

Alkylation of α -methyl-naphthalene with long-chain olefins catalyzed by rare earth lanthanum modified HY zeolite

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Abstract

Modified HY zeolites impregnated with an optimum amount of lanthanum was found to be an effective catalyst for the clean alkylation of α -methyl-naphthalene with long-chain olefins. It was found that Brönsted acid was the main catalytically active center and that the reaction required an optimal concentration of acidic sites. The deactivated LaHY zeolite catalyst can be regenerated by temperature-programmed calcination.

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Keywords: Alkylation; α -Methyl-naphthalene; Long-chain olefins; Lanthanum modified HY zeolite; Regeneration

1. Introduction

Long-chain alkylmethyl-naphthalene 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 alkylmethyl-naphthalenes are the core intermediates for AMNS. Therefore, studies on the long-chain alkylation of methyl-naphthalene are very important from both theoretical and practical viewpoints. To date, the long-chain alkylation has already been investigated widely and thoroughly for benzene [3–5], but not for naphthalene and its derivatives. To our knowledge, no comparative studies for the long-chain alkylation of methyl-naphthalene have been reported. The alkylation of α -methyl-naphthalene with long-chain olefins 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 [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 β , which have been used as environmentally friendly catalysts for alkylations of polynuclear aromatic compounds [13–17].

In our laboratory, alkylations of α -methyl-naphthalene with long-chain olefins catalyzed by large pore zeolites like HY and H β has been investigated in liquid–solid phase continuous reaction mode. Results showed that HY zeolite catalyst exhibited good catalytic activity and selectivity [18,19]. However, the stability of HY zeolite is so poor that obvious decrease in conversion is observed with increase in time on stream (TOS) above 540 min. In order to improve the stability of HY zeolite, the present paper focuses on the effects of modification of rare earth lanthanum and cerium on the alkylations. On the basis of previous studies [18], 9–10:1 of mole ratio of α -methyl-naphthalene (GC grade >98%) to long-chain olefins (C_{11-12} (wt.%) = 45/55, mixed olefins, bought from Fushun Petrochemical Company) and 6–7:1 of cyclohexane (solvent) to α -methyl-naphthalene were adopted. The modified and unmodified HY zeolite catalysts were characterized by NH_3 -TPD, pyridine-IR and XRD. Moreover, the regeneration of deactivated catalysts was also investigated.

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2. Experimental section

The three-dimensional large pore HY zeolite was used for the alkylation of α -methyl-naphthalene with long-chain olefins. The HY catalyst was prepared by calcining NH_4Y zeolite (obtained from the Chinese Wenzhou Huahua Group, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5$) in a flow of dried air at 540°C for 300 min. The prepared HY zeolite was pressed, crushed and then sieved to 20–60 meshes. The sample was dried at 120°C and then calcined at 540°C for 300 min. The modification of HY zeolite was performed by equal-volume impregnation method; by soaking in an aqueous solution of rare-earth nitrates like $\text{La}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$, for 720 min, the LaHY and CeHY zeolite catalysts were prepared, and impregnated amounts lanthanum and cerium were defined as RE_2O_3 content (wt.%). The samples were dried at 120°C and then calcined at 540°C for 300 min. Analytical grade cyclohexane, $\text{La}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ were used without further purification.

Infrared spectra were recorded at room temperature on a Fourier transform infrared spectrometer (Nicolet Impact 460) with a resolution of 4 cm^{-1} and 64 scans in the region from 1800 to 1200 cm^{-1} . The catalysts were pressed into a self-supporting wafer (ca. 15 mg cm^{-2}), and introduced into a quartz IR cell with CaF_2 windows. The samples were pretreated in situ in a stream of 30 mL min^{-1} He from RT to 500°C and then $5 \times 10^{-3}\text{ Pa}$ 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 150, 300 and 450°C for 30 min, respectively, and a corresponding spectrum was recorded to distinguish the acid site. The relative intensities of vibration bands at 1540 and 1450 cm^{-1} were ascribed to the Brønsted and Lewis acid sites, respectively. NH_3 temperature-programmed desorption (NH_3 -TPD) was performed on a conventional apparatus 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^{-1}) at 600°C for 30 min, then cooled to 150°C and saturated with NH_3 until equilibrium. It was then flushed with He (30 mL min^{-1}) again until the baseline was stable. NH_3 -TPD was then promptly started at a heating rate of 15°C/min from 150 to 600°C . All NH_3 -TPD profiles were deconvoluted into three peaks using a Gaussian and Lorentzian curve-fitting method. X-ray powder diffraction (XRD) patterns of the modified and unmodified zeolite samples were recorded on a D/MAX-2400 powder diffractometer over 2θ range of 4 – 60° at a scanning speed of 6° min^{-1} (2θ) and step size of 0.02° .

The experiments were performed in a fixed-bed continuous-flow reactor equipped with a 20 mm diameter and 400 mm length stainless steel tube, in which 2.0 g of 20–60 mesh zeolite catalysts, already having been calcined for an hour, were loaded. The reaction mixture was fed into the reactor by a measuring pump and pressure was kept by N_2 . Analyses of the products were done on a gas chromatograph (HP 6890, equipped with HP-5-column, $30\text{ mm} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$; 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, on which the conversion for olefins and selectivity for the desired products were calculated.

3. Results and discussion

The alkylation of α -methyl-naphthalene with long-chain mixed alkenes goes through a typical Friedel–Crafts reaction. It is a complex process consisting of main and side reactions. The 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, there exist some other products. On the basis of our project (the clean technology for synthesizing the intermediates for the 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 the desired products. In the present paper, in order to find an effective catalyst for synthesizing the desired alkyl methyl-naphthalene products, effects of type and impregnated amount of rare earth besides reaction conditions on the alkylations were investigated. The conversion for olefins and selectivity for alkylmethyl-naphthalene were used as the evaluation standard of the reactions. The conversion for olefins was defined as $C_L\%$, which is the wt.% of olefins consumed in the reaction. The selectivity for monoalkylmethyl-naphthalene was calculated by: $S_{\text{AMN}}\% = W_{\text{AMN}}/W_{\text{pro}} \times 100$, where W_{AMN} is the amount of the desired product, monoalkylmethyl-naphthalene, and W_{pro} is the total amount of the alkylated products, which include the desired products, a series of isomers of monoalkylated methyl-naphthalene, and some side-products, mainly a series of isomers of monoalkyl-naphthalene, monoalkyldimethyl-naphthalene, monoalkylpolymethyl-naphthalene, monoalkylmethyl-tetralin, etc [20].

3.1. Effects of type and impregnated amount of rare-earth on the alkylations

First the alkylation was performed over LaHY and CeHY (1 wt.% of impregnated amount, which is calculated based on metal oxide amount) zeolites, respectively. The reaction conditions are 10:1 of mole ratio of α -methyl-naphthalene to long-chain olefins and 6:1 of cyclohexane to α -methyl-naphthalene at 200°C and 1.0 MPa, and VHSV (which is defined for volume hour space velocity) of $4.5\text{ mL h}^{-1}\text{ g}^{-1}\text{ cat}$. Only conversions for olefins are given in Fig. 1. The selectivity for the desired products is always higher than 99%.

The stability of catalysts is improved after being modified with 1% of lanthanum or cerium, especially lanthanum, although slight decrease in the initial conversion of olefins is observed. Modification by cerium, resulted in serious isomerization. Therefore, CeHY is not suitable for alkylation. In order to explore the difference in acidic sites of catalysts, NH_3 -TPD is carried out. The results are given in Fig. 2.

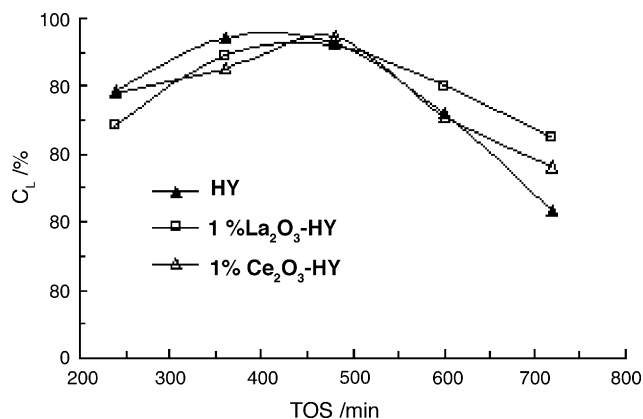


Fig. 1. Results of alkylation of methylnaphthalene catalyzed by La and Ce modified HY.

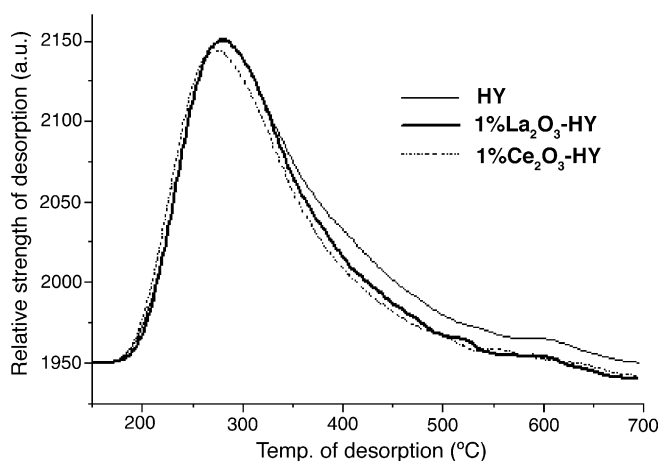


Fig. 2. NH_3 -TPD profiles of HY and rare earth modified HY.

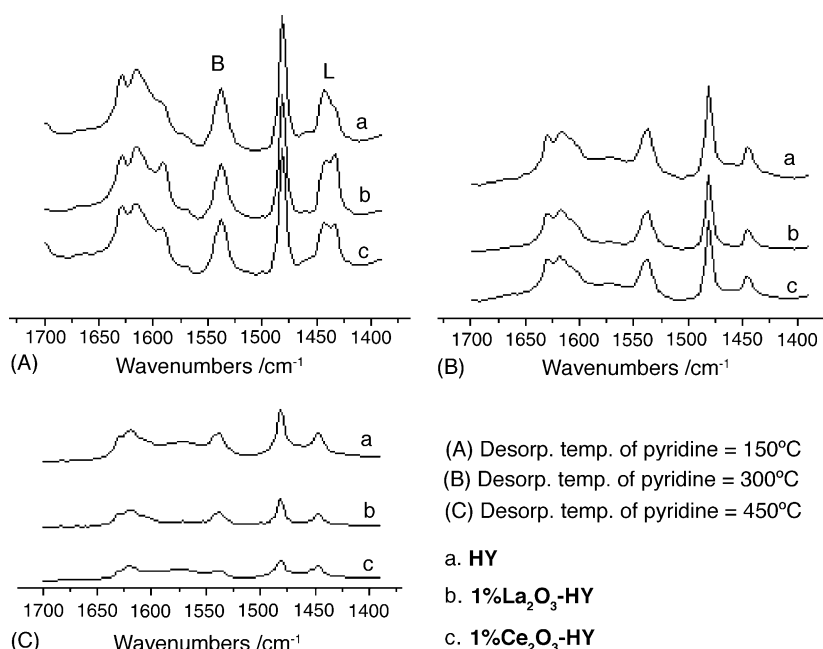


Fig. 3. In situ IR spectra of pyridine adsorbed on HY and modified HY with various impregnated amount of lanthanum.

Modification by lanthanum or cerium decreased the concentrations of acidic sites of HY zeolites, lowering the speed of coke formation. As a result, the stability of catalysts is increased. It should be noted that ammonia-TPD only provides the total number of acidic sites, and cannot differentiate between Brönsted and Lewis acidic sites. To examine the effects of acidic type on the alkylation, the zeolite catalysts were characterized by IR spectra of pyridine adsorbed. The IR spectra after evacuation at 150, 300 and 450 °C are given in Fig. 3 (desorp temp.: desorption temperature).

It has been found that both Brönsted and Lewis acidic centres are present on modified and unmodified HY zeolite catalysts. The modification caused no obvious change in the concentration of weak and moderate-strength Brönsted acidic sites, but an obvious increase in the concentration of weak Lewis acidic site. Brönsted acidic sites are active centres not only for alkylation but also for coke formation, and so the optimal acidic concentration is required for stable alkylation. Moreover, concentrations of strong Brönsted and Lewis acidic centres decrease with the modification of HY zeolite, which may depress the rate of coke formation. As a result, the stability of catalyst may be improved with the modification. Thus, the lanthanum modified zeolite catalyst has good catalytic performance.

In the present paper, effects of lanthanum impregnated amount on alkylation were also investigated. The reaction conditions are 10:1 of mole ratio of α -methylnaphthalene to long-chain olefins and 6:1 of cyclohexane to α -methylnaphthalene at 200 °C and 1.0 MPa, and VHSV of $4.5 \text{ mL h}^{-1} \text{ g}^{-1} \text{ cat}$. Reaction results are given in Fig. 4; selectivities for the desired products are not given because they are always higher than 99%.

Lanthanum impregnated amount has a slight influence on the initial activity, but an obvious influence on the stability of catalysts. The 2% lanthanum impregnated HY zeolite exhibits best stability among these catalysts. Further increase in the

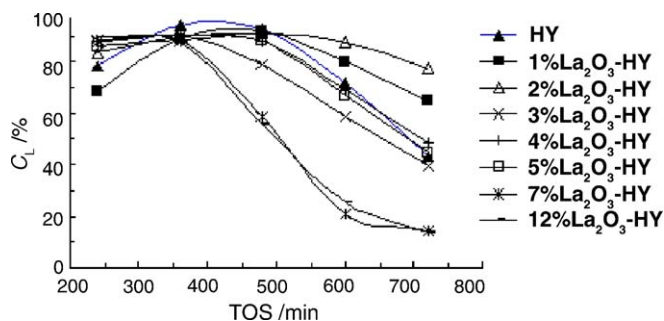


Fig. 4. Results of alkylation of methylnaphthalene catalyzed by various impregnated amount HY zeolites.

impregnated amount resulted in a deterioration of the stability of modified catalysts. The concentrations of acidic sites were characterized by ammonia-TPD, the profiles being given in Fig. 5.

As the impregnated amount is increased, acid strength weakens and acid concentration decreases, which is favorable for restraining the formation of coke. However, low acid concentration will lead to low activity for alkylation. Moreover, excessive impregnated amount may also result in the pore plugging, which is not favorable for the reaction, either. The surface acidic properties were further characterized by pyridine-IR (Fig. 6, desorp. temp.: desorption temperature).

Modification by lanthanum masks some acidic sites, and at the same time produces the new Brönsted acidic sites by the hydration of lanthanum in the presence of trace amount of water [21], and Lewis acidic sites by dehydration. As a result, weak and moderate-strong Brönsted and Lewis acidic sites increase when HY is modified with an optimal amount of lanthanum

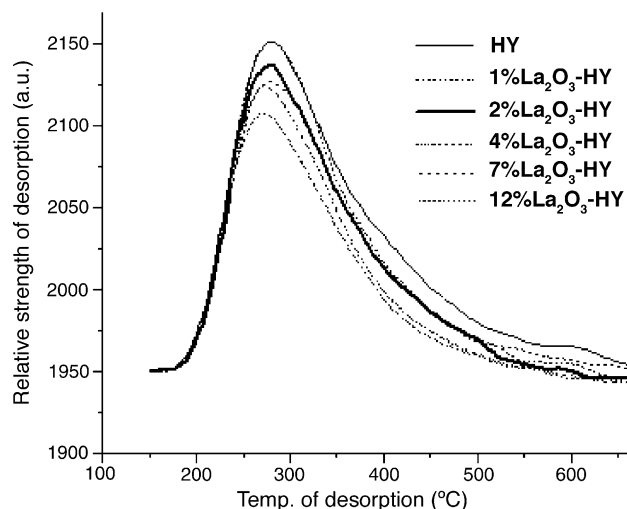


Fig. 5. NH_3 -TPD profiles of HY and modified HY with various impregnated amount of lanthanum.

(2%), which is favorable for the alkylation. When the impregnated amount is further increased, the concentrations of Brönsted and Lewis acidic sites decrease, especially that of Lewis acid. Brönsted acidic centres are main active sites. Therefore, the catalytic activity decreases with the increase in the impregnated amount. Fig. 7 gives the XRD patterns of the modified HY with various impregnated amount of lanthanum.

The XRD peak intensities of LaHY decreases when the impregnated amount is increased. The crystallinities of the catalysts are calculated on the basis of characteristic peaks of XRD. The relative crystallinities for a, b, c, d, e and f are 100, 72.2,

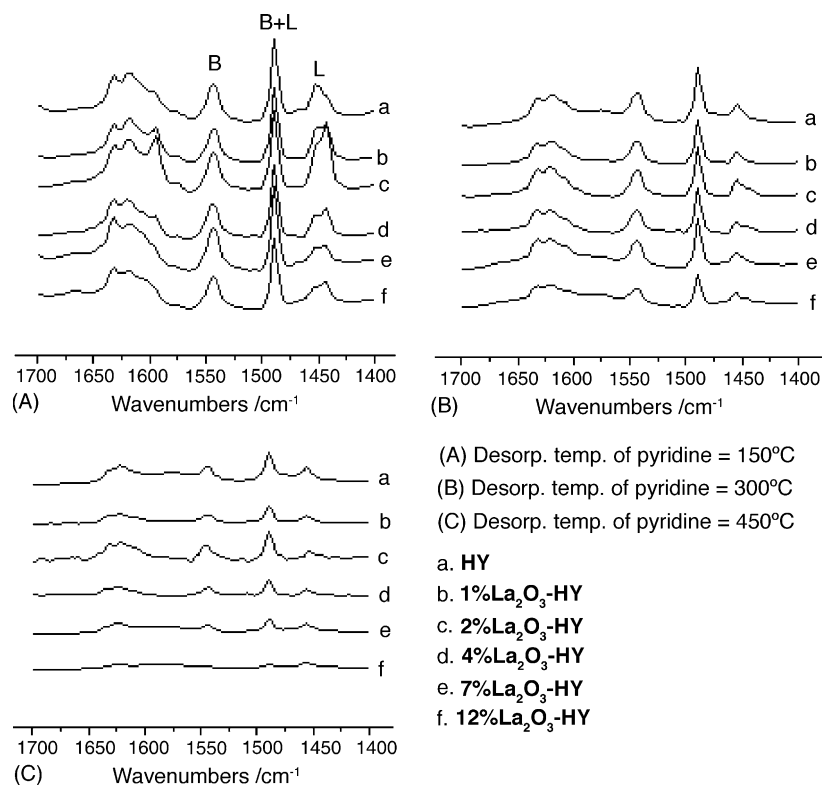


Fig. 6. In situ IR spectra of pyridine adsorbed on HY and modified HY with various impregnated amount of lanthanum.

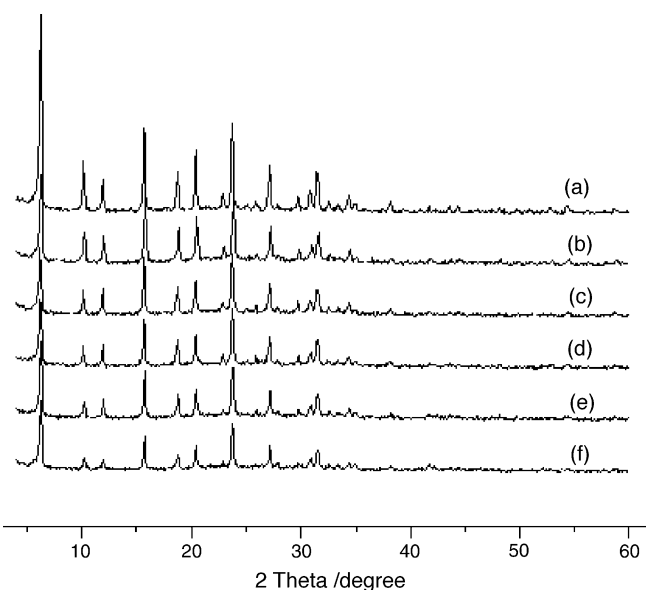


Fig. 7. XRD pattern of the modified HY with various impregnated amount of lanthanum (a, unmodified HY; b, c, d, e and f are for 1, 2, 4, 7 and 12% of impregnated amount, respectively).

63.3, 57.4, 51.5 and 43.6, respectively. The crystal structure is heavily destroyed when the impregnated amount is too large, which leads to the decrease in the stability of catalyst.

3.2. Effects of reaction conditions on the alkylation of α -methyl-naphthalene

Since reaction results indicate that 2% impregnated amount of lanthanum is optimum, the 2% LaHY zeolite is used for alkylation of methyl-naphthalene to study the effects of reaction conditions like reaction temperature, VHSV and TOS on the alkylation. Fig. 8 shows the effects of reaction temperature on the alkylations catalyzed by the 2% LaHY catalyst. The reaction conditions are 9:1 of mole ratio of α -methyl-naphthalene to long-chain olefins and 6:1 of cyclohexane to α -methyl-naphthalene at 2.0 MPa and $4.5 \text{ mL h}^{-1} \text{ g}^{-1}$ cat of VHSV.

There exists an obvious difference in stability, but only a slight difference is observed in the initial activity in the range of examined reaction temperature. The coke formation reaction takes place when the alkylation is in process. The conversion of

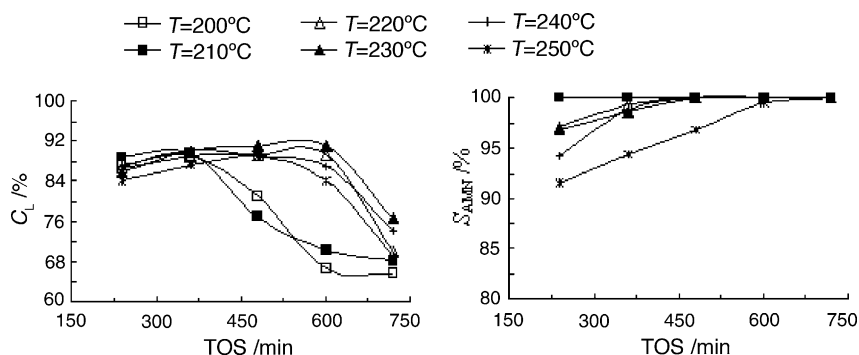


Fig. 8. Effect of reaction temperature on the alkylation of methyl-naphthalene catalyzed by 2% LaHY.

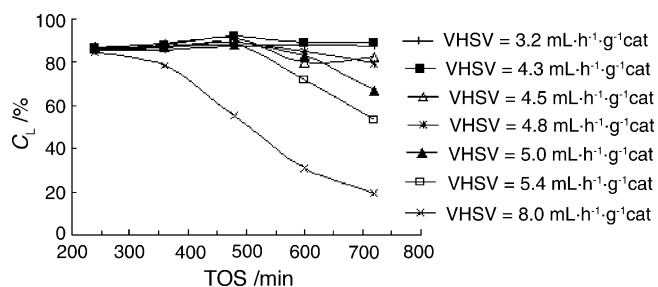


Fig. 9. Effects of VHSV on the alkylation of α -methyl-naphthalene with olefins catalyzed by 2% LaHY catalyst.

olefins decreases with prolonging time on stream (TOS). When the reaction temperature is increased, conversion of olefins can maintain a high value over the partly deactivated catalyst. But too high temperature will lead to the heavy coke formation, which results in decrease in activity and stability. Moreover, as can be seen from the curve of selectivity, with the reaction temperature increase, the initial selectivity for the desired products decreases, but with the increase in TOS, the selectivity is increased. This might be attributed to the strong acidic site being covered with coke, since some side reactions can be enhanced by strong acidic sites.

From above, 230 °C is chosen to observe the effects of VHSV on the alkylations of α -methyl-naphthalene (selectivity is more than 98%). The reaction conditions are 9:1 of mole ratio of α -methyl-naphthalene to long-chain olefins and 5:1 of cyclohexane to α -methyl-naphthalene at 230 °C and 1.5 MPa (the saturated vapour pressure of solvent is 1.3 MPa at 230 °C). The reaction results are given in Fig. 9.

VHSV has a slight influence on the initial activity, but an obvious influence on the stability in the range of 3.2–8.0 mL h⁻¹ g⁻¹ cat. The conversion of olefins can keep higher than 80% when VHSV is lower than 4.8 mL h⁻¹ g⁻¹ cat. The stability is excellent when VHSV is 4.3 mL h⁻¹ g⁻¹ cat. It is suggested that the reaction requires an optimum VHSV. The long residence time of reactants in a fixed-bed reactor would lead to many side reactions such as polymerization of reactants taking place at a very low VHSV value. As a result, carbon deposition on zeolite is serious, which would cause catalysts to be deactivated. With increasing VHSV, the contact times between reactants and catalysts are shortened obviously,

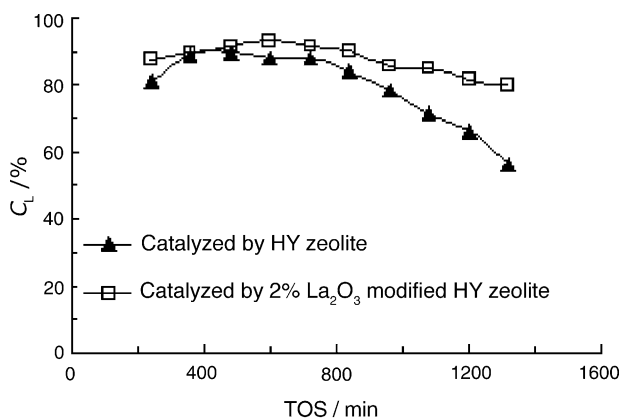


Fig. 10. Results of the alkylation of α -methylnaphthalene catalyzed by 2% impregnated amount of LaHY and HY zeolite catalysts.

and thus the conversion decreases. The optimal VHSV value is $4.3 \text{ mL h}^{-1} \text{ g}^{-1} \text{ cat}$. Effects of TOS was studied over 2% impregnated amount of LaHY and HY catalysts at 230°C and 1.5 MPa with the mole ratio α -methylnaphthalene: olefins: cyclohexane of 10:1:60 and VHSV of $4.3 \text{ mL h}^{-1} \text{ g}^{-1} \text{ cat}$. The study was conducted for 1320 min. Fig. 10 gives the catalytic activity for alkylation; selectivity for the desired products is not given since it is always higher than 99%.

The initial activity and stability of LaHY are better than those of HY. The conversions of olefins keep above 80% for 1320 min over LaHY and only 700 min over the unmodified HY zeolite. An obvious decrease in conversion with the increase in TOS was observed. The decrease in conversion with increasing time-on-stream might be attributed to a gradual increase in the blocking of the active sites by olefin oligomers and coke formation [22].

3.3. Regeneration of the deactivated LaHY zeolite catalyst

As can be seen from the above, the catalytic activity decreases when TOS is prolonged. Then, the alkylation was performed over the regenerated LaHY (2% impregnated amount) catalyst, refreshed by temperature-programmed calcination in air. The results are given in Fig. 11.

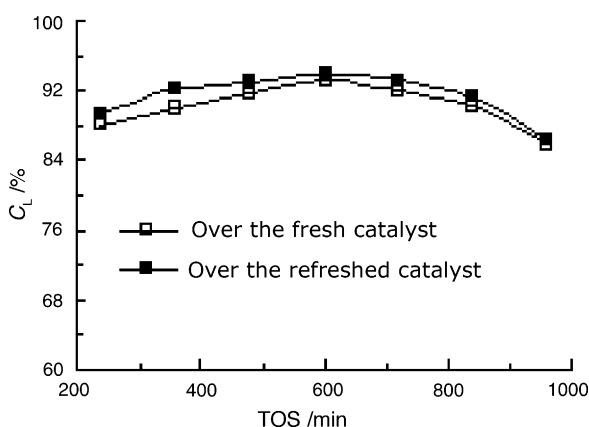


Fig. 11. Results of the alkylation of methylnaphthalene catalyzed by fresh and refreshed LaHY zeolite catalysts.

The catalytic performance of the deactivated catalyst can be refreshed by temperature-programmed calcination. The LaHY zeolite catalyst can be reused without decrease in its activity. Therefore, it could be a practical catalyst for long-chain alkylation of α -methylnaphthalene with alkenes.

4. Conclusions

The liquid–solid phase continuous alkylation reaction of α -methylnaphthalene with long-chain olefins has been investigated over HY zeolites modified with lanthanum and cerium. Effects of type and impregnated amount of alkaline earth metal oxide on the alkylation have been investigated. Results show that the 2% lanthanum modified HY zeolite catalyst exhibits the better catalytic performance than other catalysts. The catalytic performance of the deactivated catalyst can be refreshed by temperature-programmed calcination. It could be a practical catalyst for long-chain alkylation of α -methylnaphthalene with alkenes. The Brønsted acidic sites are active centres not only for the alkylation but also for coke formation and therefore the alkylation of α -methylnaphthalene needs an optimal concentration of acidic sites.

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