

Regio selective butylation of toluene on mordenite catalysts: influence of acidity

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Abstract

Vapour phase tertiary butylation of toluene with *tert*-butylalcohol was studied over high silica large pore mordenite catalysts with varying silica to alumina ratios. Influence of acidity, reaction temperature, time on stream, weight hourly space velocity and concentration of the alkylating agent on the yield and selectivity of *para-tert*-butyl toluene was investigated. Among the isomers formed during the reaction, the *para*-isomer was found to be in significant amounts followed by the *meta*-isomer, while no *ortho*-isomer was found in the products as a result of steric factors. Selectivity for *para*-isomer reduces at higher temperatures and it goes through a maximum in the temperature range 413–433 K. Mordenite catalysts with high silica to alumina ratio, with strong acidity but lower acid site density, offer good conversion, high alkylation selectivity and better *para*-selectivity. The improved *para*-selectivity on high silica mordenites is attributed to the low isomerization activity of the product *p-tert*-butyltoluene on this catalyst when compared to low silica mordenites. Lower concentration of *tert*-butylalcohol in the feed lead to better alkylation as well as *para*-butylation selectivity.

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1. Introduction

Acid catalyzed reactions such as Friedel–Crafts alkylation, acylation, isomerization, etc are important processes in organic synthesis, fine chemical production as well as in petrochemical processes [1,2]. The butylated products of toluene, particularly the *para-tert*-butyltoluene has great commercial significance as its derivatives *para-tert*-butylbenzoic acid and *para-tert*-butyl-benzaldehyde find applications as modifiers in alkylated resins, as solvents, in the production of fragrances, pharmaceuticals, herbicides and as polymerization regulators for polyesters [2,3]. Butylation of toluene has been reported [4] over homogenous catalysts like sulphuric acid, phosphoric acid and boron trifluoride. But these catalysts are not environmentally benign, difficult to regenerate and also lead to the corrosion of equipment. Therefore considerable attention has been devoted for the develop-

ment of solid acid catalysts that are environmental friendly [5–13].

A petrochemical process is evaluated not only on the basis of conversion of a given reactant, but also in terms of selectivity to the desired product. During the butylation of toluene, formation of all the three (*ortho*, *para* and *meta*) positional isomers of butyltoluene is thermodynamically feasible, however positional selectivity depends on the electrophilic and steric factors. It is found that steric factors hinder the formation of *o*-butyltoluene, while *meta*- and *para*-isomers are formed in excess. Based on reports of methylation and ethylation of toluenes [14,15], it is expected that on catalysts with high acidity (higher acid site density), *p-tert*-butyltoluene (PTBT) formed during butylation of toluene is isomerized to *m*-butyltoluene, leading to enhanced concentrations of the later isomer in the product.

Mordenite based (HM) catalysts have strong Brønsted acidity. Coupled with their high surface area, pore volume and large pore openings, they offer immense scope for the transformation of various alkyl aromatics. The present

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investigation deals with the effects of various parameters that enhance the concentration of PTBT vis-à-vis other positional isomers during butylation of toluene on HM catalysts. It is known that acidity, in terms of acid site concentration and strength vary with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Hence, efforts were made to investigate and find suitable $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio that offers not only good conversion of toluene but also high selectivity of PTBT. The mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$ offers good yield of *tert*-butyltoluene and also higher *p*-selectivity as a result of suppression of isomerization reaction. Hence, this catalyst was further explored to understand influence of various process parameters such as temperature, weight hourly space velocity (WHSV) and mole ratio of reactants on yield of *tert*-butyltoluene and selective production of *p-tert*-butyltoluene.

2. Experimental

2.1. Materials

The toluene and *tert*-butylalcohol (TBA) used in this study are of analytical reagent grade and obtained from S.D. Fine Chem Ltd. and Qualigens Fine Chemicals. They were used without further purification. Reference standards used for gas chromatographic analysis were obtained from Sigma-Aldrich Corporation. Three mordenite zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 20 (M-20), 45 (M-45) and 90 (M-90) were obtained from Zeolyst International.

2.2. Characterization

All the zeolite samples were characterized for phase purity and crystallinity by Rigaku Miniflex X-ray powder diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation. ^{27}Al MASNMR spectra were obtained at a magnetic field of 11.7 T on a Bruker DRX-500 spectrometer equipped with 4 mm BB MAS probe. Spectra were recorded at a sample rotation of 10 kHz, while chemical shifts were referenced using $\text{Al}(\text{H}_2\text{O})_6$. Specific surface areas were determined at liquid nitrogen temperatures on a Coulter 100 instrument.

The acidity was monitored through temperature programmed desorption of ammonia (NH_3 -TPD, Micromeritics autochrome 2910). About 200 mg of H-mordenite was placed in a quartz reactor and was activated at 773 K for 4 h in a helium flow of 20 ml min^{-1} . The sample was then cooled to 373 K prior to adsorption of ammonia by pulsing 10% NH_3 in helium. Followed by saturation of sample with ammonia, it was purged at 373 K in helium for one hour. The desorption experiment was carried out by heating the sample up to 1073 K at a uniform rate of 10 K min^{-1} .

For Infrared spectra of chemisorbed pyridine, self-supported thin wafers ($5\text{--}6 \text{ mg cm}^{-2}$) were prepared, evacuated (10^{-5} Torr) at 673 K for 12 h and cooled to 373 K. Then pyridine vapours were introduced into the cell and sample was equilibrated for 30 min. Subsequently, the spectra were

recorded after evacuation of the sample (for 2 h) at various desorption temperatures. All the spectra were recorded using a Nicolet 60 SXB spectrometer with 2 cm^{-1} resolution, averaging over 500 scans.

2.3. Butylation of toluene

The *tert*-butylation of toluene was carried out in a down flow fixed-bed reactor using 2 g of catalyst. The catalyst was activated at 773 K in a flow of air for 6 h prior to cooling it to reaction temperature (393–453 K) in nitrogen atmosphere. The reactant feed consisting of toluene and TBA in the desired (molar) ratio was fed to the reactor at required weight hourly space velocity (WHSV) using a liquid injection syringe pump (Isco Model 500D). The products were condensed using a chilled condenser and analysed periodically on a gas chromatograph (Shimadzu 14A) with a FID detector, equipped with BP-1 capillary (50 m length \times 0.32 mm ID) column. The conversion of toluene, alkylation selectivity and PTBT selectivity are calculated according to the following equations:

conversion of toluene (wt.%)

$$= \text{fraction of toluene converted (wt.\%)} \times 100$$

alkylation selectivity

$$= \text{fractional moles of TBA utilized for alkylation} \times 100$$

PTBT selectivity

$$= \frac{\text{PTBT in prod. (wt.\%)}}{\sum \text{tert-butyl toluenes in prod. (wt.\%)}}$$

3. Results and discussion

The powder XRD analysis of the three mordenite samples with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios show that these samples are highly crystalline pure phases. The specific surface areas of these samples were determined by N_2 adsorption and were found to be 491, 499 and $502 \text{ m}^2/\text{g}$. The results show that there is a marginal increase in surface area with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

The NH_3 -TPD profiles of the mordenite catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio are shown in Fig. 1. At least two peaks, one at low desorption temperature (α) and another at high desorption temperature (β) were observed for all the three mordenite samples. While there was a gradual decrease in the intensity of the high temperature desorption peak with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, drastic reduction in intensity of the low temperature signal was observed for high silica sample M-90. High temperature peak is assigned to desorption of ammonia from strong acid sites, while the low temperature peak is assigned for desorption of ammonia from

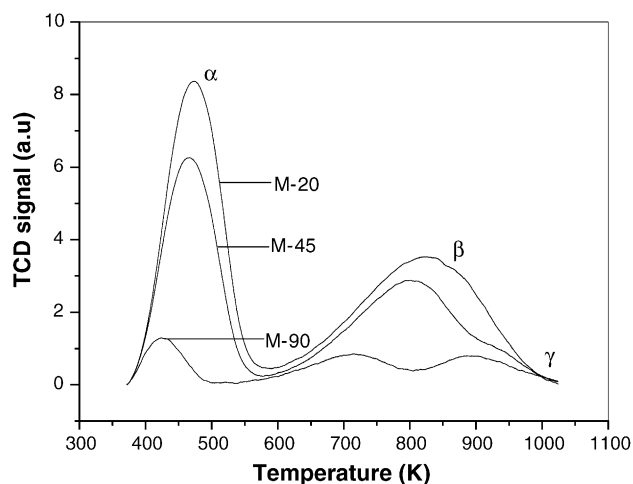


Fig. 1. NH_3 -TPD profiles of the mordenite catalysts with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

silanol and other weakly acidic centers [16]. Since, total acidity (Brönsted and Lewis) and structural aluminum content of the zeolite are linearly related, it is expected that acidity decreases for samples with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, which is confirmed by these results.

In general, two peaks are reported in the literature [17] for mordenite zeolites, one at low temperature (LT) and another at high temperature (HT). Though our results are in conformity with these reports for low silica samples, they are at variance for high silica samples as an additional peak (γ) at higher temperature was observed for these samples. As may be seen from Fig. 1 that an un-ambiguous third peak was observed for M-90 sample, while a hump indicating the presence of a third peak could be clearly seen for M-45 mordenite catalyst. Previous reports attributed this to strong Lewis acidity [17]. To probe this aspect, chemisorption of pyridine at different temperatures was monitored using FT-IR spectroscopy.

Infrared spectra of pyridine chemisorbed on the sample after evacuation at various desorption temperatures has been given in Fig. 2 for the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ mordenite M-20 sample. Pyridine bound to Brönsted (B_{Py} , 1544 cm^{-1}) and Lewis sites (L_{Py} , 1452 cm^{-1}) and the common C–C stretching band (1489 cm^{-1}) corresponding to B_{Py} and L_{Py} could be clearly seen in these spectra [16,18]. Lewis (L_{Py}) pyridine was desorbed at lower temperatures than the Brönsted (B_{Py}) pyridine on all mordenite catalysts. The variation in relative $\text{B}_{\text{Py}}/\text{L}_{\text{Py}}$ ratio with increasing evacuation temperature is given in Table 1. For all mordenite catalysts, $\text{B}_{\text{Py}}/\text{L}_{\text{Py}}$ ratio went on increasing with the evacuation temperature, except that there was slight drop at 673 K. Even at this temperature, the ratio on M-90 is close to 3.8, suggesting that Brönsted acidity is much higher than Lewis acidity even at this temperature. If the third peak (γ) in the TPD spectra of M-90 corresponds to Lewis acidity, the $\text{B}_{\text{Py}}/\text{L}_{\text{Py}}$ ratio should have been either ≤ 1 , on desorption of pyridine at 673 K. Hence, it may not be proper to attribute third peak in the TPD spectra to strong Lewis acidity.

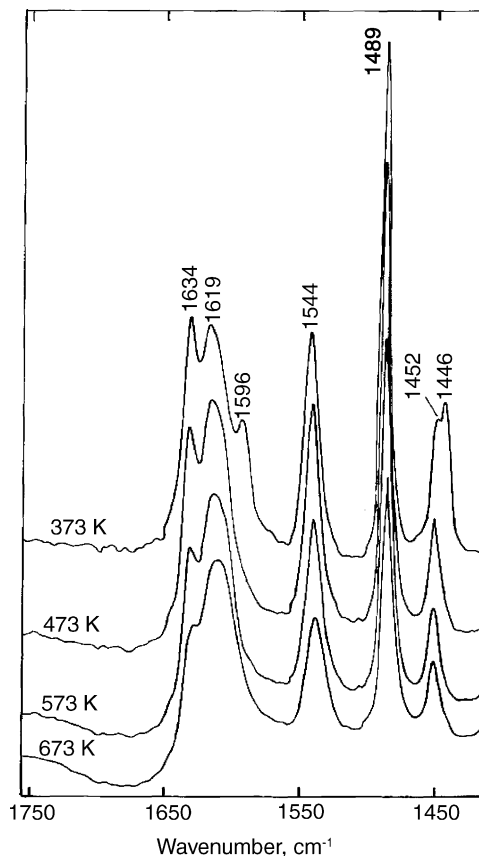


Fig. 2. IR spectra of pyridine at various desorption temperatures on M-20 catalyst.

To elucidate the origin of the third peak in the ammonia-TPD, ^{27}Al MASNMR of the mordenite catalysts were analysed. Fig. 3 shows ^{27}Al MASNMR spectra of mordenite samples of different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Two peaks, one at 55.3 ppm, assigned to aluminium in tetrahedral framework and another peak at 0.5 ppm assigned to octahedral aluminium was observed [19,20]. No other ^{27}Al peak that is attributed to other than these co-ordinations was observed. Surprisingly, ^{27}Al spectra show relatively high concentration of octahedral species for low silica samples. In fact, high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio samples are expected to have more of this octahedral aluminium species as these are usually obtained on severe de-alumination of low silica samples, followed by its extraction with various treatments.

Table 1
Brönsted to Lewis pyridine ratios at various desorption temperatures on mordenite catalysts

Temperature of desorption (K)	Brönsted to Lewis pyridine ratio (B/L)		
	M-20	M-45	M-90
373	1.751	2.168	1.205
473	3.423	3.616	4.397
573	3.455	4.077	5.283
673	2.517	3.055	3.784

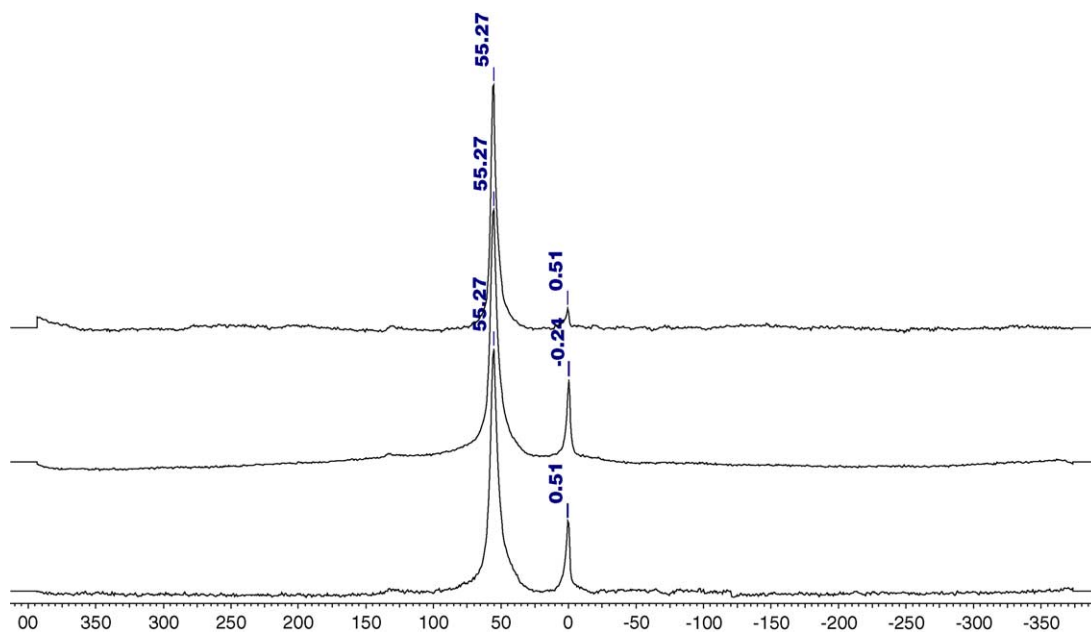


Fig. 3. ^{27}Al NMR spectra of mordenite catalysts with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. (a) M-20; (b) M-45 and (c) M-90.

Origin of the third peak in NH_3 -TPD may be ascribed to the desorption of ammonia from strong acid sites which may have been inaccessible prior to de-alumination of the parent mordenite to obtain the high silica sample. Hence, these acid sites may be structural hydroxyls that are associated with aluminium in the eight-membered rings. It is to be noted that high silica mordenites are prepared through severe de-alumination and this process may lead to development of secondary pore structure [21]. The development of secondary pore structure may have led to a better accessibility of hydroxyls present in the eight-member rings and the γ peak may be interpreted for the ammonia desorbed from these sites. However, this interpretation is being probed further.

3.1. Butylation of toluene

Toluene butylation was carried out using TBA as the alkylating agent in a down flow fixed-bed reactor. Effect of various reaction parameters has been investigated to obtain the best possible activity to produce *p-tert*-butyltoluene with high selectivity.

3.1.1. Effect of silica/alumina ratio

Acidity has two variables, the number and strength of acid sites. It is known that number of acid sites is linearly related to the amount of aluminium in the tetrahedral framework, hence, it is expected to fall with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$. Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ variation on *tert*-butylation of toluene is shown in Table 2. Conversion of TBA, the alkylating agent, which is used in highly dilute (TBA:toluene = 1:8) quantities, is complete on all mordenite catalysts. Only two isomers of butyltoluene, i.e., *p-tert*-butyltoluene (PTBT) and *m-tert*-butyltoluene (MTBT) were found in the product mix-

ture, whereas *ortho*-butyltoluene is completely absent in the product. PTBT selectivity was greater on catalysts with high silica content at any reaction temperature when compared to low silica catalysts. On an acid catalyst that has strong acidity, consecutive reactions of isomerization and de-alkylation are expected to take place, followed by alkylation. However, these consecutive reactions may be suppressed if the acid site density of the catalyst is reduced as a result of increased $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the sample. This is clearly reflected in our results, as the PTBT selectivity is high on catalysts that have high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [22,23].

The butylation reaction on the mordenite catalysts is quite selective as they hardly yield any side products. The alkylation selectivity, defined in terms of fraction of TBA utilized for alkylation was found to be greater for catalysts that have high silica content. As a result, conversion of toluene was high on these catalysts, though acidity in terms of number of acid sites dropped with increasing silicon content. This could be attributed to the suppression of side reactions that consume valuable alkylating agent leading to a fall in the toluene conversion.

Table 2

Butylation of toluene with TBA on mordenite catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios

Product composition (wt.%)	Mordenite catalyst		
	M-20	M-45	M-90
PTBT	8.26	10.43	11.89
MTBT	6.89	5.66	5.40
Toluene	84.85	83.91	82.38
Toluene conversion	15.15	16.09	17.62
PTBT selectivity	54.52	64.85	67.40
Alkylation selectivity	81.07	86.07	94.28

Temperature – 433 K, TOS second hour, WHSV – 3, toluene:TBA – 8:1.

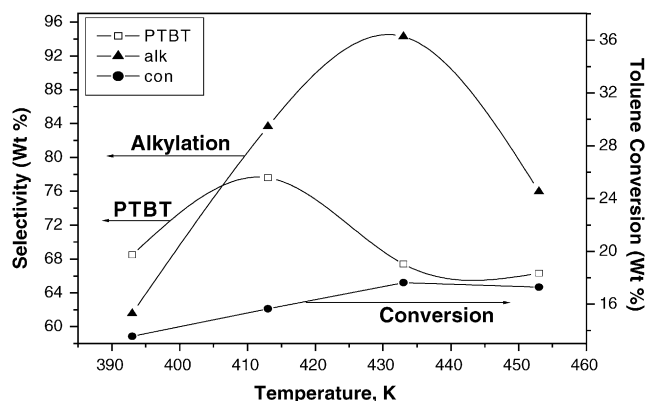


Fig. 4. *tert*-Butylation of toluene with TBA on M-90 catalyst at different reaction temperatures. Catalyst – M-90, TOS second hour, WHSV – 3, toluene:TBA – 8:1.

The above results show that mordenite catalysts with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ are better equipped for butylation of toluene than the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ samples, though the acidity is expected to be higher in the later samples. The M-90 catalyst, with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$ seems to be optimum and is best among the mordenite catalysts used in this study for the *tert*-butylation of toluene with TBA. Hence, this catalyst has been studied further by varying different reaction parameters in order to find the optimum conditions for this reaction.

3.1.2. Effect of temperature

Effect of reaction temperature on the *tert*-butylation of toluene is shown in Fig. 4. Compared to alkylation of toluene with lower ($\text{C}_1\text{--}\text{C}_3$) alcohols, alkylation with *tert*-butylalcohol (TBA) takes place at much lower (393–453 K) temperatures. It may be seen that with increasing reaction temperature, though the conversion of toluene increases, it falls at higher (453 K) temperatures. The PTBT selectivity too followed a similar trend, as it has initially increased in the 393–413 K temperature zone, while it fell at higher temperatures. The PTBT selectivity shows a plateau (~67%) at high temperatures (433–453 K). In the case of alkylation selectivity, though the trend is similar, the effective temperature shifts towards right, giving highest alkylation selectivity of 94.3% at 433 K. Increasing reaction temperature beyond 433 K led to a steep fall in its value, probably as a result of non-selective reactions that consume the alkylating agent, thus reducing its availability for butylation. It is known that butene formed through dehydration of TBA on acidic catalysts can oligomerise to C_8 and C_{12} olefins and then crack to low boilers. Since these reactions are dominant at higher reaction temperatures, a fall in the toluene conversion as well as butylation selectivity is expected.

3.1.3. Effect of WHSV

Space velocity or contact time is an important parameter as it not only influences the conversion of a reactant, it also leads to changes in selectivity of various products. Diffusion constraints have a bearing on product shape selectivity, which

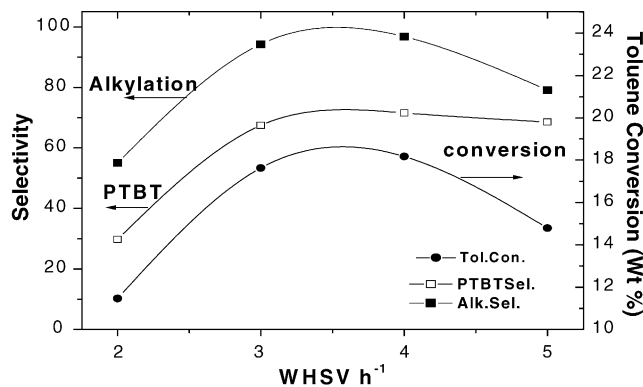


Fig. 5. *tert*-Butylation of toluene with TBA at different WHSV on M-90. Toluene:TBA – 8:1, temperature – 413 K, TOS second hour.

in turn govern the product pattern, particularly in a zeolite driven catalytic process. Space velocity also influences the secondary and consecutive reactions. As a result, desired selectivity to a particular product can be achieved by choosing right space velocity. Influence of space velocity on toluene conversion and selectivity to PTBT is given in Fig. 5. Toluene conversion has increased with space velocity, reaching a maximum in the WHSV= 3–4 region. At lower space velocities, the TBA might have under gone un-desirable non-selective reactions, leading to formation of aliphatics and as a consequence the toluene conversion is low under these conditions. This is reflected in the high concentration of aliphatics in the product at lower space velocities (not shown in the figure). A similar trend was also observed in the case of alkylation selectivity.

Lower space velocities have an adverse influence on the PTBT selectivity, as it was found to be less than 30% at WHSV=2. However, with increasing space velocity, it rises quite rapidly up to a value of WHSV=3 and remains there at that level even after further increases in space velocity [24]. These observations show that WHSV in the region of 3–4 not only offers high selectivity but also high conversion.

3.1.4. Effect of toluene to TBA ratio

Influence of toluene/TBA ratio on activity and selectivity to PTBT is shown in Fig. 6 for M-90 catalyst. Conversion of TBA is complete at all toluene to TBA mole ratios. Though toluene conversion has increased with higher alcohol content in the feed (lower mole ratio), the increase is not proportional to the alcohol content in the feed. This lower utilization of alkylating agent led to a steep fall in alkylation selectivity with higher TBA contents in the feed. In addition, at high mole ratios, PTBT selectivity has improved, though not to an appreciable extent. These results suggest that feeds at high mole ratios (low TBA content) are desirable for butylation, particularly the mole ratios in 6:1 to 8:1 region being the most appropriate. Similar observations were reported for propylation of benzene to cumene and propylation of toluene to cymene on various zeolite catalysts [25]. In fact, industrial processes based on beta zeolite for preparation of cumene

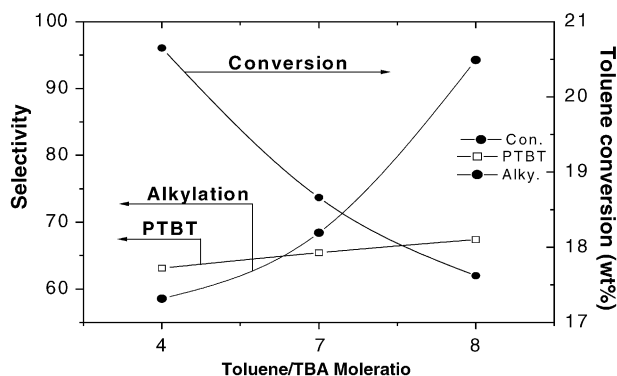


Fig. 6. Effect of toluene/TBA molar ratios on M-90 catalyst. TOS second hour, WHSV – 3, temperature – 413 K.

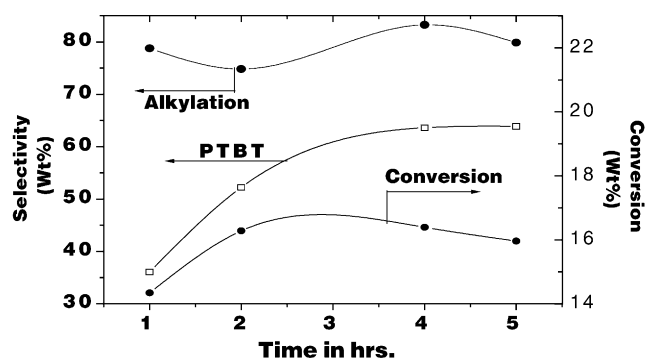


Fig. 7. Influence of time on stream on M-90 catalyst. Catalyst – M-90, WHSV – 3, temperature – 413 K, molar ratio – 8:1 (toluene:TBA).

uses low propylene concentration in the feed, to achieve high alkylation selectivity. Among the mordenites, M-90 gave the best alkylation selectivity, as catalysts with low acid site density promote selective alkylation through suppression of undesirable cracking and disproportionation reactions.

3.1.5. Effect of time on stream (TOS)

The influence of TOS was investigated on M-90 as it was found to be a better catalyst for toluene *tert*-butylation reaction (Fig. 7). There was some surge in the conversion of toluene in the initial stages, while a marginal reduction in the conversion of toluene was observed with time on stream. This kind of initial increase in activity is typical of alkylation reactions on large pore zeolites. Alkylation as well as PTBT selectivities increased to respectable levels with TOS, probably as a result of coke formation on the catalysts. This kind of increase can only be attributed to product shape selectivity effects resulting from coke deposition at pore mouths of these zeolites [26].

4. Conclusions

Alkylation of toluene with *tert*-butyl alcohol was investigated on mordenite catalysts with various $\text{SiO}_2/\text{Al}_2\text{O}_3$

ratios. These catalysts were characterized through XRD, BET surface area measurements, ^{27}Al MASNMR, TPD of ammonia and IR of chemisorbed pyridine. Ammonia TPD measurements show two desorption maxima for low silica ($\text{SiO}_2/\text{Al}_2\text{O}_3$) samples, while three desorption maxima were observed for high silica samples. Though reports attribute the third TPD peak on high silica zeolites to strong Lewis acidity, infrared studies of chemisorbed pyridine rule out this possibility. ^{27}Al MASNMR does not show any enhancement in the relative concentration of hexa-coordinated aluminium in high silica samples. Mordenite catalysts with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios offer good alkylation and PTBT selectivity's, in addition to higher toluene conversion. High reaction temperatures and contact times are not favourable for obtaining good yield of butyltoluenes and also that of PTBT. Similarly, high reaction temperature and acid site density (low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) promotes isomerization of *para*-isomer to *meta*-isomer thus reducing the PTBT selectivity. Feeds containing lower concentration of TBA are better suited for attaining high alkylation selectivity and also for the suppression of non-selective reactions. With time on stream, alkylation and PTBT selectivity's improved while slight fall in the conversion of toluene was observed.

References

- [1] G.A. Olah (Ed.), Friedel–Crafts and Related Reactions. Vol. II: Alkylation and Related Reactions, Interscience, New York, 1963.
- [2] A. Knop, L.A. Pilato, Phenolic Resins Chemistry, Springer-Verlag, Berlin, 1985.
- [3] E.D. Ozokwelu, Kirk-Othmer Encyclopedia Chem. Tech. 24 (1997) 350.
- [4] R.H. Allen, L.D. Yats, J. Am. Chem. Soc. 83 (1961) 2799.
- [5] A.J. Kolka, J.P. Napolitano, G.G. Elke, J. Org. Chem. 21 (1956) 712.
- [6] A. Corma, H. Garcia, J. Primo, J. Chem. Res.(s) 40 (1988).
- [7] A.U.B. Queiroz, L.T. Aikawa, French Patent 2 694 000 (1994).
- [8] C.D. Chang, S.D. Chang, S.D. Hellring, US Patent 5 288 927 (1994).
- [9] M. Yamamoto, A. Akyama, JP 6 122 639 (1994).
- [10] S. Subramanian, A. Mitra, C.V.V. Satyanarayana, D.K. Chakrabarty, Appl. Catal. A: Gen. 159 (1997) 229.
- [11] K. Zang, D. Xu, H. Zhang, S. Lu, C. Huang, H. Xiang, H. Li, Appl. Catal. A: Gen. 166 (1998) 89.
- [12] A. Sakthivel, N. Saritha, P. Selvam, Catal. Lett. 72 (2001) 225.
- [13] E.M. Viorcia, E.S.A. Merouiu, H. Justin, O. Maria, C. Eleonora, Rom. Pat. 73 (1981).
- [14] F. Lonyi, J. Engelhardt, D. Hardo, Zeolites 11 (1991) 169.
- [15] D. Frenkel, M. Levy, J. Catal. 118 (1981) 10.
- [16] C.V.V. Satyanarayana, D.K. Chakrabarty, Indian J. Chem. Sec. A 30 (1991) 422.
- [17] F. Lonyi, J. Valyon, Micropor. Mesopor. Mater. 47 (2001) 293.
- [18] M. Kojima, M.W. Rantenbach, C.T. O'Connor, J. Catal. 112 (1988) 505.
- [19] C.A. Fyfe, G.C. Gobbi, J.S. Hartman, J. Klinowski, J.M. Thomas, J. Phys. Chem. 86 (1982) 1247.
- [20] J. Klinowski, J.M. Thomas, C.A. Fyfe, G.C. Gobbi, Nature 296 (1982) 530.
- [21] G.R. Meima, M.J.M. van der Aaist, M.S.U. Samson, J.M. Garces, J.G. Lee, et al., in: R. von Ballmoos (Ed.), Proceedings of the Ninth

- International Zeolite Conference '1992, Reed Publishing, 1993, p. 327.
- [22] Y.S. Bhat, J. Das, A.B. Halgeri, *App. Catal. A: Gen.* 122 (1995) 161.
- [23] C. Bezouhanova, C. Dimitrov, V. Nenova, B. Spassov, H. Lahert, *Appl. Catal.* 21 (1986) 149.
- [24] P.A. Parikh, N. Subrahmanyam, Y.S. Bhat, A.B. Halgeri, *Appl. Catal. A: Gen.* 90 (1992) 1.
- [25] K.S.N. Reddy, B.S. Rao, V.P. Shiralkar, *Appl. Catal. A: Gen.* 121 (1995) 191.
- [26] W.W. Kaeding, C.C. Chu, L.B. Young, S.A. Butler, *J. Catal.* 69 (1981) 392.