Methylation of Naphthalene with Methanol over SAPO-11 Zeolite

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ABSTRACT: *Shape-selective methylation of naphthalene (NAPH) over SAPO-11 zeolite was carried out in a fixed-bed flow reactor under atmospheric pressure. Some zeolites, such as H-beta (Hβ), HUSY and ZSM-5 were also evaluated for comparison with SAPO-11 zeolite. The results showed that SAPO-11 exhibited higher stability, higher selectivity of 2,6-dimethylnaphthalene (2,6-DMN), and higher 2,6-/2,7-DMN ratio than Hβ, HUSY and ZSM-5. The improvement in catalytic performance of SAPO-11 is mainly attributed to the specific pore structure, weak acid strength and low acid amount on SAPO-11.*

KEY WORDS: *SAPO-11; Methylation; Naphthalene; Shape-selective*.

INTRODUCTION

2,6-Dimethylnaphthalene (2,6-DMN) is an important intermediate in the synthesis of polyethylene naphthalate (PEN). PEN is a new polyester which possesses superior properties, such as high tensile strength, heat resistance and gas barrier property as compared with polyethylene terephthalate (PET).

At present, 2,6-DMN is mainly produced by BP-Amoco through four-step reactions from o-xylene and butadiene. This process is an environmentally unfriendly and expensive process [1]. To reduce the cost of 2,6-DMN production, it is proposed a process of preparing 2,6-DMN by the methylation of naphthalene (NAPH) or 2-methylnaphthalene (2-MN) over zeolite, which is a simple and desirable synthetic route. However, the key role of the process is to find a zeolite with high selectivity of 2,6-DMN at acceptable conversion of NAPH or 2-MN to 2,6-DMN because the products of the methylation are very complicated.

Recently, the methylation of NAPH or 2-MN has been studied over various medium and large-pore zeolites. However, it is difficult for these zeolites to have both high catalytic activity and high selectivity of 2,6-DMN in the methylation of NAPH or 2-MN. For example, Fraenkel et al. [2] reported that medium pore zeolite ZSM-5 showed the high selectivity of 2,6+2,7-DMN and the low conversion of NAPH. They thought

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1021-9986/15/3/19 *6/$/2.60*

that the alkylation of NAPH over ZSM-5 is attributed to a 'half-cavities' effect occurred on the external surface which perfectly suit small-size NAPH molecules. However, the large pore zeolites (HY and H-mordenite(HM)) exhibited the low selectivity of 2,6+2,7-DMN and higher activity, which are wide enough to allow the products diffusion of molecules despite their acidic sites are easily accessible. *Park et al.* [3] reported that only 16% of the selectivity for 2,6+2,7-DMN could be achieved on medium pore zeolite MCM-22 at 1 h TOS. They concluded that the methylated NAPH products on MCM-22 must be directly generated on its external surface without shape selectivity due to its small pore channels. They also reported that dealuminated large pore zeolite HM substantially improved the conversion of 2-MN, the selectivity of 2,6-DMN and stability, which is ascribed to the acid amount of HM decreased and the mesopores created [4]. *Jin et al.* [5] reported that Zr/(Al)ZSM-5 can improve the selectivity of 2,6-DMN and stability of the catalyst. They attributed it to the weakening of the acid strength and enlargement of the pore dimensions from the partly incorporation of Zr in the framework instead of Al. In addition, *Yoo et al.* [6] reported that the high stability of medium pore zeolite ZSM-12 for the alkylation is a result of its pore structure. ZSM-12 possesses one dimensional non-interpenetrating channels which behave as “perfect tubes” and do not lead to the accumulation of coke precursors. Based on these reports, it is concluded that zeolites possess one dimensional non-interpenetrating channels with proper pore openings, weak acid strength and low acid amount, which maybe exhibit high catalytic activity and high selectivity of 2,6-DMN in the methylation of NAPH or 2-MN.

SAPO-11 is a one-dimensional pore zeolite with pore opening of 0.39 nm × 0.64nm [7], which are between the pore size of large-pore and medium-pore zeolites, making it an interesting material for catalytic cracking, reforming and alkylation [8-10]. *Komatsu et al.* [11] reported that the weak acid sites only catalyze alkylation while isomerization tends to occur on strong acid sites. According to this, the weak acid strength and low acid amount on SAPO-11 is possibly helpful to inhibit the isomerization of 2,6-DMN and improve the selectivity of 2,6-DMN in the methylation of NAPH or 2-MN. In addition, Similiar to ZSM-12, SAPO-11 also possesses one dimensional non-intersecting channels [12], which shows excellent resistance to deactivation by carbonaceous deposits. Therefore, SAPO-11 may be considered as the most promising candidate for the selective methylation of NAPH or 2-MN to 2,6-DMN. However, the selective methylation of NAPH or 2-MN with methanol over SAPO-11 has not been reported in the open literature so far.

The aim of the paper is to study the methylation of NAPH with methanol over SAPO-11. Moreover, Hβ, HUSY and ZSM-5 are also evaluated for comparison with SAPO-11.

EXPERIMENTAL SECTION

Catalyst Preparation

ZSM-5, Hβ and HUSY were obtained from the Catalyst Plant of Nankai University.

SAPO-11 was synthesized by hydrothermally crystallizing a sol-gel mixture with a composition of $1.0Al_2O_3$:$1.0P_2O_5$:$0.6SiO_2$:1.2template:$49H_2O$ [13]. Pseudoboehmite (30wt% Al_2O_3), orthophosphoric acid (85% H_3PO_4) and silica sol (30wt% SiO_2) were used as source of Al, P and Si. Di-n-propylamine was used as the template. The final crystallization temperature of 180-200 °C and crystallization time of 20-28 h were employed. The products were washed with distilled water, then dried at 120 °C for 5 h and calcined at 600 °C for 4 h.

Catalyst Characterization

X-Ray Powder Diffraction (XRD) analysis was performed on RigakuD/maxrB X-ray diffractometer. The morphology of the samples was examined by Hitachi S-4800 Scanning Electron Microscopy (SEM). The surface areas and Pore volume of the samples were measured by BET method using a Micromertitics ASAP-2000 sorptometer at liquid nitrogen temperature. The acidity was examined by temperature programmed desorption of pre-adsorbed ammonia (NH_3-TPD). The desorption of NH_3 was monitored on-line by a thermal conductivity detector.

Catalytic evaluation

Reactions were carried out under atmospheric pressure in a fixed-bed reactor. The Weight Hourly Space Velocity (WHSV) of NAPH was 0.19 h^{-1} in all experiments. Reactive temperature was 425°C and the liquid reactant including NAPH, methanol, mesitylene (solvent) in a molar ratio of 1:5:3.5 was preheated before

passing to the reactor. Reaction products are analyzed by gas chromatography (GC9560) with a Beta-Dex120 capillary column. The conversion of *NAPH* was calculated as follows:

$$\text{NAPH conv.}(\%) = \left(\frac{n_{N,0} - n_N}{n_{N,0}} \right) \times 100 \quad (1)$$

where $n_{N,0}$ and n_N are the molar percentage of *NAPH* before and after the reaction. The selectivity of 2,6-DMN is the corresponding molar percentage in the sum of all DMN isomers. 2,6-/2,7-DMN stands for the molar ratio of 2,6-DMN to 2,7-DMN. 2,6-DMN yield = (NAPH conversion×2,6-DMN distribution) /100%.

RESULTS AND DISCUSSION

Characterization of catalysts

XRD pattern of as-synthesized SAPO-11 sample is shown in Fig. 1. Compared with the literature [14], the pattern shows the presence of highly crystalline SAPO phases and no impurity phases are detected. It is a well-crystallized sphere-shaped material with a size of about 2-5μm as determined by our SEM studies (see Fig. 2).

The physicochemical properties of different zeolites are summarized in Table 1. For these zeolites, both Hβ and HUSY are all large pore zeolites. Hβ and HUSY have tridimensional structure, but in the case of HUSY large internal cavities (supercages) are formed at the channels intersections. Medium pore zeolite ZSM-5 has bidimensional structure. SAPO-11 has unidimensional structure with a pore size of 0.39 nm × 0.64nm, which are between the pore size of large pore zeolites (Hβ, HUSY) and medium pore zeolite (ZSM-5). As observed in Table 1, the surface area and the pore volume of SAPO-11 is considerably lower than that of the other three zeolites.

The acid amount and strength of different zeolites are determined by TPD of ammonia(see Fig. 3). From Fig. 3 we can see that the total amount is in the order of SAPO-11< Hβ< ZSM-5< HUSY and the strong acid strength is in the order of SAPO-11< Hβ< ZSM-5< HUSY.

Catalytic performance of the methylation of NAPH

Catalytic conversion and stability of four zeolites are compared in Fig. 4. As shown in Fig. 4, Hβ and HUSY show initially high conversion of NAPH and low stability. This is because some of the reactant molecules or the intermediates formed in the intrazeolitic cavity might block the pores and prevent the further diffusion

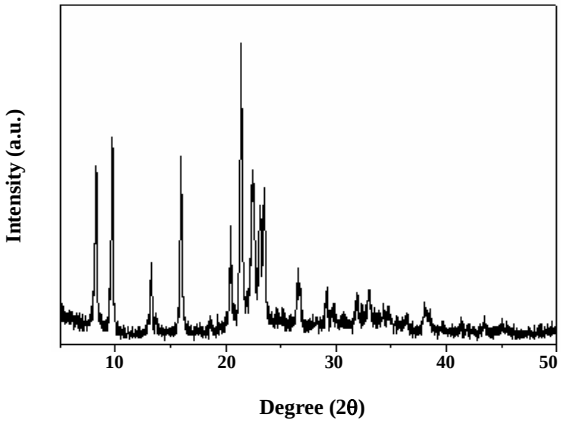

Fig. 1: XRD Pattern for SAPO-11 sample.

of the reactant molecules. ZSM-5 shows high stability, but its conversion of NAPH is rather low. It is reported that the external acidic sites of ZSM-5 are located in "half" channel intersection cavities residing in plane (001), these "half" cavities are characterized by larger-than-10-ring opening hence they can apparently "sieve" molecules up to 0.60nm [2]. The kinetic diameter of naphthalene molecule (0.62nm) and the critical size of the methylation products (at least 0.62 nm) are relatively large compared with the opening diameter of these "half" cavities, which increases them diffusion resistance in these "half" cavities and leads to lower conversion of *NAPH*.

Among these zeolites, SAPO-11 is found not only active but also high stable for the reaction. Indeed, the kinetic diameter of naphthalene molecule (0.62nm) and the critical size of the methylation products (at least 0.62 nm) are very close to the pore size of SAPO-11 (0.39 nm×0.64 nm) [15]. Thus, SAPO-11 possesses suitable pore opening (0.39 nm×0.64 nm) which are between the pore size of large-pore (Hβ and HUSY) and medium-pore (ZSM-5) zeolites, making it more favorable to the diffusion of reactants and productions. The high stability of SAPO-11 is ascribed to its weak acid strength and low acid amount (see Fig. 3) and its one-dimensional non-interpenetrating channels, which could slow down deactivation caused by coking.

The selectivity of 2,6-DMN and the 2,6-/2,7-DMN ratio on different zeolites are shown in Fig.5. Fig.5a shows that SAPO-11 exhibits higher selectivity of 2,6-DMN than that of other zeolites. The 2,6-/2,7-DMN ratio is very important in the purification of 2,6-DMN. When the 2,6-/2,7-DMN is more than 1.4, 2,6-DMN can be

Table 1: Physicochemical properties of different zeolites

Zeolites	Topology	Channel structure	Pore opening /nm	Si/Al[a]	Surface area /(m^2/g)	Pore volume /(cm^3/g)
SAPO-11	AEL	Unidimension	0.39×0.64(001)		140	0.145
Hβ	BEA	Tridimension	0.66×0.77(100)(010) 0.56×0.56(001)	40	530	0.310
HUSY	FAU	Tridimension with supercages	0.74×0.74(111)	6.2	568	0.322
ZSM-5	MFI	Bidimension with large intersection	0.51×0.54 (100) 0.54×0.56 (010)	25	340	0.185

[a] *Si:Al:P molar ratios of SAPO-11 is 0.03:0.25:0.22.*

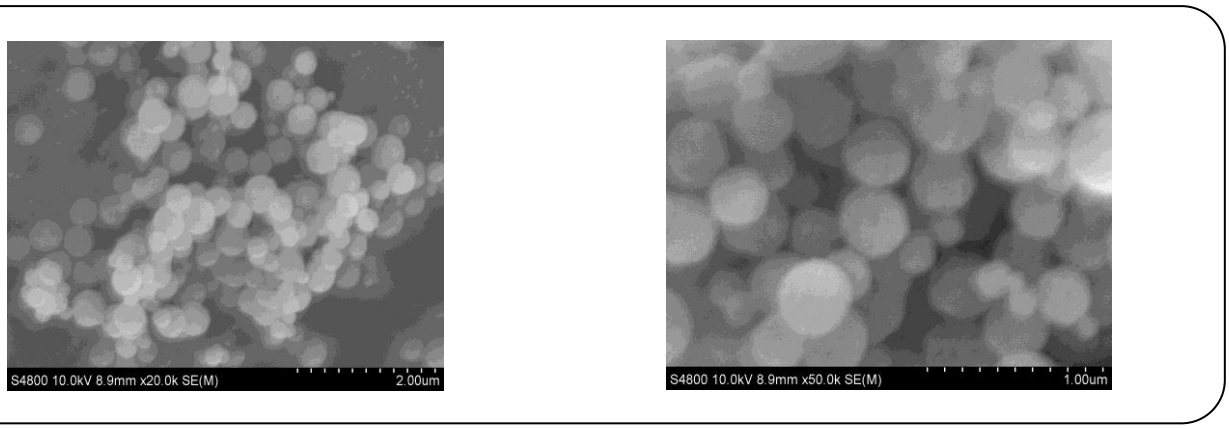

Fig.2: SEM images of SAPO-11 sample.

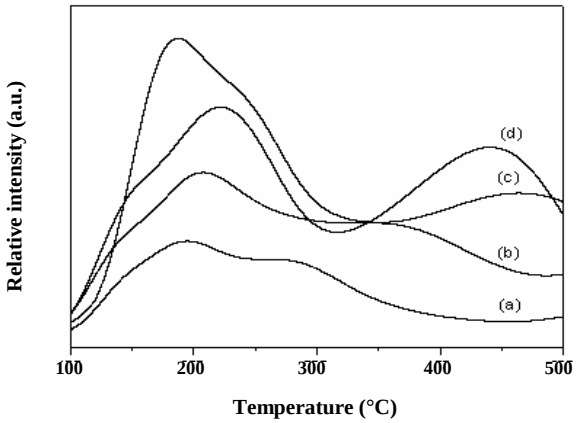

Fig.3: NH_3-TPD profiles of samples SAPO-11 (a), Hβ (b), HUSY (c), HZSM-5 (d).

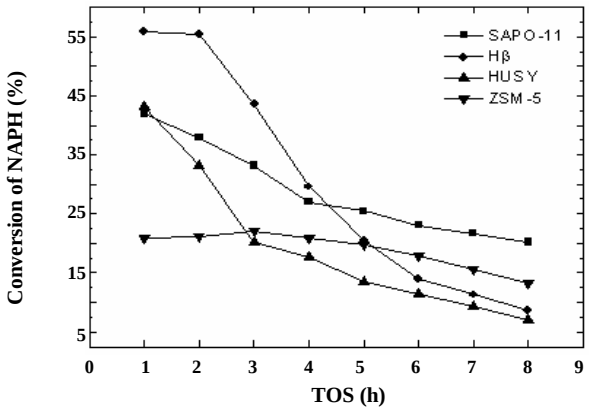

Fig.4: The conversion of NAPH on different zeolites.

more easily separated form the eutectic mixture [16]. From Fig.5b, we can see that on the SAPO-11, the ratio of 2,6-/2,7-DMN is always the highest and significantly higher than the thermodynamic of 1.0. On other zeolites, the ratio of 2,6-/2,7-DMN is near the thermodynamic value.

It is thought that the high the selectivity of 2,6-DMN and the 2,6-/2,7-DMN ratio on SAPO-11 are mainly attributed to two aspects: the acid properties and the pore structure. According to the frontier molecular orbital theory, in the case of electrophilic substitution reactions such as the alkylation studied here, the electron density in the Highest Occupied Molecular Orbital (HOMO) is a measure of the reactivity at a specific position. For 2-MN, the electron density at C-6 is significantly higher than that at C-7, which indicates a higher reactivity

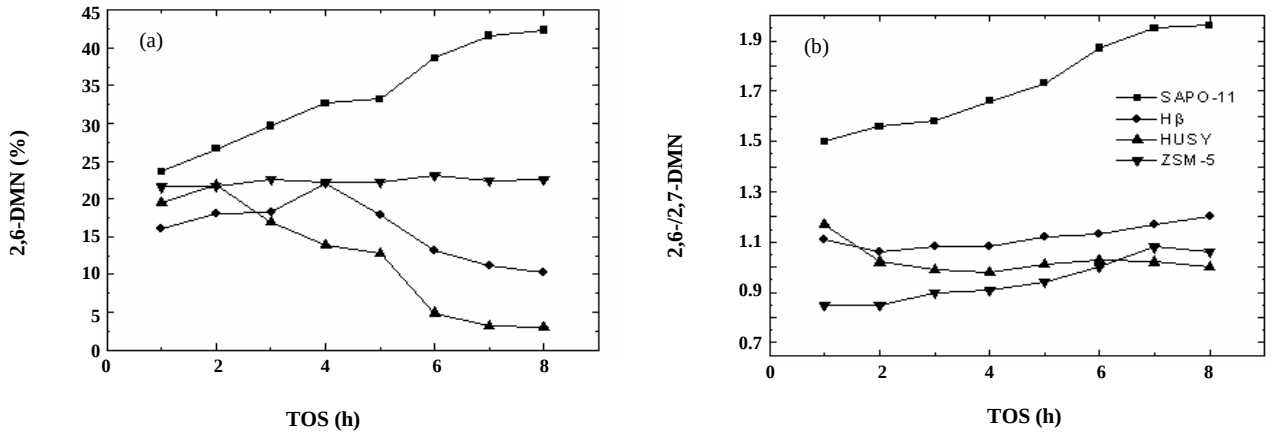

Fig. 5: Selectivity of 2,6-DMN (a), the ratio of 2,6- to 2,7-DMN (b) on different zeolites.

of the C-6 position than the C-7 position [17]. Therefore, weaker acid sites on SAPO-11 prefer to produce 2,6-DMN than 2,7-DMN (see Fig. 3 and Table 2). *Fang et al.* have calculated that 2,6-DMN is somewhat larger than 2,7-DMN in molecular dimension [18]. Therefore, 2,6-DMN suffers more diffusion resistance than 2,7-DMN does during the diffusion process. The pore opening of Hβ and HUSY, with a nominal pore opening of 0.77 and 0.74 nm, respectively, should not be selective in the methylation of NAPH. Because the channels of Hβ and HUSY are wide enough to allow the products diffusion of molecules. 2,6-DMN suffers more diffusion resistance in the relatively narrow pore channels of ZSM-5. It is seen that SAPO-11 possesses suitable pore opening (0.39 nm ×0.64nm), which is helpful to the diffusion of 2,6-DMN. Therefore, the high selectivity of 2,6-DMN and the 2,6-/2,7-DMN ratio on SAPO-11 is ascribed to its specific pore structure, weak acid strength and low acid amount.

CONCLUSIONS

In summary, the catalytic activity and stability for the methylation of NAPH do not simply have relation with the catalyst acid number and strength, but have relation with the catalyst pore structure. Based on the comparison of catalytic results, SAPO-11 exhibits higher stability, higher selectivity of 2,6-DMN, and higher 2,6-/2,7-DMN ratio than Hβ, HUSY and ZSM-5. Relation of the catalytic performances with pore structures and acidities of zeolite are discussed, the improvement in catalytic performance on SAPO-11 is mainly attributed to its specific pore structure, weak acid strength and low acid amount.

Received : Oct. 31, 2014 ; Accepted : Apr. 13, 2015

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