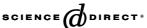
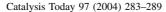


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On the isopropylation of naphthalene over zeolite catalysts in the high-pressure fixed-bed flow reactor

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Abstract

Catalytic performances of various dealuminated mordenite catalysts for the isopropylation of naphthalene by isopropyl alcohol with decalin or cyclohexane as a solvent were investigated in a high-pressure fixed-bed flow reactor. It was found that dealumination of H-mordenite could substantially improve the catalytic conversion, selectivity and stability. The catalyst with steam treatment at 700 °C followed by acid leaching was revealed to exhibit high and comparatively stable conversion of ca. 37% with the high 2,6-/2,7-DIPN ratio of ca. 3. Reaction conditions, such as reaction temperature, pressure, space velocity and solvent, could significantly influence the catalytic performance, except for the 2,6-/2,7-DIPN ratio. The catalytic behavior is discussed in relation with catalyst porosity and acidity. © 2004 Elsevier B.V. All rights reserved.

Keywords: Isopropylation of naphthalene; Diisopropylnaphthalene; Mordenite; Dealumination; Zeolite

1. Introduction

The selective alkylation of naphthalene to 2,6-dialkyl-naphthalenes is of practical importance, because they are the starting material for the manufacture of high-performance engineering plastic materials (polyethylenenaphthalate) and liquid crystal polymers [1]. The key point for large-scale application is the development of an efficient method for the preparation of 2,6-dialkylnaphthalenes. The possibility of using zeolites as environment friendly acidic catalysts has been reported in numerous studies [1–20]. Actually, for this reaction, various alkylating agents, such as methanol [2–4], ethanol [5], isopropyl alcohol [6–11], propene [12–14], isopropyl bromide [15], tert-butyl alcohol [16,17], cyclohexyl bromide [18,19] and cyclohexane [18–20], have been evaluated. Among these studies, isopropylation of naphthalene has been attracting much attention, because the iso-

propyl 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, compared with 2,6-di-*tert*-butylnaphthalene or 2,6-dicyclohexylnaphthalene, 2,6-DIPN is atomically more economical in the oxidation process, a necessary step in the manufacture of polyethylenenaphthalate, because the bulkier the alkylating agent, the higher the waste of carbon atoms when the alkyl groups are oxidized to carboxyl groups.

Mordenites have been shown to be strong candidates for such a process. Indeed, Katayama et al. first found the higher selectivity of H-mordenite for 2,6-DIPN than that of H-Y, H-L and H-ZSM-5, respectively [6]. After that, dealumination [7,12,21–24], chemical vapor deposition [15] and ceria impregnation of the external surface of mordenites [23] have been reported to improve their catalytic behavior. By contrast, some of the literature indicated that H-Y is also a promising catalyst in terms of activity [25,26].

However, the previous studies have mostly been carried out in an autoclave. Since a serious drawback of the autoclave reactor is the difficulty of evaluating the catalyst

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stability, up to now only a few papers have investigated the stability of the catalyst in this reaction. For example, Inui et al. [9] carried out the isopropylation of naphthalene by isopropyl alcohol using the atmospheric-pressure fixedbed flow reactor over Y, Beta, mordenite, MCM-41 and MCM-48 catalysts, respectively, and deactivation was found on all catalysts within the 3 h on stream; Ferino et al. [10,11,27] performed this reaction over H-Y, H-Beta and H-mordenite catalysts in a flow reactor under high-pressure, but they used a high reaction temperature of 350 °C, and a large amount of side reaction products appeared. Very recently, we [28] measured the catalytic activity of USY catalyst for the isopropylation of naphthalene by isopropyl alcohol in a fixed-bed flow reactor at 3.0 MPa and 250 °C, and found that the USY catalyst could exhibit very high and stable conversion of naphthalene of around 90% with high selectivity for DIPN of above 40% and a considerable 2,6-/ 2,7-DIPN ratio of 1.5.

In this work, we report the activity, selectivity and stability of a series of dealuminated H-mordenite catalysts for naphthalene isopropylation in the high-pressure fixed-bed flow reactor, as well as the influence of reaction conditions on the catalytic performance.

2. Experimental

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 the steam treatment of HM (H-mordenite, Zeolyst, CP814) at various temperatures for 5 h, followed by leaching in a 2 M HCl aqueous solution at 80 °C for 2 h. The resulting sample was further calcined at 550 °C for 8 h. The catalyst designation and its corresponding treatment conditions are listed in Table 1. The SiO₂/Al₂O₃ ratio of samples was obtained by an ICP spectrometer (J.Y. Ultima C., Jobin Yvon). Relative crystallinities were determined by comparing integrated XRD intensities of the (1 1 0), (0 2 0), (2 0 0), (1 5 0), (2 0 2) and (3 5 0) reflections, which were achieved on a Rigaku D/MAX-3B diffractometer using

monochromatic Cu K α radiation. BET surface area was calculated from N $_2$ adsorption isotherms using a Micromeritics model ASAP 2400. NH $_3$ -TPD was carried out in a GC apparatus with TCD as the detector in order to determine the acidity of the samples. The catalysts under study were saturated with ammonia, and fluxed with He while the temperature was increased linearly (heating rate of 10 °C/min).

Catalytic tests were carried out in a high-pressure fixedbed 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 under N₂ 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), and 1:2:6 molar ratio of naphthalene, isopropyl alcohol and decalin in the liquid feed. Also, to keep the system at the steady highpressure, 20 ml/min of N₂ was introduced concurrently with the reaction feed into the reactor at the reactor head. The reactor effluent was condensed in the sampler at -10 °C by cold ethanol and sampled hourly. Reactants and products were analyzed by a GC (HP 5890 II) using an FID as the detector furnished with a 60 m \times 0.25 mm \times 0.25 μ m SE54 (J&W Scientific) capillary column. The column oven temperature program started with the initial temperature of 40 °C for 2 min, followed with a temperature increase rate of 4 °C/min and a final temperature of 280 °C for 30 min. Conversion of naphthalene and selectivity of various products were calculated according to our previous report [28].

3. Results and discussion

3.1. Physical chemical properties of dealuminated mordenites

Table 1 displays the SiO₂/Al₂O₃ ratio, crystallinity and BET surface area of all the employed dealuminated morde-

Table 1 Dealumination conditions and properties of dealuminated mordenites

Catalyst	Steam treatment T (°C)	Acid leaching	SiO ₂ /Al ₂ O ₃ Ratio	Crystallinity ^a (%)	Surface area (m ² /g)		
					Total	Micropore ^b	Mesopore ^c
HM	no	no	25	100	450	399	51
HM550	550	no	25	99	561	486	75
HMA	no	yes	34	90	486	414	72
HM550A	550	yes	49	81	527	438	89
HM700A	700	yes	72	116	538	417	121
HM800A	800	yes	95	119	461	342	119

^a Provided that the crystallinity of HM is 100%.

^b Micropore refers to <2.0 nm (diameter) pores.

^c Mesopore refers to 2.0-60 nm pores.

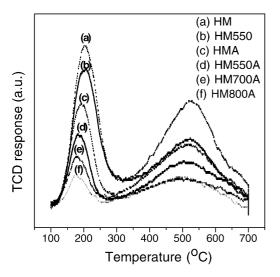


Fig. 1. NH₃-TPD profile of various dealuminated mordenite catalysts.

nites. It is observed that the SiO₂/Al₂O₃ ratio increased clearly with the increase of the steam treatment temperature when HM is subjected to steam treatment combined with HCl acid leaching. Also, more mesopores are generated for the dealuminated sample steam-treated at the higher temperature. On the other hand, after dealumination, all the samples possess high crystallinity, and the two samples steam treated at 700 °C and 800 °C even possess higher crystallinity than that of HM. It is most probable that the amorphous silica in HM could migrate into some of the dealuminated skeletal Al vacancies during steam dealumination at high temperatures with the formation of new skeletal Si units, and thus increase the crystallinity.

Fig. 1 shows the NH₃-TPD profile of various dealuminated mordenite catalysts. It can be seen that for all catalysts, two ammonia desorption peaks occur in the NH₃-TPD curve, with the one at ca. 200 °C corresponding to a weak acid site, and the one at ca. 530 °C to a strong acid site. The number of both strong and weak acid sites decreases remarkably when HM undergoes dealumination by steam treatment and/or acid leaching. Evidently, the steam treatment combined with acid leaching is a more effective way to decrease the acid number, and when the steam treatment temperature increases the acid number decreases to a lower level.

3.2. Conversion, selectivity and stability of various dealuminated mordenite catalysts

Catalytic conversion and stability of various dealuminated mordenites are plotted in Fig. 2, and their catalytic performances at 6 h on stream are compared in Table 2. For all catalysts, deactivation appears during the reaction time on stream, especially at the early reaction stage, as shown in Fig. 2. The untreated HM catalyst exhibits not only the lowest conversion of naphthalene but also severe deactivation with a conversion of <10% at 6 h on stream. After dealumination by steaming or acid leaching, HM550 or

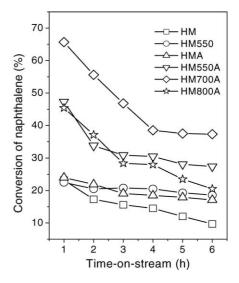


Fig. 2. Catalytic conversion and stability of various dealuminated mordenite catalysts in the isopropylation of naphthalene by isopropyl alcohol. Reaction temperature = 250 °C, reaction pressure = 3.0 MPa, WHSV = 5.3 h⁻¹ (total liquid feed), naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar).

HMA gives a comparative high conversion of ca. 18%. It is worthy of note that a much higher conversion was observed on the dealuminated mordenites treated by steaming followed by acid leaching, i.e. 27.4% of conversion on HM550A and 37.3% on HM700A was achieved at 6 h on stream. Furthermore, these two catalysts could almost attain the steady reaction state after the deactivation during the first 3 h on stream. However, with steam treatment at the very high temperature of 800 °C, HM800A shows very severe deactivation and lower conversion of ca. 21% compared with HM700A and HM550A at 6 h. As for the catalytic selectivity, Table 2 indicates that for all catalysts, only negligible PIPN (polyisopropylnaphthalene) is detected, and DIPN selectivity increases substantially when HM is dealuminated by steam treatment followed by acid leaching. Meanwhile, the ratio of 2-/1-IPN (isopropylnaphthalene) is also much higher for HM550A, HM700A and HM800A than that for other catalysts. On the other hand, β , β -selectivity on all catalysts is found to be higher than the thermodynamic equilibrium value of ca. 70% [29]. Moreover, whatever the conversion of naphthalene, all the dealuminated mordenites gives similar 2,6-/2,7-DIPN ratios of 2.7-3.0, which is slightly higher than that of HM.

It is known that mordenite consists of a unique unidimensional pore channel with a 12-membered ring window of $0.65~\text{nm}\times0.70~\text{nm}$ [26] and isopropylation of naphthalene is a consecutive reaction [10]. The first formed IPN would be further alkylated by isopropyl alcohol to DIPN, followed by PIPN. However, the formation of PIPN would be hindered largely by the pore size of mordenite, which could be confirmed by the negligible amount of PIPN shown in Table 2. Also, the selectivity to DIPN is much lower than that to IPN. Among the 10 DIPN isomers, 2,6-DIPN and 2,7-DIPN are the slimmest ones. Thus, owing to the shape selectivity

Table 2
Comparison of catalytic performance of various dealuminated mordenite catalysts in the isopropylation of naphthalene by isopropyl alcohol^a

	Catalyst					
	HM	HM550	HMA	HM550A	HM700A	HM800A
Conversion (mol%)	9.7	18.6	17.1	27.4	37.3	20.5
Selectivity (mol%)						
IPN	93.8	94.6	94.3	88.5	80.7	89.4
DIPN	6.2	5.4	5.7	11.1	17.7	10.1
PIPN	0	0	0	0.4	1.6	0.5
2-/1-IPN	1.6	1.5	1.6	2.4	4.1	2.5
2,6-/2,7-DIPN	2.5	2.9	3.0	2.7	2.7	2.9
β,β-selectivity (mol%)	100	100	89.3	83.1	91.1	88.9

^a Reaction conditions: reaction temperature = 250 °C, reaction pressure = 3.0 MPa, WHSV = 5.3 h⁻¹ (total liquid feed), time-on-stream = 6 h, naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar).

of mordenite, it is understandable why we observe the high β , β -selectivity in Table 2, where the β , β -products mainly consist of 2,6-DIPN and 2,7-DIPN, because 2,3-DIPN has rarely been detected on all catalysts. This is in contrast with the USY catalyst with an open pore structure, giving a high selectivity of DIPN and PIPN, and comparatively low β , β -selectivity [28].

It is highly desirable to achieve a high 2,6-/2,7-DIPN ratio in the reaction. For the employed mordenite catalysts, as indicated in Table 2, a 2,6-/2,7-DIPN ratio higher than 2.5 can be always observed, directing the shape-selective formation of 2,6-DIPN. This observation is in good agreement with the previous results observed in a batch reactor [13]. The molecular dimensions of 2,6-DIPN (0.661 nm \times $0.661 \text{ nm} \times 1.423 \text{ nm}$) are slightly smaller than 2,7-DIPN $(0.662 \text{ nm} \times 0.726 \text{ nm} \times 1.376 \text{ nm})$ [30], and one could deduce that in the unidimensional tunnels of mordenite, the attack of isopropyl alcohol to 2-IPN is more preferable at the position 6 of 2-IPN than that at the position 7, resulting in the selective formation of 2,6-DIPN. This proposal is suggested by the molecular graphics and molecular mechanics studies [31], which pointed out the existence of the significant energy barriers when the 2,7-isomer is diffusing in mordenite channels while the diffusion of the 2,6-isomer is unimpeded. On the other hand, based on a computational analysis using MOPAC, Song et al. [32] put forward a hypothesis termed restricted electronic transition-state selectivity affected by the frontier electron density, which demonstrates that the carbon at position 6 of 2-IPN has a higher frontier electron density than that at position 7 and thus higher reactivity towards electrophilic substitution, suggesting 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 effects of conventional shapeselectivity and specific restricted electronic transition-state selectivity.

Accompanying the high selectivity, severe deactivation and thus low activity are found for the untreated HM catalyst. Its poor activity does not correspond to its high acidity displayed in Fig. 1. Actually, it has been revealed by other researchers [11,33] that the activity of a solid acid

catalyst for this reaction is influenced largely by its porosity, rather than the acidity. The severe deactivation of HM could be interpreted by the formation of poly-nuclear crackingcocking products at the major channel mouth of its unidimensional pore, blocking the access for the reactant to the internal sites of the channel in the mordenite zeolite. The formation of the coke material is supposed to be accelerated by the high acidity of the catalyst. Dealumination of HM not only reduces the number of acid sites, but also modifies the pore distribution, resulting in an increase of mesopores as shown in Table 1 and Fig. 1. It could therefore be considered that the low acid density might lead to the slow deactivation of the catalyst, and meanwhile, the increased mesoporosity could introduce more reactants into or facilitate the products desorbing out of the mordenite major channels. Thus, over dealuminated mordenites, more contributions from the internal channel surface could be expected for the overall product distribution, as compared with unmodified ones. This explains why the activity and stability of dealuminated mordenites are higher than those of HM. Therefore, the high and stable conversion over HM700A in Fig. 2 mostly arises from its very high proportion of mesopores created by high temperature steam treatment followed by acid leaching. The further increase of steam treatment temperature up to 800 °C leads to a lower activity, the reason for which is not clear so far.

3.3. Influence of reaction conditions

Table 3 shows the influence of reaction time-on-stream on the catalytic behavior of HM550A. Only negligible PIPN is detected up to 6 h. The selectivity of DIPN decreases and IPN increases gradually with the time-on-stream, and the conversion also decreases due to coking. While the catalyst is on stream, coke is gradually formed and deposits inside the zeolite channel. As a consequence, the number of diffusion pathways for product molecules increases. Slim molecules, such as IPN, are less affected than bulkier ones, such as DIPN, and therefore the increased IPN can easily be explained by this coke selectivity. On the other hand, at the initial reaction stage at high conversion level, the 2-/1-IPN ratio is much higher than that of the later reaction stage with

Table 3
Catalytic performance of HM550A as a function of reaction time-on-stream in the isopropylation of naphthalene by isopropyl alcohol^a

	Time-on-stream (h)					
	1	2	3	4	5	6
Conversion (mol%)	47.3	33.8	30.9	30.5	28.1	27.4
Selectivity (mol%)						
IPN	73.4	82.6	79.0	85.1	87.5	88.5
DIPN	25.1	16.2	19.6	12.2	11.3	11.1
PIPN	1.4	1.2	1.4	2.7	1.2	0.4
2-/1-IPN	3.7	2.5	2.9	2.3	2.3	2.4
2,6-/2,7-DIPN	3.0	2.8	3.0	2.9	2.9	2.7
β , β -selectivity (mol%)	91.9	82.0	87.5	82.7	82.5	83.1

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

low conversion. The α -position of naphthalene is more reactive and the α -substituted products are thermodynamically less stable than the β -position. It is proposed that at low conversion, the kinetically controlled α -isomer is formed initially, and it tends to be rearranged into the thermodynamically favored β -isomer at high conversion. This observation is confirmed by the very high 2-/1-IPN ratio over HM700A with high conversion (Table 2). Table 3 also reveals the high 2,6-/2,7-DIPN ratio of 2.7–3.0 which does not change significantly with the variations of conversion.

Fig. 3 shows the conversion of HM550A as a function of the reaction temperature. At all temperatures, deactivation is observed. The conversion increases rapidly with the increase of reaction temperature up to 250 °C. At 280 °C, the conversion at 6 h on stream drops to a lower value than that at 250 °C because of the rapid deactivation, even if its initial

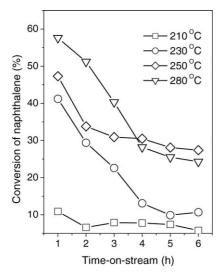


Fig. 3. Catalytic conversion of naphthalene over HM550A catalyst in the isopropylation of naphthalene by isopropyl alcohol as a function of the reaction temperature. Reaction conditions: reaction pressure = $3.0 \, \text{MPa}$, WHSV = $5.3 \, \text{h}^{-1}$ (total liquid feed), naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar).

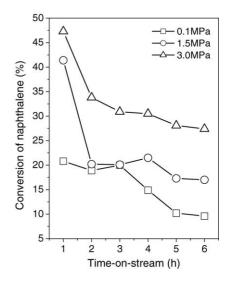


Fig. 4. Catalytic conversion of naphthalene over HM550A catalyst in the isopropylation of naphthalene by isopropyl alcohol as a function of the reaction pressure. Reaction conditions: reaction temperature = $250\,^{\circ}$ C, WHSV = $5.3\,h^{-1}$ (total liquid feed), naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar).

activity is higher. This is different from the results for USY catalyst [28], where deactivation is not so significant, and the conversion goes up with the increase of reaction temperature up to $300\,^{\circ}\text{C}$.

The effect of reaction pressure on catalytic activity and stability over HM550A is illustrated in Fig. 4. It is demonstrated that both catalytic activity and stability decreases with the decrease of reaction pressure. Although the deal-uminated mordenite 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, several previous studies [9,25] have found the deactivation of various zeolite catalysts in the gas phase fixed-bed flow reactor. Here, the high-pressure could assure homogeneity of the reactants, in either liquid or supercritical phase, and it is suggested that the liquid phase reaction allows suppression of the catalyst deactivation by dissolving some of the initially formed heavy products (the precursor of the coke) with the solvent.

Table 4 shows the effect of weighted hourly space velocity on the catalytic activity of HM550A. It is indicated that the conversion of naphthalene decreases remarkably with the increase of weight hourly space velocity (WHSV). Since the alkylation reaction is a consecutive reaction, when WHSV becomes high, only a small part of IPN have enough reaction time to be further alkylated into DIPN and PIPN subsequently, resulting in the high selectivity for IPN at high WHSV, as shown in Table 4. It is also indicated that 2-/1-IPN decreases with the enhancement of WHSV, i.e., with the decrease of conversion. This phenomenon can be explained in a similar way to those in Tables 2 and 3. Despite the large discrepancy in conversion in Table 4 (also in Tables 2 and 3), a rather high and similar 2,6-/2,7-DIPN ratio of ca. 3 can be achieved, implying that the high ratio mostly results from the

Table 4
Catalytic performance of HM550A as a function of reactant space velocity in the isopropylation of naphthalene by isopropyl alcohol^a

	WHSV (h ⁻¹)			
	2.7	5.3	10.6	
Conversion (mol%)	35.6	27.4	8.5	
Selectivity (mol%)				
IPN	76.0	88.5	90.2	
DIPN	21.9	11.1	9.8	
PIPN	2.1	0.4	0	
2-/1-IPN	2.8	2.4	1.9	
2,6-/2,7-DIPN	3.1	2.7	3.1	
β,β-selectivity (mol%)	93.0	83.1	88.0	

^a Reaction conditions: reaction temperature = 250 °C, reaction pressure = 3.0 MPa, time-on-stream = 6 h, naphthalene:isopropyl alcohol:decalin = 1:2:6 (molar).

shape selectivity of mordenite. This is in disagreement with the USY catalyst [28], where the 2,6-/2,7-DIPN ratio could be controlled largely by adjusting the reaction conditions.

Table 5 indicates the solvent effect during the isopropylation of naphthalene by isopropyl alcohol over HM550A. With decalin as the solvent, an enhancement of conversion of naphthalene is observed when the concentration of solvent in the reactant mixture is raised, while the improvements of 2,6-/2,7-DIPN and 2-/1-IPN ratios and β,β selectivity are observed. Simultaneously, the increase of PIPN and DIPN are also found. 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 contact times of the two reactants are enhanced, and thus, as an overall result, an improvement of activity could be obtained. The comparison of decalin and cyclohexane as the reaction solvent is also presented in Table 5. No significant difference in reactivity can be observed between the two different solvents. The observed effect of solvent for dealuminated mordenite catalyst is similar to the result for USY [28].

Table 5
Catalytic performance of HM550A as a function of reaction solvent in the isopropylation of naphthalene by isopropyl alcohol^a

	Molar ratio of naphthalene, isopropyl alcohol, and solvent			
	1:2:6	1:2:10	1:2:10	
Solvent	decalin	decalin	cylclohexane	
Conversion (mol%)	33.8	41.5	42.9	
Selectivity (mol%)				
IPN	82.6	75.6	74.6	
DIPN	16.2	20.3	20.7	
PIPN	1.2	4.2	4.7	
2-/1-IPN	2.5	3.1	3.1	
2,6-/2,7-DIPN	2.8	3.1	2.9	
β,β -selectivity (mol%)	82.0	94.6	94.7	

^a Reaction conditions: reaction temperature = 250 °C, reaction pressure = 3.0 MPa, time-on-stream = 2 h, WHSV = 5.3 h⁻¹ (total liquid feed).

4. Conclusions

It is found in the high-pressure fixed-bed flow reactor that the catalytic conversion, stability and selectivity of dealuminated H-mordenite catalysts for the isopropylation of naphthalene, as well as the ratios of 2,6-/2,7-DIPN and 2-/1-IPN, are improved remarkably compared with unmodified H-mordenite. Steam treatment combined with acid leaching is the most efficient dealumination method to create mesopores and lower the acid content of H-mordenite. We suggest that the mesopores created in dealumination play an essential role for the promotion effect of dealumination in this reaction. The catalytic performance can be altered largely by adjusting the reaction parameters, such as reaction temperature, pressure, space velocity, and solvent. For example, 250 °C is revealed to be the optimal reaction temperature and the high reaction temperature of 280 °C leads to severe deactivation; the high reaction pressure of 3.0 MPa can substantially improve the catalytic stability. Within the 6 h of reaction time-on-stream, the highest stabilized conversion of 37.3% with a very high 2-/ 1-IPN ratio of 4.1, 2,6-/2,7-DIPN ratio of 2.7 and β , β selectivity of 91.1% can be achieved over the dealuminated H-mordenite catalyst steam-treated at 700 °C combined with HCl acid leaching under the optimal reaction conditions as follows: reaction temperature of 250 °C, reaction pressure of 3.0 MPa, WHSV of 5.3 h⁻¹ and naphthalene, isopropyl alcohol and solvent (decalin or cyclohexane) molar ratio of 1:2:6.

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References

- [1] K. Smith, S.D. Roberts, Catal. Today 60 (2000) 227.
- [2] D. Fraenkel, M. Cherniavsky, B. Ittah, M. Ievy, J. Catal. 101 (1986)
- [3] T. Inui, S. Pu, J. Kugai, Appl. Catal. A: Gen. 146 (1996) 285.
- [4] J.N. Park, J. Wang, C.W. Lee, S.E. Park, Bull. Korean Chem. Soc. 23 (2002) 1011
- [5] G. Kamalakar, M. Ramakrishna Prasad, S.J. Kulkarni, S. Narayanan, K.V. Raghavan, Microporous Mesoporous Mater. 38 (2000) 125
- [6] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa, S. Mitamura, J. Chem. Soc. Chem. Commun. (1991) 39.
- [7] C. Song, S. Kirby, Microporous Mater. 2 (1994) 467.
- [8] S. Chu, Y. Chen, Appl. Catal. A: Gen. 123 (1995) 51.
- [9] S. Pu, J. Kim, M. Seno, T. Inui, Microporous Mater. 10 (1997) 25.

- [10] G. Colon, I. Ferino, E. Rombi, E. Selli, L. Forni, P. Magnoux, M. Guisnet, Appl. Catal. A: Gen. 168 (1998) 81.
- [11] I. Ferino, R. Monaci, E. Rombi, V. Solinas, P. Magnoux, M. Guisnet, Appl. Catal. A: Gen. 183 (1999) 303.
- [12] J.H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, Microporous Mater. 5 (1995) 113.
- [13] A.D. Schmitz, C. Song, Catal. Lett. 40 (1996) 59.
- [14] R. Brzozowski, W. Tecza, Appl. Catal. A: Gen. 166 (1998) 21.
- [15] P. Moreau, A. Finiels, P. Geneste, J. Solofo, J. Catal. 136 (1992) 487.
- [16] Z. Liu, P. Moreau, F. Fajula, Chem. Commun. 2653. (1996).
- [17] G. Kamalakar, M. Ramakrishna Prasad, S.J. Kulkarni, K.V. Raghavan, Microporous Mesoporous Mater. 52 (2002) 151.
- [18] P. Moreau, A. Finiels, P. Geneste, F. Moreau, J. Solofo, J. Org. Chem. 57 (1992) 5040.
- [19] D. Mravec, M. Michvocik, M. Hronec, P. Moreau, A. Finiels, P. Geneste, Catal. Lett. 38 (1996) 267.
- [20] P. Moreau, A. Finiels, P. Geneste, F. Moreau, J. Solofo, Stud. Surf. Sci. Catal. 83 (1993) 575.
- [21] Y. Sugi, M. Toba, Catal. Today 19 (1994) 187.
- [22] Y. Sugi, J.H. Kim, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, Stud. Surf. Sci. Catal. 84 (1994) 1837.

- [23] J.H. Kim, Y. Sugi, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu, M. Matsumoto, S. Nakata, A. Kato, G. Seo, C. Pak, Appl. Catal. A: Gen. 131 (1995) 15.
- [24] A.D. Schmitz, C. Song, Catal. Today 31 (1996) 19.
- [25] G. Kamalakar, S.J. Kulkarni, K.V. Raghavan, S. Unnikrishnan, A.B. Halgeri, J. Mol. Catal. A: Chem. 149 (1999) 283.
- [26] P. Moreau, C. He, Z. Liu, F. Fajula, J. Mol. Catal. A: Chem. 168 (2001) 105
- [27] M.G. Cutrufello, I. Ferino, R. Monaci, E. Rombi, V. Solinas, P. Magnoux, M. Guisnet, Appl. Catal. A: Gen. 241 (2003) 91.
- [28] J. Wang, J.N. Park, Y.K. Park, C.W. Lee, J. Catal. 220 (2003) 265.
- [29] R. Brzozowski, J.C. Dobrowolski, M.H. Jamroz, W. Skupinski, J. Mol. Catal. A: Chem. 170 (2001) 95.
- [30] G. Tasi, I. Palinko, F. Mizukami, React. Kinet. Catal. Lett. 74 (2001) 317
- [31] J.A. Horsley, J.D. Fellmann, E.G. Derouane, C.M. Freeman, J. Catal. 147 (1994) 231.
- [32] C. Song, X. Ma, A.D. Schmitz, H.H. Schobert, Appl. Catal. A: Gen. 182 (1999) 175.
- [33] C. Song, W.C. Lai, A.D. Schmitz, K.M. Reddy, Am. Chem. Soc. Div. Fuel Chem. Prepr. 41 (1996) 71.