

Vapor-phase tert-butylation of *p*-hydroxytoluene over Al-MCM-41 and PWA supported Al-MCM-41 mesoporous molecular sieve catalysts

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Abstract

Mesoporous Al-MCM-41 and PWA, impregnated with different weight percent catalysts have been prepared and investigated by combining structural and textural properties of both the catalysts. The catalytic behavior of both the Al-MCM-41 and PWA impregnated catalysts were evaluated for tert-butylation of *p*-hydroxy toluene. Among the series of catalysts, 20 wt% PWA impregnated catalyst was found to have superior activity for the alkylation of *p*-hydroxytoluene. The activity was increased with more PWA content upto 20 wt%. This implied that the PWA loaded Al-MCM-41 catalysts had enhanced acid strength, thereby increasing the Bronsted acid sites for the tertiarybutylation of *p*-hydroxytoluene. Various parameters viz. feed rate, temperature, feed ratio of *p*-HT and MTBE, Time on stream and WHSV were optimized for the reaction.

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1. Introduction

Alkylation of substituted phenol is an important industrial reaction. For example, both mono and di-tert-butylhydroxytoluene find many applications in the manufacture of resins, antioxidants and also inhibitors [1]. Chaudhuri et al. studied the alkylation of substituted phenols, such as *m*- and *p*-hydroxytoluenes with olefins such as α -methylstyrene (AMS) and di-isobutylene (DIB) in the presence of homogeneous catalyst *p*-toluenesulfonic acid [2]. Further they explored the same reaction with heterogeneous catalyst, Amberlyst-15 in the temperature range of 60–160 °C. In the reaction of *p*-hydroxytoluene with isobutylene and Amberlyst-15, O-alkylation was predominated to give 4-methylphenyl tert-butyl ether. Hart et al. revealed the alkylation of *o*-cresol with phosphoric acid catalyst [3]. For *p*-hydroxytoluene butylation, the use of isobutylenes, tert-butanol and methyltertiarybutylether (MTBE) as alkylation agents have been reported by many researchers. *p*-

hydroxytoluene butylation by MTBE has been reported by Yadav et al. using sulphated Zirconia [4]. Several cation exchange resins have been used for the butylation of *p*-cresol. But these commercial catalysts are thermally unstable. Use of zeolites in such process was restricted because of the deactivation associated with pore plugging via formation of coke deposits. Devassy et al. studied the tert-butylation of *p*-hydroxytoluene with tert-butanol over PWA supported on ZrO₂ catalyst. He observed that a higher percentage (15%) loading of PWA favors the formation of dialkylated products [5]. Above this higher loading it tends to decrease at the optimum temperature of 130 °C. Further, they reported maximum *p*-hydroxytoluene conversion (~60%) at 15% loadings of PWA and conversion was found decreased with increasing the PWA loadings. It was understood from the literature survey that variety of commercial solid acid catalysts namely Indion-130, Filtrol-24, Lewatit AC-10, Wofitit OK-80 have also employed for the tertiary butylation of *p*-hydroxytoluene. Mesoporous UDCaT-1 and PWA supported on K-10 catalyst are also employed to alkylate the *p*-hydroxytoluene [6,7]. Thus, the use of mesoporous material with high thermal stability has visualized. Recently,

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mesoporous catalysts are largely exploited in the petro chemical industry where solid acid catalysts has curtailed the difficulties associated with conventional homogenous catalyst. Particularly heteropolyacids supported on mesoporous MCM-41 catalysts were proved to have excellent catalytic activity towards alkylation and esterification reactions. Hence, in the present study, it is proposed to evaluate the activity of Al-MCM-41 and various PWA loaded Al-MCM-41, to generate higher acid sites, towards the tert-butylation of *p*-hydroxytoluene with methyltertiarybutylether (MTBE). It has many advantages over other alkylating agents. Alcohols that are used conventionally produces water as co-product thus possibly deactivating the catalyst by adsorbing on to the Bronsted acid sites. The use of MTBE produce methanol as co-product, which is also important raw material and does not affect the catalytic activity.

The present study reveals the possibility of Al-MCM-41 and PWA loaded MCM-41 catalyst in the tert-butylation of *p*-cresol. Further parameters were also optimized to get higher conversion with good selectivity. We have shown that PWA/Al-MCM-41 catalyst is highly active and stable catalyst and could be used efficiently in the synthesis of butylatedhydroxytoluene (BHT).

2. Experimental

2.1. Preparation of catalyst

The entire Al-MCM-41 catalysts were prepared by the method described earlier [8]. In a typical synthesis, sodium-metasilicate and aluminium sulphate were used as the sources of silica and alumina. Hexadecyltrimethylammonium bromide (HTABr) was used as the template. In a typical synthesis, 21.2 g of sodiummetasilicate was dissolved in 80 ml deionised water. Desired amount of metal ion source was added to get Si/Al = 50, 25 ratio and homogenized by stirring for 30 min. Gelation was then aided with drop wise addition of 7.8 g sulphuric acid. To this homogenous gel, 7.3 g of HTABr dissolved in 24 ml of deionized water was added and stirring was further continued for 4 h. The composition of gel was $\text{SiO}_2 \cdot x\text{Al}_2\text{O}_3 \cdot 0.2\text{HTABr} \cdot 0.89\text{H}_2\text{SO}_4 \cdot 120\text{H}_2\text{O}$. The sol was then transferred to a teflon lined autoclave and heated at 140 °C for 30 h. The resulting mixture was filtered, washed and dried at 90 °C. This was calcined at 550 °C in a static atmosphere for 6 h to remove the template. The PWA impregnated catalysts were prepared by adding desired amount of phosphotungstic acid (PWA) in aqueous medium. The PWA loading in the Al-MCM-41 (25) catalysts was 10, 20 and 30 wt%. The solids were then dried at 80 °C and put forwarded to various physiochemical characterizations. These materials were then tested for the catalytic activity towards tert-butylation of *p*-hydroxytoluene (HT).

2.2. Catalytic activity

The tert-butylation of *p*-hydroxytoluene (HT) with MTBE was carried out in a vapour phase fixed-bed

down-flow quartz reactor. The reactions were carried out over calcined Al-MCM-41(50), Al-MCM-41 (25), 10 wt% PWA loaded Al-MCM-41 (25), 20 wt% PWA loaded Al-MCM-41 (25) and 30 wt% PWA loaded Al-MCM-41 (25) catalysts under atmospheric pressure condition. Pre-heated vaporized HT/MTBE mixture was passed through the catalyst bed of the reactor and reaction products were collected using ice cooled condensers. The product mixtures were then analyzed by gas chromatography Clarus500 (Perkin–Elmer) equipped with a flame ionization detector and an Elite 5 ms capillary column. The identification of products was done by GC–MS (Perkin–Elmer Elite series PE-5, capillary column 30 m, 0.25 mm). The material mass-balance calculation showed that more than 95% of the reactants were recovered as products.

2.3. Physico chemical characterisation

Powder X-ray diffraction patterns were recorded on a low angle Philips x-pert diffractometer using Cu K α radiation. N₂ Adsorption measurements were performed at –196 °C with micromeritics ASAP 2010 instrument. Prior to the analysis, all the samples were pretreated at 200 °C for 3 h. The diffuse reflectance UV–Vis spectra were recorded in the range 200–600 nm with Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment using solid sample holder. ²⁷Al and ³¹P MAS NMR spectra were obtained for heteropolyacid (PWA) supported Al-MCM-41 catalysts, using MSL 400 spectrometer equipped with a magic angle-spinning (MAS) unit. The thermogravimetric analyses were carried out on SDTQ600 with V8.0 BUILD95 software under a flow of air (2.5 L/h) at a heating rate of 10 K min^{–1} between 50 and 600 °C. The FT-IR spectra were recorded in the 400–4000 cm^{–1} range on a Shimadzu FT-IR-8201PC. The SEM micrographs with EDX study of the samples were recorded on Stereoscan440 scanning electron microscope. The samples were loaded on stubs and sputtered with thin gold film to prevent surface charging.

3. Result and discussion

3.1. Characterisation of catalysts

3.1.1. X-ray diffraction study

It can be seen in Fig. 1 that all the Al-MCM-41 molecular sieves and PWA loaded Al-MCM-41 materials show well-ordered pattern. In addition, because of the geometry of its pattern, Al-MCM-41 can be indexed with a hexagonal unit cell, with $a = b$ and $c = \alpha$. This is because, the parameters a and b are in the order of nanometers instead of tenths of nanometers as usually encountered in crystals, the X-rays are diffracted over small angles only [9]. Therefore, Al-MCM-41 and PWA supported catalysts yields a diffractogram with a limited number of reflections [100], [110] and [200] planes, all being located at low angles ($2\theta = 1\text{--}10^\circ$). From the reflection angles, the size of the

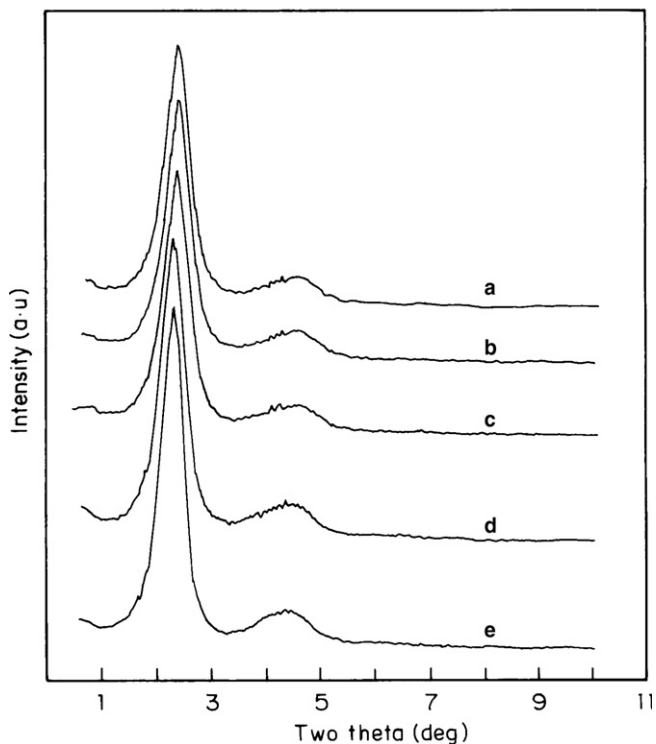


Fig. 1. X-ray powder diffraction patterns of calcined: (a) Al-MCM-41 (30 Imp); (b) Al-MCM-41 (20 Imp); (c) Al-MCM-41 (10 Imp); (d) Al-MCM-41 (25) and (e) Al-MCM-41 (50).

hexagonal unit cell of Al-MCM-41 was calculated. A marginal loss of long-range ordering was observed with increased content of PWA in the Al-MCM-41 samples [10]. This was probably due to the increasing number of defective sites and bond strain in these materials, as evidenced by the decreased intensities of the [100] peak.

3.1.2. Fourier transform infrared spectroscopy

The FT-IR spectra of the both the synthesized and impregnated samples (Fig. 2) show an absorption band at 3500 cm^{-1} . This was ascribed to hydrogen bonded silanol groups [11]. All the Al-MCM-41 samples exhibit bands at 1550 cm^{-1} and 1450 cm^{-1} , which were assigned to Brønsted and Lewis acid sites, respectively. The calcined Al-MCM-41 and different PWA loaded Al-MCM-41 molecular sieves show characteristic, strong IR bands in the range of $1200\text{--}500\text{ cm}^{-1}$. However, a peak broadening at 860 and 950 cm^{-1} for PWA/Al-MCM-41 (25) catalysts were observed. This might be due to the overlapping of heteropoly acid bands with the Al-MCM-41 molecular sieves.

3.1.3. Nitrogen adsorption measurements

Nitrogen adsorption measurements probe the textural properties of materials, viz. surface area, pore volume, and pore size distribution. Further, the technique also discloses, to what extent the measured surface area is associated with micro-, meso- and/or macropores. The measurements of surface area of both Phosphotungstic acid (PWA) loaded and hydrothermally synthesized Al-MCM-

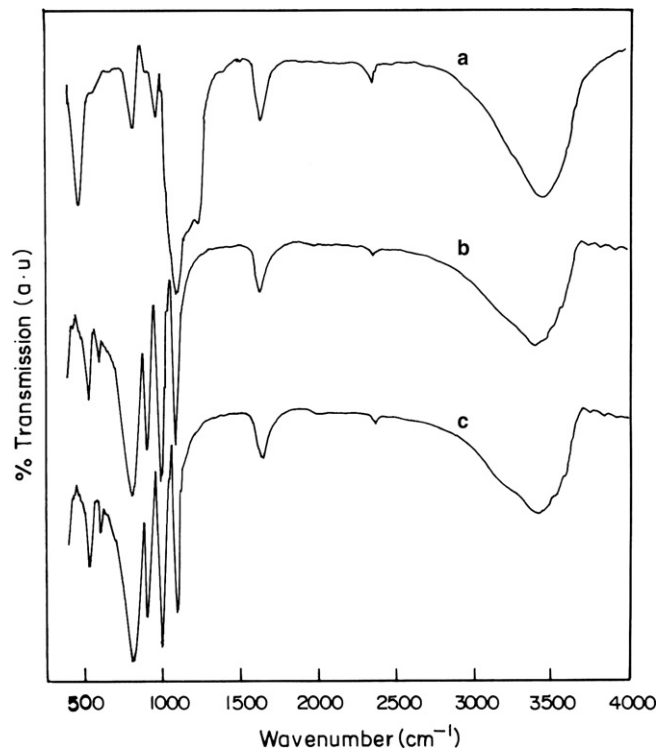


Fig. 2. FT-IR spectra of calcined: (a) Al-MCM-41 (25); (b) Al-MCM-41 (20 Imp) and (c) Al-MCM-41 (10 Imp).

41 materials were done by the BET method. The calculated surface areas are depicted in Table 1, for all the catalysts used in the study. It has been observed that the BET surface area gradually decreases with an increase in the PWA content of Al-MCM-41 samples (Fig. 8). In the case of PWA impregnated Al-MCM-41 sample, the decrease in pore size might be due to the deposition of heteropolyanion species onto the surface of the channels of Al-MCM-41 molecular sieves [13].

3.1.4. ^{27}Al MAS and ^{31}P MAS NMR studies

The ^{31}P -MAS NMR is the most informative method for probing the state of phosphorous in the heteropolyacids (PWA). Fig. 3 shows the ^{31}P MAS NMR spectra of the 10, 20 and 30 wt% loaded Al-MCM-41 catalysts. All the spectra recorded showed similar patterns with a well defined signal centered at 15.2 ppm, attributed to Keggin structure of the heteropoly acid [14]. The position of aluminium in the framework of Al-MCM-41 was analyzed

Table 1
Textural properties of catalyst studied

Catalysts/textural properties	BET surface area (m^2/g)	Pore volume (cc/g)	Average poresize (nm)
Al-MCM-41 (50)	1044	0.98	2.67
Al-MCM-41 (25)	1016	0.96	2.66
10 wt% PWA/Al-MCM-41 (25)	956	0.92	2.46
20 wt% PWA/Al-MCM-41 (25)	873	0.90	2.39
30 wt% PWA/Al-MCM-41 (25)	815	0.78	2.34

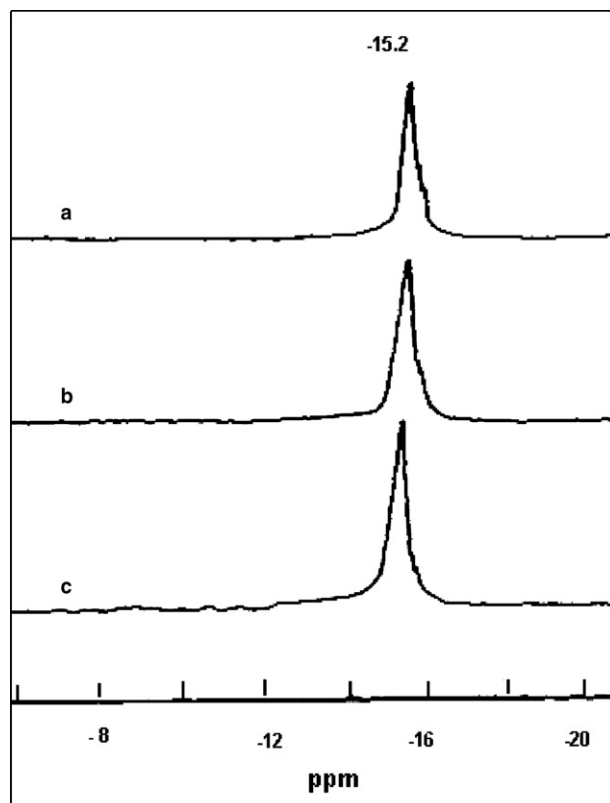


Fig. 3. The ^{13}P MAS NMR spectrum of the catalysts: (a) Al-MCM-41 (30 Imp); (b) Al-MCM-41 (20 Imp) and (c) Al-MCM-41 (10 Imp).

by ^{27}Al MAS NMR spectroscopy and the spectrum of the Al-MCM-41 (25) is shown in Fig. 4. The spectrum showed a sharp resonance peak at $\delta = 53.4$ ppm that was assigned to the tetrahedrally coordinated aluminium in the framework [15,16]. The weak line at 0.6 ppm was caused by octahedrally coordinated aluminum atoms [8] indicating that not all the aluminum atoms were incorporated into the framework.

3.1.5. DRS-UV spectroscopy

The diffuse reflectance UV-Vis spectroscopy is recognized to be a very sensitive and constructive technique for the identification of the metal ion coordination and its existence in the framework or extra-framework position of modified molecular sieves [17]. The diffuse reflectance UV-Vis spectra of 10 wt% PWA-Al-MCM-41 (25), 20 wt% PWA-Al-MCM-41 (25), pure PWA samples are shown in Fig. 5a and b. The presence of PWA in Al-MCM-41 matrix was evidenced by diffused reflectance spectra (DRS) of 10 and 20 wt% PWA impregnated samples (Fig. 5a, b). A strong band at 220 and 370 nm was observed for pure PWA material (Fig. 5c).

3.1.6. SEM analysis with EDX spectrum

The morphology of Al-MCM-41 materials and 20 wt% PWA/Al-MCM-41 samples were determined by scanning electron microscopy. The SEM micrographs of Al-MCM-

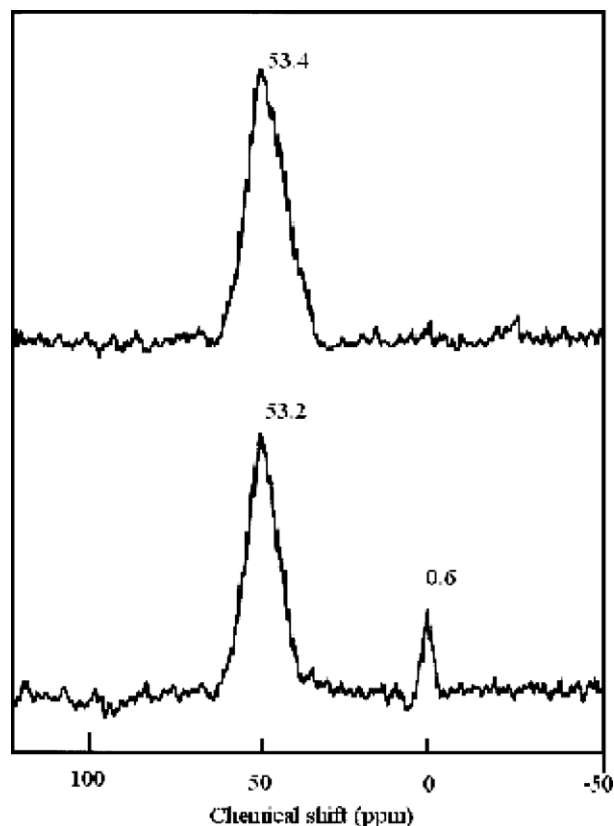


Fig. 4. The Al-MAS NMR spectrum of: (a) Al-MCM-41 (30 Imp); (b) Al-MCM-41 (20 Imp) and (c) Al-MCM-41 (10 Imp).

41 and 20 wt% PWA/Al-MCM-41 samples are shown in Fig. 6a, b. The energy dispersive X-ray analysis (EDX) of the 20 wt% PWA/Al-MCM-41 sample showed that different oxidation states of tungsten exist in keggin structure as given in Fig. 6c.

3.1.7. TG-DTA studies

The TG and DT analysis sensed three significant weight losses in the temperature regions 40–160, 160–350, 350–450 °C (Fig. 7a, b). The peak near 100 °C in DTA spectra was due to the water desorption. The peaks between 160 and 450 °C were attributed to the dehydration of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ phase and decomposition of organic templates [18,19]. The total weight loss of about 40 wt% of organic species indicated that the un-calcined sample contained large amount of organic surfactant, used to build the mesoporous structure with large pore volume [20].

3.2. Catalytic study

Tertiarybutylation of *p*-hydroxytoluene (HT) with MTBE was carried out over calcined Al-MCM-41 and PWA loaded Al-MCM-41 catalysts in the temperature range of 200–400 °C for Al-MCM-41 catalysts at the temperatures of 200, 225, 250 and 275 °C. The catalytic runs at each temperature and at each feed ratios were carried out after regenerating the used catalyst by heating at 500 °C

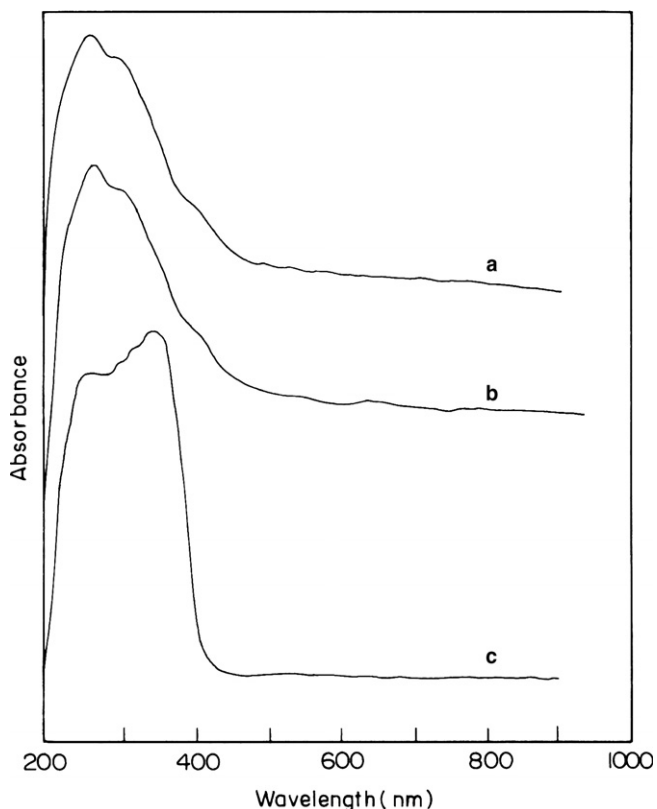


Fig. 5. Diffused reflectance spectra of: (a) Al-MCM-41 (30 Imp); (b) Al-MCM-41 (20 Imp) and (c) pure phosphotungstic acid.

in presence of CO_2 free air. Initially the molar feed ratio of *p*-hydroxytoluene (HT) to MTBE and WHSV were optimized by varying HT and MTBE ratio of 1:2, 1:3, 1:4, 2:1 and the flow rate of the feed. The optimized HT/MTBE molar ratio (1:3) and WHSV (1.65 h^{-1}) was followed for all the experiments.

3.2.1. Effect of mole ratio

The catalytic behavior of Al-MCM-41 (25) and 20 wt% PWA loaded Al-MCM-41 (25) catalysts for the tert-butylation of *p*-hydroxytoluene was evaluated. This was done as a function of different molar feed ratio (1:2, 1:3, 1:4, 2:1) at constant WHSV^{h⁻¹} of 1.65 and the trend is given in Fig. 9. The catalytic activity as a function of PWA loading appreciably increased the activity, as the wide dispersion of PWA on the surface of MCM-41 catalysts exhibited higher acidity than bulk PWA [21]. The most important factor in determining the selectivity of both the mono and di-alkylation of *p*-hydroxy toluene was the ratio of HT to MTBE in the feed. At the lowest level of feed ratio (1:2) it gave a conversion of 47.3% and showed a maximum of 55.2%, at the feed ratio of 1:4. Then it was found to be 40.3% for 2:1 ratio. At the feed ratio of 1:2, the selectivity of 2-TBHT was 64.2% whereas at 1:3, the optimum condition for higher conversion with good selectivity was 67.3%. It was observed from Fig. 9 that a decrease in *p*-hydroxytoluene and MTBE ratio has increased the *p*-hydroxytoluene

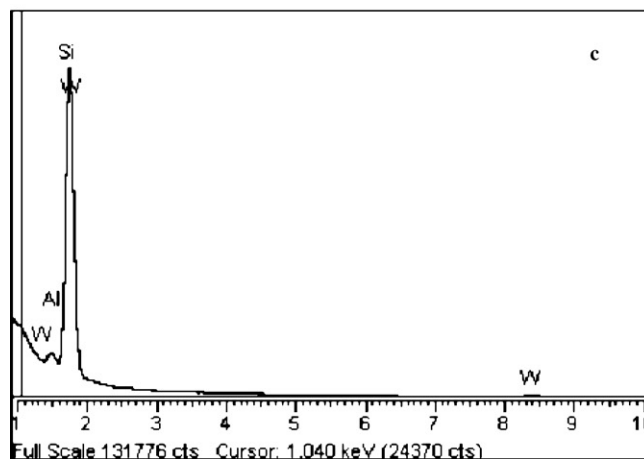
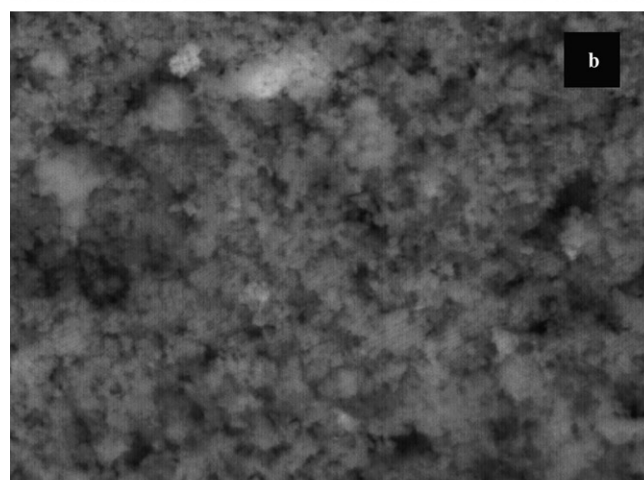
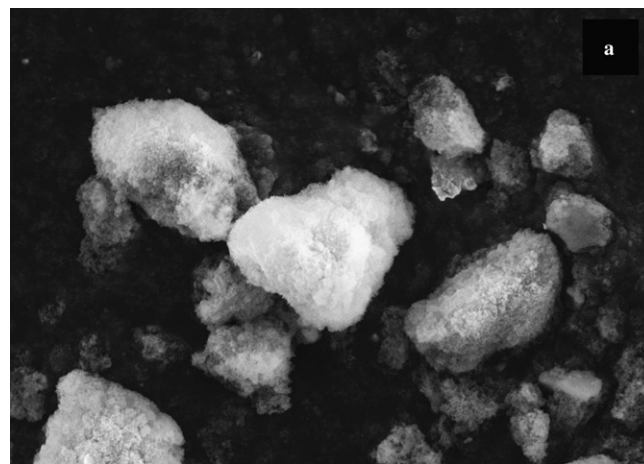


Fig. 6. Scanning electron microscope of Al-MCM-41 (20 Imp), (a) EDX spectrum of Al-MCM-41 (20 Imp).

conversion. The selectivity of mono and ditertiarybutyl *p*-hydroxytoluene was found to increase with increasing MTBE content in the feed. This increase showed a maximum for 20 wt% PWA loaded Al-MCM-41 (25) catalyst. The selectivity of 2TBHT and 2,6 DTBHT over Al-MCM-41 (25) and 20 wt% PWA/Al-MCM-41 (25) catalysts were 28.3, 36.1% and 30.4, 37.15, respectively, at the feed ratio of 1:4. The increase in 2,6 DTBHT selectivity

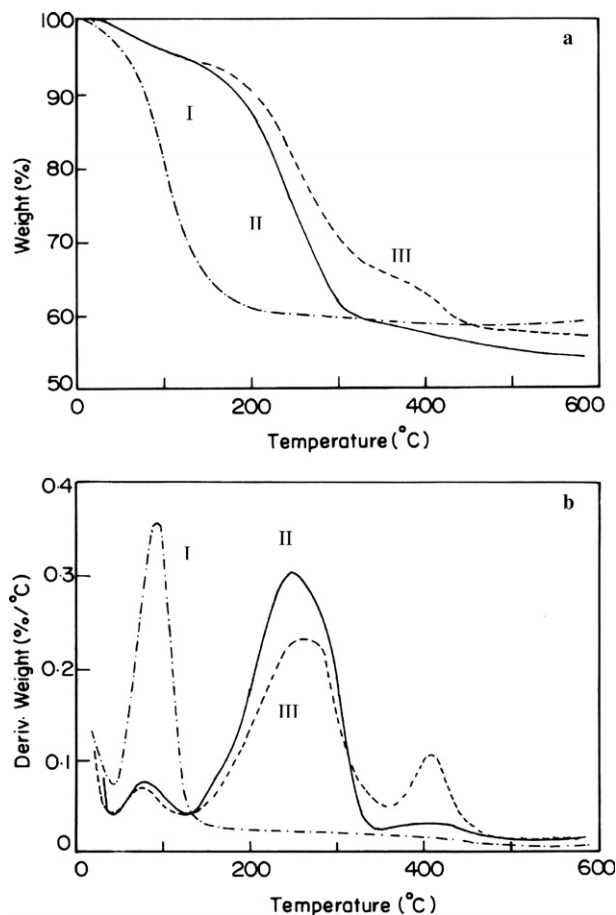


Fig. 7. (a) TGA curve of (I) Al-MCM-41 (20 Imp), (II) Al-MCM-41 (25) and (III) Al-MCM-41 (50); (b) DTA curve of (I) Al-MCM-41 (20 Imp), (II) Al-MCM-41 (25) and (III) Al-MCM-41 (50).

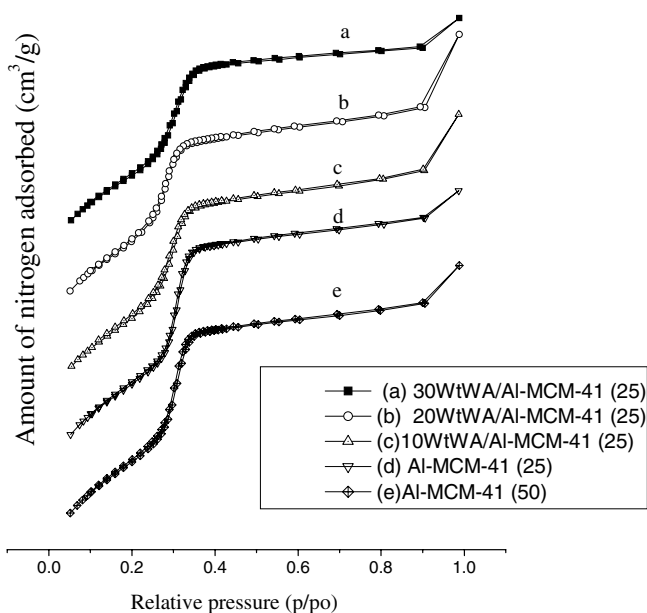


Fig. 8. Nitrogen adsorption-desorption isotherm of calcined: (a) Al-MCM-41 (30 Imp); (b) Al-MCM-41 (20 Imp); (c) Al-MCM-41 (10 Imp); (d) Al-MCM-41 (25) and (e) Al-MCM-41 (50).

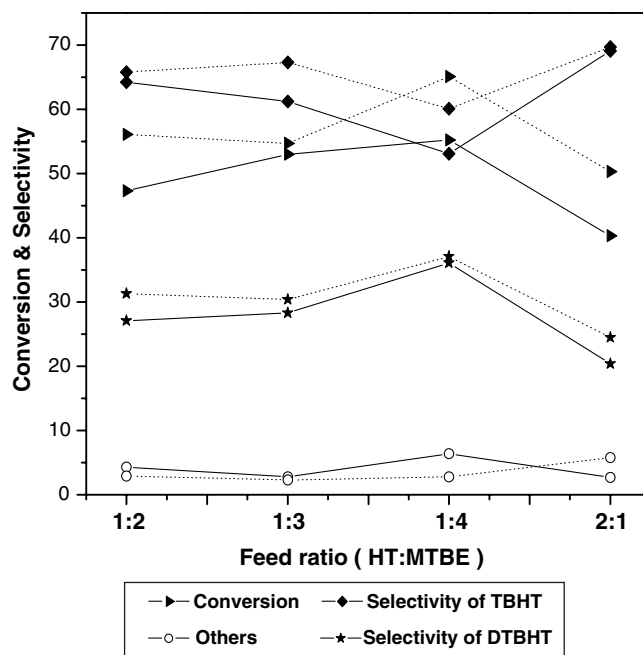


Fig. 9. Effect of feed ratio on conversion and selectivity of products over Al-MCM-41 (25) (—) and Al-MCM-41 (20 Imp) (----).

with lower HT/MTBE ratio (1:4) might be due to the higher concentration of MTBE. Based on the *p*-hydroxytoluene conversion and selectivity towards mono and dialkylated products, the optimized HT/MTBE ratio of 1:3 was selected for temperature, WHSV, and time on stream studies.

3.2.2. Effect of temperature

The conversion of HT at different temperatures over all the catalyst is presented in Table 1. The *p*-hydroxytoluene conversion was found to increase moderately up to 350 °C above, which it gets decreased. This decrease might be due to the dealkylation of alkylated product at this temperature range, which is much pronounced in the Al-MCM-41 (25) catalyst. This was not observed with PWA loaded Al-MCM-41 catalysts. The same trend was also observed for tert-butylation reaction over Al-MCM-41 and Fe-MCM-41 catalysts by savitha et al. [8]. The increase in conversion with temperature for PWA loaded Al-MCM-41 catalysts were due to the increased acidity of the catalyst. It was observed that the activity of 20 wt% PWA loaded Al-MCM-41 (25) was shown to have higher than that of remaining catalysts studied. At 225 °C, 20 wt% catalyst showed a maximum conversion of 54.7% with the selectivity of 67% towards monoalkylated product. A marked influence of PWA loading on the nature of product distribution and selectivity was observed in the tertiary butylation of *p*-hydroxytoluene. The conversion of *p*-hydroxytoluene was also increased over PWA loaded catalysts with increasing temperature. While comparing all the 3 various loaded catalysts, 20 wt% PWA/Al-MCM-41 catalyst showed higher conversion than the highly loaded

30 wt% PWA loaded catalyst which showed lower conversion (41.3%). Similar results were also observed over TPA/ZrO₂ catalysts by Devassy et al. [5]. The selectivity of 2-tert-butyl *p*-hydroxytoluene (2TBHT) 67 and 62.3% was observed over 20% PWA loaded and Al-MCM-41 (25) catalysts, respectively, which was remarkably higher than that of the other catalysts tested. This might be due to the strong Bronsted acidity generated by PWA loading. In the study, all the catalysts produced O-alkylated product in different amounts with different temperature and acidity [22]. Its selectivity was much reflected in lower reaction temperature. This trend also exhibited by higher acidic catalysts of all the three PWA loaded catalysts. Oligomers like di-isobutylene and tri-isobutylene were formed at higher temperatures (Table 2).

3.2.3. Effect of WHSV

The influence of weight hourly space velocities (WHSV) on conversion and product distribution is presented in Fig. 10. An increase in WHSV⁻¹ from 1.1 to 1.65 was found to decrease the conversion only marginally from 5% to 4.3% over Al-MCM-41 (25) and 20 wt% loaded catalysts. Further increase in WHSV⁻¹ to 2.1 showed a remarkable decrease in the conversion of 15.6 and 16.2 for Al-MCM-41 (25) and 20 wt% PWA loaded Al-MCM-41 (25) catalysts, respectively. This sudden decrease in the conversion might be attributed to the small resident time of *p*-hydroxytoluene at higher space velocity. The selectiv-

Table 2

Effect of temperature on conversion of *p*-hydroxytoluene at WHSV of 1.65 H⁻¹

Catalyst/temperature (°C)	200	250	300	350	400
<i>Al-MCM-41 (50)</i>					
Conversion of HT	15.4	32.1	39.3	42.6	40.2
2TBHT	48.3	56.3	58.8	62.3	67.3
2,6DTBHT	23.4	28.1	26.6	35.2	25.2
Others	28.3	15.6	14.6	2.5	7.5
<i>Al-MCM-41 (25)</i>					
Conversion of HT	19.4	38.1	50	56.7	50.3
2TBHT	53.1	59.3	61.2	62.3	58.3
2,6DTBHT	25.4	23.4	26.3	25.7	28.3
Others	21.5	17.3	12.5	12	13.4
Catalyst/temperature (°C)	200	225	250	275	—
<i>PWA/Al-MCM-41 (10 Imp)</i>					
Conversion of HT	31	38.3	39.4	41.3	—
2TBHT	54.1	50.2	51.7	48.9	—
2,6DTBHT	23.6	26.7	26.8	28.4	—
Others	18.3	23.1	21.5	22.7	—
<i>PWA/Al-MCM-41 (20 Imp)</i>					
Conversion of HT	34.5	54.7	57.7	59.2	—
2TBHT	59.1	67	65.3	61.2	—
2,6DTBHT	28.1	30.1	28.6	26.0	—
Others	12.8	2.9	7.1	12.8	—
<i>PWA/Al-MCM-41 (30 Imp)</i>					
Conversion of HT	38.6	41.3	48.1	49.3	—
2TBHT	49.3	50.1	51.3	48.4	—
2,6DTBHT	24.7	30.8	36	32.2	—
Others	16	14.3	12.7	19.4	—

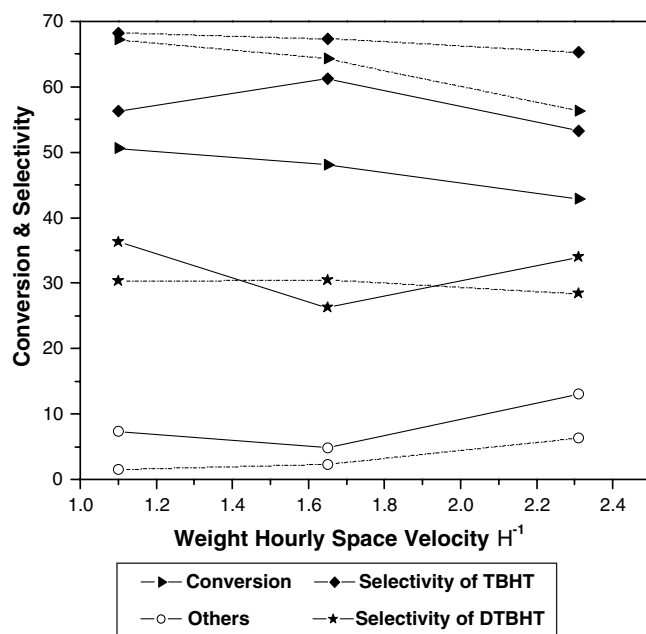


Fig. 10. Variation of conversion and product selectivity with time on stream over Al-MCM-41 (25) (—) and Al-MCM-41 (20 Imp) (- - - -).

ity of mono and dialkylated products (2TBHT and 2,6DTBHT) registered a decrease with increased WHSV⁻¹ (2.21 h) for both the catalysts, indicating that shorter resident time of *p*-hydroxytoluene. In spite of undergoing consecutive reaction (alkylation of tert-butyl *p*-hydroxytoluene to di-tert-butyl *p*-hydroxytoluene), the selectivity of ether increased with higher space velocities. From this study, it was concluded that 20 wt% PWA loaded Al-MCM-41

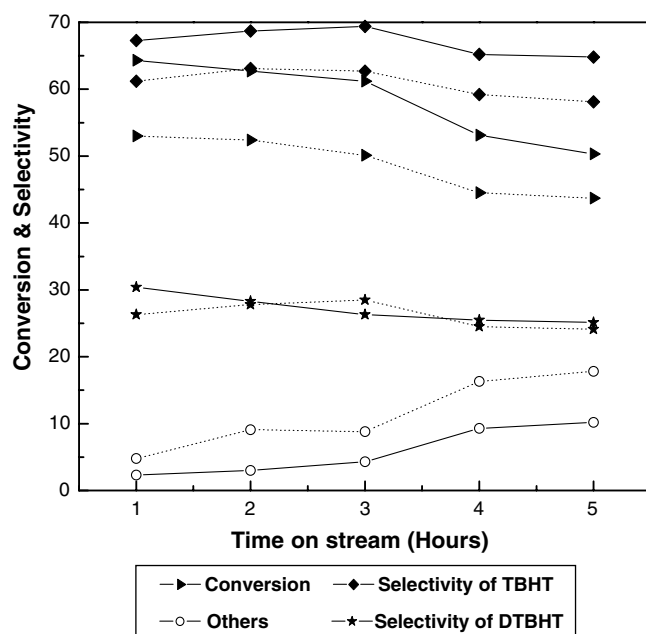
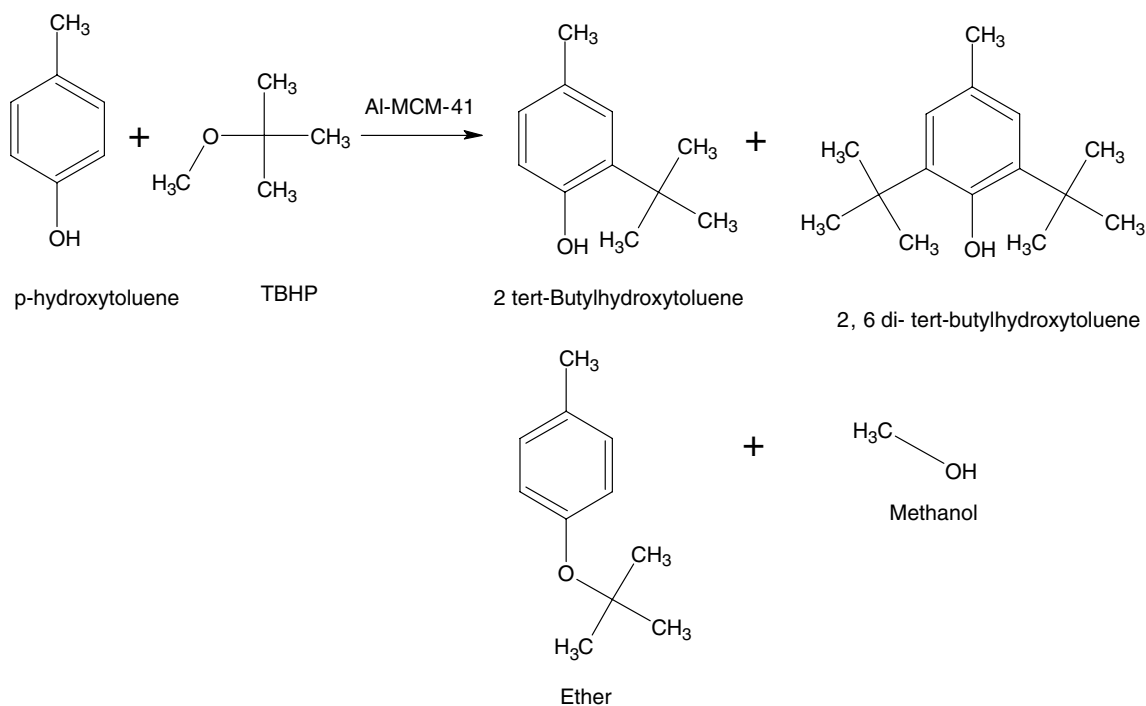


Fig. 11. Effect of weight hourly space velocity on conversion and product selectivity over Al-MCM-41 (25) (—) and Al-MCM-41 (20 Imp) (- - - -).



Scheme 1.

(25) was observed to have better activity, as it yielded higher conversion with better selectivity at 1.65 WHSV^{-1} .

3.2.4. Study of time on stream

The effect of time on stream with a constant WHSV^{-1} of 1.65 h at 300°C and 225°C was performed to understand the variation in conversion and selectivity with time over Al-MCM-41 (25) and 20 wt% PWA loaded Al-MCM-41 (25) catalysts. The results are depicted in Fig. 11. The conversion of *p*-hydroxytoluene with time on stream registered a decrease over both the catalysts. The selectivity of 2-tert-butyl *p*-hydroxytoluene (2TBHT) showed a marginal increase up to 3 h, beyond which it was decreased for both the catalysts. The apparent increase in conversion for 3 h meant the faster desorption of tert-butyl *p*-hydroxytoluene (Scheme 1).

4. Conclusion

From the catalytic data it was proved that Al-MCM-41 catalysts showed remarkable catalytic activity towards tert-butylation of *p*-hydroxytoluene. The treatment of Al-MCM-41 (25) with different weight percent of PWA yielded catalysts with varying acid strength. These catalysts demonstrated to have good catalytic conversions with high yields. Among those PWA loaded catalysts, 20 wt% catalysts were found to show higher activity for tert-butylation of *p*-hydroxytoluene with MTBE. The condition of 225°C with 1.65 WHSV^{-1} was optimized for higher conversion with good selectivity. The yield of ether registered to about 6–10% over all the catalysts. Hence, it was concluded that

PWA loaded Al-MCM-41 catalysts has enhanced preferable acid strength for the tertiary butylation of *p*-hydroxytoluene thereby increasing the bronsted acid sites.

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