

Butylation of toluene: Influence of zeolite structure and acidity on 4-*tert*-butyltoluene selectivity

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Abstract

Vapour phase alkylation of toluene with *tert*-butyl alcohol was studied over the large pore zeolites H β , HY and HMCM-22. The influence of the acidity, reaction temperature, run duration, feed rate (WHSV) and molar ratio of the reactants on conversion of toluene and selectivity for 4-*tert*-butyl toluene was studied. Among the isomers formed during the reaction, the *para*-isomer was the predominant one, followed by the *meta*-isomer, while no *ortho*-isomer was found in the products due to steric factors. 4-*tert*-Butyl toluene selectivity decreases at higher temperatures, while going through a maximum in the 413–433 K temperature range. Zeolite HY with a high silica to alumina ratio (SiO₂/Al₂O₃ = 80), that has strong acidity, but lower acid site density, possesses high activity for toluene conversion, high alkylation selectivity and also high *para*-selectivity. The improved *para*-selectivity of high silica HY zeolite is attributed to the low isomerization activity that results in the suppression of the secondary isomerization of 4-*tert*-butyl toluene. Both alkylation and selectivity are higher with feed mixtures containing a lower fraction of *tert*-butyl alcohol.

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1. Introduction

The alkylation of aromatic hydrocarbons with olefins/alcohols to obtain mono- and di-alkylated aromatics is applied on a large scale in the industry [1]. The *para*-dialkylated aromatics like *p*-xylene, *p*-di-isopropylbenzene, *p*-ethyltoluene, *p*-diethylbenzene, *p*- and *m*-cymenes and 4-*tert*-butyltoluene (4-TBT) are very important in fine chemical and petrochemical industry [2,3]. 4-TBT, which is an intermediate for 4-*tert*-butylbenzoic acid and 4-*tert*-butylbenzaldehyde, is produced by the alkylation of toluene with isobutylene, di-isobutylene, MTBE and *tert*-butyl alcohol (TBA). Ioffe et al. [4] studied different catalytic systems, such as AlCl₃, AlCl₃–CH₃NO₂, sulphuric acid and polyphosphoric acid in the liquid phase for alkylation of toluene by C₄ alcohols. Using TBA as the alkylating agent and AlCl₃ as the catalyst, at 298 K, a mixture of *tert*-butyltoluenes (67.5% *meta*- and 32.5% *para*-isomer) was obtained with 64% yield and with isomer distribution close to the equilibrium composition (64% *meta*- and 36%

para-isomer). However, no *ortho*-isomer was observed in the product [4]. Butylation of toluene has been reported [5] over homogenous catalysts like sulphuric acid, phosphoric acid and boron trifluoride. But these mineral acid catalysts are not environmentally benign, not re-usable and also lead to corrosion of the equipment. Therefore, considerable attention has been devoted to the development of solid acid catalysts that are environment friendly [6–8]. Toluene butylation has been carried out in the liquid phase in the presence of activated clay and silica-alumina catalysts at 423–503 K [9]. Butylation of toluene with *tert*-butylchloride at room temperature, catalysed by calcined iron sulphate treated with hydrogen chloride led to 86% conversion of toluene and a product distribution of 5% *meta*- and 95% *para*-isomer [10]. The isopropylation of toluene has been reported over a number of zeolites, e.g. ZSM-5 [13], β , mordenite, ZSM-12 [14–16] and the mesoporous material MCM-41 [3]. However, the use of zeolites as catalysts in *tert*-butylation of toluene has not been extensively reported. The use of NiY for this reaction has been reported, but catalytic activity and selectivity to the desired 4-*tert*-butyltoluene were very low [11]. Recently, a study comparing the activity of large pore zeolites for toluene butylation in the liquid phase has been published [12].

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In a previous study [17], we have reported toluene butylation over mordenite catalysts with different silica to alumina ratios. We were able to achieve up to 68% 4-TBT selectivity over a mordenite catalyst with large silica to alumina ratio. In the present study, we report further improvements in the 4-TBT selectivity. The study deals with an extensive investigation of the *tert*-butylation of toluene over three large-pore zeolites (HY, H β and HMCM-22) possessing three-dimensional pore structure.

2. Experimental

The synthesis methods used and the physico-chemical methods employed for the characterization of various zeolite catalysts are given in the following sections.

2.1. Synthesis of MCM-22

Large pore HY zeolite with different SiO₂/Al₂O₃ ratios, as well as H β were procured from Zeolyst International. MCM-22 was synthesized according to a method published by Corma et al. [18] using hexamethyleneimine as the organic template. In a typical procedure, sodium aluminate (1.0 g, Riedel-de Haen, ~55% of Al₂O₃, 45% of Na₂O) was added to a solution of 0.6 g of sodium hydroxide in 125 g of distilled water and stirred until it dissolved. To this, 8.6 g of hexamethyleneimine (Fluka) was added and the resulting mixture was thoroughly stirred for at least 30 min. Finally, 9.2 g of fumed silica (Cab-O-Sil M5) was added and the resulting mixture was homogenized for 60 min. The crystallization was conducted in a Teflon-lined stainless steel autoclave under autogenous pressure in a tumbling oven at 438 K for 8 days. The crystalline product was filtered, dried at 373 K and calcined at 823 K for 6 h. This NaMCM-22 was converted into the NH₄⁺ form using a solution (1 M) of NH₄NO₃. The NH₄-MCM-22 was dried at 373 K and calcined at 773 K to yield HMCM-22. All the commercial zeolites were employed without further modification.

2.2. Physico-chemical characterization of catalysts

The crystallinity and phase purity of the zeolite samples were evaluated by powder XRD (Rigaku, Miniflex) using monochromatized Cu K α (30 kVA, 15 A) X-rays. The structural acidity was determined by temperature programmed desorption of ammonia using Micromeritics 2910 instrument. For NH₃-TPD studies, the catalyst was activated in helium flow for 2 h at 823 K. Then the sample was cooled to 373 K before the adsorption of ammonia. Subsequently, 10% NH₃ in helium (10 ml/min) was passed through the sample for 30 min followed by which the sample was treated in helium flow for 1 h. The desorption experiments were carried out in the temperature range of 373–873 K at a heating rate of 10 K/min. BET surface area measurements were carried out on a Nova 1200 instrument by nitrogen sorption at 77 K. Prior to the sorption of N₂, the samples were heated in vacuum at 573 K for 3 h.

2.3. Butylation reaction procedure and product analysis

Butylation of toluene was carried out at atmospheric pressure, in a fixed bed, down flow, integral silica reactor. Prior to the reaction, the catalyst was calcined at 823 K for 3 h. About 1.5 g of catalyst (10–20 mesh) was placed at the center of the silica reactor supported by quartz wool and porcelain beads. The reactor was placed vertically in a two-zone furnace (Geomechanique, France) controlled by temperature programmers (Eurotherm). Liquid reactant mixture containing toluene + TBA was fed with a high-precision syringe pump (ISCO 500D). The reaction products were condensed using chilled water condenser and the samples were collected at regular intervals. The products were analysed by GC (HP-6890) equipped with FID and capillary column (BP-5, 50 m, 0.32 μ m film thickness). The reaction products were identified by GC–MS (QP5000, Shimadzu), GC–IR (Perkin-Elmer) and by using authentic (Aldrich) standards.

3. Results and discussion

3.1. Characteristics of zeolites used in the study

Zeolite β has a three-dimensional interconnecting pore system with pores of 0.55 nm \times 0.55 nm and 0.76 nm \times 0.64 nm, whereas Y zeolite has a three-dimensional interconnecting pore system with super cages of 1.18 nm connected by circular 12-ring 0.74-nm windows. The structure of zeolite MCM-22 consists of two independent pore systems. One pore system is defined by two-dimensional sinusoidal 10-membered ring channels (0.40 nm \times 0.59 nm), while the second pore system consists of large super cages with a free inner diameter of 0.71 nm, circumscribed by 12-membered rings. The size of the large super cages is 1.82 nm. However, these huge intra-crystalline voids are accessible only through 10-membered-ring apertures.

All the zeolite samples used in this study were subjected to powder XRD. The crystallinities of the samples, including the MCM-22 synthesized for this study was found to be good and comparable to those reported in the literature [19]. The HMCM-22 sample was also investigated for its SiO₂/Al₂O₃ ratio by chemical analysis/XRF.

3.2. Acidity of zeolites

The ammonia-TPD studies provide valuable information on relative acid strength, number and distribution of the acid sites. Fig. 1 shows the NH₃-TPD pattern of zeolite samples with different structural characteristics and acidities. TPD of ammonia is most useful for comparing the acidity characteristics of zeolite samples of the same structure, but possessing different acidities as a result of variation in Si/Al ratio. However, it can also be used for a quantitative comparison of the acidity of various zeolites, but not have the same structure. The position of the temperature maxima (T_{\max}) depends on the strength and concentration of acid sites. Hence, T_{\max} alone cannot be used to comment on the strength of acid sites while comparing various zeolite structures. Two TPD peaks, characterized by two temperature maxima (Table 1), were observed in the NH₃-TPD

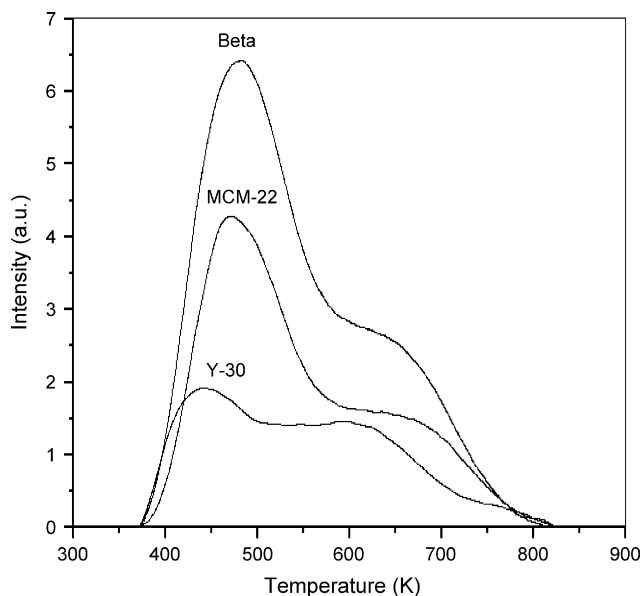


Fig. 1. Ammonia TPD pattern of various large pore zeolites with similar Si/Al ratios.

spectra of all the representative samples. Even though, zeolites HY (Y-30) and H β are characterized to have similar silica to alumina ratio, β shows a much higher acidity in terms of ammonia desorbed. Infact, similar observations were earlier made by Mravec et al. [12]. This difference in acidity may be attributed to structural characteristics. Fig. 2 shows the TPD profiles of HY zeolites that have different silica to alumina ratios. As the silica to alumina ratio increases, the total acidity of the zeolites clearly reduces, the decrease being more prominent for the low temperature peak that is associated with the interaction of NH₃ with silanols and other adsorption centers. The variation of acidity with SiO₂/Al₂O₃ ratio in millimoles of NH₃ desorbed is shown as inset in Fig. 2.

3.3. Catalytic activity

Butylation of toluene using TBA as the alkylating agent was carried out over three zeolites with different frameworks, but with similar SiO₂/Al₂O₃ ratios viz., H β (25), HY (30) and HMCM-22, in the temperature range 393–453 K. The main reaction products observed were 4-*tert*-butyltoluene (4-TBT) and 3-*tert*-butyltoluene (3-TBT); 2-*tert*-butyltoluene (2-TBT) was completely absent in the product. The main alkylation product

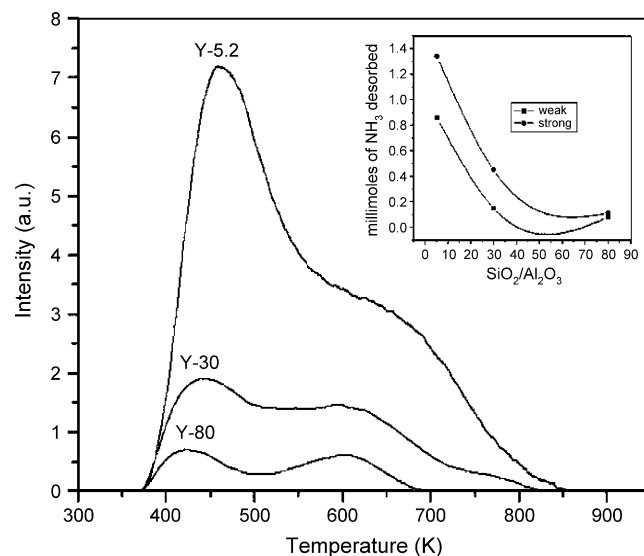


Fig. 2. Ammonia TPD pattern of HY zeolite with different silica to alumina ratios.

is expected to be 4-TBT as it is kinetically favoured. Due to steric hindrance of the methyl group on one side and the presence of the voluminous *tert*-butyl group on the other side, 2-TBT is not expected to form except through consecutive isomerization steps on the outer surface of zeolites. Shape-selectivity also plays a role, though it depends on the particular pore structure. In the higher boiling fraction of the product, 3,5-di-*tert*-butyltoluene, which has all alkyl groups in the *meta*-position to each other was present in trace amounts over HY and H β zeolites. This 3,5-di-*tert*-butyltoluene is most probably formed outside the pore structure of the zeolite as its diffusion from the channels is hindered due to its bulkiness. What is common in all cases is that selectivity to 4-TBT is much higher than the thermodynamic equilibrium value under all the reaction conditions.

3.3.1. Butylation of toluene—comparison of various large pore zeolites

When the comparison is made among the three different large-pore 3-D zeolites (Fig. 3), the most active catalysts for toluene butylation are HY and H β . Over all the catalysts, the initial toluene conversion was low, while it continuously increased with time on stream, reaching a maximum after considerable time on stream. This kind of phenomenon was reported by Karge et al. [20] for large pore zeolites, which was termed as the induc-

Table 1
Physico-chemical characteristics of the zeolites used in toluene butylation

Catalyst	SiO ₂ /Al ₂ O ₃	Pore system and size (nm)	SA (g/m ²)	TPD, T _{max} (K)	Acidity (mmol)	
					W	S
Y-5	5.2	0.74 × 0.74 × 0.74	750	464, 602	0.86	1.34
Y-30	30	0.74 × 0.74 × 0.74	780	440, 576	0.15	0.45
Y-80	80	0.74 × 0.74 × 0.74	780	431, 588	0.08	0.11
H β	25	0.55 × 0.55, 0.76 × 0.64	685	476, 614	0.65	0.55
HMCM-22	52	0.41 × 0.51, 0.71 × 0.71 × 1.8	544	476, 620	0.32	0.28

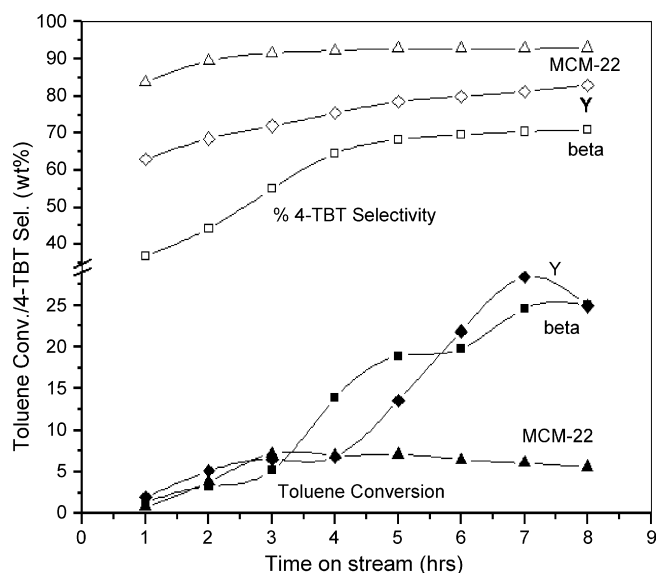


Fig. 3. Comparison of toluene butylation on various zeolite catalysts. WHSV = 2 h⁻¹, Tol:TBA = 4:1, temperature 393 K.

tion period. As the reaction proceeded further, the conversion of toluene increased over all the three zeolites to various extents. The toluene conversions on H β , HY and HMCM-22 were 14, 6.8 and 7.1% after 4 h on stream. Afterwards, the conversion on MCM-22 stayed steady at around 6–7% and then started to decrease with time. On the contrary, there was a steep rise in the toluene conversion on H β and HY from the fourth hour. But the selectivity for 4-TBT on MCM-22 (92%) was much higher than that over the H β zeolite. However, as the selectivity can be compared only at similar conversions, it is better to compare H β and HY as the conversions are similar over these samples. Compared to H β , the selectivity for 4-TBT is relatively higher on Y zeolite. It may be recalled that HY zeolite was characterized with lower acidity compared to H β . This lower acidity might help suppress the isomerization of 4-TBT that is formed in the first instance as a result of kinetic considerations. Zeolite β was

stable up to 8 h on stream, while HY zeolite showed deactivation after 7 h.

3.3.2. Effect of temperature on various zeolite catalysts

The reaction temperature was increased from 393 to 453 K for all the zeolites investigated. The results are shown in Table 2. The conversion of toluene (22%) was highest at 393 K on β and Y zeolites, while it dropped to 16 and 14%, respectively, at 453 K. However, the conversion of TBA was complete at all temperatures. There was a marginal increase in 4-TBT selectivity with increasing reaction temperature on zeolite β , while the trend was exactly opposite on HY zeolite. This may be attributed to the larger pore aperture of zeolite HY that does not constrain or pose any diffusion barriers for 3-TBT. There was a continuous drop in the yield of tertiary butyl toluenes with increasing reaction temperature, probably as a result of drop in the toluene alkylation activity. This drop was steep at high temperatures (>433 K). One reason that can be attributed to this is the domination 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 C₈ and C₁₂ olefins that can either form coke or 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. Conversion is also expected to fall at higher temperatures because of dealkylation of TBTs. Zeolite MCM-22, on the other hand, behaves in a different manner, though it is also a 3-D zeolite like β and Y. The toluene conversion increases from 393 to 433 K, while it decreases above that temperature. TBA conversion was always 100% even on this zeolite at all temperatures. The 3-TBT fractions in the product increases continuously with reaction temperature. This may be due to the isomerization of 4-TBT to 3-TBT. The selectivity decreases from 90.6% at 393 K to 77.4% at 453 K. The crystallite size of MCM-22 is smaller than the other zeolites; as a result, less constraints are expected for the diffusion of 3-TBT. In addition, isomerization of 4-TBT is favoured outside the pore structure.

Table 2
Comparison of toluene butylation on different zeolites at various reaction temperatures

Zeolite Si/Al	Temperature (K)	Product (wt%)			Toluene conversion (wt%)	4-TBT selectivity (wt%)
		3-TBT	4-TBT	Others		
H β (25)	393	7.9	12.9	0.3	21.1	62.3
	413	7.1	12.5	0.2	19.8	63.0
	433	6.1	12.2	0.0	18.5	66.6
	453	4.7	10.7	0.0	15.8	69.6
HY (30)	393	4.2	16.9	0.6	21.9	79.9
	413	10.5	9.7	0.6	20.9	48.3
	433	8.2	11.1	0.9	20.6	57.7
	453	5.4	7.7	0.4	13.9	59.0
HMCM-22 (52)	393	0.4	4.4	0.0	4.9	90.6
	413	1.2	9.9	0.6	12.2	89.2
	433	2.1	12.3	0.4	15.3	85.2
	453	2.6	9.1	0.2	12.5	77.4

Silica/alumina ratio in parenthesis; reaction conditions: TBA/Tol mole ratio = 1:4, WHSV = 2 h⁻¹.

3.3.3. Tertiary butylation of toluene on zeolite Y

Since, HY zeolites offer relatively high conversion and better 4-TBT selectivity, a detailed study of this zeolite for this reaction was taken up. The influence of various reaction parameters like silica to alumina ratio, space velocity and toluene to TBA mole ratio on conversion and selectivity to the various products was investigated.

3.3.3.1. Influence of silica to alumina ratio of HY zeolites.

Acidity has two variables, the number and the strength of acid sites. It is well known that the number of acid sites is related to the amount of tetrahedral aluminium in the framework. Hence, the conversion of toluene 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 3. Conversion of *tert*-butyl alcohol, which is used in dilute (TBA:toluene = 1:4) concentration, is complete on all the catalysts. As mentioned previously, only two isomers, 4-TBT and 3-TBT, were found in the product. Selectivity to 4-TBT was higher than the equilibrium concentration (36%) at this temperature, increasing substantially on the high silica catalysts. On an acid catalyst, that has high acidity, consecutive reactions of isomerization and de-alkylation are expected to take place, followed by alkylation. However, these consecutive reactions are likely to be suppressed if the acid site density of the catalyst is reduced with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the sample. This is clearly reflected in our results, as 4-TBT selectivity is high on catalysts that have high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [21,22]. The conversion of toluene goes through a maximum at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$. These results show that HY 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 later have high acidity. The Y-80 catalyst, with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$ seems to offer optimum acidity and is best among the HY catalysts used in this study. Hence, this catalyst has been studied further by varying the different reaction parameters in order to find the optimum conditions for this reaction.

3.3.3.2. Effect of space velocity. Space velocity or contact time is an important parameter as it not only influences the conversion of reactant(s), it also has an effect on selectivity to a particular product. Diffusion constraints have a bearing on product shape selectivity, which in turn govern the product pattern, particularly in a zeolite driven catalytic process. Space velocity also

Table 3
Influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ on *tert*-butylation of toluene

Product (wt%)	$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio		
	5.2	30	80
NA	0.2	0.3	0.3
Toluene	74.4	70.9	77.2
3-TBT	8.0	7.1	2.8
4-TBT	15.6	19.5	17.7
HB	1.8	2.2	1.9
Toluene conversion	25.4	28.9	22.2
%PTBT selectivity	66.1	73.4	85.9

NA: non-aromatics, WHSV = 2 h^{-1} , Tol:TBA = 4:1, temperature 393 K.

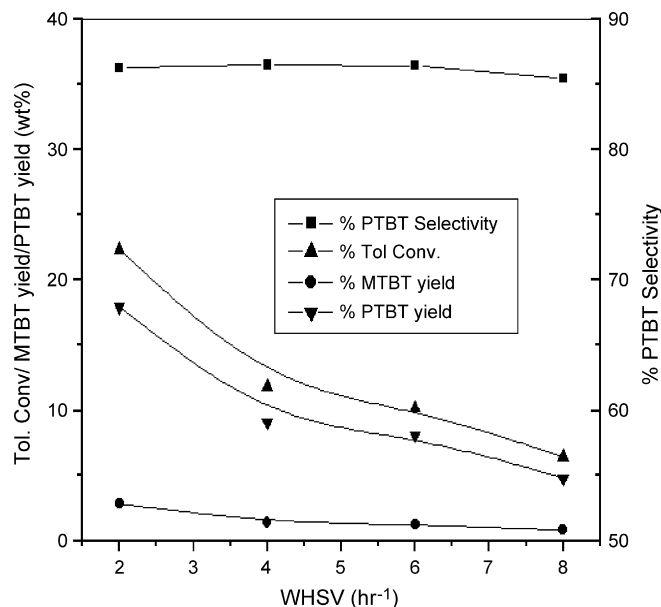


Fig. 4. Effect of space velocity during butylation of toluene on Y-80 zeolite. Tol:TBA = 4:1, temperature 393 K.

influences the secondary and consecutive reactions. As a result, desired selectivity to a particular product can be achieved only by choosing the right space velocity. With increasing the space velocity from WHSV = 2 to WHSV = 4 there was a drop in the conversion of toluene from 22.4 to 11.8% (Fig. 4). We have also observed a faster rate of deactivation at higher space velocities. This may be due to the fact that a lower contact time favours the oligomerisation of isobutylene rather than the toluene alkylation reaction. In many alkylation reactions, the selectivity to the desired product increases with increasing space velocity, but in this case no such effect was observed in 4-TBT selectivity. This could be attributed to the structure of zeolite Y, which has supercages that do not hinder the formation of the bulky transition state required for 3-TBT formation. Also, no diffusional constraints are in place in the pore system, thus facilitating easy diffusion of 3-TBT. However, the concentration of high boilers decreased after longer hours on stream, probably due to catalyst deactivation (not shown in Fig. 4).

3.3.3.3. Influence of toluene to TBA mole ratio. The influence of toluene/TBA ratio on activity and 4-TBT selectivity is shown in Table 4, for the Y-80 catalyst. Conversion of TBA is complete at all toluene to TBA mole ratios. The effect of excess TBA is observed at toluene:TBA mole ratios of 1 and 2. Unlike mordenite catalysts [17], where toluene conversion increased with higher alcohol content in the feed, there was a reduction in the toluene conversion on HY zeolites. It may be seen that as the concentration of TBA in the feed increases, the aliphatics concentration in the product increases. At higher TBA concentrations, the oligomerisation of isobutylene that is formed on dehydration of TBA is in competition with the main alkylation reaction. The lower utilization of the alkylating agent leads to a steep fall in the alkylation selectivity with higher TBA containing feeds. In addition, at high toluene/TBA mole ratios, 4-TBT

Table 4
Effect of toluene to TBA mole ratio during butylation of toluene on Y-80 catalyst

Product (wt%)	Toluene: <i>tert</i> -butyl alcohol (mol)				
	1:1	2:1	4:1	6:1	8:1
NA	17.5	11.4	1.4	0.4	0.2
Toluene	71.3	75.4	76.6	80.2	84.9
3-TBT	0.7	1.3	2.9	2.9	3.3
4-TBT	3.4	8.3	17.9	15.4	11.1
HB	7.0	3.6	1.2	0.9	0.6
Toluene conversion	13.5	14.9	22.4	19.4	14.9
%PTBT selectivity	83.8	86.2	86.2	83.9	77.3

WHSV = 2 h⁻¹, temperature 393 K.

selectivity increases, though not to an appreciable extent. These results suggest that feeds rich in toluene (low TBA content) are better for butylation. The mole ratios in the range of 4:1–6:1 are the most appropriate. Similar observations were already reported for the propylation of benzene to cumene and propylation of toluene to cymene on various zeolite catalysts [14]. In fact, industrial processes based on β zeolite for the preparation of cumene use very low propylene concentration (8:1, benzene to propylene) in the feed, to achieve high alkylation selectivity. Among the HY zeolites used, Y-80 gave the best alkylation selectivity, as catalysts with low acid site density promote selective alkylation by suppressing undesirable oligomerisation, cracking and disproportionation reactions. In addition, high boilers are produced in larger quantities, when feeds that contain high TBA content are employed, as a result of consecutive alkylations.

3.3.3.4. Influence of time on stream (TOS). The influence of TOS was investigated on Y-80 as it was a better catalyst for the toluene *tert*-butylation reaction. The time on stream data for the butylation of toluene on this zeolite is presented in Fig. 5. 4-*tert*-Butyltoluene selectivity reached maximum within 4 h on stream and remained steady thereafter at 87%. There was a rapid increase in the conversion of toluene in the initial hours, while

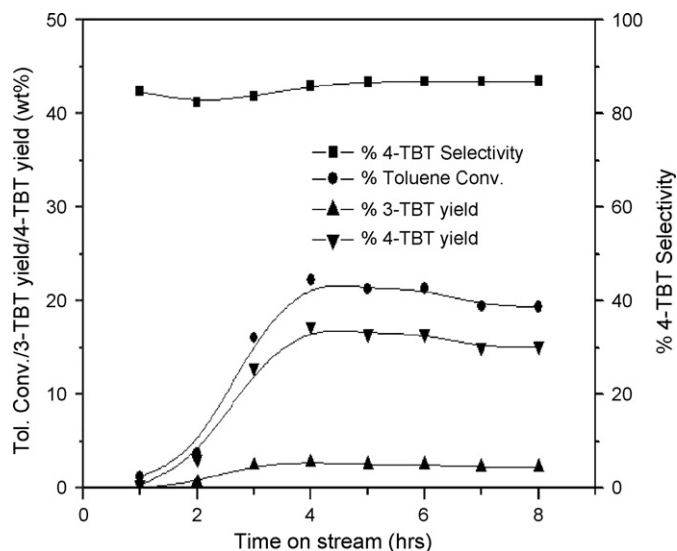


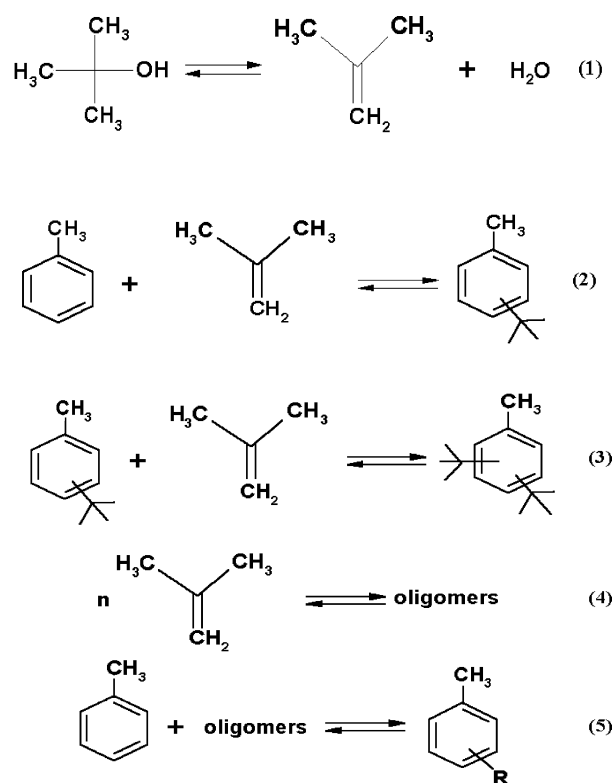
Fig. 5. Influence of time on stream on toluene butylation over Y-80 zeolite. WHSV = 2 h⁻¹, Tol:TBA = 4:1, temperature 393 K.

a marginal decline in conversion was observed after reaching steady state, though it was to a much lower extent compared to β zeolite. This is probably because of the more open structure of zeolite Y as compared to β , as the former does not trap the bulky multi-alkylated products in its channels. The 3-TBT and 4-TBT yield increases during the first 4 h on stream and then there is a marginal slide after that. This kind of initial increase in activity is typical of alkylation reactions on large pore zeolites. During the tertiary butylation of toluene [12] in the liquid phase, the decrease in toluene conversion is accompanied by a corresponding increase in the yield of 3-TBT with a simultaneous fall in the 4-TBT yield. But in this case, no fall in 4-TBT selectivity was found with time on stream. The selectivity reached a steady level of 87% after 8 h at 393 K. These differences may be attributed to the change in contact time of liquid and vapour phase processes.

3.3.4. Selectivity in butylation (alkylation)

Several acid-catalysed equilibrium reactions take place during toluene alkylation by TBA. These reactions (1)–(5) are shown in Scheme 1. The first reaction to be considered is the dehydration of TBA (reaction (1)). The reaction of interest is the alkylation of toluene with the isobutylene that is produced on dehydration of TBA (reaction (2)). The reactions (3)–(5) are unwanted.

The composition of the reaction mixture is defined by the content of TBA. The rate of formation of each product is influenced by its thermodynamic stability, while in the case of zeolites, the



R – alkyl groups

Scheme 1.

Table 5
Effect of different alkylating agents on butylation of toluene

Alkylating agent	Temperature (K)	Toluene conversion (wt%)	4-TBT selectivity (wt%)
Isobutyl alcohol	433	6.6	46.4
Tertiary butyl alcohol	393	21.3	86.6
Methyl tertiary butyl ether	393	10.0	86.8

WHSV = 2 h⁻¹, toluene:alkylating agent = 4:1, catalyst Y-80.

diffusion rate of molecules within the pores also play a role. Since, most of the acid sites in zeolites are located in the internal surface, mainly processes that take place within the pores of zeolites influence the composition of the reaction products. It is known that the diffusion rate of compounds in zeolites is influenced by the ratio of the pore diameter to molecular dimensions. 4-TBT is the narrowest of TBT isomers and has the highest diffusion rate in the zeolite channels. Hence, as a result has the highest probability of diffusing out of the pores, while 3-TBT because of larger molecular dimensions is expected to have lower diffusion rates. Since, the 3-TBT is the thermodynamically most favoured mono-*tert*-butyltoluene, the kinetically favoured 4-TBT is transformed to 3-TBT. This isomerization takes place more easily on the external surface, where it is not sterically hindered. The kinetically, as well as thermodynamically favoured 3,5-di-*tert*-butyltoluene may not diffuse out of pores, and as a result it is embedded in the channels of zeolite because of its large size. The channels of the zeolite may also be clogged by oligomers of isobutylene. Probably, the formation of the latter two products is the main reason for catalyst deactivation. The formation of classical coke at temperatures below 473 K is less probable. However, the rate of oligomerization of isobutylene is significant at higher temperatures, resulting in shift of equilibria (2) and (3) to the left, favouring dealkylation. The overall conversion of toluene versus the reaction time on all the catalysts investigated shows that the toluene conversion in the presence of the HY and β zeolites is much higher than on MCM-22 catalysts. The experimental results indicate the following order of catalytic activity: β -25 \approx Y-30 > MCM-22. Zeolites β and Y have three-dimensional open structures and hence even if their acidities are different they have similar activities. Due to open structures, there is a better interaction of the reactant molecules with the acid sites and the diffusivity of the product molecules is also better. The structure of zeolite MCM-22 consists of two independent pore systems, one of which is defined by two-dimensional sinusoidal 10-membered ring channels (0.40 nm \times 0.59 nm). The second pore system consists of large supercages with a free inner diameter of 0.71 nm with a length of 1.82 nm. However, these huge intra-crystalline voids are accessible through 10-membered-ring apertures (0.40 nm \times 0.59 nm) only [23]. The lower catalytic activity of MCM-22 may be attributed to its pore structure. One of the pore systems in MCM-22 has only 10-membered rings. Hence, in spite of three-dimensional pore structures, the diffusion of reactants towards the internal acid sites is limited. Cejka et al. [24] have carried out toluene isopropylation on MCM-22 and found that it behaves like a large pore zeolite with no selectivity to *p*-cymene. But in the case of toluene butylation, we have found that MCM-22 gives good

selectivity for 4-TBT, though the toluene conversion is low. The combination of 10- and 12-membered rings impose a diffusional barrier to 3-TBT, thus allowing 4-TBT to come out faster than 3-TBT. The time on stream stability of this catalyst is good, as it deactivates at a slow rate.

3.3.5. Effect of different alkylating agents on butylation of toluene

The tertiary butylation of toluene was carried out in the presence of isobutyl alcohol (IBA) and methyl tertiary butyl ether (MTBE) on zeolite Y-80 to find out the effect of alkylating agent on the selectivity and stability of the catalyst. The results are shown in Table 5. With IBA as the alkylating agent, higher reaction temperatures were needed to obtain reasonable toluene conversion. This is because IBA generates a primary carbocation, which is stable only at higher temperatures. The observed conversion is because of the isomerization of the primary carbocation to the tertiary carbocation, followed by its addition to toluene. Another probability could be that the statistical probability of dehydration to isobutylene is thrice for TBA than that for IBA. As a result, selectivity to 4-TBT is poor. MTBE as an alkylating agent has also yielded lower TBTs compared to alkylation with TBA. In view of problems associated with the availability, transportation and handling of isobutylene, particularly in low-tonnage usage by fine and speciality chemical industry, it is advantageous to generate isobutylene in situ. Amongst them cracking of MTBE and dehydration of TBA are attractive [25–27]. MTBE is a good source for the in situ generation of pure isobutylene and the co-product, methanol, can be recycled, as it is not expected to undergo any reactions under toluene butylation conditions. The comparison of both alkylating agents is shown in Fig. 6. In case of TBA, the conversion is low in the initial stages (up to 1.5 h) and then there is a steep rise in the toluene conversion up to 4 h then reaching a stable value. In the case of MTBE, the initial activity is higher than compared with TBA, but the stable activity is much lower. Though the mole ratio of the alkylating agent used in the reaction mixture was same in both cases, the amount of isobutylene available for the reaction must have been different. This is because the mechanism of isobutylene generation is different in the two cases. Isobutylene generation by dehydration of TBA on acid sites of zeolites is more facile than the hydrolysis of MTBE. The catalyst has a better stability with MTBE as a result of the slow release of isobutylene to the reaction medium. Thus, the side reactions that lead to coke formation and deactivation are controlled. However, no influence of the alkylating agent on 4-TBT selectivity was observed on this catalyst.

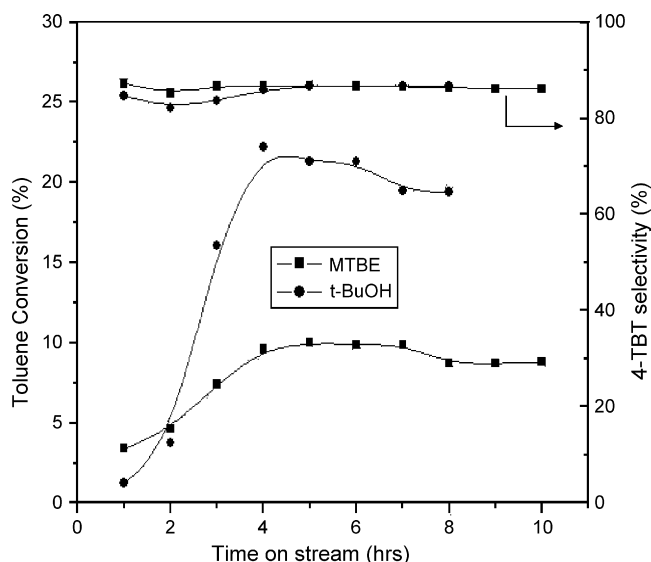


Fig. 6. Comparison of TBA and MTBE as toluene butylation agents. Temperature 393 K, WHSV = 2 h⁻¹, Tol:alkylating agent = 4:1.

4. Conclusions

Alkylation of toluene with *tert*-butyl alcohol has been investigated on three large pore zeolites, viz., β , HY and HMC-22 that have 3-D pore structures. The ammonia TPD studies show that zeolite β and MCM-22 possess higher acid strengths than zeolite HY. Though zeolites HY and β have similar silica to alumina ratios, the latter has a higher acidity in terms of chemisorbed ammonia. Vapour phase alkylation studies of toluene with TBA on different large pore zeolites reveal very good catalytic activity on β and HY, but a low activity on MCM-22, though all the zeolites have the same 12-membered ring large pores. The main product of the reaction, 4-*tert*-butyltoluene is kinetically favoured. The steric hindrance of the methyl group on one side and the voluminous *tert*-butyl group on the other side favours its formation. Shape-selectivity also plays a role depending on the structure of zeolite. High reaction temperature and acid site density (low SiO₂/Al₂O₃ ratio) promote isomerization of the *para*-isomer to the *meta*-isomer, reducing 4-TBT selectivity. On Y-80 zeolite catalyst, the toluene conversion decreased with increasing space velocity without much change in the 4-TBT selectivity. Feeds containing a lower concentration of TBA are better for obtaining high alkylation selectivity. The experimental results indicate the following order of catalytic activity: β -25 \approx Y-30 > MCM-22. Though MCM-22 has

a three-dimensional structure, the diffusion of reactants towards the internal acid sites is limited because of the 10-membered ring pores. TBA is a better alkylating agent than MTBE or isobutyl alcohol. However, MTBE is advantageous as it prevents rapid deactivation, which improves catalyst stability.

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