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Isopropylation of naphthalene by isopropyl alcohol over USY catalyst: an investigation in the high-pressure fixed-bed flow reactor

Jun Wang,[1] Jung-Nam Park, Yong-Ki Park, and Chul Wee Lee *

Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology (KRICT), PO Box 107, Yusung, Daejeon 305-600, South Korea

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Abstract

Catalytic performances of USY, H-mordenite, dealuminated H-mordenite, and H-MCM-22 zeolite catalysts in the isopropylation of naphthalene by isopropyl alcohol with decalin or cyclohexane as a solvent were compared in a high-pressure fixed-bed flow reactor. For the USY catalyst, reaction conditions, such as reaction temperature and pressure, reactant ratio and space velocity, and solvent concentration and type, were controlled to investigate in detail the effect of reaction conditions on the catalytic activity. Over H-mordenite, it was found that 2,6-diisopropylnaphthalene (2,6-DIPN) could be selectively synthesized with a 2,6-/2,7-DIPN ratio of 2.46, and dealumination could enhance not only the selectivity of 2,6-DIPN, with a 2,6-/2,7-DIPN ratio of 2.67, but also the conversion of naphthalene, which was 27.4%, three times as high as that over the unmodified one at 6 h of reaction time on stream. However, neither the H-mordenite or the dealuminated one were catalytically stable and the selectivity of DIPN was at a very low level of less than 12%. In contrast, over the USY catalyst, a high and stable conversion of about 90%, a high selectivity of DIPN of more than 40%, and a considerable 2,6-/2,7-DIPN ratio of 1.46 could be achieved by adjusting the reaction conditions, although no shape selectivity was observed on USY. On the other hand, only a low 2,6-/2,7-DIPN ratio of 0.47 with a low conversion of about 30% was revealed over H-MCM-22, which indicates that the reaction takes place on the external surface of this zeolite. An attempt has been made to explain the catalytic activity, selectivity, and stability in relation to the zeolite structures, product properties, and reaction conditions.
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Keywords: Isopropylation of naphthalene; Diisopropylnaphthalene; USY; Mordenite; MCM-22; Zeolite; Alkylation

1. Introduction

Alkylation of naphthalene is of industrial importance for producing 2,6-dialkylnaphthalenes (2,6-DAN), the precursor of naphthalene-2,6-dicarboxylic acid used in the synthesis of advanced aromatic polymer materials such as polyethylene naphthalate, polybutylene naphthalate, and thermotropic liquid crystalline polymers. Further expansion in the utilization of these materials depends on the development of an efficient method for preparation of 2,6-DAN.

There are as many as 10 possible DAN including α,α-(1,4-; 1,5-; 1,8-), α,β-(1,6-; 1,7-; 1,3-; 1,2-), and β,β-(2,6-; 2,7-; 2,3-) disubstituted isomers, and in fact, 1,2-, 1,8-, and 2,3-isomers are not frequently detected in the reaction product mixture due to the placement of alkyl groups at adjacent nucleus positions [1]. Because of the difficulty of completely separating these isomers, especially β,β-isomers [2], the selective production of 2,6-DAN with a high 2,6-/2,7-DAN ratio by alkylation of naphthalene is highly desired. However, selective synthesis of 2,6-DAN is difficult by alkylation of naphthalene with conventional Friedel–Crafts catalysts [3,4] or over silica–alumina catalyst [5,6], which lead to low β,β-selectivity and equal amounts of 2,6- and 2,7-isomers. Therefore, the use of shape-selective properties of zeolites in the alkylation of naphthalene should be helpful in the synthesis of 2,6-DAN, although the average molecular dimensions of the β,β-isomers are very similar.

Various alkylating agents, such as methanol [7–9], ethanol [10], isopropyl alcohol [11–16], propene [11,17–19], isopropyl bromide [20], *tert*-butyl alcohol [21–23], cyclohexyl bromide [24,25], and cyclohexene [24–26], have been evaluated in this type of reaction over various zeolite catalysts. Among these studies, isopropylation of naphtha-

* Corresponding author.
E-mail address: chulwee@pado.krict.re.kr (C.W. Lee).
[1] On a study leave from the Department of Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China.

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lene has been attracting much attention for both practical and fundamental reasons. On the one hand, the isopropyl group is more sterically hindered than the methyl group, implying a high possibility of the selective synthesis of 2,6-diisopropylnaphthalene (2,6-DIPN) in the suitable intracrystalline channel of zeolite. On the other hand, 2,6-DIPN is more easily oxidized into naphthalene-2,6-dicarboxylic acid as compared with 2,6-dimethylnaphthalene, and has more atomic economy in the oxidation process as compared with 2,6-di-*tert*-butylnaphthalene or 2,6-dicyclohexylnaphthalene. Indeed, Katayama et al. first found a higher selectivity of H-mordenite for 2,6-DIPN than for H-Y, H-L, and H-ZSM-5, respectively [11]. After that, dealuminated mordenite was revealed to be more active and selective for 2,6-DIPN than the unmodified one [12,17,18,27–30]. By contrast, some literature demonstrated that H-Y is also a promising catalyst in terms of activity, β,β-selectivity, and/or 2,6-/2,7-DIPN ratio in both liquid and gas-phase reactions [13,20,31,32].

However, most of the previous studies have been carried out in an autoclave. Since the serious drawback of the autoclave reactor is the difficulty of evaluating the catalyst stability, up to now, only a few papers have investigated the stability of the catalyst in this reaction. For example, Inui and coworkers [14] 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. Colon et al. [15,16] performed this reaction over H-Y and H-Beta catalysts in a flow reactor under high pressure, but they used a high reaction temperature of 350 °C, and a high number of side reactions occurred. Very recently, Kamalakar et al. [23] attempted the vapor-phase *tert*-butylation of naphthalene over cerium-modified Y zeolites and revealed a clear decrease of conversion of naphthalene with time on stream.

In this work, we have investigated, in detail, the catalytic activity, selectivity, and stability of a commercially available USY (ultrastable H-Y zeolite) in the isopropylation of naphthalene by isopropyl alcohol using a high-pressure fixed-bed flow reactor. In order to understand the catalytic behavior of the USY catalyst, a comparative investigation is also performed with H-mordenite and H-MCM-22 zeolite catalysts.

2. Experimental

USY (CBV780, $SiO_2/Al_2O_3 = 80$) and H-M (H-mordenite, CP814, $SiO_2/Al_2O_3 = 25$) were from Zeolyst. Naphthalene was from Junsei Chem. Co. Ltd., Japan; isopropyl alcohol from Duksan Pure Chem. Co. Ltd., Korea; decalin from Kanto Chem. Co. Inc., Japan; and cyclohexane from Aldrich. All chemicals were guaranteed reagent grade and used as purchased. The dealuminated H-mordenite was prepared by treatment of H-M in a 2 M HCl aqueous solution at 80 °C for 2 h, followed by calcination in a muffle furnace at 550 °C for 8 h. The above procedure was repeated once more. The obtained sample was designated as H-MD. The SiO_2/Al_2O_3 ratio of 49 for H-MD was obtained by the ICP-AES analysis. Na-MCM-22 ($SiO_2/Al_2O_3 = 30$) was synthesized according to previous literature [33]. H-MCM-22 was prepared by the repeated ion exchange of Na-MCM-22 with an aqueous solution of ammonium nitrate, followed by drying and calcination.

All experiments were carried out in a high-pressure fixed-bed down-flow microreactor with an inner diameter of 10 mm. The reactant mixture of naphthalene, isopropyl alcohol, and decalin or cyclohexane was injected by a high-pressure pump into the tubular stainless-steel reactor, the middle stage of which was charged with 1.0 g of catalyst in the form of granules (20–40 mesh). The catalyst was initially pretreated in situ in N_2 flow at 550 °C for 6 h before reactants were injected into the reactor. The typical reaction conditions were as follows: 250 °C reaction temperature, 3.0 MPa reaction pressure, 5.3 h^{-1} weight hourly space velocity (WHSV, total liquid feed), 6 h reaction time on stream (TOS), and 1:2:6 molar ratio of naphthalene, isopropyl alcohol, and decalin (or cyclohexane) in liquid feed. Also, to keep the system at a steady high pressure, 20 ml/min of N_2 was introduced cocurrently with the reaction feed into the reactor at the reactor head. Under these reaction conditions, the reaction could take place in the liquid phase. For USY catalysts, the reaction conditions were altered systematically to test the effect of reaction conditions. The reactor effluent was condensed in the sampler at −10 °C by cold ethanol and sampled hourly. Reactants and products were analyzed by GC (HP 5890 II) using FID as the detector furnished with a 60 m × 0.25 mm × 0.25 μm SE54 (J&W Scientific) capillary column. The analytical conditions was as follows: flow rate of He (carrier gas) in the column of 0.78 ml/min; split ratio of 80; sample injection volume of 0.1 μl; detector temperature of 300 °C; and injection temperature of 250 °C. The column oven temperature program started with an initial temperature of 40 °C for 2 min, followed by a temperature increase rate of 4 °C/min and a final temperature of 280 °C for 30 min. The conversion and selectivity were calculated as follows. Conv. $= (M_{n0} - M_n)/M_{n0} \times 100\%$, where Conv. is conversion of naphthalene, M_{n0} is the molar percentage of naphthalene before reaction, and M_n is the molar percentage of naphthalene after reaction. Sel. $= M_1/M_t \times 100\%$, where Sel. is the selectivity of IPN (monoisopropylnaphthalene), DIPN, or PIPN (polyisopropylnaphthalene), M_1 is the molar percentage of IPN, DIPN, or PIPN, and M_t is the sum of molar percentage of the above three kinds isopropylated products. β,β-Selectivity $= (M_{2,6\text{-DIPN}} + M_{2,7\text{-DIPN}} + M_{2,3\text{-DIPN}})/M_{t\text{DIPN}} \times 100\%$, where $M_{2,6\text{-DIPN}}$, $M_{2,7\text{-DIPN}}$, and $M_{2,3\text{-DIPN}}$ are the molar percentages of 2,6-DIPN, 2,7-DIPN, and 2,3-DIPN, respectively, and $M_{t\text{DIPN}}$ is the sum of the molar percentage of all the DIPN isomers. 2,6-/2,7-DIPN stands for the molar ratio of 2,6-DIPN to 2,7-DIPN, and 2-/1-IPN for 2-IPN to 1-IPN. Since only a negligible amount of 2,3-DIPN was observed in this work, β,β-

selectivity could be understood as the selectivity of 2,6-DIPN and 2,7-DIPN.

3. Results and discussion

3.1. Conversion, selectivity, and stability of various zeolite catalysts

Table 1 compares the product selectivity over various zeolite catalysts at a similar conversion level in the range of 17.3–22.6%. It is observed that IPN is the major product on all catalysts, while less than 1% of PIPN is detected on H-M, H-MD, or H-MCM-22 catalysts, and the DIPN and β,β-selectivity on USY is the highest among the four different catalysts. Moreover, H-MD gives both the highest 2,6-/2,7-DIPN, and 2-/1-IPN ratios and β,β-selectivity while those on H-MCM-22 are very low. Although a very high β,β-selectivity of 85% is observed on USY, 2,6-/2,7-DIPN is rather low at 0.34. When the conversion and selectivity are compared under the same reaction conditions, as shown in Table 2, it is indicated that the naphthalene conversion decreases in the order of USY > H-MCM-22 > H-MD > H-M, and DIPN becomes the major product only on USY. Furthermore, H-MD still possesses the highest 2,6-/2,7-DIPN, 2-/1-IPN, and β,β-selectivity, while those on H-MCM-22 are still at a low level of 0.98. However, with a very high conversion of 89.9%, USY exhibits a much higher 2,6-/2,7-DIPN ratio of 1.28 than that in Table 1 of 0.34, and at the same time, β,β-selectivity drops to a comparatively low level of 52.8%. These results imply that for the USY catalyst the reaction conditions could impose a significant effect on the product distribution.

Catalytic activity and stability of four different zeolites under typical reaction conditions are plotted and compared in Fig. 1. It is obvious that USY is a very stable and active catalyst with conversion of about 90%, and by contrast, H-MD deactivates to a conversion of lower than 10% after 6 h TOS. Through dealumination, the activity of H-MD increases substantially; however, it still exhibits deactivation with reaction time on stream. For H-MCM-22, the activity is rather stable, but at a low conversion of 20–30%.

Table 1
Comparison of catalytic selectivity of various zeolites at a conversion of about 20% in the isopropylation of naphthalene by isopropyl alcohol[a]

	Catalyst			
	USY[b]	H-M[c]	H-MD[d]	H-MCM-22[c]
Conv. (mol%)	18.5	17.3	22.6	21.1
Sel. (mol%)				
IPN	65.4	86.4	84.3	91.3
DIPN	23.0	13.6	14.9	8.1
PIPN	11.7	0	0.8	0.6
2-/1-IPN	0.36	1.61	3.55	0.86
2,6-/2,7-DIPN	0.34	2.02	3.12	0.47
β,β-Selectivity (mol%)	85.0	78.5	86.3	34.9

[a] Reaction conditions: reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} (total liquid feed), naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar), others are indicated below.
[b] Reaction temperature = 200 °C, TOS = 1 h.
[c] Reaction temperature = 250 °C, TOS = 2 h.
[d] Reaction temperature = 230 °C, TOS = 2 h.

Table 2
Catalytic activity and selectivity of different zeolites in the isopropylation of naphthalene by isopropyl alcohol under typical reaction conditions[a]

	Catalyst			
	USY	H-M	H-MD	H-MCM-22
Conv. (mol%)	89.9	9.7	27.4	31.3
Sel. (mol%)				
IPN	31.9	93.8	88.5	93.1
DIPN	40.1	6.2	11.1	6.7
PIPN	28.0	0	0.4	0.2
2-/1-IPN	1.25	1.61	2.36	1.30
2,6-/2,7-DIPN	1.28	2.46	2.67	0.98
β,β-Selectivity (mol%)	52.8	100	83.1	55.3

[a] Reaction conditions: reaction temperature = 250 °C, reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} (total liquid feed), TOS = 6 h, naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar).

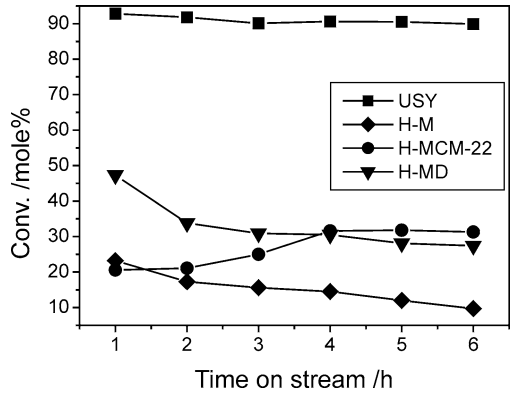

Fig. 1. Catalytic activity and stability of four different zeolite catalysts in the isopropylation of naphthalene by isopropyl alcohol under typical reaction conditions (reaction temperature = 250 °C, reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} (total liquid feed), TOS = 6 h, naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar)).

2,6-DIPN and 2,7-DIPN are the slimmest among the 10 DIPN isomers, with the molecular dimension of the former (0.661 × 0.661 × 1.423 nm) being only slightly smaller than the latter (0.662 × 0.726 × 1.376 nm) [34], and thus, it should be difficult to obtain a high 2,6-/2,7-DIPN ratio even with shape-selective zeolite catalysts. As shown in Tables 1 and 2, whatever the conversion, a 2,6-/2,7-DIPN ratio higher than 2.0 can always be observed on the two employed mordenite catalysts, indicating the shape-selective formation of 2,6-DIPN. This observation is in a good agreement with the previous results [11,12,17,18]. It is known that mordenite consists of a unique unidimensional pore channel with the 12-membered ring (12MR) window of 0.65 × 0.70 nm [32]. Considering the more linear structure of 2,6-DIPN than that of 2,7-DIPN, it is reasonable to deduce that in the unidimensional tunnels of mordenite, the attack of isopropyl alcohol to 2-IPN is more preferable at position 6 of 2-IPN than that

at position 7, resulting in the selective formation of 2,6-DIPN. This proposal is suggested by molecular graphics and molecular mechanics studies [35], which pointed out the existence of significant energy barriers when the 2,7-isomer is diffusing in mordenite channels while the diffusion of the 2,6-isomer is unimpeded, and very recently reconfirmed by the first principal quantum chemical method [34], which revealed that the 2,6-isomer could diffuse through the mordenite main channels the easiest among the possible isomers. This shape-selective effect of mordenite also causes the very low selectivity of PIPN (Tables 1 and 2). Despite the experimental and theoretical evidence for the shape selectivity of mordenite in this reaction, and considering the very slight difference in their molecular size, one still tends to suspect that this size effect cannot sufficiently account for the fact that the ratio of 2,6-/2,7-DIPN is higher than 2.0. However, based on computational analysis using MOPAC, Song et al. [36] put forward a hypothesis termed as restricted electronic transition-state selectivity effected by frontier electron density, which demonstrates that the carbon at position 6 of 2-IPN has a higher frontier electron density than that of position 7 and thus higher reactivity toward electrophilic substitution, suggesting that the formation of 2,6-DIPN is more electronically favored than that of 2,7-DIPN. As a consequence, the high 2,6-/2,7-DIPN ratio on mordenite must arise from the combined effect of the conventional shape selectivity and the specific restricted electronic transition-state selectivity.

Accompanied with high selectivity, severe deactivation and thus low activity are found for H-M. Due to its unidimensional pore structure, the deactivation of H-M seems to be accelerated by the formation of polynuclear cracking-coking products at the major channel mouth, blocking access for the reactant to the internal sites of the channel in the mordenite zeolite. Dealumination of H-M not only reduces the number of acid sites but also modifies the pore distribution, resulting in an increase of mesopore structure [17]. It could therefore be considered that low acid density might lead to the slow deactivation of the catalyst. Meanwhile, increased mesoporosity could introduce more reactants into or facilitate the products desorbing out of the mordenite major channels. Thus, over H-MD, more contributions from the internal channel surface could be expected for the overall product distribution, as compared with unmodified H-M. This could be a possible interpretation for the higher activity, stability, and 2,6-/2,7-DIPN ratio over H-MD than those over H-M (Tables 1 and 2 and Fig. 1).

MCM-22 is a medium-sized pore zeolite with a supercage ($0.71 \times 0.71 \times 1.82$ nm) and narrow pore window (10MR, 0.52 nm) [37]. Theoretically, the narrow pore windows of MCM-22 make it impossible for the reactant to diffuse into and the product to desorb out of the zeolite channels, and therefore, the reaction likely occurs at the acid sites on the external surface. This is the reason why H-MCM-22 shows a low β,β-selectivity and 2,6-/2,7-DIPN ratio and is stable with low conversion (Tables 1 and 2). However, what is unexpected on H-MCM-22 is the observation of much lower PIPN selectivity, which is very similar to those on the two different mordenite catalysts. It was found recently [38] that H-MCM-22 possesses a high concentration of strong acid sites; however, they locate mostly inside the supercages and narrow channels, and are inaccessible to the reactant. On the other hand, only some medium-strength acid sites are located on the external surface of this zeolite, and these medium strength acid sites are supposed to contribute to the formation of IPN, and not PIPN [23,31], resulting in the low selectivity of PIPN.

In contrast to the low and unstable activity and low selectivity for DIPN over mordenite catalysts, USY exhibits a high conversion of 90% up to the employed 6 h TOS with 40% of DIPN a main product. Moreover, under suitable reaction conditions, a considerable 2,6-/2,7-DIPN ratio of 1.28 is achieved, which is higher than that in the equilibrium of DIPN isomer mixtures (about 1) [1]. Y zeolite has a three-dimensional 12MR channel (0.74 nm) with large interval cavities (1.3 nm). When USY is prepared from (NH_4^+, Na)-Y zeolite by hydrothermal treatment [39,40], a large amount of mesopores could be generated with the decrease of acid density and the increase of acid strength. As a consequence, the high and stable activity of USY in Fig. 1 could be ascribed to its easily accessible pore channel and low acid density. On the other hand, the strong acidity of USY might associate with the comparatively high selectivity of PIPN (28.7%) in Table 2 [23,31]. It is also noteworthy in Table 2 that the β,β-selectivity of 52.8% over USY is lower than the thermodynamic equilibrium value ($> 70\%$) [1]. This observation possibly arises from the shape selectivity that occurs in the entrance to the pores of large-pore zeolites, which causes relatively high selectivity for 1,3- and 1,4-DIPN, and simultaneously decreases the β,β-selectivity [41].

Now that the high and stable activity, as well as the high 2,6-/2,7-DIPN ratio, can be achieved over USY, and moreover, catalytic activities can be altered to a great extent by changing reaction conditions, further investigation under various reaction conditions is then focused on the USY catalyst as below.

3.2. Effect of the reaction temperature

Fig. 2 shows the activity and selectivity of USY as a function of the reaction temperature during the isopropylation of naphthalene. It is observed in Fig. 2A that the conversion increases rapidly with the reaction temperature up to 230 °C, and it goes up very slowly beyond 230 °C, showing that the conversion reaches to 93% at 300 °C. At the same time, IPN decreases, and DIPN and PIPN increase drastically with temperatures up to 230 °C, and at higher temperatures, this trend becomes slow. When the temperature is as high as 300 °C, a small amount of cracking of solvent is observed. Moreover, it is found in Fig. 2B that 2-/1-IPN increases very quickly with reaction temperature, while 2,6-/2,7-DIPN possesses a maximum point at 250 °C.

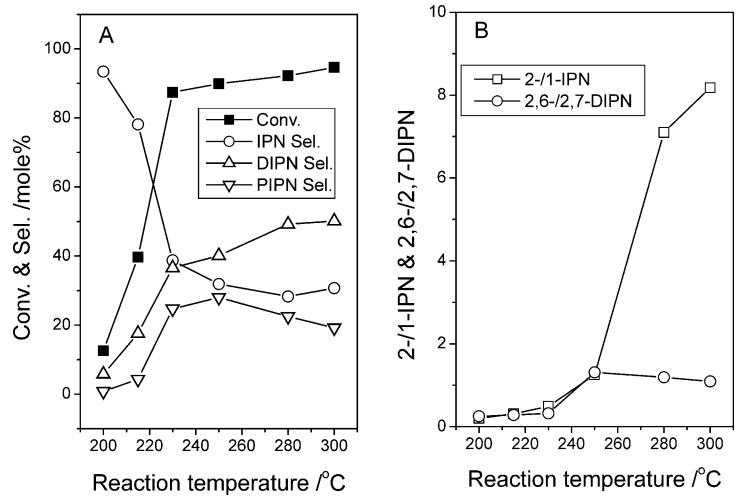

Fig. 2. Catalytic performances of the USY catalyst in the isopropylation of naphthalene by isopropyl alcohol as a function of the reaction temperature (reaction conditions: reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} (total liquid feed), TOS = 6 h, naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar)).

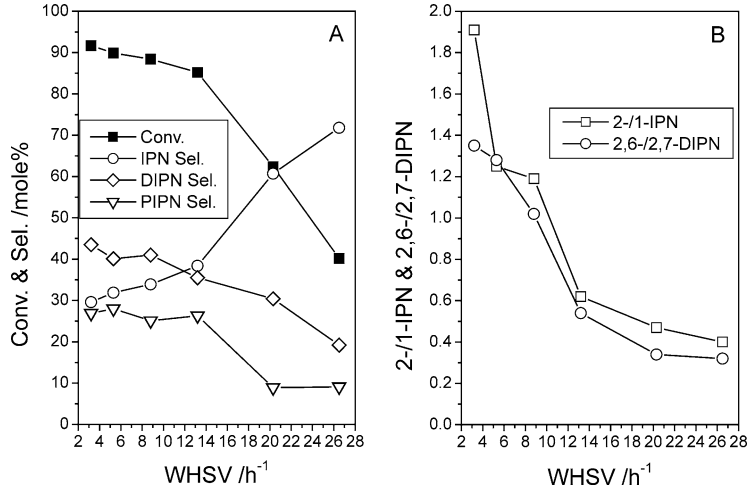

Fig. 3. Catalytic performances of the USY catalyst in the isopropylation of naphthalene by isopropyl alcohol as a function of WHSV (reaction conditions: reaction temperature = 250 °C, reaction pressure = 3.0 MPa, TOS = 6 h, naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar)).

It is known that this reaction is a consecutive reaction [15]. The high reaction temperature would facilitate the further alkylation of IPN by isopropyl alcohol to DIPN, followed by PIPN, which is observed in Fig. 2A. On the other hand, the α-position of naphthalene is more reactive and the α-substituted products are thermodynamically less stable than the β-position. At a low reaction temperature, the kinetically controlled α-isomer is formed initially. It is rearranged into the thermodynamically favored β-isomer at high reaction temperatures. This is the reason why the 2-/1-IPN ratio is much higher at high reaction temperatures. However, this high 2-/1-IPN ratio does not necessarily indicate the shape selectivity of the USY zeolite here, although 2-IPN is slimmer than 1-IPN. Furthermore, the comparatively high ratio of 2,6-/2,7-DIPN (> 1) is also found at high reaction temperatures. Taking into account conversion, selectivity of DIPN, 2-/1-IPN, and 2,6-/2,7-DIPN ratios, 250 °C can be suggested as the optimal reaction temperature.

3.3. Effect of the reactant space velocity

Fig. 3 illustrates the effect of weight hourly space velocity on the catalytic activity of USY. Fig. 3A indicates that the catalytic activity decreases very slowly when WHSV is less than 12.5 h^{-1}, and the decreasing rate quickens at a high WHSV. Since the alkylation reaction is a consecutive reaction, when WHSV becomes high, only a small part of IPN has enough reaction time to be further alkylated into DIPN and TIPN subsequently, indicating the high selectivity for IPN at high WHSV. Regarding the conversion and selectivity for DIPN, it is reasonable to choose the low WHSV for this reaction. Fig. 3B reveals that both 2-/1-IPN and 2,6-/2,7-DIPN decreases with the enhancement of WHSV. It is suggested that the high WHSV allows first the formation of thermodynamically favorable 1-IPN, and the low WHSV facilitates the rearrangement of 1-IPN into 2-IPN. Based on the above understandings, a WHSV of 5–6 h^{-1} is preferred

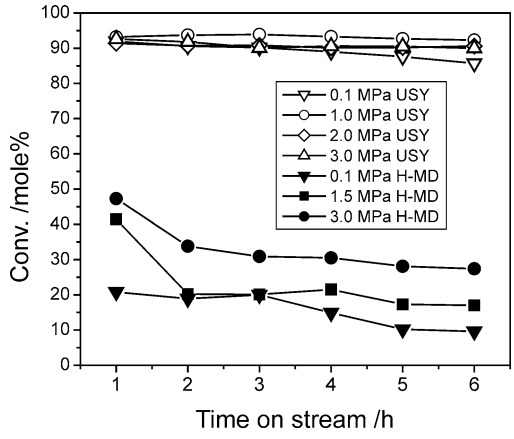

Fig. 4. Catalytic activity and stability of USY (hollow symbol) and dealuminated mordenite (black symbol) catalysts in the isopropylation of naphthalene by isopropyl alcohol as a function of the reaction pressure (reaction conditions: reaction temperature = 250 °C, WHSV = 5.3 h^{-1} (total liquid feed), TOS = 6 h, naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar)).

for achieving a high conversion and high 2-IPN and 2,6-DIPN selectivities, respectively.

3.4. Effect of the reaction pressure

The effect of reaction pressure on catalytic activity and stability under typical reaction conditions is displayed in Fig. 4. It can be seen that at pressures higher than 1.0 MPa, USY exhibits high and stable activity with a conversion of around 90%. At atmospheric pressure, a little deactivation appears, with a conversion of 85% at 6 h TOS. By contrast, for H-MD catalyst it is demonstrated in Fig. 4 that both catalytic activity and stability decrease with the decrease of reaction pressure. Although H-MD is not stable at any of the employed reaction pressures, its stability is improved remarkably at high pressure such as 3.0 MPa. For this reaction, some previous literature [14,31] has found the deactivation of Y and other catalysts in the gas-phase flow fixed-bed reactor. Here, the high pressure could assure homogeneity of the reactants, in either the liquid or the supercritical phase, and it is suggested that the liquid-phase reaction allows suppression of catalyst deactivation by dissolving some of the initially formed heavy products (the precursor of the coke) with the solvent. The role of solvent has not been evaluated, in this reaction, with this effect of reaction pressure before; however, it has been reported in benzene alkylation reactions [42,43].

3.5. Effect of the solvent concentration and type

Table 3 compares the reaction results on USY with 1:2:6 and 1:2:10 molar ratios of naphthalene, isopropyl alcohol, and decalin. At both high and low reaction temperatures, an enhancement of conversion of naphthalene is observed when the concentration of solvent in the reactant mixture is raised, while slight improvements of 2,6-/2,7-DIPN and 2-/1-IPN ratios and β,β-selectivity are also observed. However, an apparently increase of PIPN is found simultaneously. When the concentration of solvent is raised, the relative concentrations of the two reactants decrease, which should cause the decrease of conversion. On the other hand, in case of the same WHSV value (total liquid feed) for all reactions, the space velocities of the two reactants are enhanced, and thus, as an overall result, an improvement of activity is given in Table 3, especially at a reaction temperature of 200 °C.

Table 3
Catalytic performance of USY in the isopropylation of naphthalene by isopropyl alcohol as a function of solvent concentration[a]

	Molar ratio of naphthalene, isopropyl alcohol, and decalin			
	1:2:6	1:2:10	1:2:6	1:2:10
Reaction temperature (°C)	200	200	250	250
Conv. (mol%)	12.6	34.9	89.9	93.5
Sel. (mol%)				
IPN	93.4	76.2	31.9	22.6
DIPN	5.8	18.1	40.1	43.4
PIPN	0.8	5.7	28.0	34.0
2-/1-IPN	0.2	0.28	1.25	1.48
2,6-/2,7-DIPN	0.25	0.3	1.28	1.46
β,β-Selectivity (mol%)	83.3	83.8	52.8	58.0

[a] Reaction conditions: reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} (total liquid feed), TOS = 6 h.

Table 4
Comparison of catalytic performance of USY in the isopropylation of naphthalene by isopropyl alcohol with decalin and cyclohexane as the solvent[a]

	Solvent			
	Decalin	Cyclohexane	Decalin	Cyclohexane
Reaction temperature (°C)	200	200	250	250
Conv. (mol%)	34.9	30.2	93.5	92.9
Sel. (mol%)				
IPN	76.2	84.6	22.6	25.9
DIPN	18.1	13.7	43.4	42.2
PIPN	5.7	1.7	34.0	31.8
2-/1-IPN	0.28	0.28	1.48	3.38
2,6-/2,7-DIPN	0.3	0.26	1.46	1.50
β,β-Selectivity (mol%)	83.8	81.3	58.0	61.2

[a] Reaction conditions: reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} (total liquid feed), TOS = 6 h, naphthalene:isopropyl alcohol:decalin (or cyclohexane) = 1:2:10 (molar).

The comparison of decalin and cyclohexane as the reaction solvent over USY catalyst is presented in Table 4. No significant difference in reactivity can be observed between the two different kinds of solvents, except that the β,β-selectivity and 2,6-/2,7-DIPN ratio increase in a very small amount.

3.6. Effect of the reactant ratio

The molar ratio of naphthalene and isopropyl alcohol is changed to test the impact of reactant ratio upon the reactivity of USY catalyst, as shown in Table 5. It is found that both activity and selectivity are influenced drastically by the change of reactant ratio. With the increase of iso-

Table 5
Catalytic performance of USY in the isopropylation of naphthalene by isopropyl alcohol as a function of reactant ratio[a]

	Molar ratio of naphthalene, isopropyl alcohol, and decalin		
	1:1:10	1:2:10	1:4:10
Conv. (mol%)	66.7	93.5	100
Sel. (mol%)			
IPN	44.6	22.6	5.7
DIPN	40.4	43.4	29.9
PIPN	15.1	34.0	64.4
2-/1-IPN	2.95	1.48	1.26
2,6-/2,7-DIPN	1.31	1.46	0.93
β,β-Selectivity (mol%)	70.3	58.0	33.5

[a] Reaction conditions: reaction temperature = 250 °C, reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} (total liquid feed), TOS = 6 h.

propyl alcohol in the reactant mixture, the conversion and PIPN selectivity rapidly increase, and a decrease in IPN and β,β-selectivity and 2-/1-IPN ratio can been observed. Moreover, the highest value of DIPN selectivity (43.4%) and 2,6-/2,7-DIPN ratio (1.46) can be achieved with the molar ratio of naphthalene and isopropyl alcohol being 1:2. However, at a 1:1 naphthalene and isopropyl alcohol molar ratio, a comparatively high β,β-selectivity (70.3%) and considerable 2,6-/2,7-DIPN ratio (1.31) can be obtained, even if its conversion is not so high (66.7%). The increase of conversion of naphthalene and selectivity for PIPN at the low naphthalene/isopropyl alcohol ratio are easily explained by the consecutive alkylation of IPN by isopropyl alcohol into DIPN and then into PIPN, which is facilitated by the high concentration of isopropyl alcohol in the reaction mixture. At the same time, the initially produced α-IPN, which is more thermodynamically preferred than β-IPN, tends to be further alkylated into α,β- and/or α,α-DIPN isomers with excess alkylating reagent in the reaction mixture before there is enough time to be transferred into β-IPN through isomerization. This might account for the low β,β-selectivity at the low reactant ratio in Table 5.

4. Conclusions

In a high-pressure fixed-bed flow reactor, selective synthesis of 2,6-DIPN is achieved over both unmodified and dealuminated H-mordenite, with the selectivity of 2,6-DIPN almost independent of the catalyst activity. By dealumination, the conversion and selectivity of 2,6-DIPN are improved remarkably, with 2,6-/2,7-DIPN being around 3. However, the mordenite catalyst shows significant deactivation even at high reaction pressures, accompanied with the disadvantage of very low selectivity of DIPN. For H-MCM-22 catalysts, isopropylation can only take place at its acid sites on the external surface, leading to a stable but low activity, and very low 2,6-/2,7-DIPN ratio.

Although no shape selectivity for 2,6-DIPN is found over USY catalysts, very high and stable conversion (> 90%) and high selectivity for DIPN (> 40%) can be produced. Moreover, both conversion and selectivity can be altered by adjusting the reaction parameters, such as reaction temperature, pressure, reactant ratio, space velocity, and solvent concentration and type. By optimizing the reaction conditions, it is also possible to achieve a considerable 2,6-/2,7-DIPN ratio of 1.5 (Table 4), which is clearly higher than that in the equilibrium DIPN isomer mixtures containing an equal amount of 2,6- and 2,7-DIPN.

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