Selective alkylation of naphthalene with *tert*-butyl alcohol over HY zeolites modified with acid and alkali

Yingli Wang [a,b], Lei Xu [a], Zhengxi Yu [a], Xinzhi Zhang [a], Zhongmin Liu [a,*]

[a] *Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China*
[b] *Graduate University of the Chinese Academy of Sciences, Beijing 100049, PR China*

ABSTRACT

Liquid phase alkylation of naphthalene with *tert*-butyl alcohol over HY zeolites modified with acid and alkali had been studied. A highest naphthalene conversion of more than 90 mol% was achieved over HY zeolites modified with hydrochloric acid (HY-H). 2,6-di-*tert*-butylnaphthalene(DTBN) was synthesized selectively over HY zeolites modified with oxalic acid (OY) and with stepwise acid and alkali (OSY-BS-H), with 2,6-/2,7-DTBN ratios of 5.93 and 6.11, respectively. Correlations between 2,6-selectivity and zeolite structures, catalysts acidity, products properties were obtained.

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1 Introduction

2,6-Dialkylnaphthalene (2,6-DAN) is potentially useful raw material for production of advanced aromatic polyester plastics such as polyethylene naphthalate (PEN) and thermotropic liquid crystalline polymers. Alkylation of naphthalene is of industrial importance for producing 2,6-DAN. The synthesis of 2,6-DAN is complicated for the formation of as many as 10 possible DANs [1] including α,α-, α,β-, and β,β-disubstituted isomers on alkylation of naphthalene. Because of the difficulty of separating 2,6-DAN from these isomers, especially β,β-isomers [2], the selective production of 2,6-DAN with a high 2,6-/2,7-DAN ratio on alkylation of naphthalene is highly expected. It was found that a shape-selective effect was in operation on alkylation of naphthalene over zeolite catalysts [3–7]. And higher selectivity for β-position products, especially 2-AN, 2,6- and 2,7-DAN, were obtained with the larger alkyl groups. Nevertheless, the selective formation of the 2,6-DAN was not as good as expected. The best results of 2,6-/2,7-DAN ratio on methylation, isopropylation, cyclohexylation of naphthalene shown in the literatures to date were 2.0 [3], 2.7 [5], 1.4 [7], respectively.

Such results led us to focus our attention on other hindered alkylating substituents, especially *tert*-butyl group, being a much bulkier substituent than isopropyl or cyclohexyl, from which it was expected that high β,β-selectivities, especially high 2,6-selec-

tivity could be achieved [8–10]. And our interest on *tert*-butylation of naphthalene was stimulated by the finding that, 2,6-DTBN could be isolated from the reaction mixtures by recrystallization [10,11]. HY zeolites had been shown to be effective for the selective synthesis of 2,6-DTBN in the liquid phase *tert*-butylation of naphthalene. The naphthalene conversion of about 50%, with 2,6-/2,7-DTBN ratios from 5.6 to 5.9, was obtained over HY zeolites under mild reaction conditions [11,12]. Several modification techniques could improve the catalytic performance for zeolite catalysts. In the present study, the effects of acid and alkali modification over HY zeolites on the structural and acidic characteristics and on the catalytic performance in the shape-selective *tert*-butylation of naphthalene were investigated.

2 Experimental

2.1. Catalyst preparation

The HY zeolites were obtained from catalyst factory. The acid and alkali treatment procedure included modification of the zeolite powders (10 g) in 100 ml solutions under stirring. The commercial HY was modified with 0.05 mol/l hydrochloric acid (HCl) and 0.2 mol/l oxalic acid ($H_2C_2O_4$) to generate HY-H and OY sample, respectively. The OY was steamed at 650 °C for 1 h to give OSY sample. The OSY was added into 0.1 mol/l NaOH solution to stir for 2 h and OSY-B sample was obtained. Then the OSY-B was exposed to a steam atmosphere at 650 °C for 1 h to prepare OSY-BS sample. The OSY-BS was treated with 0.05 mol/l HCl solution to

* Corresponding author. Tel: +86 411 84685510; fax: +86 411 84691570.
E-mail address: Liuzm@dicp.ac.cn (Z. Liu).

prepare OSY-BS-H sample. Besides the steamed samples, the others were followed by calcination at 550 °C for 4 h. Table 1 summarized sample codes and corresponding treatment conditions.

2.2. Characterization

The crystal structure was analyzed on a Rigaku D/MAX-γB powder X-ray diffractometer (XRD) with Cu Kα radiation. The relative crystallinity was determined by comparing integrated intensities of the (311), (511,333), (440), (533), (642), (822,660), (555,751) and (664) reflections and the (533) half-height line widths according to ASTM D3906-2003. ASTM D3942-2003 was used for determination of lattice constants a_0. The framework Si/Al molar ratios were calculated with formulae below [13]:

$$Al_F = 107.1(a_0 - 24.238) \qquad Si/Al = (192 - Al_F)/Al_F$$

NH$_3$-TPD was carried out on TPRWin v2.0 chemical Autosorb Instrument from Quantachrome to discern the distribution of acid amount and acid strength. The surface Si/Al molar ratios were determined on a VG ESCALAB MKII X-ray photoelectron spectroscopy (XPS) spectrometer with Al Kα radiation. The bulk Si/Al molar ratios were determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer.

2.3. Catalytic reaction

Alkylation of naphthalene was carried out in a 75 ml stirred micro-autoclave reactor. For a typical run, 0.29 g (2.25 mmol) naphthalene and 16.62 g (200 mmol) cyclohexane as solvent were mixed together in the autoclave, then 0.50 g freshly calcinated catalyst and 0.50 g (3.00 mmol) of tert-butyl alcohol was added sequentially. The autoclave was sealed, purged with N$_2$ for several times and filled with N$_2$ to 2.0 Mpa. At the end of the reaction, the reactor was quenched in cold water. The catalyst was centrifugalized after venting the headspace gas, and then the products were analyzed on a Varian3800 gas chromatograph equipped with Varian cp-sil-19 column (25 m) and FID detector. The oven temperature program was 50–220 °C at 4 °C/min heating rate. GC–MS (HP5970) was used for identification of the products.

3 Results and discussion

3.1. Characterization of catalysts

The XRD patterns (not shown) showed that the typical diffraction peaks of FAU structure were largely preserved, which indicated the stability of HY zeolites under the different modification conditions. The framework Si/Al molar ratios, unit cell constant and relative crystallinity, drawn from a detailed XRD crystallographic calculation, were listed in Table 2. The first step of acid leaching modification resulted in: (1) an increase of framework Si/Al molar ratios. It showed dealumination was accomplished over HY zeolites modified with HCl acid or H$_2$C$_2$O$_4$ acid; (2) a reduction
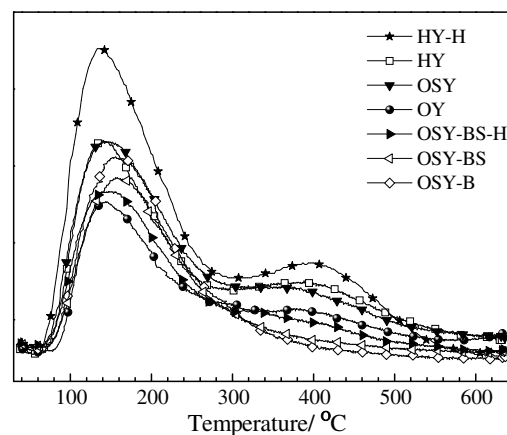
Table 2
Crystallographic calculation results of HY zeolites modified with acid and alkali

Sample	a_0 (Å)	Framework Si/Al from XRD	Relative crystallinity
HY	24.53	5.20	100[a]
HY-H	24.46	7.04	141.9
OY	24.42	8.66	130.7
OSY	24.33	17.76	124.2
OSY-B	24.38	11.85	126.7
OSY-BS	24.37	12.19	117.2
OSY-BS-H	24.33	18.83	112.1

[a] Commercial HY zeolites as the reference material.

of unit cell constant. Dealumination would induce a contraction in unit cell, as is expected for the removal of aluminum atoms whose T–O–T bond length is longer than that of silicon: 0.175 nm versus 0.162 nm [14]; and (3) an enhancement of relative crystallinity. This was probably owing to the removal of amorphous impurity of the commercial HY. During the following stepwise modifications, the structural factors kept a similar running tendency, except a back run in the step of NaOH extracting modification: framework Si/Al molar ratio of OSY-B resulted in a significant decrease to 11.85.

The NH$_3$-TPD curves of HY zeolites modified with acid and alkali were presented in Fig. 1. The profiles exhibited typical double-peak characteristics of zeolites with the FAU-structure. The lower temperature desorption peaks at 150 °C was usually ascribed to physically adsorbed ammonia or the weak adsorption sites of zeolites, and this kind of acid sites is unable to activate alkylation reaction. The higher temperature desorption peak at 370 °C was deserved to strong acid sites. Usually, the area of a specific peak was closely related to the amount of ammonia desorbed and could be taken as a quantitative measure of the number of acid sites of the sample concerned [15]. It was observed that the numbers of strong acid sites were varied over HY zeolites modified with acid and alkali.

Fig. 1. NH$_3$-TPD curves of HY zeolites modified with acid and alkali.

Table 1
Acid and alkali treatment conditions over HY zeolites

Sample	Parent materials	Treatment conditions			Calcination temperature (°C)
		Treatment methods	Temperature (°C)	Time (h)	
HY	Commercial HY	–	–	–	550
HY-H	HY	0.05 mol/l HCl	85	2	550
OY	HY	0.2 mol/l H$_2$C$_2$O$_4$	80	4	550
OSY	OY	Water vapor	650	1	–
OSY-B	OSY	0.1 mol/l NaOH	50	2	550
OSY-BS	OSY-B	Water vapor	650	1	–
OSY-BS-H	OSY-BS	0.05 mol/l HCl	85	2	550

The modified HY zeolites with HCl acid showed an increase in the strong acid number, while the number of strong acid sites was decreased obviously in the step of $H_2C_2O_4$ acid leaching modification. And the strong acid number over HY zeolites modified with NaOH could be negligible.

3.2. Catalytic performance

Table 3 compared the conversion and products distribution over HY zeolites modified with acid and alkali under the same conditions. In accordance with the other researchers [11,16], only two DTBN were observed on *tert*-butylation of naphthalene. These results showed that a shape-selective effect had strongly taken place on *tert*-butylation of naphthalene over HY zeolites. The others products listed in Table 3 were attributed to derivatives of polynuclear aromatic hydrocarbons by the fragmentation patterns in the mass spectra. As shown in Table 3, TBN was the major product over OSY-B, OSY-BS, and OSY-BS-H, while the others products were not detected. Moreover, OSY-BS-H gave the highest 2,6-/2,7-DTBN ratio of 6.11 and a naphthalene conversion of about 45 mol% while those over OSY-B, OSY-BS were very low. Although a naphthalene conversion more than 90 mol% was observed over HY-H, a 2,6-/2,7-DTBN ratio was rather low at 2.34. In contrast to the low activity and/or low selectivity for DTBN over the catalysts above, OY exhibited a higher naphthalene conversion of 53.5 mol% with 59.7 mol% of DTBN a main product, as well as a higher 2,6-/2,7-DTBN ratio of 5.93. Therefore, it was proposed that $H_2C_2O_4$ acid leaching modification was the most effective and direct approach to obtain an activated shape-selective catalyst among the different modifications.

3.2.1. Structure–selectivity relationships

The Si/Al molar ratios of some modified samples were shown in Fig. 2. Si/Al molar ratios were determined by XPS (surface Si/Al), by XRF (bulk Si/Al), by XRD (framework Si/Al). It was observed that surface Si/Al molar ratio showed a little higher than bulk and framework Si/Al molar ratio over HY, which represented the non-uniform distribution in parent HY sample; When HY was modified with $H_2C_2O_4$ acid leaching, the high aluminum-extraction efficiency from FAU framework was observed. Especially, the value of surface Si/Al molar ratio was up to 36.98. Such results suggested that the aluminum atoms from external surface were removed selectively. This could be explained by the dual nature of $H_2C_2O_4$ acid, i.e. it acted both as a hydrolyzing as well as a chelating agent during dealumination, forming a tris-oxalate aluminum complex with a high complexation constant [17]. Complexation was the driving force of the high aluminum-extraction efficiency of $H_2C_2O_4$ acid. And the big bulk of tris-oxalate aluminum complex would prevent dealumination from the internal crystal and resulted in dealumination gradient [18]. Thus, a silicon-rich surface would come into being in the step of $H_2C_2O_4$ acid leaching modification, which could deactivate nonselective acid sites on
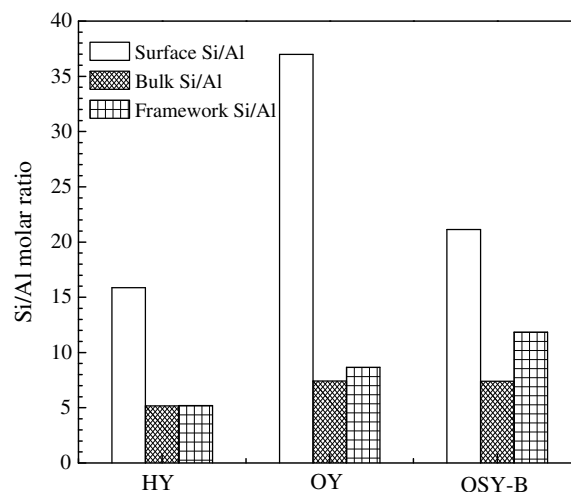

Fig. 2. Si/Al molar ratios of HY zeolites modified with acid and alkali; Surface Si/Al were determined by x-ray photoelectron spectroscopy; Bulk Si/Al were determined by x-ray fluorescence analysis; Framework Si/Al were determined by x-ray diffrator analysis.

the external surface. And more contributions from the internal channel surface could be expected to improve 2,6-/2,7-DTBN ratio over OY; In the step of NaOH extracting modification, the value of surface Si/Al molar ratio was decreased. Such results testified the silicon-rich surface was dissolved and the extraframework aluminum was reinserted into the FAU framework, which was reported by Liu et al. [18]. The shape-selective effect from the internal channel was weakened and a lower 2,6-/2,7-DTBN ratio of 3.26 was obtained over OSY-B. A speculated schematic picture was given in Scheme 1, in which the grid denoted the zeolite framework and the black squares were framework aluminum atoms. HY zeolites structure was depicted with the parent situation in the left. In the step of $H_2C_2O_4$ acid leaching modification, dealumination gradient (oblique arrow) resulted in the formation of the silicon-rich surface and some extraframework aluminum (open squares), which showed in the middle. In the step of NaOH extracting modification, silicon atoms dissolution (dotted lines) and extraframework aluminum reinsertion (curve arrow) produced the zeolite structure in the right.

#### 3.2.2. Acidity–selectivity relationships

The NH_3-TPD profiles were deconvoluted by the Gauss curve fitting method. Quantitative results of the number of strong acid sites were obtained from measurement the amount of ammonia adsorbed at higher temperature. Fig. 3 compared naphthalene conversion, product selectivity and 2,6-/2,7-DTBN ratio as a function of the amount of ammonia adsorbed at higher temperature. The

Table 3
Reaction results over HY zeolites modified with acid and alkali on *tert*-butylation of naphthalene [a]

Sample ID	Naphthalene conversion/mol%	Product distribution/mol%			β,β-Selectivity in DTBN/mol%		2,6-/2,7-DTBN
		TBN	DTBN	Others[b]	2,6-	2,7-	
HY	83.4	37.7	53.6	8.7	80.6	19.4	4.16
HY-H	91.2	47.3	44.5	8.2	70.0	30.0	2.34
OY	53.5	40.3	59.7	–	85.6	14.4	5.93
OSY	76.7	37.3	57.8	4.9	79.9	20.1	3.97
OSY-B	5.51	65.6	34.4	–	76.5	23.5	3.26
OSY-BS	5.29	70.5	29.5	–	76.9	23.1	3.33
OSY-BS-H	45.7	50.4	49.6	–	85.9	14.1	6.11

[a] Reaction conditions: reaction temperature, 160 °C; reaction pressure, 2.0 MPa; reaction time, 2.0 h; naphthalene: *tert*-butyl alcohol: cyclohexane, 2.25:3:200 (molar).
[b] Derivatives of polynuclear aromatic hydrocarbons identified with MS.
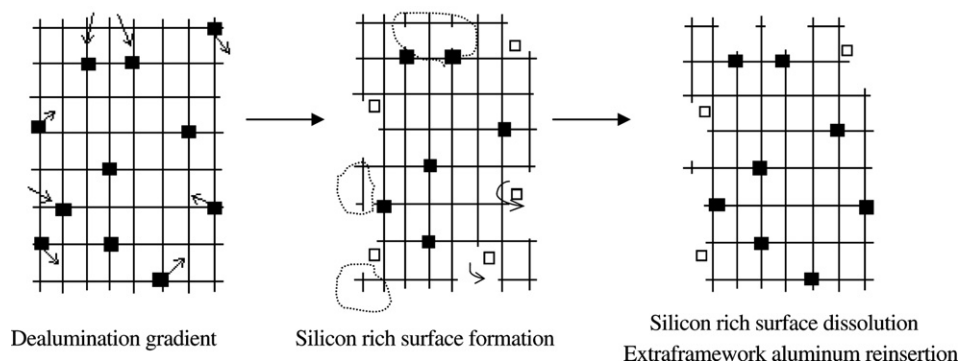
Scheme 1. Schematic picture of the structural modification over HY zeolite modified with $H_2C_2O_4$ acid and NaOH.
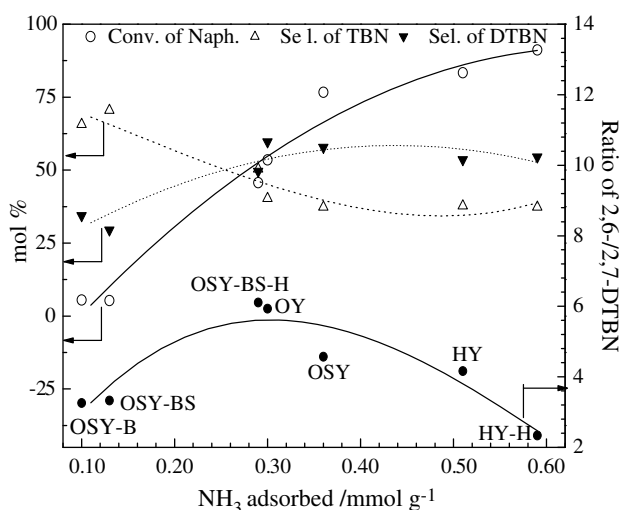
Fig. 3. Naphthalene conversion, product selectivity and 2,6-/2,7-DTBN ratio as a function of NH_3 adsorbed of HY zeolites modified with acid and alkali.

naphthalene conversion was enhanced with the increasing numbers of strong acid sites. Possible reason was that the strong acid sites must be the active sites of in alkylation of naphthalene. Then the increased number of strong acid sites was in favor of the accessibility of the active sites, resulting in the enhancement of the naphthalene conversion.

The relationship between 2,6-/2,7-DTBN ratios and the numbers of strong acid sites was also discussed in Fig. 3. It was observed that 2,6-/2,7-DTBN ratio was more sensitive to the change of strong acid sites number, and the moderate numbers of strong acid sites might associate with comparatively higher selectivity for 2,6-DTBN. There were two directional requirements for achieving high catalytic selectivity for 2,6-DTBN: the selective formation of 2,6-DTBN and the prevention of further reaction or conversion of 2,6-DTBN once it was formed. Due to large numbers of strong acid sites over HY-H, low 2,6-/2,7-DTBN ratio of 2.34 seemed to be ascribed to increase the chance of secondary reactions, such as isomerization of 2,6-DTBN. On the other hand, small amounts of strong acid sites might lead to the lack of active sites to alkylation of naphthalene and/or TBN into DTBN, which would inhibit the formation of 2,6-DTBN. This could be considered as the reason that higher selectivity for TBN and lower selectivity for DTBN were observed over OSY-B and OSY-BS, which occupied few numbers of strong acid sites. The shape-selective effect from the zeolite channel was the only explanation for a 2,6-/2,7-DTBN ratio of 3.26 over OSY-B. Moreover, OY and OSY-BS-H showed a much higher 2,6-/

2,7-DTBN ratio (5.93 and 6.11, respectively) under the same reaction condition. Reduction in the number of strong acid sites to a certain extent was likely to be partially responsible for enhanced 2,6-selectivity.

3.2.3. Products properties–selectivity relationships

Intercomparsion of selectivity for 2,6-DAN and alkylating agents on the basis of the previous studies, it was observed that a more remarkable shape-selective effect happened on alkylation of naphthalene with *tert*-butyl alcohol than with other alkylating agents. It is well-known that 2,6- and 2,7-DAN were the slimmest among the 10 DAN isomers, with the molecular dimension of the former being only slightly smaller than the latter, so it should be difficult to obtain a high 2,6-/2,7-DAN ratio even with shape-selective zeolites catalysts. Although the structural and acidic modification over HY zeolites for the shape selectivity, one still tended to suspect that all these effects could not sufficiently account for the fact that 2,6-/2,7-DTBN ratio was so much as higher to six, while the best results of 2,6-/2,7-DAN ratio on methylation, isopropylation, cyclohexylation of naphthalene were 2.0 [3], 2.7 [5], 1.4 [7], respectively. In the present study, we did a simple contrast of the β,β-isomers between isopropyl and *tert*-butyl group on their differentiation in molecular dimensions based on computational analysis using MOPAC. As shown in Table 4, the differentiation in molecular dimensions between 2,6- and 2,7-DAN was broaden with the increase of the volume augmentation of the alkyl group (0.05 Å for isopropyl- and 0.4 Å for *tert*-butyl- isomers). In this regard, *tert*-butyl group possessed immense superiority than other alkyl group on shape-selective alkylation of naphthalene. Table 4 also showed the enthalpy values of these isomers. In general, the molecular is slightly more stable with lower heat of formation. Thus, 2,6-di-isopropylnaphthalene (DIPN) and 2,7-DIPN were equally stable in terms of heat of formation. However, heat of formation of 2,6- and 2,7-DTBN were discriminating and 2,6-DTBN was more stable than 2,7-DTBN. The results of the differentiation in molecular dimensions and enthalpy values could be another interpretation for that a more higher 2,6-/2,7-DAN ratio was obtained on shape-selective *tert*-butylation of naphthalene from products properties.

Table 4
Effect of the alkyl group on the properties of β,β-isomers

	Isopropyl-[19]		*tert*-Butyl-[11]	
	2,6-	2,7-	2,6-	2,7-
Critical diameter (Å)	7.21	7.26	7.1	7.5
Molecular length (Å)	13.14	13.14	11.7	11.1
Molecular thickness (Å)	6.52	6.52	4.3	4.3
Heat of formation (kcal/mol)	3.44	3.44	3.04	3.06

4. Conclusion

Shape-selective *tert*-butylation of naphthalene was achieved over HY zeolites modified with acid and alkali. Over HY-H, a naphthalene conversion more than 90 mol%, while a 2,6-/2,7-DTBN ratio of 2.34 could be achieved. Over OY and OSY-BS-H, it was found that 2,6-DTBN could be selectively synthesized with 2,6-/2,7-DTBN ratios of 5.93 and 6.11, respectively. The lowest naphthalene conversion of about 5 mol% with a 2,6-/2,7-DTBN ratio of 3.26 was obtained over OSY-B. Our work revealed that $H_2C_2O_4$ acid leaching modification was an effective and direct approach to obtain a silicon-rich surface zeolite catalyst, which could enhance 2,6-selectivity for deactivating nonselective acid sites on the external surface. And the increased number of strong acid sites could be in favor of conversion of naphthalene, while the decreased number of strong acid sites could inhibit the subsequent second reactions of 2,6-DTBN. Therefore, for 2,6-DTBN selectivity, the key factor was not the total number of acid sites, but the number (moderate) and distribution (internal channel surface) of catalytic effective sites (strong acid sites) that controlled the catalytic activity.

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