

# Alkylation of $\alpha$ -methylnaphthalene with long-chain olefins over large-pore zeolites

Zhong-Kui Zhao, Zong-Shi Li\*, Wei-Hong Qiao, Gui-Ru Wang and Lü-Bo Cheng

State key Laboratory of Fine Chemicals, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, P.R. China

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The liquid-phase alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins ( $C_{11-12}$ ) has been investigated firstly in the presence of H-Y and H-Beta zeolites with different pore architectures. The H-Y zeolites exhibited outstanding catalytic performances. The influences of various reaction parameters like temperature, pressure, mole ratio of  $\alpha$ -methylnaphthalene to olefins ( $n_{\text{rea}}$ ), solvent concentration, volume hour space velocity (VHSV) and time on stream on the reaction were studied in detail. Under the optimal reaction parameters, more than 90% conversion of olefins and 100% selectivity for the desired mono-alkyl methylnaphthalene were achieved.

**KEY WORDS:** Alkylation;  $\alpha$ -methylnaphthalene; Long-chain olefins; H-Y; H-Beta.

## 1. Introduction

Alkyl naphthalene sulfonates are one of the most important anionic surfactants, and their surface activities are obviously better than those of alkylbenzene sulfonates. With the usage of alkyl naphthalene sulfonates as a chemical oil-displacing agent for enhanced oil recovery, satisfactory results could be obtained and the ultralow interfacial tension between oil and water achieved. Moreover, because of their outstanding surface activity, they may be used in many fields such as cleaning, dye printing, emulsifying, ore milling, and nanotechnology, etc. Long-chain monoalkyl methylnaphthalenes are the core intermediates for alkyl naphthalene sulfonate surfactants. To date, the long-chain alkylation of benzene has already been widely and thoroughly investigated [1–3], but not for naphthalene and its derivatives. To our knowledge, no relative studies for the long-chain alkylation of methylnaphthalene have been reported. The alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins goes through a carbonium ion mechanism, and has conventionally been catalyzed by homogeneous acid catalysts, such as  $H_2SO_4$ ,  $BF_3$ ,  $HF$ ,  $AlCl_3$ ,  $FeCl_3$ , etc., which give rise to many problems concerning the handling, health, safety, corrosion and waste disposal of the catalysts [4,5]. In order to overcome these problems, many efforts have been devoted to the search of various heterogeneous acid catalysts to replace the homogeneous acid catalysts, which include clays, amorphous silica-alumina, mixed oxides and zeolites. Among solid acid catalysts, zeolites are extensively used on a large scale for the alkylations of aromatics [6–9]. Venuto *et al.*

observed Beta and Y zeolites to be better catalysts for benzene alkylation with olefins than amorphous silica-alumina gels [10]. The large pore zeolites may catalyze reactions of large-size moleculars. More and more attention has recently been paid to large pore zeolites such as H-mordenite, H-Y, and H-Beta used as environmentally friendly catalysts for alkylations of polynuclear aromatic compounds [11–15]. Fraenkel *et al.* firstly investigated the gas phase alkylation of naphthalene [16–18] with methanol over H-ZSM-5, H-Mordenites and H-Y zeolites. The medium pore size H-ZSM-5 showed a high  $\beta$ -selectivity, but only of moderate activity; while the large pore size zeolites, HY and H-M, owing to the existence of supercages providing enough space for multiple reactions would lead to lower  $\beta$ -selectivity, and higher activity. Moreau *et al.* recently reported that HY, in terms of activity or selectivity, is a better catalyst than H-M or H- $\beta$  in the selective synthesis of 2,6-dialkyl naphthalenes in liquid phase isopropylation, cyclohexylation or *tert*-butylation [16–24]. Moreover, Inui and coworkers carried out the isopropylation of naphthalene by isopropyl alcohol using the atmospheric pressure flow fixed-bed reactor over Y, Beta, mordenite, MCM-41, and MCM-48 catalysts, respectively, and deactivation was found on all catalysts within 3 h of reaction time on stream, with Y zeolite being comparatively stable [25].

In the present paper, we have first studied the alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins ( $C_{11-12}$  mixture), catalyzed by large pore zeolites such as H-Y and H-Beta zeolites as acid catalysts, with the usage of a fixed-bed continuous-flow reactor. Gas chromatography and gas chromatography mass spectrometry were used as the appraisal method for alkylation technology [26,27]. The influences of various reaction parameters like reaction temperature (T/K), system

\*To whom correspondence should be addressed.

E-mail: zkzhao2000@yahoo.com

pressure (P/MPa), mole ratio of  $\alpha$ -methylnaphthalene to olefins ( $n_{\text{rea}}$ ), solvent concentration (mole ratio of cyclohexane to  $\alpha$ -methylnaphthalene,  $n_{\text{sol}}$ ), volume hour space velocity (VHSV) and time on stream (TOS/min) on the reaction were investigated in detail. The optimal reaction parameters were achieved, and the results had been analyzed and discussed.

## 2. Experimental

The three-dimensional large pore zeolites H-Y and H-Beta were used in the alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins. The H-Y catalyst was prepared by calcining  $\text{NH}_4\text{-Y}$  (obtained from the Chinese Wenzhou Huahua Group,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5$ ) in a flow of dried air at 813 K for 5 h. H-Beta were prepared by the conventional liquid-state ion-exchange method. Na-Beta (offered by the Institute of Industrial Catalysis, DUT,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 27$ ) zeolite was soaked in 0.6 M aqueous solution of  $\text{NH}_4\text{NO}_3$  by a ratio of 4 ml/g and stirred at 363 K for 1 h. After being repeated for four times, the zeolite was washed thoroughly with deionized water to get rid of any residual ions which may have been occluded in zeolite pores. The washed sample was then dried at 393 K and calcined in a flow of dried air at 813 K for 5 h. The prepared H-Y and H-Beta zeolites were pressed, crushed and then sieved to 20–60 meshes. After this, the sample was dried at 393 K and then calcined at 813 K for 5 h.

Infrared spectra were recorded at room temperature on a Fourier transform infrared spectrometer (Nicolet Impact 410) with a resolution of  $4\text{ cm}^{-1}$  and 64 scans in the region from 4000 to  $400\text{ cm}^{-1}$ . The H-Y and H-Beta were pressed into a self-supporting wafer (ca.  $15\text{ mg cm}^{-2}$ ), and introduced into a quartz IR cell with  $\text{CaF}_2$  windows. The samples were pretreated *in situ* in a stream of 30 ml/min He from RT to 773 K and  $5 \times 10^{-3}\text{ Pa}$  for 90 min. The cell was subsequently cooled to room temperature and pyridine vapor was passed into the cell and adsorbed onto the zeolite for a period of 30 min. After removal of the excess pyridine, the spectrum was recorded. Then the sample was evacuated at 473 K for 30 min and a corresponding spectrum was recorded to distinguish the acid site. The relative intensities of vibration bands at  $1540\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  were ascribed to the Brønsted and Lewis acid site respectively.  $\text{NH}_3$  temperature-programmed desorption ( $\text{NH}_3\text{-TPD}$ ) was performed on a conventional set-up equipped with a thermal conductivity detector (TCD). The catalyst charge was 0.2 g with particle size of 20–60 meshes. The sample was first flushed with He (30 ml/min) at 873 K for 30 min, then cooled to 423 K and saturated with  $\text{NH}_3$  until equilibrium. It was then flushed with He (30 ml/min) again until the integrator baseline was stable.  $\text{NH}_3\text{-TPD}$  was then promptly started at a heating rate of  $15\text{ K/min}$  from 423 to

873 K. All  $\text{NH}_3\text{-TPD}$  profiled were deconvoluted into three peaks using a Gaussian and Lorentzian curve-fitting method.

The experiments were performed in a fixed-bed continuous-flow reactor equipped with 20 mm diameter and 400 mm length stainless steel tube, 2.0 g of 20–60 mesh zeolite catalysts, already having been calcined for 1 h, were loaded in the reaction tube. The reaction mixture was fed into the reactor by a quantity measuring pump and pressure was kept by  $\text{N}_2$ . Analyses of the products were done on a gas chromatograph (HP 6890, equipped with HP-5column,  $30 \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$ ; FID detector) and further product identification was done on a GC-MS (HP 5973 mass selective detector, column: HP-5MS column,  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ). The concentration of reactants and products were directly given by the system of GC chemstation from the area of each chromatograph peak. The conversion of alkenes, and selectivity of alkylmethylnaphthalene were used as the evaluation standard of this technology. The conversion of olefins was defined as  $C_L\%$ , which is the wt% of olefins consumed in the reaction. The selectivity of monoalkyl methylnaphthalene was calculated by:  $S_{\text{AMN}}\% = W_{\text{AMN}}/W_{\text{pro}} \times 100$ , where  $W_{\text{AMN}}$  is the amount of the desired product, monoalkylmethylnaphthalene, and  $W_{\text{pro}}$  is the total amount of the alkylated products.

$\alpha$ -Methylnaphthalene (GC grade  $> 98\%$ ) and industrial grade of long-chain olefins ( $\text{C}_{11-12}$ , wt% = 45/55, mixed olefins, bought from Fushun Petrochemical Company) mixture were used. Analytical grade cyclohexane and  $\text{NH}_4\text{NO}_3$  were used without further purification.

## 3. Results and discussion

### 3.1. Effect of catalyst type

Typical reaction results for the large pore zeolites with different pore architectures, H-Y and H-Beta, catalysts used in the alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins under standard conditions are listed in table 1.

It is obvious to observe that H-Y catalyst exhibits better catalytic performances for the reaction than those of H-Beta. If the reaction was catalyzed by H-Y, 90.0% conversion for olefins and about 99.0% selectivity for

Table 1  
The alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins over different catalysts

Entry	Catalyst	$C_L\%$	$C_{MN}\%$	$S_{AMN}\%$
1	H-Y	90.0	8.9	99.0
2	H-Beta	34.0	1.7	39.8

Reaction conditions: catalyst, 2.0 g;  $T = 473\text{ K}$ ;  $P = 1.0\text{ MPa}$ ; HSV =  $6\text{ mL}\cdot\text{h}^{-1}\text{ g}^{-1}\text{ cat}$ ;  $n_{\text{rea}} = 10:1$ ;  $n_{\text{sol}} = 2:1$ ; TOS = 240 min.

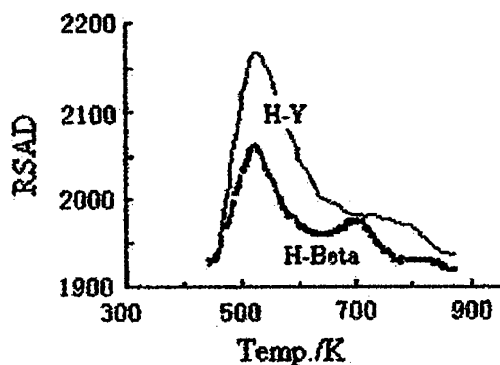


Figure 1.  $\text{NH}_3$ -TPD profiles of H-Y and H-Beta catalysts (RSAD is defined as relative strength of  $\text{NH}_3$  desorption).

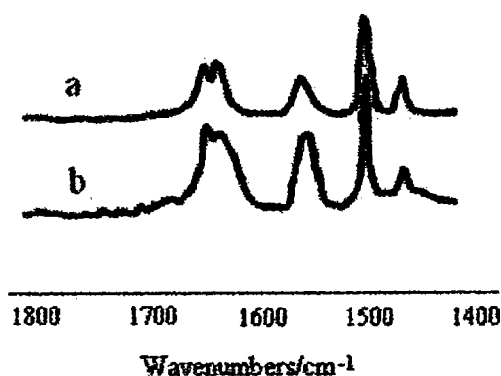


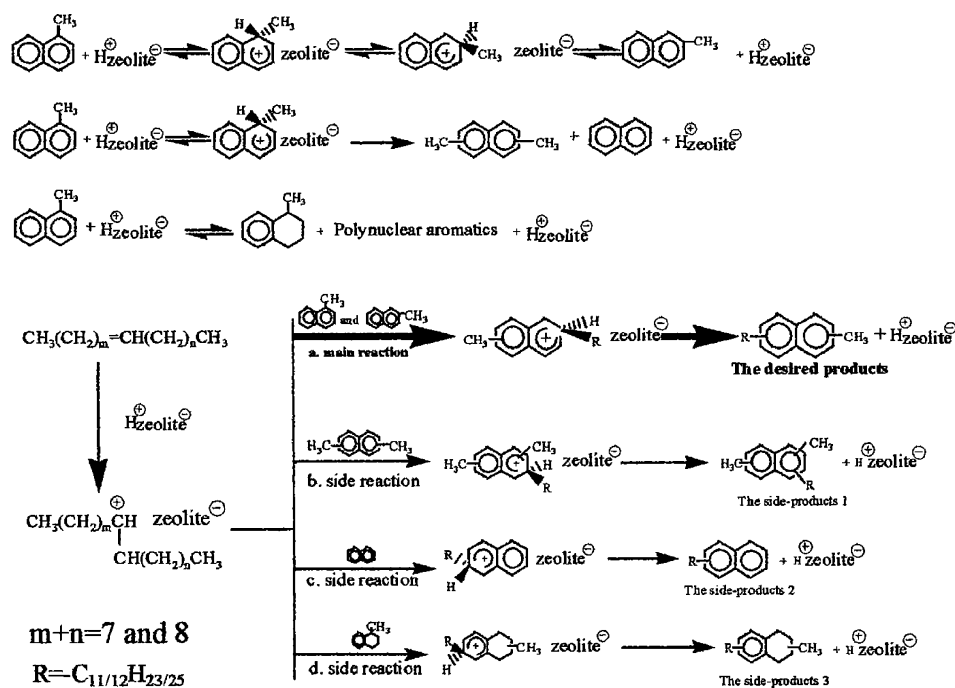
Figure 2. *In situ* IR spectra of pyridine adsorbed on H-Y and H-Beta zeolite catalysts.

monoalkylated products have been obtained. However, catalyzed by H-Beta, only 34.0% conversion for olefins and 39.8% selectivity for the desired products are obtained. This result can be explained by the TPD profiles of the two samples presented in figure 1. The higher Si/Al ratio H-Beta sample exhibited three  $\text{NH}_3$  desorption peak at ca. 543 K, 673 K and 873 K, which could be assigned to the site of weak, moderate-strong and strong acidity, respectively. The H-Y sample also provided the site of weak acidity at ca. 543 K and a relatively broader range of moderate-strong acidity site between 623 K and 753 K shown. Moreover, the amount of acid site determined by the  $\text{NH}_3$ -TPD shows much more for HY zeolite than that for H $\beta$ , which is in agreement with their activity. This suggests that the catalytic activity is proportionally increasing with the amount of acid sites, especially with the amount of moderate-strong acidity sites. The *in situ* IR spectra of pyridine adsorbed on different zeolite catalysts are shown in figure 2, from which one could readily find that H-Y (b) contained more Brönsted acidity sites ( $1540\text{ cm}^{-1}$ ) than H-Beta (a), while the amount of Lewis acidity sites ( $1450\text{ cm}^{-1}$ ) almost remains the same. Therefore, it can be safely say that the Brönsted acidic sites are active sites for the alkylation over both H-Y and H-Beta zeolites. Moreover, as can be seen from figure 1, there exists a strong acidity site at 873 K in H-Beta but not in HY, which leads to low selectivity for desired products since the strong acidity sites could enhance cracking and polymerization reactions. Therefore, a series of byproducts such as the short-chain alkyl methylnaphthalene, alkylnaphthalene, alkylmethyl tetrahydronaphthalene, alkyl dimethylnaphthalene, multi-alkylated short-chain products etc. were detected when catalyzed by H-Beta. As for H-Y, olefin polymers were hardly found over the relatively strong acidity sites along with the moderate-strong acidity sites. In addition, the pore size of H-Y is about 0.8–0.9 nm, which is appropriate for the products to diffuse out from the pre-channel, while that of H-Beta was about 0.6–0.75 nm,

which is small for alkylmethylnaphthalene and long chain olefins. The longer staying time in the pore passage of H-Beta may cause the products to crack to short-chain polyalkylated by-products or cause the olefins to polymerize. That is why the selectivity of desired products catalyzed by H-Beta is lower than that of H-Y. As can be seen from above, H-Y zeolite exhibited outstanding catalytic performances. Therefore, H-Y zeolite was chosen for alkylation of  $\alpha$ -methylnaphthalene. The outstanding catalytic performances of H-Y are undoubtedly related to the large-pore tri-dimensional zeolite network and the presence of supercages, which allow the reaction to occur onto the hindered substrate within the framework without diffusional restrictions.

On the basis of the above discussion, the catalytic alkylation over H-Y zeolite is supposed to be catalyzed by Brönsted acidity sites, which goes through a carbonium ion mechanism, the possible mechanism is shown in scheme 1 [28].

The reaction mixtures were analyzed by GC/MS [26]. The results exhibit that, except for the desired products, a series of isomers of monoalkylated methylnaphthalene, some side-products, mainly include isomers of monoalkyl dimethylnaphthalene (the side-products 1), monoalkyl naphthalene (the side-products 2), monoalkyl methyltetrahydronaphthalene (the side-products 3), etc. The confined channels of zeolite restrict the further alkylation of long-chain alkyl methylnaphthalene. As a result, no polyalkylated methylnaphthalene was detected. The formations of side-products 1 and 2 are easy to be explained based on the isomerization and disproportionation of  $\alpha$ -methylnaphthalene [26,27]. At present, the hydrogenation in alkylation of aromatic hydrocarbon was not reported, to our knowledge. On the basis of the GC/MS analytical results, the possible hydrogenation mechanism was supposed. It is the polymerization that provides hydrogen, which leads to the formation of alkyl methyltetrahydronaphthalene.



### 3.2. Effect of reaction temperature

The effect of reaction temperature on both activity and selectivity in the long-chain alkylation  $\alpha$ -methyl-naphthalene with olefins over the H-Y zeolite was investigated in the range of 353–523 K, and the results are shown in table 2. It indicates that, there is a considerable effect on conversion for olefins and a slight effect on selectivity for desired products were observed. It is observed that the conversion increases rapidly with the reaction temperature up to 473 K, and it goes up very slowly beyond 473 K. As T is further increased, both conversion and selectivity tend to drop. At temperature above 503 K the catalytic activity is decreasing and this may be due to the availability of strong acid sites at high reaction temperature [29–31], which enhanced polymerizations of methyl-naphthalene and olefins resulting in the pore blockage. The decrease in conversion for olefins may also be due to the coke formation.

Table 2

Effects of reaction temperature on both activity and selectivity in the alkylation of  $\alpha$ -methyl-naphthalene with long-chain olefins

Entry	T/K	C <sub>L</sub> %	S <sub>AMN</sub> %	Entry	T/K	C <sub>L</sub> %	S <sub>AMN</sub> %
1	353	8.6	100	5	453	80.9	100
2	373	9.0	100	6	473	84.9	99.0
3	403	31.9	100	7	503	84.8	97.7
4	423	66.5	100	8	523	73.8	90.0

Reaction conditions: catalyst, 2.0 g;  $P = 1.0$  MPa; VHSV = 7 mL·h<sup>-1</sup> g<sup>-1</sup> cat;  $n_{\text{rea}} = 8:1$ ;  $n_{\text{sol}} = 2:1$ ; TOS = 240 min.

### 3.3. Effects of system pressure

The influence of system pressure on the alkylation was studied at different pressure in the range 0.5–2.5 MPa. The results obtained are summarized in table 3.

From the table, it is observed that there is a noticeable increase in conversion for olefins from 68.4% to 81.7% when the pressure is increased from 0.5 MPa to 1.0 MPa. It may be explained that the phase change of the solvent plays an important role in the reactions. As system pressure is lower than 0.9 MPa, the saturated vapour pressure of cyclohexane at 473 K a dramatic increase in conversion of olefins observed by increasing the pressure from 0.8 MPa to 1.0 MPa. With further increase in pressure from 1.0 MPa to 2.5 MPa, only slight change in the conversion for olefins was observed. In the gas-phase solvent, long-chain olefins are liable to polymerization, which produces the main precursors of carbon deposition. The catalysts are

Table 3

Effects of system pressure on both activity and selectivity in the alkylation of  $\alpha$ -methyl-naphthalene with long-chain olefins

Entry	P/Mpa	C <sub>L</sub> %	S <sub>AMN</sub> %	Entry	P/Mpa	C <sub>L</sub> %	S <sub>AMN</sub> %
1	0.5	68.4	100	4	1.5	81.7	100
2	0.8	70.1	100	5	2.0	82.0	100
3	1.0	81.7	100	6	2.5	82.0	100

Reaction conditions: catalyst, 2.0 g;  $T = 473$  K; VHSV = 7 mL·h<sup>-1</sup> g<sup>-1</sup> cat;  $n_{\text{rea}} = 8:1$ ;  $n_{\text{sol}} = 2:1$ ; TOS = 240 min.

Table 4

Influence of mole ratio of reactants on  $\alpha$ -methylnaphthalene alkylation with long-chain olefins over H-Y zeolite

Entry	$n_{\text{rea}}$	$C_L$ %	$S_{\text{AMN}}$ %	Entry	$n_{\text{rea}}$	$C_L$ %	$S_{\text{AMN}}$ %
1	2:1	55.8	100	4	8:1	88.4	100
2	4:1	66.1	100	5	10:1	91.1	100
3	6:1	85.9	100	6	12:1	83.4	100

Reaction conditions: catalyst, 2.0 g;  $P = 1.0$  MPa;  $T = 473$  K; VHSV =  $5.5 \text{ mL} \cdot \text{h}^{-1} \text{ g}^{-1} \text{ cat}$ ;  $n_{\text{sol}} = 5:1$ ; TOS = 480 min.

covered and to be deactivated. After the pressure reached 1.0 MPa, beyond the saturated vapour pressure of solvent, the solvent has already been in the liquid state. The phase change of the solvent plays an important role in the reactions. After the pressure reached to 1.0 MPa, beyond the saturated vapour pressure of solvent, the solvent has already been in the liquid state. Therefore, only a slight increase in conversions of reactants would be observed. The long-chain alkylation of  $\alpha$ -methylnaphthalene is different from that of benzene, in which benzene is used as both reagent and solvent. Because of too large molecular size and viscosity for  $\alpha$ -methylnaphthalene, only be dispersed into solvent, the reaction would take place. The main role of increasing pressure is only accelerating the diffusion of both reactants and products in the channel of zeolite. Therefore, only a slight increase in conversions of reactants would be observed. Just in this sense we can safely conclude that it is very important in the reaction that the solvent be kept in the liquid phase. 1.0 MPa was set to be the optimal pressure.

### 3.4. Effect of molar ratio of $\alpha$ -methylnaphthalene to long-chain olefins

The mole ratio of  $\alpha$ -methylnaphthalene to long-chain olefins ( $n_{\text{rea}}$ ) is changed to test the impact of reactant ratio upon the alkylation reaction. Table 4 summarizes the results at various mole ratio of  $\alpha$ -methylnaphthalene to long-chain olefins from 2:1 to 12:1. In all cases, 100% selectivity for desired products were achieved. It is found that the activity is influenced dramatically by the change of  $n_{\text{rea}}$ . With the increase of  $n_{\text{rea}}$  the conversion of olefins rapidly increased. When  $n_{\text{rea}}$  reaches 10:1, more than

90% conversion of olefins has been obtained. The results may be explained as follows. As  $n_{\text{rea}}$  increasing, the relative amount of olefins flowing through the catalysts would be small, the main reaction is hastened, and simultaneously, the side reactions, such as polymerization of olefins, etc., are restricted. The stability of catalyst is also improved. If  $n_{\text{rea}}$  is further increased from 10:1 to 12:1, an obvious decrease in conversion of olefins was found. Therefore, the  $n_{\text{rea}}$  value can't be too large, 8–10:1 was the optimal molar ratio of  $\alpha$ -methylnaphthalene to olefins.

### 3.5. Effect of solvent concentration

Table 5 indicates the influence of the solvent concentration (mole ratio of cyclohexane to  $\alpha$ -methylnaphthalene,  $n_{\text{sol}}$ ) on  $\alpha$ -methylnaphthalene alkylation with long-chain olefins over H-Y zeolite. The effect was investigated by varying molar ratios of cyclohexane and  $\alpha$ -methylnaphthalene from 0 to 9. In all cases, 100% selectivity for desired products were achieved. It is observed that  $n_{\text{sol}}$  value plays a vital role in conversion of long chain olefins. An enhancement of conversion for long-chain olefins is observed when the concentration of solvent in the reactant mixture is raised. When  $n_{\text{sol}}$  value is 7:1, approximately 90% conversion of olefins could be obtained. As far as the circulating load is concerned, the optimal  $n_{\text{sol}}$  value is 5–7:1.

### 3.6. Effect of VHSV

Table 6 illustrates the effect of VHSV on the alkylation of  $\alpha$ -methylnaphthalene with long chain olefins upon H-Y zeolite.

As can be seen from the table, VHSV has a considerable effect on conversion for olefins. It is observed that the conversion increases obviously with the VHSV up to  $4.5 \text{ mL} \cdot \text{h}^{-1} \text{ g}^{-1} \text{ cat}$ . As it is further increased, the conversion tends to drop. It is suggested that neither too high nor too low flow rate is optimum to the reaction. If the VHSV value is too small, the long residence time of reactants in fixed-bed reactor would lead to many side reactions such as polymerization of reactants take place. As a result, carbon deposition on zeolite

Table 5

Influence of solvent concentration on  $\alpha$ -methylnaphthalene alkylation with long-chain olefins over H-Y zeolite

Entry	$n_{\text{sol}}$	$C_L$ %	$S_{\text{AMN}}$ %	Entry	$n_{\text{sol}}$	$C_L$ %	$S_{\text{AMN}}$ %
1	0:1	40.6	100	4	5:1	87.3	100
2	2:1	64.9	100	5	7:1	89.3	100
3	3:1	80.7	100	6	9:1	93.7	100

Reaction conditions: catalyst, 2.0 g;  $P = 1.0$  MPa;  $T = 473$  K; VHSV =  $5.5 \text{ mL} \cdot \text{h}^{-1} \text{ g}^{-1} \text{ cat}$ ;  $n_{\text{rea}} = 10:1$ ; TOS = 480 min.

Table 6

Influence of VHSV on  $\alpha$ -methylnaphthalene alkylation with long-chain olefins over H-Y zeolite

Entry	VHSV/ $\text{mL} \cdot \text{h}^{-1}$ $\text{g}^{-1} \text{ cat}$	$C_L$ %	$S_{\text{AMN}}$ %	Entry	VHSV/ $\text{mL} \cdot \text{h}^{-1}$ $\text{g}^{-1} \text{ cat}$	$C_L$ %	$S_{\text{AMN}}$ %
1	2.0	87.5	100	5	5.0	94.8	100
2	3.0	89.4	100	6	7.0	80.6	100
3	4.0	95.3	100	7	10.0	62.7	100
4	4.5	100.0	100	8	15.0	44.5	100

Reaction conditions: catalyst, 2.0 g;  $P = 1.0$  MPa;  $T = 473$  K;  $n_{\text{rea}} = 10:1$ ;  $n_{\text{sol}} = 6:1$ ; TOS = 480 min.

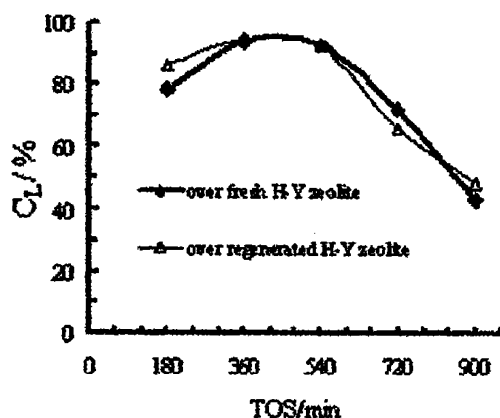


Figure 3. Effect of TOS on the alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins (approximately 100% of selectivity for monoalkyl methylnaphthalene).

is serious, which would cause catalysts to be deactivated. As the VHSV value increasing, the contact times between reactants and catalysts are shortened, and the conversion decreased. The optimal VHSV value is 4–5 mL h<sup>-1</sup> g<sup>-1</sup> cat.

### 3.7. Effect of time on stream

The effect of time on stream (TOS) was studied over the fresh H-Y and regenerated H-Y zeolite catalysts at 473 K with the mole ratio  $\alpha$ -methylnaphthalene: long-chain olefins: cyclohexane of 10:1:60 and VHSV 4.5 mL h<sup>-1</sup> g<sup>-1</sup> cat. The study was conducted for 900 min, and approximately 100% of selectivity for monoalkyl methylnaphthalene was obtained in the whole TOS. The catalytic activity of the alkylation is exhibited in figure 3. It was observed in the table that the conversion of long-chain olefins increased with an increase in TOS from 180 min to 360 min. In contrast, obvious decrease in conversion with increase in TOS above 540 min was observed. The decrease in conversion with increasing in time-on-stream might be attributed to a gradual increase in the blocking of the active sites by olefin oligomers and coke formation [32]. Furthermore, the catalytic activity of regenerated zeolite catalyst is also exhibited in the figure. As can be seen that, the catalytic performance of the regenerated H-Y zeolite catalyst is equal to that of the fresh H-Y zeolite. We can safely conclude that the catalytic performance of the deactivated H-Y zeolite can be regenerated completely by temperature-programmed calcinations. Hence, H-Y zeolite can be a viable alternative for substituting the traditional AlCl<sub>3</sub> catalyst.

## 4. Conclusions

The liquid phase alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins has been investigated over the large-pore zeolites, such as H-Y and H- $\beta$ , in a fixed-bed continuous-flow reactor. The catalytic

performance of H-Y zeolite in terms of both conversion for olefins and selectivity for monoalkylated methylnaphthalene was found to be better than that of H- $\beta$  zeolite. The alkylation of  $\alpha$ -methylnaphthalene with long-chain olefins leads to the formation of a mixture, including the desired products, a series of isomers of monoalkylated methylnaphthalene, and some side-products monoalkyl naphthalene, monoalkyl dimethylnaphthalene, monoalkyl methyltetrahydronaphthalene, etc. The further long-chain alkylation of monoalkylmethylnaphthalene was stopped due to the restriction of the confined channels of zeolite. The optimum reaction conditions are 8–10: 1 of molar ratio of  $\alpha$ -methylnaphthalene to olefins, 5–7: 1 of molar ratio of cyclohexane to  $\alpha$ -methylnaphthalene at 453–473 K and 1.0 MPa and VHSV to be 4–5 mL h<sup>-1</sup> g<sup>-1</sup> cat. Under the optimal reaction conditions, 100% selectivity for the desired products was achieved. The deactivated H-Y zeolite can be regenerated completely by temperature-programmed calcinations. The use of H-Y zeolite in the Friedel–Crafts alkylation reaction of aromatic hydrocarbon could be considered as an environmentally friendly alternative to the existing homogeneous catalysts. It could be a practical catalyst for long-chain alkylation of  $\alpha$ -methylnaphthalene with alkenes.

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