

# HY zeolite promoted free-solvent alkylation of $\alpha$ -methylnaphthalene with long chain olefins in liquid–solid intermittent reaction

Zhongkui Zhao\*, Weihong Qiao, Xiuna Wang, Guiru Wang, Zongshi Li, Lübo Cheng

State Key Laboratory of Fine Chemicals, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, PR China

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## Abstract

HY zeolite promoted liquid–solid free-solvent alkylations of  $\alpha$ -methylnaphthalene with long chain olefins have been performed in intermittent reactor. Effects of various reaction conditions like reaction temperature, dosage of catalyst and reaction time on the alkylation reaction were investigated. The alkylations were also carried out over alkaline earth and rare earth metal oxide modified HY, and effects of impregnated amount on the reactions were investigated simultaneously. It is found that 0.5% of  $\text{La}_2\text{O}_3$  modified HY exhibits outstanding catalytic performances, 94.0% of conversion for olefins and 100% of selectivity for the desired products were achieved. Moreover, the generation and reusability of deactivated HY zeolite catalyst were also studied. Results show that the catalytic performances of deactivated catalyst can be refreshed completely, and the regenerated catalyst can be further reused many times without decrease in its catalytic activity.

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**Keywords:** Alkylation;  $\alpha$ -Methylnaphthalene; Long chain olefins; HY zeolite; Modification; Regeneration and reusability

## 1. Introduction

Long chain alkyl methylnaphthalene sulfonate (AMNS) surfactants possess outstanding capability and efficiency of lowering the aqueous solution surface tension and the dynamic interfacial tension between oil and water [1,2]. AMNS have a great potential for enhanced oil recovery with low costs and high efficiency. Long chain alkylmethylnaphthalenes are the core intermediates for AMNS. Therefore, studies on the long chain alkylation of methylnaphthalene are very important from both theoretical and practical viewpoints. To date, the long chain alkylation of benzene has already been widely and thoroughly investigated [3–5], 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  $\text{H}_2\text{SO}_4$ ,  $\text{BF}_3$ , HF,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , etc., which give rise to many problems concerning the handling, health, safety, corrosion and waste disposal of

the catalysts [6,7]. 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 [8–11]. Venuto et al. observed Beta and Y zeolites to be better catalysts for benzene alkylation with olefins than amorphous silica–alumina gels [12]. The large pore zeolites may catalyze reactions of large-size molecules. More and more attention has recently been paid to large pore zeolites such as H-mordenite, HY and H $\beta$  used as environmentally friendly catalysts for alkylations of polynuclear aromatic compounds [13–17].

In our laboratory, large pore zeolite catalysts like HY and H $\beta$  enhanced alkylations of  $\alpha$ -methylnaphthalene with long chain olefins had been investigated in liquid–solid phase continuous reaction mode. Results showed that HY zeolite catalyst exhibited good catalytic performances [18,19]. Towards large-scale production, continuous reaction operating mode is good. However, towards small-scale production, the intermittent reactor may be adopted, since device cost and operating cost are quite high for continuous reaction producing mode. Therefore, in the present paper, HY enhanced alkylations of  $\alpha$ -methylnaphthalene with long chain olefins had been investigated in liquid–solid phase

\* Corresponding author. Tel.: +86 411 88993878; fax: +86 411 83683229.  
E-mail address: [zkzhao2000@yahoo.com](mailto:zkzhao2000@yahoo.com) (Z. Zhao).

intermittent reaction mode. Here reaction conditions, modification of HY zeolite and regeneration and reusability of catalyst were investigated. Now that the optimum mole ratios of  $\alpha$ -methyl-naphthalene to long chain olefins (5–7:1) are similar in different catalytic systems, the effect of mole ratios of  $\alpha$ -methyl-naphthalene to long chain olefins on the reaction was not further investigated. In the reaction,  $\alpha$ -methyl-naphthalene is both reaction reagent and solvent, no other organic solvents were added.

## 2. Experimental

The three-dimensional large pore zeolites HY was used in the alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins. The HY 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 300 min. 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 300 min.

First, 30 g of  $\alpha$ -methyl-naphthalene (>98%) and mixed alkenes  $\text{C}_{11-12}$  ( $\text{C}_{11}:\text{C}_{12}$  weight ratio 45:55, purchased from Fushun Petrochemical Company) were put into a 100 mL three-necked flask, the molar ratio of aromatic hydrocarbon and alkenes being 5–7. Then a certain amount of HY or modified HY zeolite as catalyst was added. After stirring for about 30 min at room temperature to make the agents homodispersed. The reaction time was counted when the mixture was heated to the required reaction temperature. The reaction mixtures were stirred at 453–523 K for about 10–720 min. After the total alkylation, the catalyst was separated from reaction mixture by filtration. 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-5-column, 30 mm  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ; FID detector) and further product identification was done on a GC-MS (HP 5973 mass selective detector, column: HP-5MS column, 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). 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 alkylmethyl-naphthalene were used as the evaluation standard of this technology. The conversion of olefins was defined as  $C_L\%$ , which is the weight percent of olefins consumed in the reaction. The selectivity for the desired products, alkylmethyl-naphthalene was calculated by:  $S_{\text{AMN}}\% = W_{\text{AMN}}/W_{\text{pro}} \times 100$ , where  $W_{\text{AMN}}$  is the amount of desired monoalkylated products, and  $W_{\text{pro}}$  is the total amount of the alkylated products, including alkyl-naphthalene, alkylmethyl-tetrahydronaphthalene, alkyl-dimethyl-naphthalene, alkyl-polymethyl-naphthalene, etc., other than the desired products.

## 3. Results and discussion

The alkylation of  $\alpha$ -methyl-naphthalene with long chain mixed alkenes goes through a typical Friedel–Crafts reaction. It

is a complex process consisting of various side reactions, besides the main reaction, alkylation. The reaction products were characterized by GC/MS [18,20]. The results exhibit that, except for the desired products, a series of isomers of monoalkylated methyl-naphthalene. On the basis of our project (the environmental friendly technology for synthesizing the intermediates for long chain alkylmethyl-naphthalene sulfonate surfactants), the alkylated position on the methyl-naphthalene ring is not required, and all the isomers of monoalkylated methyl-naphthalene are our desired products), some side-products, mainly include isomers of monoalkyl dimethyl-naphthalene, monoalkyl naphthalene, monoalkyl methyl-tetrahydronaphthalene, etc. The confined channels of zeolite restrict the further alkylation of long chain alkyl methyl-naphthalene. As a result, no polyalkylated methyl-naphthalene was detected. HY zeolite was used as catalyst for alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins. The effects of various parameters on the reaction were investigated.

### 3.1. Effect of reaction temperature on the alkylation of $\alpha$ -methyl-naphthalene

Table 1 shows the effects of reaction temperature on the alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins.

Results show that the conversion for olefins are increased obviously while the reaction temperature is increased from 453 to 503 K. Only slight increase can be seen with the reaction temperature being further increased, and the selectivity for the desired products decreases. Thus, the optimum reaction temperature is 503 K.

### 3.2. Effect of dosage of HY zeolite catalyst on the alkylation of $\alpha$ -methyl-naphthalene

Effects of dosage of HY zeolite catalyst on the alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins was investigated by varying the dosage from 6.4 to 24.0%. The dosage of catalyst ( $W_{\text{cat}}$ ) is the mass concentration of HY zeolite in the reaction mixture. The results are given in Table 2.

Results show that dosage of HY zeolite catalyst has an obvious effect on the alkylation of  $\alpha$ -methyl-naphthalene. The conversion can reach 92.7% at 16.0% of  $W_{\text{cat}}$ . Only slight increase in conversion can be seen with the  $W_{\text{cat}}$  being further increased, and the selectivity for the desired products decreases. Thus, the optimum dosage of catalyst is 16.0%.

Table 1

Effect of reaction temperature on the alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins

Entry	$T$ (K)	$C_L$ (%)	$S_{\text{AMN}}$ (%)	Entry	$T$ (K)	$C_L$ (%)	$S_{\text{AMN}}$ (%)
1	453	32.0	100	5	493	89.2	100
2	463	56.9	100	6	503	93.8	100
3	473	82.5	100	7	513	94.4	97.5
4	483	85.6	100	8	523	94.1	93.2

Reaction conditions: Molar ratio  $\alpha$ -methyl-naphthalene to long chain olefins = 5:1;  $W_{\text{cat}} = 16.8\%$ ;  $t = 600$  min.

Table 2  
Effect of dosage of HY on alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins

Entry	$W_{\text{cat}}$ (%)	$C_L$ (%)	$S_{\text{AMN}}$ (%)	Entry	$W_{\text{cat}}$ (%)	$C_L$ (%)	$S_{\text{AMN}}$ (%)
1	6.4	22.1	100	5	14.4	89.7	100
2	8.0	48.2	100	6	16.0	92.7	100
3	9.6	56.5	98.1	7	17.6	93.6	97.5
4	12.0	75.8	100	8	24.0	95.1	90.6

Reaction conditions: Molar ratio  $\alpha$ -methyl-naphthalene to long chain olefins = 7:1;  $T = 503$  K;  $t = 600$  min.

Table 3  
Effect of reaction time on the alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins

Entry	$t$ (min)	$C_L$ (%)	$S_{\text{AMN}}$ (%)	Entry	$t$ (min)	$C_L$ (%)	$S_{\text{AMN}}$ (%)
1	10	16.4	100	5	240	92.8	100
2	30	42.7	100	6	360	93.6	100
3	60	66.6	100	7	480	94.6	97.0
4	120	87.9	100	8	720	96.6	93.0

Reaction conditions: Molar ratio  $\alpha$ -methyl-naphthalene to long chain olefins = 7:1;  $W_{\text{cat}} = 16.0\%$ ;  $T = 503$  K.

### 3.3. Effect of reaction time on the alkylation of $\alpha$ -methyl-naphthalene

Table 3 shows the effects of reaction time on the alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins. It can be seen that, the conversion for olefins increases by prolonging the reaction time. More than 90% of conversion can be obtained when the reaction time is not less than 240 min. The selectivity for the desired products decreases while the reaction time is too long. Thus, the optimum reaction time is 240–360 min.

On the basis of the above studies, it is found that the optimum reactions for the HY zeolite enhanced alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins in liquid–solid phase intermittent reaction mode are 5–7:1 of  $\alpha$ -methyl-naphthalene

Table 4  
Effect of alkaline and rare earth modification on the alkylation of  $\alpha$ -methyl-naphthalene

Entry	Catalysts	$C_L$ (%)	$S_{\text{AMN}}$ (%)	Entry	Catalysts	$C_L$ (%)	$S_{\text{AMN}}$ (%)
1	0.5% MgO-HY	91.5	100	13	0.5% BaO-HY	88.5	100
2	1.0% MgO-HY	93.1	100	14	1.0% BaO-HY	82.4	100
3	2.0% MgO-HY	70.1	100	15	2.0% BaO-HY	80.8	100
4	4.0% MgO-HY	48.6	100	16	4.0% BaO-HY	76.4	100
5	0.5% CaO-HY	91.7	100	17	0.5% La <sub>2</sub> O <sub>3</sub> -HY	94.0	100
6	1.0% CaO-HY	91.8	100	18	1.0% La <sub>2</sub> O <sub>3</sub> -HY	90.8	100
7	2.0% CaO-HY	68.8	100	19	2.0% La <sub>2</sub> O <sub>3</sub> -HY	89.5	100
8	4.0% CaO-HY	60.4	100	20	4.0% La <sub>2</sub> O <sub>3</sub> -HY	90.0	100
9	0.5% SrO-HY	79.5	100	21	0.5% Ce <sub>2</sub> O <sub>3</sub> -HY	92.2	100
10	1.0% SrO-HY	88.0	100	22	1.0% Ce <sub>2</sub> O <sub>3</sub> -HY	90.9	100
11	2.0% SrO-HY	68.2	100	23	2.0% Ce <sub>2</sub> O <sub>3</sub> -HY	87.7	100
12	4.0% SrO-HY	75.0	100	24	4.0% Ce <sub>2</sub> O <sub>3</sub> -HY	78.8	100

Reaction conditions: Molar ratio of methyl-naphthalene to olefins = 7:1,  $T = 503$  K,  $t = 240$  min,  $W_{\text{cat}} = 16.0\%$ .

to long chain olefins, 16.0% of dosage of catalyst at 503 K for 240–360 min. Adopting the optimum reactions, the modification of HY zeolite, regeneration and reusability of the deactivated HY zeolite catalyst were investigated.

### 3.4. Results for the alkylation over the alkaline earth and rare earth metal oxide modified HY zeolite catalyst

In order to further improve the catalytic performances of HY zeolite catalyst, the alkylations of  $\alpha$ -methyl-naphthalene with long chain olefins have also been performed over the alkaline earth and rare earth metal oxides modified HY zeolite catalyst. The results are given in Table 4.

Results show that the catalytic performances of HY zeolite may be improved while being modified with optimum impregnated amount of alkaline earth and rare earth metal oxides. Especially being modified with 0.5% La<sub>2</sub>O<sub>3</sub>, the catalyst exhibits the best catalytic performances. It is found that the modification has not an effect on the selectivity for the desired products. After being modified, some acidic sites are covered, at the same time, the new Brønsted acidic sites may be produced by the hydrolyzation of lanthanum in the presence of trace quantity [21], and Lewis acidic sites may be produced by dehydration. Brønsted acidic sites are activated centres not only for alkylation but also for coke formation, and the optimal acidic concentration and acidic strength are favourable for alkylation reactions. Therefore, neither the too large impregnated amount nor the too small impregnated amount is favourable for the alkylation of methyl-naphthalene, and which needs an optimum impregnated amount. Moreover, the type of metal ions has also a great influence on the reaction. Only the magnesium and lanthanum modified HY zeolite catalysts exhibit the good catalytic performance. The reason would be further studied in our laboratory.

### 3.5. Regeneration and reusability of the deactivated HY zeolite catalyst for the alkylation of $\alpha$ -methyl-naphthalene

The easy separation and the separated catalyst being reused are the prominent strongpoint for solid acid cata-

Table 5  
Results of refreshed catalysts by various regenerating methods

Entry	Calcination method	$C_L$ (%)	$S_{AMN}$ (%)
1	Fresh HY zeolite catalyst	92.5	100
2	Being calcined at 813 K for 720 min after drying (method 1)	91.9	100
3	Being calcined at 813 K for 480 min after drying (method 2)	92.0	100
4 <sup>a</sup>	Being temperature-programmed calcined after drying (method 3)	93.5	100

<sup>a</sup> Calcination temperature was increased from 473 to 773 K at 50 K/60 min, then being calcinated at 813 K for 60 min.

Table 6  
Reusability of refreshed HY zeolite catalysts on alkylation of  $\alpha$ -methyl-naphthalene

Entry	Run times	$C_L$ (%)	$S_{AMN}$ (%)	Entry	Run times	$C_L$ (%)	$S_{AMN}$ (%)
1	0	92.5	100	5	4	89.6	100
2	1	93.5	100	6	5	91.0	100
3	2	92.0	100	7	6	92.6	100
4	3	88.3	100	8	8	92.5	100

lysts. The catalytic activation of separated catalyst decreases after the liquid–solid intermittent alkylation reaction of  $\alpha$ -methyl-naphthalene with long chain olefins. The decrease in conversion might be attributed to a gradual increase in the blocking of the active sites by olefin oligomers and coke formation [22]. Here, the regeneration and reusability of the deactivated HY zeolite catalyst were investigated. Table 5 gives the comparison of refreshed method for the deactivated HY zeolite catalyst.

As can be seen that, the catalytic performances of the deactivated catalyst can be refreshed being calcined. The whole results show the deactivated catalysts may be regenerated completely by the three different methods. Moreover, the table also gives the comparison of the various methods, which are different in operation and energy consumption, besides refreshing effect. The results show that the method 3 is best method among the various methods, which is an easy regeneration method, except for saving time and energy consumption. By adopting the method 3, the reusability of refreshed HY zeolite catalysts on alkylation of  $\alpha$ -methyl-naphthalene was investigated. The results are given in Table 6.

The HY zeolite catalyst can be reused eight times without decrease in its catalytic activation. Therefore, HY zeolite catalyst might be a practical catalyst for liquid–solid intermittent alkylation reaction of  $\alpha$ -methyl-naphthalene with long chain olefins.

#### 4. Conclusions

The liquid–solid phase intermittent alkylation reaction of  $\alpha$ -methyl-naphthalene with long chain olefins has been investigated

over HY zeolite catalyst. HY zeolite exhibits good catalytic performances. The alkylation of  $\alpha$ -methyl-naphthalene with long chain olefins leads to the formation of a mixture, including the desired products, a series of isomers of monoalkylated methyl-naphthalene, and some side-products monoalkyl naphthalene, monoalkyl dimethyl-naphthalene, monoalkyl methyl-tetrahydro-naphthalene, etc. The further long chain alkylation of monoalkyl-methyl-naphthalene was stopped due to the restriction of the confined channels of zeolite. The optimum reaction conditions are 5–7:1 of  $\alpha$ -methyl-naphthalene to long chain olefins, 16.0% of dosage of catalyst at 503 K for 240–360 min. The catalytic performances of HY zeolite catalyst may be improved being modified with an optimal amount of alkaline earth and rare earth metal oxide. Especially being modified with 0.5%  $La_2O_3$ , the catalyst exhibits the best catalytic performances. 94.0% of conversion for olefins and 100% of selectivity for the desired products can be achieved. The catalytic performances of the deactivated catalyst can be refreshed being temperature-programmed calcined. The HY zeolite catalyst can be reused many times without decrease in its activation. It could be a practical catalyst for long chain alkylation of  $\alpha$ -methyl-naphthalene with alkenes in the intermittent reactor.

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