MCM-22, Mordenite, USY 촉매를 이용한 나프탈렌의 이소프로필화 반응

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Isopropylation of Naphthalene with Isopropanol over MCM-22, Mordenite and USY Catalysts

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Introduction

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

In recent years, isopropylation of naphthalene has been extensively studied over zeolite catalysts, aiming at the selective synthesis of 2,6-diisopropylnaphthalene (2,6-DIPN). Katayama and his coworkers first found the higher selectivity of H-mordenite for 2,6-DIPN than that of H-Y, H-L and H-ZSM-5, respectively [Katayama et al., 1991], and later, dealuminated mordenite proved to be more active and selective for 2,6-DIPN [Song, et al., 1999]. By contrast, some literatures also demonstrated that H-Y is a promising candidate for the selective synthesis of 2,6-DIPN in both liquid and gas phase reaction [Moreau et al., 2001].

However, most of the previous studies have been carried out in autoclave reactors. A serious drawback of this simple apparatus is the difficulty of evaluating the catalytic stability. So far, very few papers have investigated isopropylation of naphthalene with isopropanol using the flow fixed bed reactor. Colon and his coworkers recently carried out this reaction in a flow reactor under high pressure, but they used a high reaction temperature of 350 ºC, and a significant amount of side reactions occurred. In this work, we study the catalytic activity, selectivity and stability of USY, H-mordenite and H-MCM-22 catalysts for isopropylation of naphthalene using a high pressure flow fixed bed reactor. The effect of reaction conditions is also measured in detail on the USY catalyst.

Experimental

USY (CBV780, $SiO_2/Al_2O_3 = 80$) and H-Mor (H-mordenite, CP814, $SiO_2/Al_2O_3 = 25$) were from Zeolyst. Na-MCM-22 ($SiO_2/Al_2O_3 = 30$) was synthesized according to the previous literature [Corma et al., 1995]. H-MCM-22 was prepared by the repeated ion-exchange of Na-MCM-22 with the aqueous solution of ammonium nitrate, followed by drying and calcination.

All experiments were carried out in a high-pressure flow fixed bed microreactor. The reactant mixture of naphthalene, isopropanol and decalin (solvent) was injected by a high-pressure pump into the fixed bed tubular stainless-steel reactor, in 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 ºC for 6 h before reactants entered the reactor. The typical reaction conditions were as follows: 250 ºC reaction temperature, 3.0 MPa reaction pressure, 5.3 h^{-1} weight hourly space velocity (WHSV, total liquid feed) and 1:2:6 of the molar ratio of naphthalene, isopropanol and decalin in liquid feed. Also, to keep the system at the required high pressure, a small flow of N_2 was maintained from the reactor head. For USY catalyst, the reaction conditions were altered systematically to test the effect of reaction conditions. Reaction conditions other than typical ones are indicated in corresponding tables and figures. The reactor effluent was condensed at -10 ºC and sampled hourly. Reactants and products were analyzed by the gas chromatograph (HP 5890 II) using FID as the detector furnished with a 60 m SE54 capillary column.

Results and Discussion

Table 1 compares the product selectivity over different zeolite catalysts at the same conversion level. It can be seen in Table 1 that IPN is the major product on all catalysts, with no TIPN detected on H-Mor. Moreover, H-Mor gives the highest 2,6-/2,7-DIPN and 2-/1-IPN ratios, while those on USY and H-MCM-22 are less than 1. When the catalytic activity and selectivity are compared at same reaction conditions in Table 2, it is observed that the catalytic activity decreases in the order USY>H-MCM-22>H-Mor, and DIPN becomes the major product on USY. Furthermore, H-Mor still possesses the highest 2,6-/2,7-DIPN and 2-/1-IPN ratios, while those on H-MCM-22 are still at a low level. However, with a very high activity (89.9%), USY exhibits a much higher 2,6-/2,7-DIPN ratio (1.28) than that in Table 1 (0.34), which implies that the reaction conditions could impose a significant effect on the product distribution.

Table 1. Comparison of catalytic selectivity of different zeolites at the conversion of around 20%

Catalyst	NA[a] Conv. /mole%	Prod. Sel. /%			IPN Sel. /%		DIPN Sel. %		
		IPN[b]	DIPN[c]	TIPN[d]	2-	2-/1-	2,6-	2,7-	2,6-/2,7-
USY[e]	18.5	65.4	23.0	11.7	26.6	0.36	20.9	61.4	0.34
H-Mor[f]	17.3	86.4	13.6	0	61.7	1.61	52.5	26.0	2.02
H-MCM-22[g]	21.1	91.3	8.1	0.6	46.2	0.86	11.2	23.8	0.47

[a] Naphthalene, [b] isopropylnaphthalene, [c] diisopropylnaphthalene, [d] triisopropylnaphthalene, [e] Time on stream (TOS)=1 h, reaction temperature=200 °C, [f] TOS=2 h, [g] TOS=2 h.

Catalytic activity and stability of different zeolites are shown in Fig. 1. It is obvious that USY is a very stable and active catalyst, H-Mor deactivates to a very low conversion level after 6 h TOS, and H-MCM-22 is also very catalytically stable but with low activity.

Table 2. Catalytic activity and selectivity of different zeolites at 6 h TOS

Catalyst	NA Conv. /mole%	Prod. Sel. /%			IPN Sel. /%		DIPN Sel. %		
		IPN	DIPN	TIPN	2-	2-/1-	2,6-	2,7-	2,6-/2,7-
USY	89.9	31.9	40.1	28.7	55.6	1.25	27.6	21.5	1.28
H-Mor	9.7	93.8	6.2	0	61.6	1.61	71.1	28.9	2.46
H-MCM-22	31.3	93.1	6.7	0.2	56.5	1.30	27.4	27.9	0.98

2,6-DIPN and 2,7-DIPN are slimmest among the 10 DIPN isomers, with the molecular size of the former being only slightly smaller than that of the later, and thus, it is very difficult to obtain a high 2,6-/2,7-DIPN ratio even on zeolite catalysts. High 2,6-/2,7-DIPN ratio is always found on H-Mor (Tables 1 and 2), indicating the selective formation of 2,6-DIPN due to its unique unidimensional pore channel with the 12-membered ring (12MR) window (0.65×0.70 nm). This observation is in

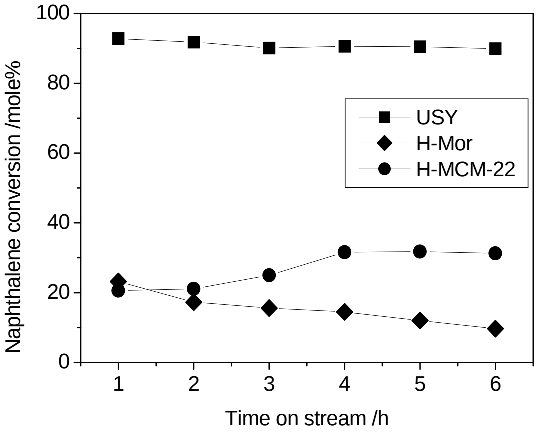

Fig. 1. Catalytic activity and stability of different zeolites.

agreement with the previous results [Katayama et al., 1991]. However, H-Mor exhibits very low activity and DIPN selectivity, leading to a very low yield of 2,6-DIPN. On the other hand, with more narrow pore window (0.52 nm) than H-Mor, H-MCM-22 shows much low 2,6-/2,7-DIPN ratio and low and stable activity, implying that the alkylation reaction must take place on acid sites of external surface with low selectivity. Y zeolite has three-dimensional 12MR channel (0.74 nm) with large cavities (1.3 nm) interval. When USY is prepared from Y zeolite, a large amount of mesopores could be generated with the decrease of acid density. 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. It has been found recently that the selective formation of 2,6-DIPN on dealuminated mordenite is not only because of the shape selectivity of zeolite pore, but also, more importantly, because the formation of 2,6-DIPN is electronically more favored than that of 2,7-DIPN. Thus, one would consider that, inside USY channel, which is not shape selective for 2,6-DIPN shown by the result in Table 1, it is still possible to selectively produce 2,6-DIPN taking the advantage of the electronic property on 6 position of 2-IPN. This is true when high conversion is obtained on USY in Table 2, where a considerable 2,6-/2,7-DIPN ratio of 1.28 is achieved, which is higher than that (about 1) in the equilibrium DIPN isomers mixture.

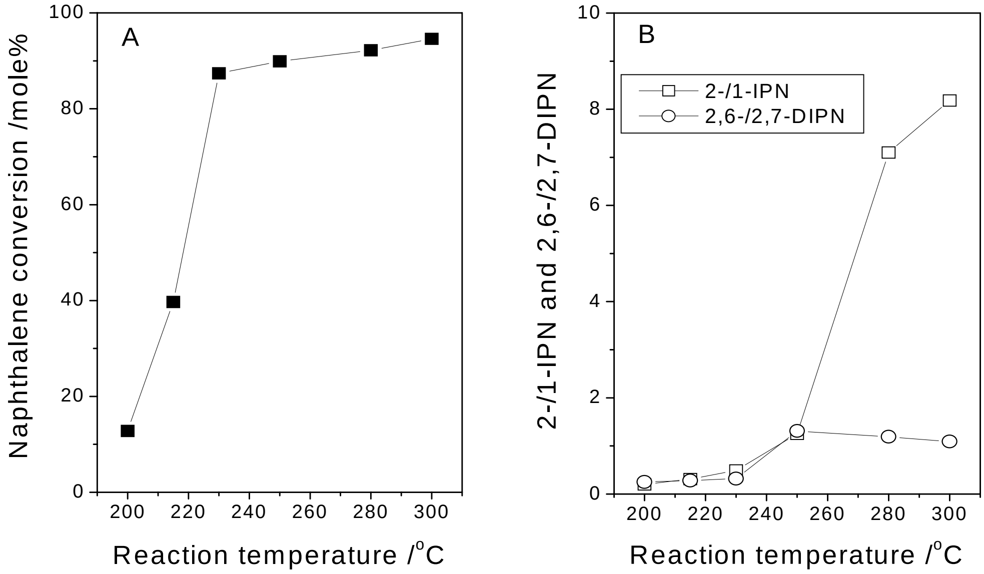

Fig. 2. Catalytic performance of USY as a function of reaction temperature.

Now that the high and stable activity, as well as the high 2,6-/2,7-DIPN ratio can be achieved over USY, the effect of reaction conditions is then performed on this catalyst.

Fig. 2 shows the activity and selectivity of USY as a function of the reaction temperature. It is observed in Fig. 2A that the conversion increases rapidly with the increase of temperature up to 230 ºC, and it is very high and goes up very slowly at high temperatures. 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 ºC. It is known that the formation of 1-IPN is dynamically favored and 2-IPN is more thermodynamically stable. At the high reaction temperature, isomerization of 1-IPN to 2-IPN should occur more drastically, resulting in a very high 2-/1-IPN ratio. Therefore, high ratio of 2-/1-IPN does not necessarily mean the shape selectivity of zeolite, although 2-IPN is slimmer than 1-IPN.

Fig. 3 illustrates the effect of weight hourly space velocity (WHSV) on the catalytic performance of USY. Fig. 3A indicates that the activity decreases very slowly when WHSV is less than 12.5 h^{-1}, and the decreasing rate quickens at the high WHSV. Since the alkylation reaction is a consecutive reaction, when WHSV becomes high, only a small amount of IPN have got enough reaction time to be further alkylated into DIPN and TIPN. This could account for the high selectivity of IPN at high WHSV in Fig. 3A. Regarding the activity and selectivity for DIPN, it is reasonable to choose the low WHSV for this reaction. Also, taking into account of the 2,6-/2,7-DIPN ratio according to Fig. 3B, a WHSV of less than 6 h^{-1} is more preferred to achieve a high 2,6-DIPN selectivity.

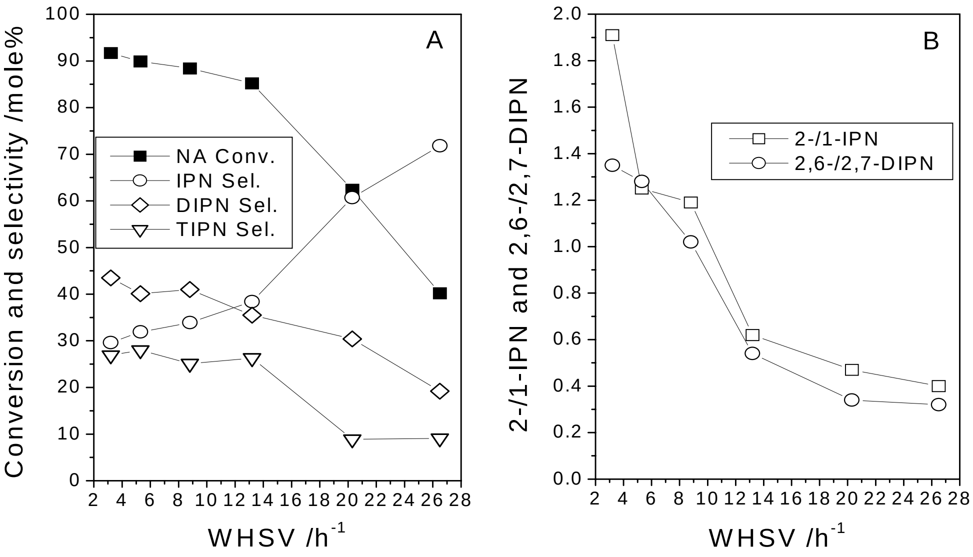

Fig. 3. Catalytic performance of USY as a function of WHSV.

Effect of reaction pressure and solvent are also evaluated on USY. At atmospheric reaction pressure, a conversion of 85% and a 2,6-/2,7-DIPN ratio of 1.02 are obtained, which is clearly lower than those observed at high reaction pressure. On the other hand, when the reaction is carried out with more diluent decalin concentration in liquid feed (molar ratio of naphthalene: isopropanol: decalin = 1: 2: 10), a higher activity (93.5%) and higher 2,6-/2,7-DIPN ratio (1.46) can be obtained than those obtained at typical reaction conditions. In addition to decalin, cyclohexane is also tried as a solvent for this reaction (molar ratio of naphthalene: isopropanol: cyclohexane = 1: 2: 10), and also high catalytic activity (92.9%) and high selectivity (2,6-/2,7-DIPN ratio = 1.50) can be achieved, however, partly decomposition of cyclohexane is observed. Thus decalin is thought to be a more suitable solvent here.

Based on the above measurements, the suitable reaction conditions for isopropylation of naphthalene on the USY catalyst in the high-pressure fixed bed reactor can be as follows: reaction temperature = 250 ºC, reaction pressure = 3.0 MPa, WHSV = 5.3 h^{-1} and molar ratio of naphthalene: isopropanol: decalin = 1: 2: 10. At this reaction conditions, the high and stable catalytic activity (93.5%) can be achieved, with DIPN dominating products, and with the selective produce of 2,6-DIPN (2,6-/2,7-DIPN =1.46).

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