Tertiary butylation of phenol over HY and dealuminated HY zeolites

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Abstract

The catalytic properties of HY and dealuminated HY zeolites in the vapor phase *t*-butylation of phenol with *t*-butyl alcohol in the temperature range 100–200 °C are reported. The influence of various reaction parameters such as temperature, space velocity, molar ratio of the reactants are discussed. The main products are *p-t*-butyl phenol (*p*-TBP), *o-t*-butyl phenol (*o*-TBP) and 2,4-di-*t*-butyl phenol (2,4-DTBP). The product distribution depends on the reaction temperature, number of acid sites and the ratio of Bronsted to Lewis acid sites, which changes with the steaming temperature. Lower molar ratio of reactants and higher space velocity facilitated mono alkylated products.
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1. Introduction

p-t-Butyl phenol (p-TBP), the mono alkylated product of *t*-butylation of phenol has wide spread application in the manufacture of varnish and lacquer resins, antioxidant for soaps, ingredient in de-emulsifiers for oil field, motor oil additives etc. di-*t*-Butyl phenols are used in the production of substituted triaryl phospites and antioxidant in foods and other consumable items [1,2]. The catalysts used are liquid acid, metal oxides, Al-salt catalyst and cation exchange resins, and solid acid catalysts, especially zeolites Hβ, HY and mesoporous molecular sieves [3–17] were reported for this reaction either in gas or liquid phase. There were drawbacks in using liquid catalysts due to hazardous nature and tedious work-up for its separation. Cation exchange resins cannot be used at higher temperatures. Switching over to solid acid catalysts, in recent days, much attention was given to environmentally friendly catalysts like zeolites.

It is well known that zeolite HY on steaming at various temperatures yields wide spectrum of acid site distribution. In the literature, *t*-butylation of phenol over faujasite is mentioned, however, the data on variable acid sites distribution having impact on product distribution in title reaction is not documented. Keeping this in view, we have carried out systematically the steaming of HY zeolite to yield different aluminum deficient samples having variable acid sites. In this paper, we report the influence of nature of acid site distribution over mono and di-alkylation

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of phenol with *t*-butyl alcohol (TBA). The important variables affecting conversion and selectivity of the reaction such as reaction temperature, space velocity, molar ratios of TBA to phenol are studied.

2. Experimental

2.1. Preparation and characterization

The Linde Na-Y (SK-40) was converted to HY via ammonium exchange with ammonium nitrate solution for four times followed by calcination at 500 °C. A multi-step temperature programmed (MSTP) steaming was adopted. The HY zeolite was steam-treated at different temperatures (550–850 °C) to yield various degrees of dealuminated HY zeolites with varying Si/Al ratio. The scheme of modification is explained in Table 1. These samples were characterized by XRD (Rigaku Dmax/IIIVC diffractometer using Ni-filtered Cu Kα; λ = 1.5404 Å radiation) for crystallinity and unit cell constants, ^{29}Si and ^{27}Al MAS NMR (Bruker MSL 300 spectrometer) for Si/Al framework ratio and N_2 sorption (Omnisorb Coulter 100CX, USA) for pore volume and BET surface area.

2.2. Acidity measurement

Acid strength distribution of HY and dealuminated HY samples was estimated by FTIR spectra (NICOLET SXB spectrometer) of adsorbed pyridine by adopting the procedure reported elsewhere [18]. In a typical procedure, self-supported wafers of the samples weighing nearly 5–6 mg/cm^2 were made by pressing a thin layer of the sample at a pressure of

7 tonnes/in.^{2}. The wafer was placed on the sample holder. It was then placed inside the heating compartment of the transmittance cell connected to a high vacuum system. The sample was evacuated to 10^{-6} Torr at 400 °C for 3 h and then cooled to 100 °C before recording the spectrum of the pure sample. Then the sample was allowed to adsorb pyridine at an equilibrium pressure of 20 mm Hg for 30 min. The loosely adsorbed and free vapor of pyridine was removed by evacuating the cell for 1 h. Then the spectrum was recorded. Thereafter, the sample was further heated to 200, 300 and 400 °C successively for 1 h at each temperature before recording the spectrum again. The spectrum was recorded with 2 cm^{-1} resolution after averaging over 500 scans. The physico-chemcial characteristics and relative concentration of both Bronsted and Lewis acid sites of HY and modified HY samples are shown in Table 2.

2.3. Catalytic reaction

The catalytic alkylation of phenol (E-Merck >99%) with *t*-butyl alcohol (E-Merck >99%) at 170 °C was carried out at atmospheric pressure using a fixed-bed vertical flow reactor. A mixture of phenol and *t*-butyl alcohol with a molar ratio of 1:2 was introduced into the reactor by means of a syringe pump (Sage Instruments, USA) with a WHSV of 2.4 h^{-1}. The liquid products were collected in an ice-cold trap and analyzed by gas chromatography (Shimadzu 15A) using a flame ionization detector furnished with HP-1 30 m capillary column. Reaction products were identified by GC–MS (Shimadzu QP 5000) and GC–FTIR (Perkin-Elmer Spectrum 2000).

Table 1
Scheme of sample treatment

Zeolite	Treatment	Unit cell composition (anhydrous)[a]
HY	NH$_4$Y calcined at 550 °C for 4 h	Na$_{2.3}$[(AlO$_2$)$_{54}$(SiO$_2$)$_{138}$]
HY-550	NH$_4$Y steamed at 550 °C for 4 h followed by exchange with NH$_4$NO$_3$ solution (1N, 20 ml/g of zeolite) at 98 °C for 4 h followed by calcination at 550 °C for 12 h	Na$_2$[(AlO$_2$)$_{20}$(SiO$_2$)$_{172}$]
HY-700	HY-550 sample steamed at 700 °C for 4 h followed by exchange with NH$_4$NO$_3$ solution (1N, 20 ml/g of zeolite) at 98 °C for 4 h followed by calcination at 500 °C for 12 h	Na$_{1.49}$[(AlO$_2$)$_{10}$(SiO$_2$)$_{182}$]
HY-850	HY-700 sample steamed at 850 for 4 h followed by exchange with NH$_4$NO$_3$ solution (1N, 20 ml/g of zeolite) at 98 °C for 4 h. Further calcination at 500 °C for 12 h followed by acid leaching by 0.01N HNO$_3$ at 98 °C (4 h). This was further steamed at 550 °C (4 h) and subsequently acid leached. This was repeated three times	Na$_{1.20}$[(AlO$_2$)$_7$(SiO$_2$)$_{185}$]

[a] Other balancing cation is H$^+$.

Table 2
Physical characteristics and acid site distributions of zeolites under study

Zeolite	HY	HY-550	HY-700	HY-850
Si/Al (bulk)[a]	2.65	2.70	3.17	3.70
Si/Al (framework)[b]	2.56	8.7	18.6	26.3
Pore volume (ml/g)	0.307	0.268	0.276	0.261
Unit Cell Constant (Å)	24.68	24.38	24.34	24.21
Unit Cell Volume (Å^3)	15,036	14,493	14,428	14,202
BET surface area (m^2/g)	836.8	551.6	555.8	433.0
Relative concentration of Bronsted acid sites	44	40.6	17	3
Relative concentration of Lewis acid sites	28	22	9	6
B/L ratio	1.56	1.8	1.87	0.5

[a] Calculated by XRF analysis.
[b] Calculated from NMR.

3. Results and discussions

The XRD crystallinity measurements showed that the parent HY and the dealuminated HY zeolites (obtained by steaming at varying temperature) were found to be highly crystalline with a decrease in peak intensities ranging from 1.4 to 2.0% depending on the severity of the steam treatment (Fig. 1). The percentage of Al in tetrahedral coordination for each sample was calculated from the relative area of a peak, centered at 60 ppm in the ^{27}Al MAS NMR spectra (not shown). Almost all of the Al in HY zeolite was
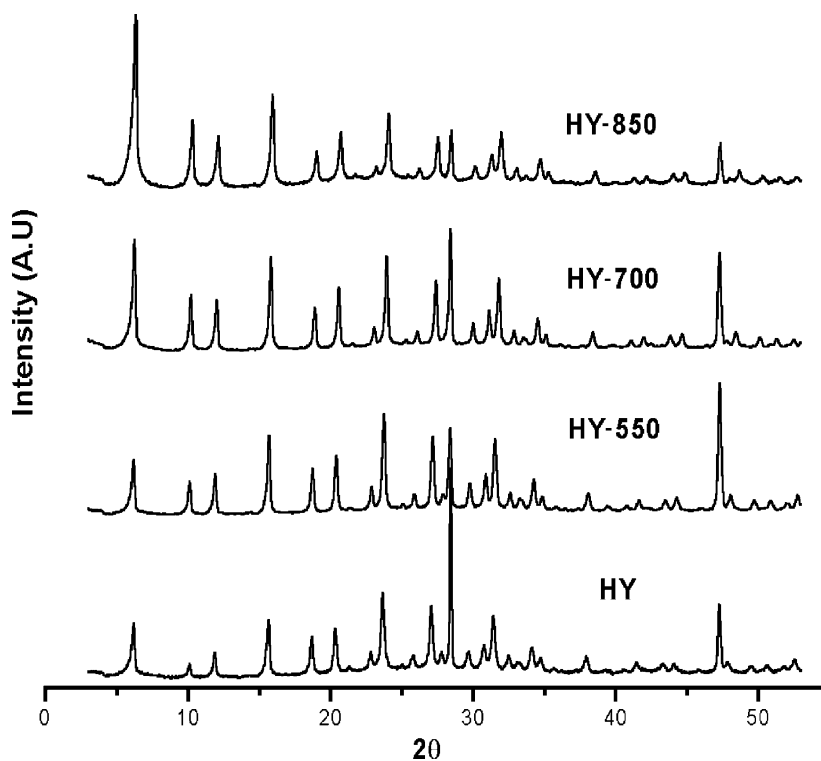

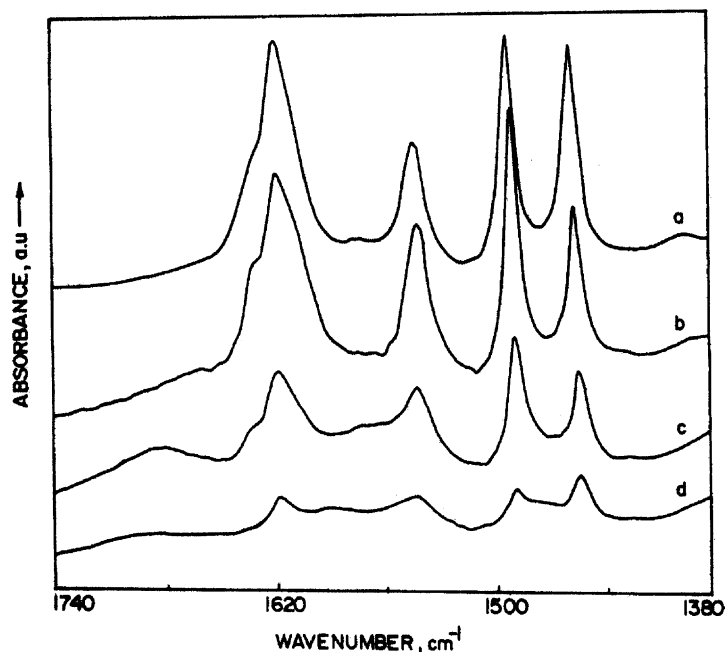Fig. 1. XRD spectra of HY and dealuminated HY zeolite.

Fig. 2. FTIR spectra of pyridine adsorbed at 200 °C over HY and dealuminated HY zeolites (a) H-Y; (b) HY-550; (c) HY-700; and (d) HY-850.

tetrahedral, where as in the steam treated samples with increasing steaming temperature, increasing emergence of the pentacoordinated aluminum ($\sim$30 ppm) and octahedral aluminum ($\sim$0 ppm) is noticed [19]. Increase in Si/Al ratio from 8.7 (for HY-550) to 26.3 (for HY-850) indicates increasing dealumination with increasing steaming severity. This is also due to the extraction of extra-framework aluminum from HY-850 zeolite by acid leaching with HNO_3 (Table 1).

The FTIR spectra of pyridine adsorbed at 200 °C on HY and dealuminated HY zeolites are shown in Fig. 2. All zeolites showed bands at 1540 and 1450 cm^{-1} corresponding to concentration of Bronsted and Lewis acid. The relative concentrations of these acid sites (Table 2) suggest an increase in the acid strength of Bronsted acid site with decreasing framework aluminum content. Since the sample HY-850 is also treated with dilute HNO_3 after stream-treatment to remove extra-framework aluminum both the relative concentrations of Bronsted and Lewis acid sites decreased as seen in the Fig. 2 and Table 2.

In general, the alkylation of phenol with TBA over HY and dealuminated HY zeolite catalyst resulted in the formation of p-t-butyl phenol (p-TBP), o-t-butyl phenol (o-TBP), 2,4-di-t-butyl phenol (2,4-DTBP) and hydrocarbons along with very small quantity of t-butyl phenyl ether (TBP-ether, O-alkylated phenol) as identified by GC–MS and GC–FTIR. The meta isomer m-TBP is not formed even at the high temperature and phenol conversion as claimed by Selvam and co-workers [16,17]. The hydrocarbons are formed by the undesired reaction of C_4 hydrocarbons (formed from TBA) to produce C_8 and C_{12} fractions.

The effect of reaction temperature in the range 100–200 °C on the activity and selectivity of HY and dealuminated HY zeolites is exhibited in Table 3. It is seen that with rise in temperature from 100 to 130 °C, the phenol conversion increased with increase in dealkylated product selectivity, however, the conversion decreased with further increase in temperature. The selectivity to p-TBP increased and that of 2,4-DTBP decreased at higher reaction temperatures (170–200 °C).

It can be seen from the table that the phenol conversion is comparatively less (>46%) over HY than the other dealuminated HY zeolites which exhibited

Table 3
Effect of reaction temperature on *t*-butylation of phenol with TBA over HY and dealuminated HY zeolites

Catalyst	Temperature (°C)	Phenol conversion	Product selectivities (%)					*p/o* ratio
			TBP-ether	*o*-TBP	*p*-TBP	2,4-DTBP	Others[a]	
HY	100	33	16.7	4	59.9	0.6	18.8	15.0
	130	35.9	0.9	25.6	49.8	14.2	9.5	1.9
	170	45.5	0.6	12.6	62.6	18.1	6.1	5.0
	200	28.6	0	11.7	69.7	14.6	4	6.0
HY-550	100	72.1	0.5	5.6	57.1	7	29.8	10.2
	130	91.7	0.1	4.5	49.7	33.8	11.9	11.0
	170	76	0.2	5.5	46.5	38.1	9.7	8.5
	200	62.5	0.3	8.5	75.9	9.5	5.8	8.9
HY-700	100	77	11.7	5	18.4	4.4	60.5	3.7
	130	80.5	3.8	4.3	47.9	13.3	30.7	11.1
	170	69.4	0.5	6.4	68.8	9.8	14.5	10.8
	200	47.4	0.8	7.2	77.7	4.9	9.4	10.8
HY-850	100	72.6	7.8	3.9	47.4	3.3	37.6	12.2
	130	83.5	0.8	5.3	53.2	19.8	20.9	10.0
	170	68.6	0.5	6.7	68.3	9.2	15.3	10.2
	200	48.4	0.3	9.9	65.8	10.1	13.9	6.6

Reaction conditions: WHSV = 2.4 h^{-1}; TBA/phenol molar ratio = 2; TOS = 4 h.

[a] Hydrocarbons and unidentifiers.

conversion up to 91% at 130 °C (HY-550). At lower temperatures, all the dealuminated HY zeolites produced a large amount of hydrocarbons at 100 °C: 29.8, 60.5 and 37.6% over HY-550, HY-700 and HY-850 respectively even though all these zeolite exhibited higher conversion of phenol (<72%). The phenol conversion increases with steaming temperature up to 700 °C, with a further increase in steaming temperature to 850 °C, the phenol conversion dropped marginally indicating that loss of acid sites by steaming at higher temperature and is unfavorable to the reaction. The selectivity to *o*-TBP is almost same at all the temperatures indicating that medium acid sites can promote the conversion of *o*-TBP to *p*-TBP. A decrease in conversion as reaction temperature increased (200 °C) was observed with all the HY zeolites. However, a slight increase in *p*-TBP and a decrease in 2,4-DTBP was noted which implies that secondary reactions, such as dealkylation and transalkylation, should occur over these zeolites under given experimental conditions.

It was observed in the transformation of *o*-TBP catalyzed by montmorillonite KSF catalyst under conventional and microwave conditions [20], that the reaction mixture composition reaches equilibrium and when

p-TBP was used as the starting compound, the final composition reached the same value, i.e. 76–82 mol% *p*-TBP and 20 mol% *o*-TBP; a *p/o* ratio of ∼4. It can be seen from the values of *p/o* ratio (Table 3), that the system is far removed from this thermodynamic equilibrium.

The activity enhancement in dealuminated samples can be attributed to increase in strength of Bronsted acid sites [21]. Steam dealumination generates non-framework Al species, which could withdraw electron density from nearby Bronsted acid sites, causing an enhancement in the strength of the site [21,22] and their strong Lewis acid sites may enhance activity by promoting hydride abstraction and help to initiate the cracking reaction [23] which is observed in the very less formation of 2,4-DTBP at higher reaction temperatures. So a moderate reaction temperature (170 °C) and the zeolite HY-700 (steam treated at 700 °C) was chosen for further studies wherein the phenol conversion as well the selectivity to *p*-TBP is higher with minimum side products.

Table 4 summarizes the results of butylation reaction carried out with various TBA to phenol molar ratios at 170 °C with a WHSV of 2.4 h^{-1}. In all the cases, *p*-TBP was obtained as the major product along

Table 4
Effect of molar ratio of TBA/phenol on *t*-butylation of phenol with TBA over HY-700 zeolites

(TBA/phenol) molar ratio	Phenol conversion	Product selectivities (%)				
		TBP-ether	*o*-TBP	*p*-TBP	2,4-DTBP	Others[a]
1	48.6	0.2	7.7	78.8	5.9	7.4
2	69.4	0.5	6.4	68.8	9.8	14.5
3	80.2	0.1	5.7	60.5	12.3	21.4
4	81.8	0.4	5	52.8	10.4	31.4

Reaction conditions: temperature = 170 °C; WHSV = 2.4 h^{-1}; TOS = 4 h.
    [a] Hydrocarbons and unidentifiers.

with small amounts of *o*-TBP and 2,4-DTBP. With an increase in the molar ratio of *t*-butyl alcohol to phenol from 1 to 4, phenol conversion and selectivity to 2,4-DTBP increases due to higher concentration of TBA available for alkylation. However, the selectivity to monoalkylated products (*o*-TBP + *p*-TBP) decreased from 86.5 to 57.8%. A marked increase in the formation of hydrocarbons with an increase in TBA content in the reaction mixture was also noticed. Thus, keeping in view of *p*-TBP selectivity, it can be concluded that optimum molar ratio of *t*-butyl alcohol to phenol was found to be 2.

The catalytic performance as a function of time of over HY-700 for phenol alkylation with TBA at 170 °C, WHSV of 2.4 h^{-1} was depicted in Fig. 3. There is no appreciable change in phenol conversion, however, the selectivity of *p*-TBP and 2,4-DTBP

slightly increased with time indicating deactivation has not taken place during the course of study.

The influence of space velocity on phenol alkylation with TBA and product selectivity over HY-700 zeolite at 170 °C for a TBA/phenol (molar ratio) of 2 was depicted in Fig. 4. The phenol conversion increased from 52 to 72.7% with an increase in contact time (on decreasing WHSV from 9.6 to 1.83 h^{-1}), however, the product selectivity to *p*-TBP remains unchanged. There was an increase in selectivity of *o*-TBP at WHSV 9.6 h^{-1} showing that even weak acid sites can promote the formation of *o*-TBP at such high space velocities. Also both the *p/o* ratio and 2,4-DTBP increases with decrease in WHSV implying secondary reactions such as isomerization and dealkylation.
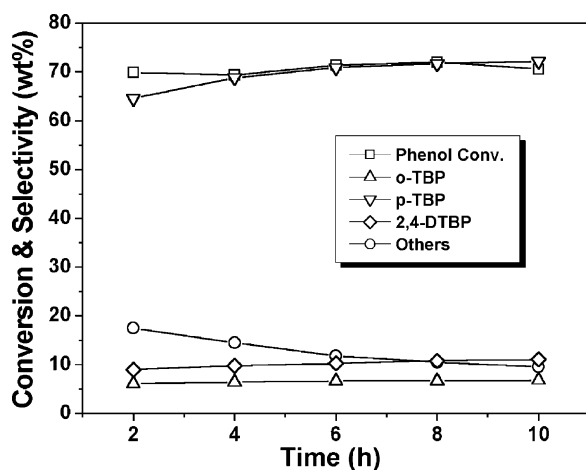

Fig. 3. Effect of reaction time on *t*-butylation of phenol with TBA over HY-700 zeolite. Reaction conditions: temperature = 170 °C; WHSV = 2.4 h^{-1}; TBA/phenol molar ratio = 2.
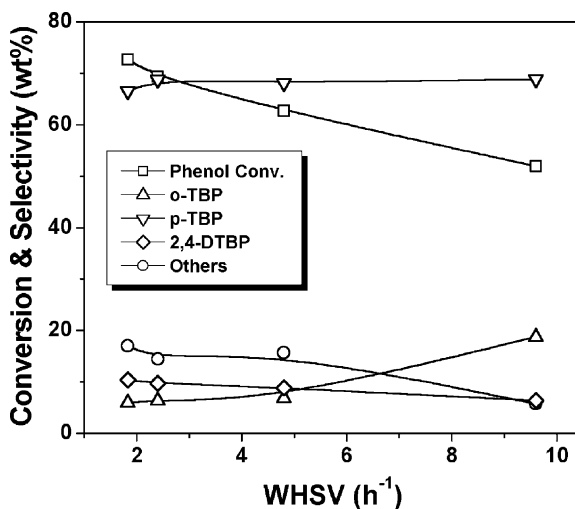

Fig. 4. Effect of contact time on *t*-butylation of phenol with TBA over HY-700 zeolite. Reaction conditions: temperature = 170 °C; TOS = 4 h; TBA/phenol molar ratio = 2.

4. Conclusion

Hydrothermal treatment of zeolite HY causes appreciable framework dealumination. The degree of dealumination depends on the severity of the treatment. Steaming at higher temperature (over $700\,^{\circ}$C) is unfavorable to the alkylation of phenol with TBA due to decrease in number of Bronsted acid sites. Lower reactant molar ratio (1:2) of TBA/phenol and space velocities ($2\,h^{-1}$) predominate mono-ring alkylation, and di-alkylation is facilitated at higher reactant ratio and higher contact time.

Acknowledgements

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