve of 50-SBA-15 with a small initial addition amount of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is quite different from that of SBA-15. The smaller hysteresis loop of 50-SBA-15 further demonstrates that the ZSM-5 crystallized (structural unit) on the pore wall occupies the pore interior space. On the other hand, the isothermal curve of 50-SBA-15 gradually changes from type IV to I, suggesting that the mesoporous of SBA-15 is destroyed when the mesoporous wall is crystallized into the ZSM-5 crystal. Figure 3b shows the BJH pore size distribution of the samples. With the increasing ratio of Si/Al, the pore size of mesopores gradually decreases. This result may be related to the enhanced amount of ZSM-5 structural units and the increased crystallinity on the walls of SBA-15 pores, consequently leading to congested pores.

3.4 Transmission electron microscope (TEM) results

Transmission electron microscopy (TEM) technique has been employed to describe the morphologies of samples in Figure 4. The TEM image of 15-SBA-15 in Figure 4a shows relatively low (basically no crystals)

Figure 3. (a) N₂ adsorption and desorption isotherms and (b) BJH pore size distribution of samples: SBA-15 (black line) and n-SBA-15 (n = 15, red line; 25, green line; and 50, blue line).

Figure 4. TEM images of samples: (a) 15-SBA-15; (b) 25-SBA-15; (c) 50-SBA-15; (d) SAED pattern of 25-SBA-15 and (e) element mapping and EDS layered image of 25-SBA-15.

crystallized pore wall due to the sample with higher aluminum. The SBA-15 still possesses the long-range and orderly two-dimensional hexagonal mesoporous structure that is similar to parent SBA-15. The TEM image of 25-SBA-15 in Figure 4b demonstrates the appearance of channel characteristics in the parent SBA-15. The distribution of the pores is relatively uniform, but the order of pores is reduced, owing to the SBA-15 crystallized to ZSM-5 zeolite (structural unit). The electron diffraction results of 25-SBA-15 are shown in Figure 4d. The weak electron diffraction of 25-SBA-15 indicates that the pore walls of the sample crystallize into a smaller size crystal. This phenomenon is consistent with the previous characterization test. Based on the TEM image of 50-SBA-15 in Figure 4c, it

can be seen that the long-range ordered structure of SBA-15 almost disappears, resulting in some disordered pore structure. The TEM analysis shows that the two-dimensional hexagonal mesoporous structures of 15-SBA-15 and 25-SBA-15 maintain well with tiny ZSM-5 crystals. The mesoporous structure of 50-SBA-15 essentially destroyed. This result is consistent with data from XRD, FT-IR, and N₂ adsorption-desorption results. Furthermore, the element mapping and energy dispersive spectrometer (EDS) layered image of 25-SBA-15 catalyst in Figure 4e, Figure S2 and Table S1 (Supplementary Information) show the uniform distribution of O, Al and Si and the measured content of elemental composition and content. The element content was detected in Table S1 (Supplementary Information)

Figure 5. (a) ^{27}Al MAS NMR spectra and (b) NH_3 -TPD spectra of samples: 15-SBA-15 (black line), 25-SBA-15 (red line) and 50-SBA-15 (blue line).

exhibits that some Al was lost during the preparation progress.

3.5 ^{27}Al MAS NMR and NH_3 -TPD results analysis

Figure 5a is the ^{27}Al NMR spectra of materials. The signal of 15-SBA-15 can be observed at two points of $\delta = 55$ ppm and $\delta = 0$ ppm. The signal of $\delta = 55$ ppm is related to the skeleton tetra-coordinated aluminum, and the aluminum entering the material skeleton can produce strong acid centers.³⁴ The signal of $\delta = 0$ ppm derives from the non-skeleton six coordination aluminum, while the non-skeleton aluminum possesses lower acid. 25-worm-like and 50-worm-like samples only produce a signal at the position of $\delta = 55$ ppm in the spectra, indicating that Al exists in the material skeleton in a tetra-coordinated state with a stronger acid. Moreover, the peak intensity of 50-worm-like sample is higher than that of 25-SBA-15, indicating that the high content of aluminum has been entered into the skeleton, which is consistent with the above XRD analysis.

Figure 5b shows the NH_3 -TPD spectra of samples with a different molar ratio of Si/Al. The results demonstrate that 15-SBA-15 exhibits a wide NH_3 desorption peak at about 725 K, indicating that aluminum has been entered the mesoporous framework and produced a certain acid center. There were two NH_3 desorption peaks in 50-SBA-15 at 525 K and 820 K, belonging to weak and strong acid, respectively. The high crystallinity of 50-SBA-15 belongs to the acidic character of ZSM-5. The NH_3 desorption peak of 25-SBA-15 indicates strong acid. Besides, the high-temperature desorption peak (770 K) is slightly lower than that of 50-SBA-15.

3.6 Analysis of tert-butylated phenol reaction

Mesoporous molecular sieve SBA-15 and pore wall crystallized SBA-15 were investigated for the reaction of phenol and tert-butanol. It can be seen from the results of the tert-butylation of phenol in Table 1. The catalyst SBA-15 has very low activity with phenol conversion of only 2.2%. The phenol can be converted over catalysts of n-SBA-15 to 2-tert-butylphenol (2-TBP), 4-tert-butylphenol (4-TBP), 2,4-di-tert-butylphenol (2,4-di-TBP) and others. It is indicated that the introduction of Al element within the microporous zeolite structure enhances the acidity of the material and increases the conversion of phenol. In addition, the co-existence of the parent SBA-15 mesoporous structure in the catalysts not only provides the large specific surface area and a spacious channel but also gives a good environment for the generation and transmission of macromolecule products. The sample of 25-SBA-15 with higher content of aluminum possesses higher catalytic performance, in which the conversion of phenol is over 96%, and the selectivity of 2,4-di-TBP is larger than 50%. The high catalytic activity is mainly attributed to the fact that the two-dimensional hexagonal mesoporous structure of the parent SBA-15 maintains well and the parent SBA-15 pore wall partially crystallizes into ZSM-5 crystals and/or structural units. However, as to 50-SBA-15, the two-dimensional hexagonal pore of SBA-15 disappears due to the high crystallization of 50-SBA-15, which is a disadvantage of the product diffusion. The catalytic performance over 50-SBA-15 cuts down in terms of phenol conversion (61.7%) and the selectivity of 2,4-di-tert-butylphenol (48.6%). For 15-SBA-15, the two-dimensional hexagonal pores maintain well, but 15-SBA-15 with no crystallization hampers the

Table 1. Results of alkylation of phenol tert-butanol.

Catalysis	Conversion (%)	Selectivity (%)
		2-TBP	4-TBP	2,4-di-TBP	2,4,6-tri-TBP
SBA-15	2.2	64.1	1.9	34.0	—
15-SBA-15	85.8	4.4	44.0	51.4	0.2
25-SBA-15	96.2	4.2	42.2	53.5	0.1
50-SBA-15	61.7	4.1	47.1	48.6	0.1

Reaction temperature = 418 K; Phenol: TBA = 1: 2.5 (molar ratio); WHSV = 2.20 h⁻¹; TBP corresponding to tert-butyl phenol. The products were withdrawn and quantified after the reaction for 2 h.

Figure 6. The probable mechanism of tert-butylation of phenol.

reaction of phenol and tert-butanol due to the weak acid sites.

As can be seen from Table 1, increasing aluminum content in the catalyst increases the conversion initially. This phenomenon can be explained as follows: the acidity of the catalyst with low aluminum percentage is weak, which leads to a relatively low catalytic activity and selectivity of 2,4-di-TBP. Compared with the catalyst 50-SBA-15 with low aluminum percentage, more Al atoms are incorporated into the silica framework of the 25-SBA-15 and a stronger acidity is formed. Thus, the catalytic performance over the catalyst 25-SBA-15 is obviously higher than those over the catalyst 50-SBA-15. In addition, a further increase in aluminum content in the catalyst 15-SBA-15 decreases the conversion. This phenomenon can be ascribed to the fact that more Al atoms are not incorporated into the silica framework of the 15-SBA-15. These results can be confirmed by ²⁷Al-MAS NMR and NH₃-TPD results.

The probable mechanism of the catalytic transformations is shown in Figure 6. It was reported that the alkylation of phenol by tert-butanol is an acid-catalyzed reaction. In principle, the strong acidity of microporous molecular sieves is beneficial to this reaction. Therefore, the crystalline skeleton of microporous molecular sieves can provide acidic sites of tert-butylation of phenol. However, the small pore size of micropores molecular sieves (< 2 nm) makes it very difficult for the large size molecular to diffuse effectively in the pore system. Accordingly, the reaction activity of tert-butylation of phenol over the microporous molecular sieves is low. In addition, mesoporous molecular sieve, such as Al-MCM-41, has large pore channels. However, its catalytic activity is still low, which should be ascribed to weak acidity of amorphous mesoporous walls. Hence, the coexistences of mesopore in the microporous molecular sieves enable easier diffusion of reactants and

Figure 7. Effect of time-on-stream on phenol conversion and selectivity of products over 25-SBA-15 (Reaction condition: WHSV = 2.2 h^{-1} , reaction temperature = 418 K, N_2 flow velocity = 20 mL min^{-1} , $n_{\text{tert-butanol}}/n_{\text{phenol}}$ = 2.5: 1).

products, favoring a high phenol conversion and 2,4-di-TBP selectivity.

Based on the results in Table 1, the catalyst 25-SBA-15 displays better catalytic performance than others. In addition, comparing with others reported work in Table S2,^{3, 35–42} the obtained catalyst in our study exhibits competitive catalytic performance for the catalytic activity on the reaction for tert-butylation of phenol. Furthermore, the reaction parameters, including reaction time, temperature and the molar ratio of tert-butanol/phenol were evaluated over the catalyst 25-SBA-15. The catalytic activity over 25-SBA-15 as a function of time for the reaction results is shown in Figure 7. The products were collected at a time interval of an hour. As shown in Figure 7, after 2 h on stream, both the catalytic activity and product selectivity reach an equilibrium level. The phenol conversion is over 96% without significant change for time-on-stream, indicating that the catalyst 25-SBA-15 is stable at relatively high phenol conversion. The behavior of catalyst 25-SBA-15 is assigned to its large pore size (as shown in N_2 adsorption-desorption results) and/or relatively strong acidity (as shown in NH_3 -TPD results). In addition, the product selectivity to 2-TBP, 4-TBP and 2,4-di-TBP maintains stability within 6 h, which exhibits that there is no secondary reaction, like dealkylation or transalkylation, over the catalyst 25-SBA-15.

Similar results were obtained for the alkylations of benzene with isopropanol using hierarchical zeolites. Higher activity and selectivity for the main product were achieved.⁴⁰ As reported earlier, a crucial issue is that the microporous structure is a blockage of the pore mouths as a result of coke deposition, resulting in catalyst deactivation. The coke poisons the activity sites and

Figure 8. Effect of reaction temperature on phenol conversion and selectivity of products over 25-SBA-15 (Reaction condition: WHSV = 2.2 h^{-1} , N_2 flow velocity = 20 mL min^{-1} , $n_{\text{tert-butanol}}/n_{\text{phenol}}$ = 2.5: 1).

cannot be recovered. Many studies have shown that coke formation can be avoided using the large pore systems in mesoporous zeolite.^{41–44}

Moreover, Figure 8 shows the effect of reaction temperature on the phenol conversion and product selectivity over 25-SBA-15 at a WHSV of 2.2 h^{-1} , N_2 flow velocity = 20 mL min^{-1} and $n_{\text{tert-butanol}}/n_{\text{phenol}}$ ratio of 2.5: 1. The reaction temperature is one of the most important parameters on the conversion of phenol.^{45–47} The conversion of phenol first increases and then decreases with increasing reaction temperature. At a low reaction temperature of 378 K, it exhibits poor catalytic performance with a low conversion of phenol (16.1%). It can be explained that the low temperature is harmful to reactants activation as a consequence of the slow diffusion within the pores/channels of the catalyst. Additionally, the conversion of phenol increases from 36.8% to 96.2% with increasing reaction temperature from 398 to 418 K. This result clearly indicates that the high temperature favors the reactants activation and diffusion. However, the conversion of phenol decreases to 46.2% at a temperature of 458 K. The low conversion may be ascribed to both the predominant dealkylation and the diminishing availability of tert-butanol due to side reactions, like oligomerization or aromatization.⁴⁸

Similarly, the reaction temperature is an important influenced factor on the selectivity of products. With increasing reaction temperature, the selectivity to 2-TBP is higher at lower reaction temperature and decreases with the increasing reaction temperature. The selectivity to 4-TBP is similar to the wave line. The results in 4-TBP selectivity can be explained by the different diffusion kinetics of 4-TBP as compared to the

Figure 9. Effect of $n_{\text{tert-butanol}}/n_{\text{phenol}}$ on phenol conversion and selectivity of products over 25-SBA-15 (Reaction condition: WHSV = 2.2 h^{-1} , reaction temperature = 418 K, N_2 flow velocity = 20 mL min^{-1} , time-on-stream = 2 h).

other products.⁴⁹ This is probably attributed to the high stability of tert-butyl cation at a low reaction temperature. Furthermore, the selectivity to 2,4-di-TBP increases and reaches a maximum of 53.5% at a reaction temperature of 418 K. Accordingly, a moderate reaction temperature (418 K) is helpful for the enhancement of the product selectivity to bulky 2, 4-di-TBP.

Figure 9 shows the impact of $n_{\text{tert-butanol}}/n_{\text{phenol}}$ ratio on the catalytic results of 25-SBA-15 for the reaction at 418 K with N_2 flow velocity of 20 mL min^{-1} and a space velocity of 2.2 h^{-1} for time-on-stream of 2 h. It shows that the phenol conversion increases with increasing molar ratio of tert-butyl alcohol to phenol. The reaction reaches the equilibrium and the conversion of phenol reaches the maximum with the $n_{\text{tert-butanol}}/n_{\text{phenol}}$ of 2.5. It is well-known that the presence of competition between the polar molecule tert-butanol and phenol for adsorption sites. More tert-butanol molecules adsorb on the acid sites with increasing ratio of $n_{\text{tert-butanol}}/n_{\text{phenol}}$. The content of reaction intermediate iso-butene formed by dehydration of tert-butanol finally promotes the alkylation reaction. Therefore, the conversion of phenol increases with increasing the molar ratio of tert-butanol in the reactants. The results obtained in this study are in good agreement with the reported literature.⁵⁰ Furthermore, the selectivity of 2-TBP and 4-TBP decreases and the selectivity of 2,4-di-TBP increases with an increase in a molar ratio of tert-butyl alcohol to phenol. It may be the reason that the increase of the tert-butanol content can further improve the alkylation of monoalkylated products, such as 2-TBP and 4-TBP to 2,4-di-TBP.

4. Conclusions

Using the mesoporous molecular sieve SBA-15 as a precursor, a microporous-mesoporous molecular sieve ZSM-5/SBA-15 with different wall crystallinity can be obtained by hydrothermal crystallization. The increase in initial aluminum content results in low crystallinity of pores. Moreover, the mesoporous structure remains well, favoring high catalytic activity in the reaction of phenol tert-butanol. When lowering the initial content of aluminum, the crystallinity of the pore wall becomes high, and the two-dimensional hexagonal structure of the parent SBA-15 is destroyed. Such activity of phenol tert-butanol is reduced due to the absence of a large-sized mesoporous channel.

Supplementary Information (SI)

Figures S1–S2 and Tables S1–S2 are available at www.ias.ac.in/chemsci.

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