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Dealumination of Zeolite BEA under Microwave Irradiation

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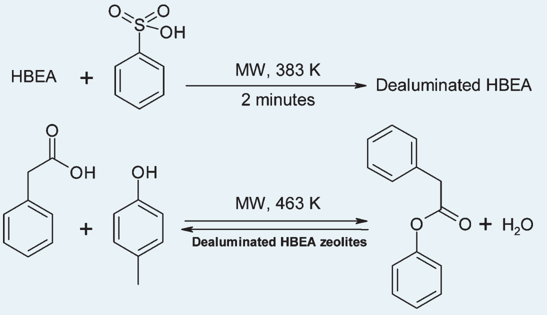
Supporting Information

ABSTRACT: An efficient, quicker, milder, and easier method for controlled dealumination of zeolite BEA using an aqueous solution of toluene-4-sulfonic acid under microwave irradiation is reported. The effect of various parameters like concentration of toluene-4-sulfonic acid solution, reaction time, and temperature on the extent of dealumination was investigated. Dealumination with microwave heating was found to be much more effective and faster than with conventional thermal heating. Aluminum removed from the framework of the zeolite was readily extracted and estimated by back-titration method. BEA zeolite samples before and after dealumination were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), ^{27}Al MAS NMR, Temperature Programmed Desorption of ammonia, low temperature nitrogen adsorption, and Brunauer−Emmett−Teller (BET) surface area. To understand the relationship between acidity and activity of parent and dealuminated zeolites, the esterification of *p*-cresol with phenylacetic acid has been studied under microwave irradiation. BEA dealuminated with 0.1 M solution of toluene-4-sulfonic acid for just 2 min under microwave heating showed highest activity for the said esterification.



KEYWORDS: dealumination, toluene-4-sulfonic acid, BEA zeolite, microwave irradiation., esterification

1. INTRODUCTION

BEA zeolite is a solid acid useful in chemical synthesis because of its tunable acidity and three-dimensional large pore system.[1,2] To have a longer life in the commercial reactors the zeolites are subjected to dealumination to even out acid site distribution all over the material. Acidity of BEA zeolite can be modulated by various dealumination techniques like steaming,[3] leaching with mineral acid such as HCl,[4] or with chemical treatments such as ammonium hexafluorosilicate,[3] $SiCl_4$[5], and dicarboxylic acids.[6] Most of these techniques require harsh experimental conditions which result in loss of crystallinity and difficulty in removing aluminum out of pores. Dealumination of BEA zeolite using methane sulfonic acid has been described in the patent literature, but this treatment uses a large quantity of methane sulfonic acid per gram of BEA zeolite for a longer duration.[7]

p-Cresylphenyl acetate is an important perfumery grade ester having narcissus odor with a honey note. It is used in floral soaps, fine fragrance, beauty care products, and as a fixative.[8] Al^{3+}-montmorillonite[9] and ion exchange resins[10] have been investigated as heterogeneous catalysts for the esterification of *p*-cresol and phenylacetic acid under conventional heating with a solvent. In both cases longer reaction time is required to reach equilibrium conversion. Zeolite BEA has been used as catalyst in few esterification reactions.[11−14] The effect of dealumination of BEA zeolite to optimize its activity for esterification and acylation reactions is reported in the literature.[15]

Microwave heating is reported to be advantageous in many applications including organic and inorganic synthesis because of reduced reaction time and more uniform and rapid heating.[16,17] However, to the best of our knowledge, post synthesis modification of zeolite like dealumination using microwave heating has not received much attention in the literature. The effect of microwave heating in the dealumination of mordenite using HCl solution has been reported recently. Dealumination using microwave heating is reported to be faster with more pronounced effect on the surface and acidic properties of the zeolite than conventional heating.[18]

The objective of this paper is to study the dealumination of BEA zeolite under microwave irradiation and its effect on solventless catalytic activity for esterification. Dealumination of BEA zeolite is investigated using toluene-4-sulfonic acid (*p*-TSA) solution of different concentrations under microwave heating. This method has the potential to dealuminate BEA zeolite in a controlled and predictable manner. For comparison BEA zeolite was also dealuminated under conventional heating. Earlier reports of esterification of *p*-cresol with phenylacetic acid by conventional heating required longer duration and makes use of solvent. Microwave irradiation is known to accelerate the reaction rate significantly. Hence in this report, microwave assisted catalytic activity of original and dealuminated BEA samples for the synthesis of *p*-cresylphenyl acetate has been investigated under solventless condition.

2. EXPERIMENTAL SECTION

2.1. Catalysts and Chemicals. The ammonium form of BEA zeolite (Si/Al = 30) was kindly provided by Süd-Chemie India Ltd. It was converted into H-form by calcination at 813 K in dry

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air for 8 h. All required chemicals were procured from SD fine chemicals, India. *p*-Cresol was distilled before use, and all other chemicals were used without further purification.

2.2. Dealumination of BEA Zeolite. Under microwave heating, dealumination was effected in Microwave lab station START-S with built-in Infrared automatic temperature control and magnetic stirrer. Variable power up to 1000 W was applied by a microprocessor controlled single magnetron system. Dealumination under conventional thermal heating was carried out by refluxing over rota mantle. In a typical procedure, 10 g of BEA zeolite and 100 mL of *p*-TSA solution in water were taken in a round-bottom flask and refluxed. After the reaction, the mixture was centrifuged; the solid thus obtained was washed thoroughly with hot water until the centrifugate was neutral. The centrifugate was collected in a 1000 mL volumetric flask and diluted up to the mark. Aluminum present in the above solution was estimated by the back-titration method.[19] The effect of time, temperature, and concentration of *p*-TSA solution on the extent of dealumination was investigated under microwave heating. The effect of contact time on dealumination was also studied for comparison under conventional heating. For the catalytic study, four dealuminated samples of BEA were obtained by refluxing 10 g of BEA zeolite and 100 mL of *p*-TSA solution of 0.1, 0.2, 0.5, and 1.0 M concentration, under microwave heating for 2 min. The reason for selecting these conditions for dealumination is given later in the paper. After the treatment, the reaction mixture was centrifuged; the solid thus obtained was washed thoroughly with hot water until the centrifugate was neutral. Then, the samples were ammonium exchanged thrice with 1.0 M ammonium nitrate solution to reduce Na^+ content of the zeolite. Finally the samples were dried and calcined at 813 K for 8 h to obtain the proton acid form of BEA. Samples treated with 0.1, 0.2, 0.5, and 1.0 M *p*-TSA solutions were designated as HB0.1M, HB0.2M, HB0.5M, and HB1.0M, respectively. The original BEA zeolite was designated as HB.

2.3. Characterization. Samples HB, HB0.1M, HB0.2M, HB0.5M, and HB1.0M were characterized by various techniques to compare structural and chemical features before and after dealumination. Powder X-ray diffraction (XRD) data were recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 1.5405 Å). The data were recorded by step-scanning at 0.025° 2θ per step from 2 to 40°. ^{27}Al MAS NMR spectra were obtained on a Bruker DSX-300 solid state NMR spectrometer. Brunauer−Emmett−Teller (BET) specific surface area, average pore diameter, and total pore volume were determined by nitrogen sorption measurements at 77 K in a NOVA 1000 Quanta chrome instrument version 3.7. Starting from room temperature, samples were outgassed at about 350 K until a residual pressure of 10^{-2} Pa was obtained, and then the temperature was slowly increased to 713 K and maintained at this temperature for 4 h before use. SEM micrographs were taken to see possible changes, if any, in morphology and crystal size. Total acidity of samples was examined by Temperature Programmed Desorption (TPD) with ammonia. TPD of NH_3 experiments were carried out with AMI 200 equipment (Alta Mira). The sample was first activated at 773 K (10 K/min) for 2 h and cooled to 423 K in a stream of flowing helium. Then the sample was saturated with the basic probe at 423 K by continuously flowing ammonia. The temperature-programmed desorption was performed by ramping the sample temperature at 10 K/minute to 1123 K monitoring the concentration of the desorbed species by built-in thermal conductivity detector.

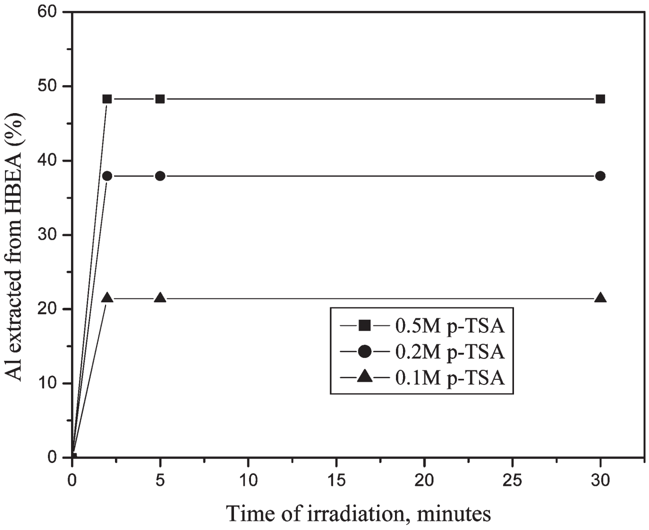

Figure 1. Dealumination. Effect of reaction time on dealumination from HB. Microwave heating: 100 mL of 0.5 M *p*-TSA solution/10 g of HBEA, temperature 383 K, maximum power 800 W.

2.4. Catalytic Reaction. Esterification of *p*-cresol with phenylacetic acid to give *p*-cresylphenyl acetate was studied under microwave heating without using solvent. The effect of various reaction parameters like reaction time, temperature, mole ratio of reactants, and catalyst amount on the conversion of phenylacetic acid were investigated on HB, HB0.1M, HB0.2M, HB0.5M, and HB1.0M samples. Reaction feed before and after the reaction was analyzed with a Chemito GC1000 gas chromatograph using capillary column (BP-20, 30 m × 0.32 mm) and flame ionization detector.

3. RESULTS AND DISCUSSIONS

3.1. Dealumination. *3.1.1. Effect of Reaction Time.* The effect of contact time on the rate of dealumination under microwave heating was studied by varying time from 2 to 30 min with *p*-TSA solutions of different concentrations. For comparison, dealumination was also studied under conventional heating by varying time from 30 to 120 min. Results are shown in Figures 1 and 2. Dealumination was observed to be faster and effective with microwave heating than with conventional heating. This is due to intensive, localized, and uniform heating of the reaction mixture by microwaves. With microwave heating, for a particular concentration of *p*-TSA, maximum dealumination was achieved in just 2 min, while the conventional thermal method required more than 120 min. Irrespective of the reaction time, the amount of aluminum removed from the framework was constant for a particular concentration of *p*-TSA. This shows the dependency of dealumination on the concentration of *p*-TSA solution. Hence, this method could be used potentially for controlled dealumination of zeolite BEA.

3.1.2. Effect of Concentration of p-TSA. Figure 3 gives the effect of the concentration of *p*-TSA on the amount of aluminum removed from the framework. The amount of aluminum removed increased with increase in concentration of *p*-TSA until 0.5 M, and it was constant at higher concentrations. The degree of dealumination reaching a limit with *p*-TSA was thought to be due to some steric constraints associated with this acid. To verify this, dealumination of HBEA was studied with 0.5 M methane

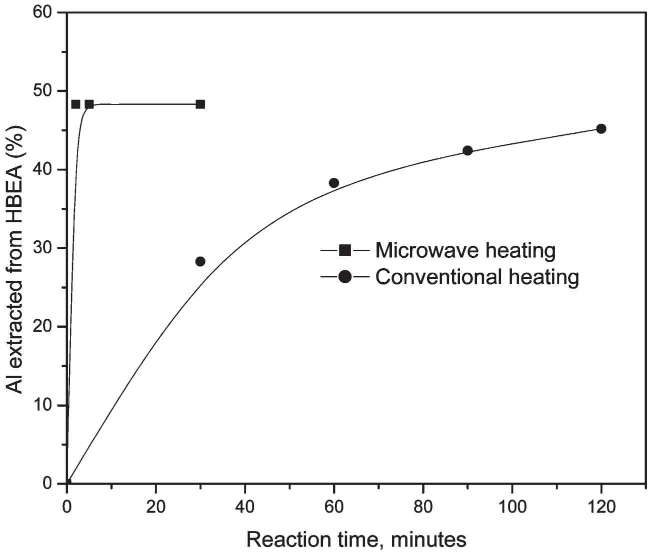

Figure 2. Dealumination. Effect of reaction time on dealumination. Microwave versus conventional heating: 100 mL of 0.5 M *p*-TSA solution/10 g of HBEA, refluxing.

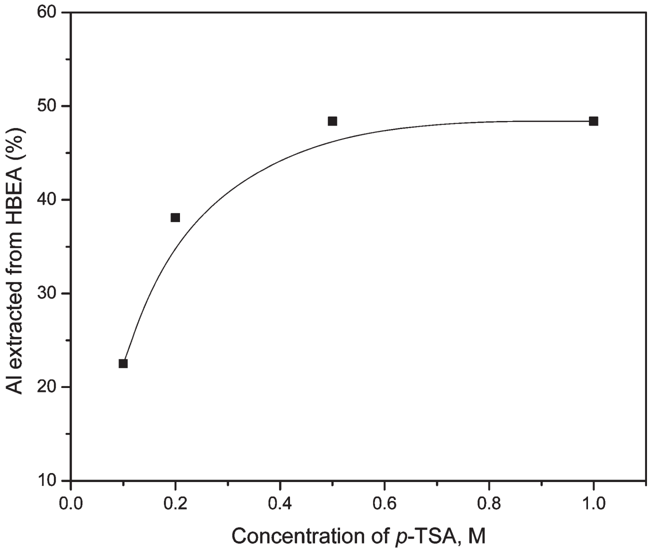

Figure 3. Dealumination. Effect of the concentration of *p*-TSA on dealumination. Microwave heating: 100 mL of *p*-TSA solution/10 g of HBEA, temperature 383 K, reaction time 2 min, maximum power 800 W.

sulfonic acid which is a much smaller molecule than *p*-TSA. The percentage of Al removed from HBEA with the former was found to be same as that with the latter. This suggests that dealumination involves some sort of interaction between the $-SO_3^-$ group of *p*-TSA and the framework aluminum. Hence, only those aluminum atoms present in specific tetrahedral sites which can interact with the $-SO_3^-$ group of *p*-TSA appears to have been removed, while other aluminum atoms are intact even at higher concentration of *p*-TSA.

3.1.3. Effect of Temperature. The effect of temperature on the extent of dealumination is shown in Figure 4. Temperature was varied from 303 to 383 K. The amount of aluminum removed increased with increase in temperature. This may be attributed to increased interaction between framework aluminum and *p*-TSA molecules because of increased diffusion of *p*-TSA molecules into pores of the zeolite with increase in temperature.

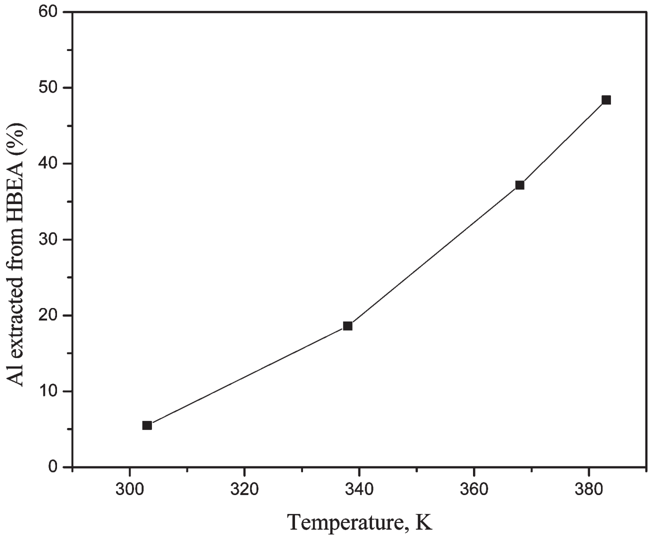

Figure 4. Dealumination. Effect of temperature on dealumination. Microwave heating: 100 mL of 0.5 M *p*-TSA solution/10 g of HBEA, reaction time 2 min, maximum power 800 W.

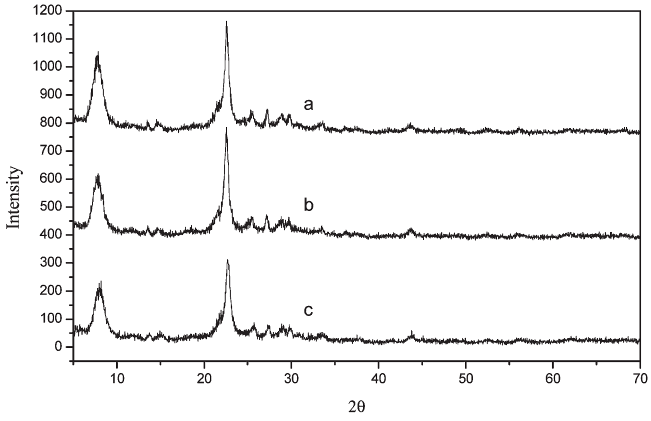

Figure 5. Characterization. XRD patterns of (a) HB, (b) HB0.2M, and (c) HB0.5M samples.

3.2. Characterization. The effect of the concentration of *p*-TSA solution on the integrity of zeolite samples as measured by XRD is shown in Figure 5. The most significant diffraction line is observed for the HB sample at $2\theta = 22.55°$. The d302 spacing corresponding to this diffraction peak (3.940 Å) can be used to verify qualitatively the lattice contraction of the BEA zeolite upon dealumination.[20] No change was observed in intensity and position of the peak for the HB0.1M and HB0.2M samples, indicating that the dealumination under these conditions caused neither change in crystallinity nor contraction of zeolite structure. The diffraction peak for the HB0.5M sample was slightly shifted toward higher 2θ (22.71°) with decreased intensity showing some loss in crystallinity. The d302 spacing related to this peak decreased from 3.940 to 3.912 Å indicating some contraction of BEA structure. The effectiveness of *p*-TSA in removing framework aluminum in zeolite BEA is evidenced from ^{27}Al MAS NMR spectra which are shown in Figure 6. The intensity of the tetrahedral aluminum peak decreased with increase in

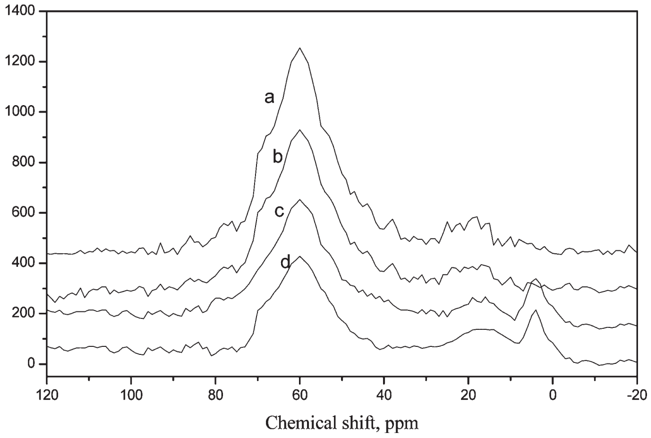

Figure 6. Characterization. ^{27}Al MAS NMR of (a) HB, (b) HB0.1M, (c) HB0.2M, and (d) HB0.5M samples.

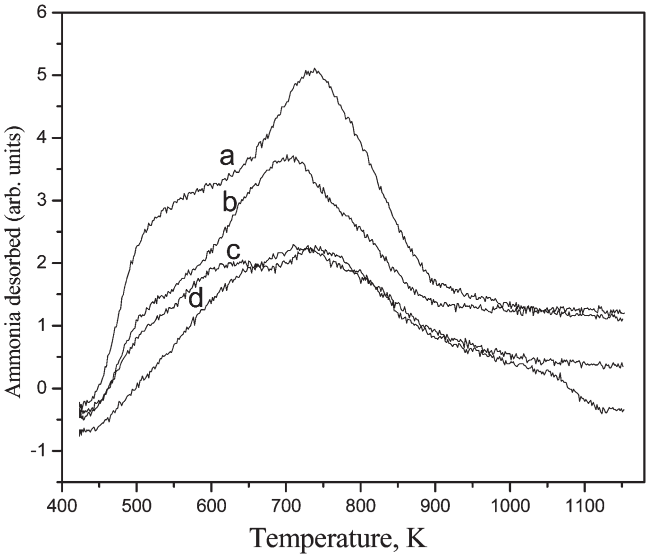

Figure 7. Characterization. TPD ammonia profiles of (a) HB, (b) HB0.1M, (c) HB0.2M, and (d) HB0.5M samples.

concentration of *p*-TSA. In the case of the HB and HB0.1M samples, only one peak corresponding to tetrahedral aluminum was observed. In the case of the HB0.2M and HB0.5M samples, a small peak corresponding to the octahedral Al species was also observed along with the tetrahedral peak. NH_3-TPD profiles of HB, HB0.1M, HB0.2M and HB0.5M are shown in Figure 7. The main desorption peak in the NH_3-TPD profile of the HB sample was observed at 738 K, and it was slightly shifted toward low temperature for the dealuminated samples. However, in all the samples desorption continued up to high temperature giving a tail like spectrum which is characteristic of BEA zeolite. Concentration of desorbed ammonia as measured from TPD of ammonia for HB, HB0.1M, HB0.2M, HB0.5M, and HB1.0M is shown in Table 1. The acidity in the BEA zeolite is due to aluminum, and the amount of acid site varies linearly with the concentration of aluminum. The concentration of desorbed ammonia is generally used to determine the amount of acid sites and hence the concentration of aluminum.[21] The decrease in concentration of desorbed ammonia from HB to HB0.5M sample confirmed the effectiveness of *p*-TSA in removing framework aluminum.

Application of BET method is not valid for microporous solids like zeolites, because the volume filling of micropores instead of the multilayer adsorption of nitrogen proceeds. Even then the values of BET specific surface areas are generally used in the characterization of samples.[22−24] BET specific surface area, total pore volume as computed from the Barrett−Joyner−Halenda (BJH) cumulative pore size distribution (desorption) plots, for parent and dealuminated samples, are given in Table 1. Increase in BET surface area and total pore volume of HB0.1M and HB0.2M samples might be due to generation of secondary pores in place of removed Al with their crystallinity intact as indicated from their XRD patterns. Whereas in the case of HB0.5M and HB1.0M, decreased surface area and pore volume may be due to some loss of crystallinity. Even though a clear trend can be observed in the variation of BET specific surface area and total pore volume, the variation is within the margin of error of the method. Therefore, no clear conclusions can be drawn from the data. Low temperature nitrogen sorption isotherms of parent and dealuminated zeolites are shown in Figure 8. They exhibited a type-IV isotherm with hysteresis loops, and the volume of nitrogen adsorbed increased with increase in dealumination. The presence of the hysteresis loop indicates the presence of mesopores. The existence of mesoporosity may be due to two phenomena. First, the intragranular mesoporosity because of the existence of mesopores in the particles of zeolite, and second, the extra-granular mesoporosity, where the mesopores are created because of the space between the grains in the case of zeolite with small particle size. The nitrogen sorption isotherm shows that the mesoporosity is already present in the sample HB before dealumination. The size of the crystallites of HBEA as determined from SEM micrographs is in the range of 0.5−0.7 μm. Hence, the mesoporosity observed in the samples must be due to space between the grains of zeolite. SEM micrographs of the HB and HB0.5M samples indicate no change in morphology and crystal size after dealumination.

The decrease in peak area in NH_3-TPD profiles and the decrease in intensity of tetrahedral aluminum peak in ^{27}Al MAS NMR spectra of the dealuminated samples corresponds to the amount of aluminum estimated from centrifugate by back-titration method. This confirms that *p*-TSA not only removes framework aluminum but also binds and brings it out of the zeolite pore. Thus, *p*-TSA seems to be playing dual role in dealumination of BEA zeolite, first as an acid hydrolyzing agent to hydrolyze Al−O−Si linkage and second as a chelating agent to complex the tetrahedral aluminum. Similar observations have been made in dealumination of BEA zeolite using dicarboxylic acid.[6] Van Bokhoven et al. have reported that BEA zeolite possesses nine crystallographic tetrahedral sites and only those tetrahedral aluminum atoms which can be converted in to octahedral coordination can be dealuminated.[25] All tetrahedral aluminum atoms in the framework of BEA zeolite may not be in a suitable position to coordinate with the $-SO_3^-$ group of *p*-TSA. Hence, *p*-TSA cannot dealuminate BEA zeolite to full extent. Only those tetrahedral aluminum atoms which can assume an octahedral configuration through coordination with a $-SO_3^-$ group of *p*-TSA appear to have been removed easily. This is further evidenced from the fact that the amount of aluminum removed from BEA zeolite, as estimated by back-titration, becomes constant after the concentration of *p*-TSA crosses 0.5 M. To know whether further dealumination is possible for the sample which is once dealuminated, the HB0.5M sample was further

Table 1. Specific Surface Area, Total Pore Volume, Si/Al Ratio, and TPD-NH_3 Data for Original and Dealuminated Samples

sample	specific surface area[a] (m^2/g)	total pore volume [b] (cc/g)	Si/Al ratio	micromoles of NH_3 desorbed [c]
HB	555	0.43	30	500
HB0.1M	564	0.45	38	381
HB0.2M	579	0.46	48	347
HB0.5M	568	0.46	58	292
HB1.0M	566	0.46	58	291

[a] Computed by BET method. [b] Computed by BJH method. [c] Per gram of beta zeolite.

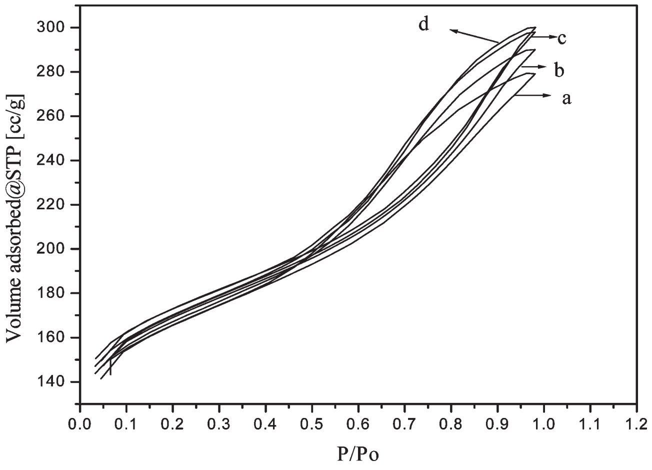

Figure 8. Characterization. Low temperature nitrogen sorption isotherms of the (a) HB, (b) HB0.1M, (c) HB0.2M, and (d) HB0.5M samples.

Table 2. Catalytic Reactions: Effect of Catalyst Amount[a]

	conversion of PAA (%) over catalyst				
catalyst amount, mg	HB	HB0.1M	HB0.2M	HB0.5M	HB1.0M
10	11.5	20.4	14.3	13.6	13.0
20	25.5	41.4	29.5	28.1	29.0
40	38.3	55.2	42.4	40.4	39.2
60	43.5	63.6	53.1	51.2	49.3
80	47.1	67.9	56.3	54.1	55.2
100	49.6	71.5	59.6	55.8	56.0

[a] Conditions: Reaction time 10 min, temperature 463 K, mole ratio (PC/PAA) 2.0, maximum power 1000 W.

Table 3. Catalytic Reactions: Effect of Temperature[a]

	conversion of PAA (%) over catalyst				
reaction temperature (K)	HB	HB0.1M	HB0.2M	HB0.5M	HB1.0M
403	6.9	12.3	8.5	6.3	6.1
423	15.2	28.5	19.7	17.7	17.0
443	28.5	50.3	37.2	32.8	34.1
463	49.6	71.5	59.6	55.8	56.0

[a] Conditions: Reaction time 10 min, catalyst amount 100 mg, mole ratio (PC/PAA) 2.0, maximum power 1000 W.

treated with 0.5 M *p*-TSA solution under microwave heating for 5 min. The aluminum removed in the second *p*-TSA treatment was negligible. This supports the observation made by Van Bokhoven et al. All these facts indicate that the formation of complex between framework aluminum and $-SO_3^-$ group of *p*-TSA is an essential step in removing aluminum out of the zeolite pore.

3.3. Catalytic Activity. The catalytic activity of zeolites is known to be influenced by dealumination. To know the influence of microwave irradiation on dealumination by *p*-TSA on the changes in pore structure and its consequent effect on the catalytic activity of the dealuminated samples, esterification of *p*-cresol (PC) with phenylacetic acid (PAA) to give *p*-cresylphenyl acetate (PCPA) was studied.

3.3.1. Effect of Catalyst Amount. The effect of catalyst amount on the esterification of PC with PAA to give PCPA was studied over a range of 0.01−0.15 g using parent and dealuminated BEA zeolite samples (Table 2). No conversion was observed in the absence of catalyst. Conversion of PAA increased with increase in catalyst amount and reaches a steady state value. Similar observations have been reported in the literature.[26] However, for the establishment of equilibrium, the amount of catalyst required was found to be different for each catalyst. It is in the order HB < HB0.1M < HB0.2M < HB0.5M ≈ HB1.0M, which is apparently due to proportional decrease in the number of active sites after dealumination.

3.3.2. Effect of Temperature. The effect of temperature on the conversion of PAA was studied by conducting reactions at 403, 423, 443, and 463 K using the HB, HB0.1M, HB0.2M, HB0.5M, and HB1.0M samples under otherwise similar conditions (Table 3). It was observed that the yield of ester increased with increase in temperature. Esterification of carboxylic acid with an alcohol is an endothermic reaction; hence, the increase in temperature favored forward reaction.[27]

3.3.3. Effect of Mole Ratio of Reactants. PC:PAA mole ratio was varied from 0.33 to 3.0 to verify its effect on yield of ester over the HB, HB0.1M, HB0.2M, HB0.5M, and HB1.0M samples (Table 4). It is very well established that the conversion in esterification is governed by an equilibrium which can be shifted toward the product side by taking one of the reactant in excess.[28] In conformity with the literature, the yield of ester enhanced with increase in concentration of either acid or alcohol. However, the increase in ester yield was more pronounced with increase in concentration of PC than PAA, which shows that PC has an important role in the rate determining step of the reaction. The mechanism of reaction involves protonation of PAA by acid site of catalyst followed by the addition of PC and elimination of water. Thus, the ready availability of PC for interaction with protonated acid increases the yield of ester. A slight increase in yield of ester with increase in concentration of PAA may be due to difficulty in solubility of a higher quantity of PAA in PC, as the reaction was conducted without using solvent.

3.3.4. Effect of Reaction Time. To check the efficacy of the parent and dealuminated beta samples on the conversion of PAA,

Table 4. Catalytic Reactions: Effect of Mole Ratio of Reactants[a]

mole ratio (PC/PAA)	yield of PCPA (%) over catalyst				
	HB	HB0.1M	HB0.2M	HB0.5M	HB1.0M
0.33	36.2	44.3	37.9	37.2	36.5
0.5	32.9	42.6	37.2	35.5	36.0
1.0	31.5	41.3	35.1	33.9	33.0
2.0	49.6	71.5	59.6	55.8	56.0
3.0	51.1	72.0	59.8	56.1	57.0

[a] Conditions: Reaction time 10 min, catalyst amount 100 mg, temperature 463 K, maximum power 1000 W.

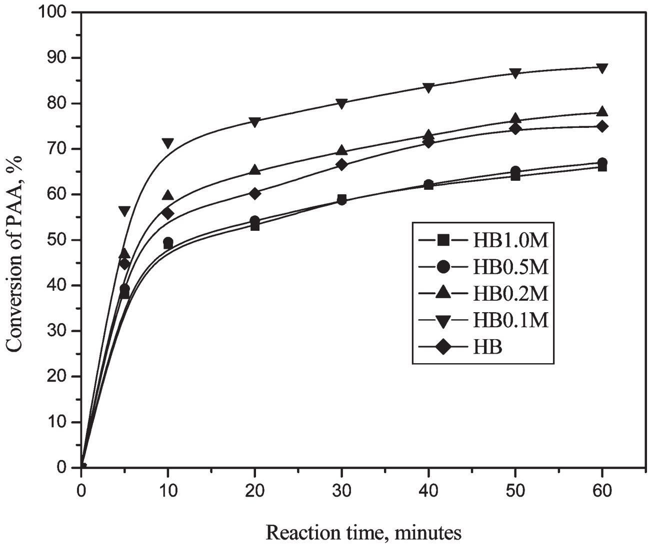

Figure 9. Catalytic reactions. Effect of reaction time: Temperature 463 K, catalyst amount 100 mg, mole ratio (PC/PAA) 2.0, maximum power 1000 W.

optimum conditions were selected (temperature 463 K, mole ratio of PC/PAA 2.0, and catalyst amount of 100 mg) and reaction time period was varied from 5 to 60 min (Figure 9). Initially the rate of reaction was faster, and as the reaction approached toward equilibrium, conversion enhanced very slowly before reaching steady state value which has been in conformity with the literature.[29] The HB0.1M sample showed the highest conversion followed by HB0.2M, HB, and HB0.5M. The activity of the HB1.0M sample was found to be similar to that of the HB0.5M sample. Variation in activity of the dealuminated samples from the original HBEA toward the esterification of PC with PAA can be attributed to changes that occur in the samples after dealumination. With dealumination, the Si/Al ratio and the hydrophobicity of the sample increase whereas the number of acid sites decreases. The kinetics of these reactions are usually controlled by the rate of adsorption of the product, which inhibits the reactions leading toward slower rates. This adsorption of the product is changed when the Si/Al atomic ratio of the catalyst is modified since it alters the hydrophobicity of the catalysts. To verify this effect on conversion of PAA, evolution of reaction rate with time was studied over original HBEA as well as dealuminated samples with initial addition of 5 mmol of product ester. After 60 min of the reaction, conversion of PAA over all the samples was found to be 12−15%. This clearly shows that adsorption of product has an inhibitive effect on the reaction. However, no difference in conversion was observed among original HBEA and dealuminated samples. The Si/Al ratio of the original HBEA used in the study is 30, and it increased to 58 in the case of the highest dealuminated sample HB0.5M. The hydrophobicity of catalysts is expected to increase in the same order. Since the original HBEA itself is hydrophobic, further dealumination of this may not have altered the hydrophobicity of the samples to a large extent. Hence, increase in hydrophobicity because of increase in Si/Al ratio on dealumination may not have significant impact on conversion of PAA. Another reason for a difference in activity of the samples may be the deactivation of the acid sites by parallel reactions involving neighboring Al sites. But the reactions conducted with used original HBEA and dealuminated samples showed no change in activity. The optimization of catalytic activity of various zeolites toward esterification by varying the Si/Al ratio has been reported in the literature. Srivastava et al. have reported the enhancement of catalytic activity of BEA zeolite dealuminated by acid treatment at controlled pH toward esterification.[15] Peters et al. have shown that the activity of H−Y zeolite toward esterification of acetic acid with *n*-butanol increases with dealumination, reaches a maximum at a Si/Al ratio of 20, and decreases thereafter.[30] Palani et al. have observed that among Al-MCM-41 synthesized hydrothermally with different Si/Al ratios (Si/Al = 25, 50, 75, and 100), the one with a Si/Al ratio of 100 showed maximum activity toward vapor phase esterification of butyric acid with 1-pentanol.[31]Hence for every reaction there may exist an optimum acid site distribution which could be achieved by controlled dealumination. Dealumination of BEA zeolite using *p*-TSA results in a distribution of acid sites. Conversion in the esterification of PAA with PC depends upon the protonation of PAA and nucleophilic interaction of PC with protonated acid. The highest activity of the HB0.1M sample for the above esterification must be due to the optimum acid site distribution achieved by partial dealumination. However, on further dealumination overall acid site concentration is decreased below the optimum level. Hence, the activity of the HB0.2M, HB0.5M, and HB1.0M samples is lower than that of the HB0.1M sample.

4. CONCLUSIONS

Treatment of BEA zeolite with *p*-TSA solution under microwave irradiation can be used for controlled dealumination. For a specific concentration of *p*-TSA, the extent of desired dealumination was achieved in only 2 min with microwave heating compared to more than 120 min using a conventional thermal heating method. Successive *p*-TSA treatment of the zeolite led us to the understanding that all tetrahedral aluminum atoms in the framework of BEA zeolite may not be in suitable position to coordinate with the $-SO_3^-$ group of *p*-TSA. Since dealumination of removable aluminum mainly depends on the concentration of *p*-TSA solution, catalytic activity of zeolite BEA in different chemical transformations can be effectively controlled. In the case of esterification of *p*-cresol with phenylacetic acid, the HB0.1M sample with optimum acid site distribution showed highest activity

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Further details are given in the supporting Figures 1 and 2 and Tables 1−3. This material is available free of charge via the Internet at http://pubs.acs.org.

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