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Alkylation of biphenyl with *t*-butylalcohol over modified Y zeolites

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Abstract

The alkylation of biphenyl with *t*-butylalcohol (TBA) over HY and ultrastable Y zeolites produced by multistep temperature programmed (MSTP) steaming procedure is studied in a stirred batch reactor using cyclohexane as solvent. 4-*t*-Butylbiphenyl (4-TBB) was observed as the major product with all the HY zeolites studied. However, the selectivity to 4,4′-di-*t*-butylbiphenyl (4,4′-DTBB) increased with framework dealumination and latter it decreases with the severity of dealumination temperature. The various reaction parameters affecting the activity and selectivity of the products such as temperature, catalyst amount, molar ratio and reaction time were investigated. The isomerization of 4,4′-DTBB over steam-treated HY zeolites is also discussed.

Keywords: Biphenyl; Alkylation; Butylation; Isomerization; TPD; Acidity; Zeolites

1. Introduction

Zeolites have been utilized for synthesis of fine chemicals involving shape selective catalysis leading to development of many industrial processes. Mono- or dialkylated binuclear aromatic compounds such as 4-*t*-butylbiphenyl (4-TBB) and 4,4′-di-*t*-butylbiphenyl (4,4′-DTBB) are valuable industrial intermediates used for polyester fibers, engineering plastics with superior properties and for production of thermotropic liquid crystals or heat resistant polymers [1,2]. The shape selective formation of 4- and 4,4′-isomers of biphenyl in the alkylation (methylation [3,4], ethylation [5], isopropylation [6–11] and *t*-butylation [12–14]) of biphenyl was reported by various authors. In the recent years, alkylation of biphenyl in the liquid phase conditions over large pore zeolites like Y and dealuminated mordenite zeolites with propylene as alkylating agent were widely studied. The study concludes that dealuminated mordenites are more shape-selective zeolites for isopropylation of biphenyl to 4- and 4,4′-positions. It was also reported that H-mordenite and HY zeolites have been shown to be more active for *t*-butylation of biphenyl to 4-TBB and 4,4′-DTBB than H-beta zeolite.

We have been studying various alkylation reactions leading to industrial important intermediates [15–17] over HY and dealuminated HY zeolites prepared by multistep temperature programmed (MSTP) steaming procedure [15,18]. The present work deals with preparation of HY and USY zeolites using MSTP steaming procedures and its application as catalysts for butylation of biphenyl with TBA under liquid phase conditions. The isomerization of 4,4′-DTBB over steam-treated HY zeolites is also discussed.

2. Experimental

2.1. Preparation and characterization

Zeolite 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 multistep temperature programmed (MSTP) steaming procedure [18] was adopted which allows controlled rate of dealumination in the initial period in order that the aluminum is not withdrawn too quickly from the framework. The HY zeolite was

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steam-treated at different temperatures to obtain aluminum deficient HY having variable Si/Al ratio. The steaming was done under stepwise temperature programmed procedure where water vapors were introduced at 100 °C and then the temperature was increased till the desired temperature (550, 700 and 850 °C for HY-550, HY-700 and HY-850, respectively) was reached. The samples were named after the steaming temperature. The end material obtained in each temperature treatment was used as the starting material for the next step. The samples were maintained at the desired temperature for 4 h before switching off the electrical heating for cooling the samples down to 100 °C and then the injection of water was stopped and the samples were then dried under air flow, followed by ammonium exchange using 1N ammonium nitrate solution for 4 h at 100 °C, washed repeatedly with copious amount of water, dried and calcined at 500 °C in a flow of dry air for 8 h to convert ammonium form into H-form.

All the materials were characterized by XRD (Rigaku Dmax/IIIVC diffractometer using Ni-filtered Cu Kα; $\lambda = 1.5404$ Å radiation), BET surface area by N_2 sorption (Omnisorb Coulter 100CX, USA), ^{29}Si and ^{27}Al MAS NMR (Bruker MSL 300 spectrometer) for Si/Al framework ratio. A detailed ^{29}Si and ^{27}Al MAS/3Q-MAS NMR studies of these samples are reported recently [18]. Surface area, Si/Al ratio, unit cell parameters and details of pore-size distribution of these catalysts are given in Table 1.

Acidity measurements were performed by temperature programmed desorption of ammonia using an AutoChem 2910 (Micromeritics, USA) instrument. A sample (50 mg) was pretreated in a helium stream (50 ml/min) at 500 °C for 1 h and then exposed to a flow of ammonia in a stream of He for 30 min at 80 °C. Subsequently, the sample was flushed with the carrier gas at 105 °C for 1 h to remove physisorbed ammonia. The TPD profile of ammonia was obtained from 50 to 700 °C at a heating rate of 10 °C/min. The ammonia concentration in the effluent stream was monitored with the thermal conductivity detector and the areas under the peaks were integrated using GRAMS/32 software to determine the amount of ammonia desorbed during TPD.

2.2. *Alkylation of biphenyl with TBA*

The alkylation reactions of biphenyl with TBA and cyclohexane as solvent were performed in a stainless steel batch reactor with stirring under nitrogen atmosphere. In a typical experiment, biphenyl, TBA and cyclohexane (solvent) with molar ratio of 1:2:10 were charged into the reactor. To this a freshly activated zeolite catalyst (200 °C, 2 h) was added. The reactor was then pressurized to the 100 psi by nitrogen and the mass was heated from ambient to the desired temperature (time taken to reach the desired temperature was approximately 15–20 min) Samples were taken periodically from the reactor and analyzed by a gas chromatograph (Shimadzu 15A) equipped with a 30 m HP-1 capillary column. Reaction products were identified by GC–MS (Shimadzu QP 5000) and GC–FT-IR (Perkin-Elmer Spectrum 2000). Isomerization of 4,4′-DTBB was carried out using a 5 wt.% solution of 4,4′-DTBB (Lancaster, 99% purity) in cyclohexane at desired temperature under 100 psi nitrogen pressure.

3. Results and discussion

3.1. *Catalyst characterization*

The physico-chemical properties of the catalyst used in this study are presented in Table 1. It is well known that the Brönsted sites left on the dehydroxylated zeolite after hydrothermal treatment are usually stronger than those of the parent zeolite [19]. Thus, the dealumination decreases the acid site density but increases the strength [20,21] and could modify the porosity [20]. It can be seen from the results of XRD patterns of the HY zeolite and dealuminated HY

Table 1
Physical characteristics and acidity of HY and dealuminated HY 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	18.2	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	15036	14493	14428	14202
Unit cell composition (anhydrous)[c]	$Na_{2.3}[(AlO_2)_{54}(SiO_2)_{138}]$	$Na_2[(AlO_2)_{20}(SiO_2)_{172}]$	$Na_{1.49}[(AlO_2)_{10}(SiO_2)_{182}]$	$Na_{1.20}[(AlO_2)_7(SiO_2)_{185}]$
BET surface area (m^2/g)	836.8	551.6	555.8	433.0
T_{d1} (°C)[d]	297.4	192.5	209.3	–
T_{d2} (°C)[d]	398.4	364.5	314.5	346.1
Total acidity (mmol/g)	4.54	1.17	1.97	0.68

[a] Calculated by XRF analysis.

[b] Calculated from NMR.

[c] Other balancing cation is H^+.

[d] $150 < T_{d1} < 300\,^\circ C$; $T_{d2} > 300$.

zeolites, a small loss of crystallinity (a drop of peak intensity from 1.4 to 2.0%) is noticed depending on the severity of the steam treatment [15,17]. Similarly, the specific surface area decrease with increase in steaming temperature due to the presence of extra-framework aluminum in the pores and channels as well as the formation of mesopores (Table 1). Almost the entire Al in HY zeolite was tetrahedral, where as in the steam treated samples with increasing steaming temperature, increasing emergence of the penta-coordinated aluminum (∼30 ppm) and octahedral aluminum (∼0 ppm) is noticed [18]. The percentage of framework dealumination increased to as high as 87% for the HY-850 zeolite was evidenced from ^{27}Al MAS NMR spectra [18] as the severity of the steaming increased.

The NH_3-TPD spectra of HY, HY-550, HY-700 and HY-850 catalysts are shown in Fig. 1, while the temperature of desorption maxima (T_{di}) and the amount of desorbed ammonia (total acidity) are summarized in Table 1. The TPD curve of HY catalyst showed two main desorption peaks at 297 and 398 °C with long tailing indicating the overlap of various components desorbing in relatively broad temperature range. The catalytic important peak in the high temperature (HT) region (>300 °C) is likely to be associated with the water desorption as a result of dehydroxylation of surface hydroxyl groups. Cattanach et al. [22] reported such a complexity in the TPD spectra of NH_3 taken from faujasite-type zeolites. HY-550 shows these peaks at 192 and 364 °C and HY-700 shows these peaks at 212 and 309 °C showing a marked decrease in acidity as compared with HY-550 (steam-treated at 550 °C) due to higher framework dealumination. A marked decrease in the area of HT peak should be noted in these steam treated zeolites as compared with the parent sample. An increase in acidity is evident by the increase in the temperature of desorption peak in HT region (346 °C) for zeolite HY-850 as compared to zeolite HY-700 (309 °C).

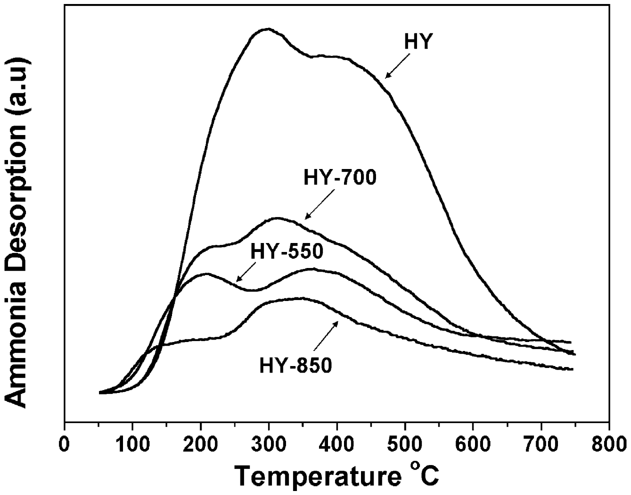

Fig. 1. Normalized NH_3-TPD spectra of HY and dealuminated HY zeolites.

3.2. Catalytic activity

The reaction of biphenyl alkylation with *t*-butanol over HY and dealuminated HY zeolites yielded 4-*t*-butylbiphenyl (4-TBB) as the major monoalkylated isomer and 4,4′-di-*t*-butylbiphenyl (4,4′-DTBB) as the major dialkylated isomer. The other higher polyalkyl biphenyls (PAB) were observed in the range of >2 wt.%. The products formed by the self-reaction/oligomerization of isobutene formed by the dehydration of *t*-butanol is also in the range of 2 wt.% and are excluded in the product distribution. Among the isomers, over all these zeolites, 4-TBB and 4,4′-DTBB were formed with a selectivity of above 95 and 85%, respectively. The preferential formation of the 4-TBB from mono-*t*-butylated isomers and consequently 4,4′-DTBB from di-*t*-butylated isomers is probably dependent on the size (kinetic diameter) of these molecules that are lower than other isomers due to their linearity and difference in diffusion kinetics [14].

Table 2 shows the effects of reaction temperature on the selectivity for 4-TBB and 4,4′-DTBB isomers in the butylation of biphenyl with TBA over HY and modified HY zeolites in the temperature range of 130–200 °C for a period of 2 h. The molar ratio of TBA to biphenyl is taken as 2. It is clearly seen from Table 2 that unmodified HY zeolite showed a maximum conversion of ∼28% and is more selective towards 4-TBB even at high temperatures (175–200 °C). Also unmodified HY zeolite did not form any polyalkylbiphenyls (PAB) and other dialkylbiphenyl except 4,4′-DTBB. At low temperature (130 °C) a high monoalkylation activity is observed over all the zeolites under study: 97.3, 83.5, 88.8 and 95% MTBB with a 4-TBB selectivity of 98.3, 96.8, 97.7 and 97.8% respectively for HY, HY-550, HY-700 and HY-850 zeolites. This monoalkylation decreases with an increase in dialkylation as well as other secondary reactions with temperature. The secondary reactions include isomerization of 4-TBB to 3-TBB and further alkylation of 4-TBB to 4,4-DTBB. This is in agreement with the results obtained that 4-TBB concentration in the product decreases with increase of temperature (200 °C).

HY zeolite upon dealumination at a temperature of 550 °C, the catalyst HY-550, showed a marked increase in both conversion and the dialkylation selectivity as compared to the unmodified HY zeolite. The catalyst is active even at lower temperature showing a maximum conversion of 51.7% at 175 °C with dialkylation selectivity around 24%. With a further increase in the dealumination temperature to 700 °C (HY-700), a decrease in conversion of biphenyl is observed at all the temperature studied as compared to HY-550. This is attributed to both decrease in acid strength and concentration of acidity in the HT region. However, this catalyst showed an increase in the dialkylation isomer (4,4′-DTBB) selectivity above 90% as compared to HY-550 along with an improved 4-TBB isomer selectivity (∼97%). This can be explained by the secondary reactions such as self-reaction of mono- and dialkylated biphenyl over

Table 2
Effect of reaction temperature on *t*-butylation of biphenyl with TBA over HY and dealuminated HY zeolites

Catalyst	*T* (°C)	Conversion of biphenyl (wt.%)	Product distribution (wt.%)			Selectivity of 4-TBB	Selectivity of 4,4′-DTBB
			∑MTBB	∑DTBB	∑PAB		
HY	130	15	97.3	2.7	0	98.3	100
	150	21.8	95.7	4.3	0	98.1	100
	175	26.4	93.9	6.1	0	98.5	100
	200	27.9	92.6	7.4	0	94.5	100
HY-550	130	25.1	83.5	16.2	0.3	96.8	92.6
	150	36.5	77.8	21.6	0.6	96.0	88.9
	175	51.7	72.9	25.9	1.2	95.3	91.9
	200	48.1	64.5	33.8	1.7	85.9	83.1
HY-700	130	22.9	88.8	11	0.2	97.7	92.7
	150	29.5	80.6	19.1	0.3	97.1	92.1
	175	45.6	78.7	20.6	0.7	97.0	91.3
	200	44.7	72.3	26.8	0.9	90.0	83.2
HY-850	130	18.1	95	5	0	97.8	82.0
	150	24.3	92.4	7.6	0	97.2	85.5
	175	34.6	89.5	10.1	0.4	96.2	86.1
	200	33.5	85.9	13.3	0.8	92.9	75.2

Reaction conditions: pressure = 100 psi (N_2); catalyst = 10 wt.%; biphenyl:TBA:cyclohexane = 1:2:10 (molar ratio); TOS = 2 h; MTBB: mono-*t*-butylbiphenyl; DTBB: di-*t*-butylbiphenyl; PAB: polyalkylatedbiphenyl.

HY-700 is less pronounced as compared to HY-550 (see Table 3). HY-850, sample HY-700 steam treated at 850 °C, showed a decrease in conversion of biphenyl as compared to other two dealuminated zeolites. This can be attributed to the decrease in the concentration of acid sties in the HT region even though an increase in acid strength is noticed. These modified zeolites did not show a very high conversion as the commercial HY zeolite used by Horniaková et al. (55.6% conversion after 2 h). However, a very high selectivity for both the isomers (97% for 4-TBB and ~90% for 4,4′-DTBB) were observed over HY-700 zeolite.

From the foregoing discussions, the HY zeolite dealuminated in the moderate temperature region (550–700 °C) are active for both conversion of biphenyl and dialkylation selectivity to 4,4′-DTBB. Considering the other by-products like PAB, it can be concluded that HY-700 is more selective towards formation of 4,4′-DTBB and further studies are carried out over these zeolites and the temperature is fixed as 175 °C.

Table 3
Self-reaction of 4,4′-DTBB over HY-550 and HY-700 catalysts

Catalyst	*T* (°C)	Conversion of 4,4′-DTBB (wt.%)	Selectivity of 4-TBB (wt.%)	Selectivity of biphenyl (wt.%)
HY-400	130	0.8	98.9	1.1
	150	6.6	90.7	9.3
	175	70.5	80.6	19.4
	200	94.0	53.1	46.9
HY-500	130	2.8	98.2	1.8
	150	23.3	94.5	5.5
	175	80.2	67.0	33.0
	200	91.8	15.5	84.5

Reaction conditions: 5 wt.% solution of 4,4′-DTBB in cyclohexane; pressure = 100 psi (N_2); catalyst = 10 wt.%; TOS = 2 h.

Fig. 2 shows the variation in the level of biphenyl conversion and in the isomer selectivity of 4-TBB and 4,4′-DTBB over HY-700 zeolite with reaction time. The conversion of biphenyl increases with time and reaches almost constant conversion level of around 45% after 1 h of reaction and during the course of study of 6 h. The selectivity for 4-TBB and 4,4′-DTBB decreases slightly over the period of time indicating the secondary reactions leading to polyalkylated products and isomerized products due to longer contact time. The above results are further supported by the studies

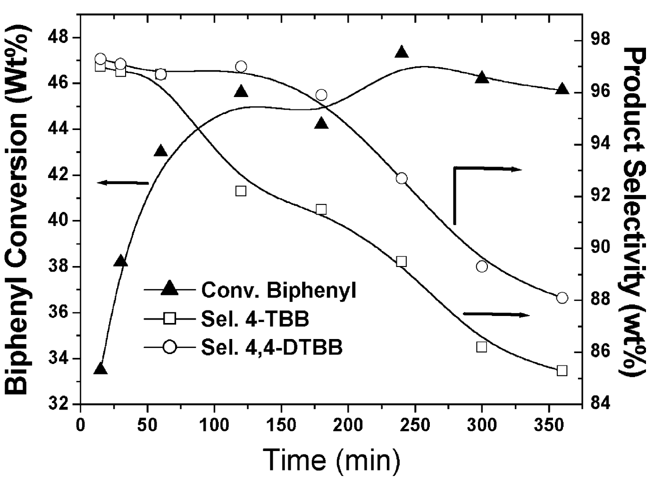

Fig. 2. Effect of reaction time on the alkylation activity and selectivity of 4-TBB and 4,4′-DTBB over HY-700 zeolite. Reaction conditions: temperature = 175 °C; pressure = 100 psi (N_2); catalyst (10 wt.%) = HY-700; TBA/biphenyl = 2.

Table 4
Effect of molar ratio in the *t*-butylation of biphenyl with TBA over HY-700 zeolite

Molar ratio biphenyl:TBA	Conversion of biphenyl (wt.%)	Product distribution (wt.%)			Selectivity of 4-TBB (wt.%)	Selectivity of 4,4′-DTBB (wt.%)
		∑MTBB	∑DTBB	∑PAB		
1:1	19.4	89.9	9.9	0.2	98.2	94.9
1:2	45.6	78.7	20.6	0.7	97.0	91.3
1:3	56.1	66.3	31	2.7	90.6	84.8
1:5	62	61	33.9	5.1	88.9	83.8

Reaction conditions: temperature = 175 °C; pressure = 100 psi (N_2); catalyst (10 wt.%) = HY-700; TOS = 2 h. Solvent (cyclohexane): 10 (molar ratio); MTBB: mono-*t*-butylbiphenyl; DTBB: di-*t*-butylbiphenyl; PAB: polyalkylatedbiphenyl.

Table 5
Effect of catalyst concentration in the *t*-butylation of biphenyl with TBA over HY-700 zeolite

Catalyst concentration (wt.%)	Conversion of biphenyl (wt.%)	Product distribution (wt.%)			Selectivity of 4-TBB (wt.%)	Selectivity of 4,4′-DTBB (wt.%)
		∑MTBB	∑DTBB	∑PAB		
5	30.8	88.3	11.4	0.3	98.5	96.5
10	45.6	78.7	20.6	0.7	97.0	91.3
15	50.1	69.9	27.1	3	89.6	81.9
20	58.9	59.7	33.6	6.7	84.3	81.3

Reaction conditions: temperature = 175 °C; pressure = 100 psi (N_2); catalyst = HY-700; biphenyl:TBA:cyclohexane = 1:2:10 (molar ratio); TOS = 2 h; TBB: mono-*t*-butylbiphenyl; DTBB: di-*t*-butylbiphenyl; PAB: polyalkylatedbiphenyl.

of isomerization of 4,4′-DTBB over HY-550 and HY-700 (Table 3). The major products are 4-TBB and biphenyl. It is evident from Table 3 that with an increase in temperature, an increase in conversion of 4,4′-DTBB was observed with cracking towards 4-TBB and biphenyl. The cracking is more pronounced at 200 °C with selectivity around 84 and 47% towards biphenyl over HY-550 and HY-700 catalysts, respectively.

The results of influence of different molar ratios of TBA to biphenyl on the alkylation of biphenyl and product selectivites over the catalyst HY-700 are summarized in Table 4. The conversion of biphenyl increased from 19.4 to 62%, whereas the selectivity to 4-TBB decreased from 88.3 to 55.2% with increasing molar ratio of TBA to biphenyl from 1 to 5 with a concomitant increase in the 4,4′-DTBB and PAB selectivity. The increase in the selectivity of 4,4′-DTBB is sharp from 9.4 to 26.3% with an increase in molar ratio of TBA to biphenyl from 1 to 3, however, it almost leveled off (28.4%) with a further increase of molar ratio to 5 due to various secondary reactions as the alkylating agent is rich in the reaction mixture.

Table 5 shows the influence of HY-700 zeolite concentration under the optimal conditions ($T = 175\,°C$; TBA/biphenyl molar ratio = 2; time = 2 h). An increase in the biphenyl conversion from 30.8 to 58.9% is observed with increase in the catalyst amount in the reaction mixture from 5 to 20 wt.%. As shown in this table, the increase in catalyst amount increases the 4,4′-DTBB selectivity along with increase in polyalkylation and other side reactions versus the monoalkylation step. This is attributed to availability of more number of acids sites for the secondary reactions to take place.

4. Conclusions

The liquid-phase butylation of biphenyl with TBA as alkylating agents was carried out efficiently over HY and dealuminated HY zeolites. The butylation of biphenyl yields both mono- and dialkylated biphenyl out of which the *para*-isomers 4-TBB and 4,4′-DTBB is found to be major products with a selectivity of above 95 and 85%, respectively. The optimum reaction conditions are $T = 175\,°C$; TBA/biphenyl molar ratio = 2 and time = 1–2 h. Higher temperatures above 175 °C lead to unnecessary secondary reactions as confirmed by the isomerization studies of 4,4′-DTBB. Conversion of biphenyl increases with time, however, the selectivities of 4-TBB and 4,4′-DTBB decreases slightly with time due to longer times leading to secondary reactions. Also HY zeolite steamed at medium temperatures (550–700 °C) showed an increase in selectivity of 4,4′-DTBB.

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