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Vapor phase ethylation of naphthalene with ethanol over molecular sieve catalysts

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Abstract

Ethylation of naphthalene was carried out in the vapor phase over various molecular sieve catalysts. Among the catalysts tested, CeMgY (5 wt.% Ce, 3 wt.% Mg) gave the highest yield of mono and diethylnaphthalenes at a reaction temperature of 250°C and a space velocity of 0.5 h^{-1}. A correlation between acidity of the catalyst and the ethylation activity was obtained. Ethylation of naphthalene was favorable on Brönsted acidic centers. The HY catalyst was modified with rare earth metal cations such as cerium to enhance activity for alkylation and Mg^{+2} to optimize the acidity of the catalyst. Alkaline earth metal ions, also help in reducing the formation of coke. The catalysts were characterized by XRD, stepwise temperature programed desorption (STPD) of ammonia, TGA, and nitrogen adsorption to measure the surface areas. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ethylation; Brönsted acidity; Lewis acidity; Naphthalenze; Ethylnaphthalene

1. Introduction

Alkylnaphthalenes are important monomers for the production of advanced polymer materials [1,2]. Vitamin A can be prepared via 2-methylnaphthalene as an intermediate and naphthalene-2,6-dicarboxylic acid (2,6-NDCA) is prepared via 2,6-dialkylnaphthalene. Naphthalene-2,6-dicarboxylic acid is used in making speciality polyesters, liquid crystal polymers and 2,6-dihydroxynaphthalene. Naphthalene-2,6-dihydroxide is used in the preparation of speciality polymers and is also an oxidation product of 2,6-dialkylaromatics [3–10]. The use of heterogeneous catalysts particularly zeolites for the preparation of dialkyl aromatics has received great attention [11–16]. In the alkylation of naphthalene with conventional Friedel–Crafts catalysts, it is very difficult to obtain good yields of dialkylated products selectively, since tri and tetra substitution occur very rapidly. Due to their uniform pore structure, the presence of active centers and their high thermal stability, zeolites are useful catalysts for alkylation reactions. Moreover, catalytic synthesis of alkylnaphthalenes using molecular sieve catalysts has become a prominent route, considering the

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increasing demand for ecofriendly routes in the chemical industry.

Very little work has been done to synthesize diethylnaphthalene using zeolites. Diethylnaphthalene (2,6-DEN) is a more preferable raw material than 2,6-diisopropylnaphthalene (2,6-DIPN) to synthesize 2,6-naphthalenedicarboxylic acid (2,6-NDCA), because 2,6-DEN results in a high yield [17,18]. An attempt has been made to correlate the acidity of the catalysts employed for this reaction and their alkylation activity.

2. Experimental

HY ($Si/Al = 30$) catalyst was obtained from PQ corporation, USA. MCM-41 and silicoaluminophosphate-5 (SAPO-5) catalysts were prepared in our laboratory. In a typical synthesis of MCM-41, 0.76 g of aluminum isopropoxide (Fluka), 0.3 g of sodium hydroxide (Loba) was placed in a 100 ml glass beaker, to which 20 ml of doubly distilled water was added, and then thoroughly stirred under heating, until a clear solution was obtained. Then, this solution was cooled to room temperature followed by the dropwise addition of 9.26 g of tetraethylammonium hydroxide (Fluka). The resultant mixture was stirred with a magnetic stirrer for 2 h. In a separate beaker 9.26 g of Ludox silica (Aldrich) was added to 30 ml of doubly distilled water and strirred until a uniform mixture was obtained. To this solution, the mixture of sodium aluminate was added dropwise. The resultant mixture was stirred for 3 h and combined with 10.55 g of cetyltrimethylammonium bromide (Fluka). After stirring for 1 h, the pH of the resulting gel was adjusted to 12 using dilute ammonia solution, and loaded in an autoclave and heated at a temperature of 100°C for 24 h. The autoclave was cooled and the resulting MCM-41 was filtered and thoroughly washed with warm double distilled water. This catalyst was dried and calcined at 550°C overnight in the presence of air. The ramp rate was $10°C\,min^{-1}$.

The SAPO-5 was prepared using the following procedure. In a 250 ml beaker 20.4 g of aluminum-isopropoxide was added to 40 ml of double distilled water and the resulting mixture was stirred for 2 h. Then, 9.8 g of phosphoric acid was added dropwise to this solution. This mixture was combined with 28.7 g of tetrapropylammonium bromide and then stirred for 2 h. To the resulting gel, 2.4 g of Ludox silica was added and stirred thoroughly and the pH was adjusted to 6.8. This reaction gel was autoclaved and heated at 200°C for 24 h. The resulting reaction mixture was cooled and washed with double distilled water. Then the catalyst was filtered, dried and calcined at 500°C overnight.

The materials were characterized by Brunner, Emmett and Teller (BET) surface area, XRD and stepwise temperature programed desorption (STPD) of ammonia. The XRD patterns were taken using a Phillips 1051 X-ray diffractometer using a Ni-filtered CuK_α radiation ($\lambda = 1.5406$ Å). The STPD of ammonia was carried out on a Micromeritics pulse Chemisorb 2700 instrument. Before starting the analysis, the instrument was calibrated using different standard loops (0.984, 0.509, 0.190 and 0.097 cm^3) for sending the ammonia pulses. The empty sample tube was maintained at 80°C. A known volume of ammonia corresponding to the loop used was flushed with helium through the empty sample tube. The volume of ammonia was detected by a thermal conductivity detector (TCD) and it was displayed using a digital counter on the instrument [19]. A number of pulses of ammonia (usually four) were flushed through the empty sample tube to get a constant reading. A powdered sample of the catalyst was taken in the U shaped quartz sample tube. It was pre-treated in flowing helium for 2 h at 400°C. The sample temperature was brought down to 150°C. Using the loop (0.984 cm^3) saturated with ammonia, several pulses were flushed through the sample tube. The sample was thus saturated with ammonia (usually pulses of a 1 min duration were given). The saturation of sample with ammonia was known from a constant reading on the digital counter. After saturation, the sample was flushed with helium. The temperature of the sample was then raised to 250°C and the reading over the digital counter was noted down. Similarly, at 350°C and 450°C, the readings were noted.

Surface areas of all these catalysts were also calculated using nitrogen monolayer adsorption at liquid nitrogen temperature. The catalysts were also characterized by the TGA analysis. The modified catalysts were prepared using the corresponding metal nitrate (Ce, La, Mg) salts by a wet impregnation method. The detailed procedure of the wet impregnation method was given elsewhere [20]. In the case of doubly modified catalysts, metal ions were impregnated one after the other. Once the catalysts were modified using the corresponding metal nitrate salts, they were washed using doubly distilled water then dried and calcined at 400°C.

The vapor phase ethylation reaction was carried out in a fixed bed, tubular, down flow, Pyrex reactor of 20 mm internal diameter. The catalyst used was in the form of sieved powder (18 × 30 mesh size). The reaction mixture of naphthalene, ethanol and solvent was introduced into the reactor from the top using a syringe pump (Braun, USA). The product samples were collected at the

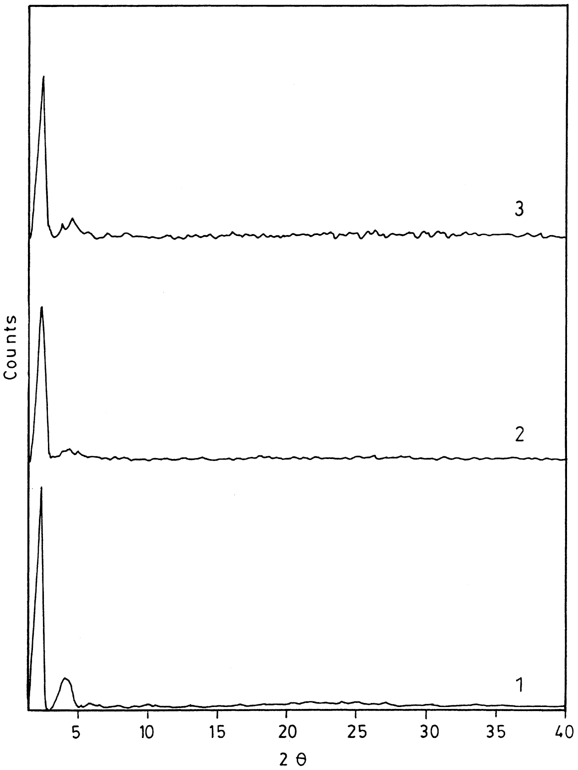

Fig. 1. XRD pattern of MCM-41 and modified MCM-41 catalysts calcined at 540°C temperature (1) HMCM-41, (2) Ce-MCM-41, (3) LaMCM-41.

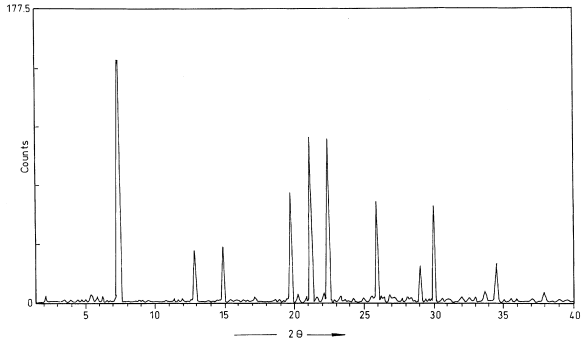

Fig. 2. XRD pattern of SAPO-5 calcined at 500°C temperature.

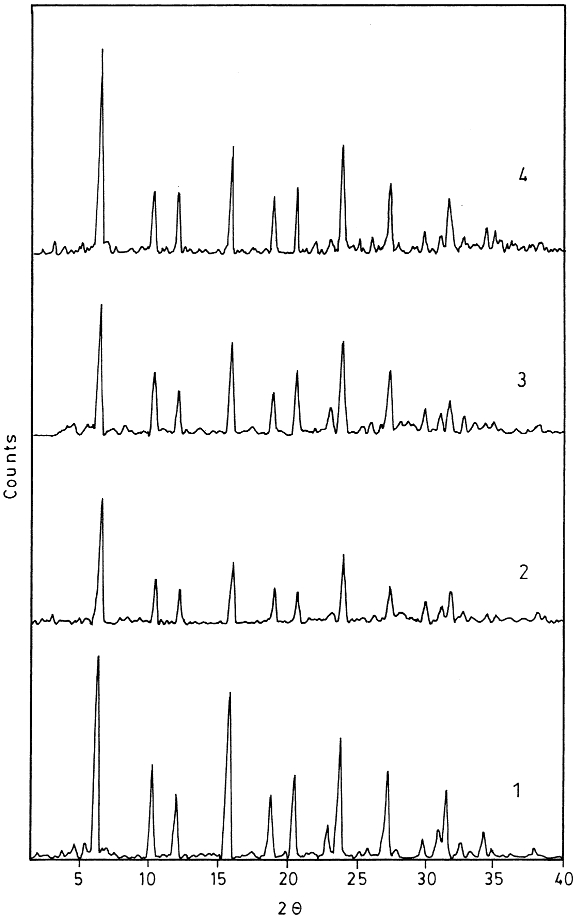

Fig. 3. XRD pattern of Y and modified Y catalysts. (1) HY, (2) CeHY, (3) LaHY, (4) CeMgY.

Table 1
Ethylation of naphthalene: variation of catalyst

S. no.	Catalyst	TOS (h)	Conversion (%)	Liquid product selectivity (%)				Total acidity mmol g^{-1} (0.01)	Surface area (m^2 g^{-1})
				$\sum$MEN	$\sum$DEN	$\sum$TEN	Others		
(1)	HY	3	43.0	46.2	36.0	7.5	10.3	67.49	593.2
		4	29.1	65.9	22.1	7.3	4.6		
(2)	CeHY(5 wt.% Ce)	1	69.2	53.1	29.4	8.3	8.8	88.80	462.2
		4	56.0	48.8	30.8	13.0	7.4		
(3)	LaHY(5 wt.% La)	4	59.8	48.7	33.0	14.5	3.8	72.12	441.2
(4)	CeMgY(5 wt.% Ce, 3 wt.% Mg)	1	73.6	49.7	40.3	6.8	3.2	85.35	480.0
		4	57.2	49.7	31.3	13.9	5.0		
(5)	LaMgY(5 wt.% La, 3 wt.% Mg)	4	72.6	40.1	30.1	14.6	15.2	70.32	448.7
(6)	CeKY(5 wt.% Ce, 3 wt.% K)	1	70.4	43.7	31.7	15.5	9.1	72.0	456.7
		4	37.2	60.0	20.5	7.0	12.5		
(7)	LaKY(5 wt.% La, 3 wt.% K)	4	58.7	44.2	26.1	19.5	10.2	71.24	449.4
(8)	HMCM-41	4	26.2	71.1	22.6	4.2	2.1	56.51	939.3
(9)	CeMCM-41(5 wt.% Ce)	4	26.8	68.9	21.0	8.4	1.7	62.18	765.2
(10)	LaMCM-41(5 wt.% La)	2	14.3	72.5	14.5	12.9	0.1	56.28	735.9
		4	10.4	81.1	15.0	–	3.9		
(11)	SAPO-5	2	31.0	72.2	17.6	6.0	4.2	54.40	188.9
		4	21.8	76.2	17.7	2.5	3.6		

Reaction temperature: 250°C, WHSV: 0.5 h^{-1}, feed composition: naphthalene (3g) + ethanol (7.0 g) (1:5 molar ratio), solvent benzene, catalyst weight: 4 g, $\sum$MEN; sum total of (1-, 2-)monoethylatednaphthalenes, $\sum$DEN; sum total of (2,6-, 2,7-)diethylatednaphthalenes, $\sum$TEN; sum total of triethylatednaphthalenes, others; polyethylatednaphthalenes.

bottom of the reactor using cold water traps and were analyzed by Gas Chromatograph (Chemito) equipped with a 2 m long 10% SE-30 column and an FID. The products were confirmed by GC–mass analysis using VG Auto Spec mass spectrometer equipped with a gas chromatogram. The mass balance was greater than 90%.

3. Results and discussion

The XRD patterns of MCM-41 calcined at 550°C, LaMCM-41 and CeMCM-41 are given in Fig. 1. The XRD spectra of SAPO-5 calcined at 500°C is given in Fig. 2. The XRD pattern of SAPO-5 is highly crystalline and its pattern is in accordance with the spectra reported in the literature [21,22]. The XRD patterns of Y and modified Y catalysts are given in Fig. 3. The catalysts are highly crystalline after modification. The enhanced thermal stability of La and Ce modified Y catalysts was discussed earlier by Lemos et al. [23].

The vapor phase ethylation reaction was carried out over various catalysts such as HY, CeHY, LaHY, CeMgY, LaMgY, CeKY, LaKY, HMCM-41, CeMCM-41, LaMCM-41 and SAPO-5. All the reaction conditions and results are given in Table 1. The reaction was also carried out over the CeMgY catalyst at various reaction temperatures, weight hourly space velocity (WHSV), feed compositions and with time on stream. The results of the STPD of ammonia reveals the strength of the acid sites over various temperature regions. The desorption of ammonia in various temperature regions is indicative of the acidic strength [19] (weak, medium and strong). The total acidity is represented by acid sites due to desorption of ammonia in temperature ranges of 150–250°C, 250–350°C and 350–450°C. The STPD results are presented in Fig. 4. The order of total acidity was observed as follows: CeHY > CeMgY > LaHY > HY > CeMCM-41 > LaMCM-41 > HMCM-41 > SAPO-5. Gauthier et al. reported [25] earlier that, as the activation temperature was increased, Brönsted acidic centers may get converted into Lewis acidic centers after dealumination. The surface areas of MCM-41 and modified MCM-41 catalysts indicate the mesoporous nature of these materials. The modified catalysts have less surface areas compared to the unmodified catalysts due to the impregnation of the metal ion. The modified catalysts were also crystalline in nature.

The HY and MCM-41 catalysts were initially modified with rare earth metal ion Ce^{+3} or La^{+3} in order to increase the alkylation activity and thermal stability of the catalyst [3,4]. The catalysts were further modified by Mg^{+2} to optimize the acidity and to decrease coke formation [3]. CeMgY was found to be the better catalyst among the catalysts tested in this work, for this reaction with a naphthalene conversion of 73.6 wt.% and the selectivity towards monoethyl naphthalene (MEN), diethyl naphthalene (DEN) and triethyl

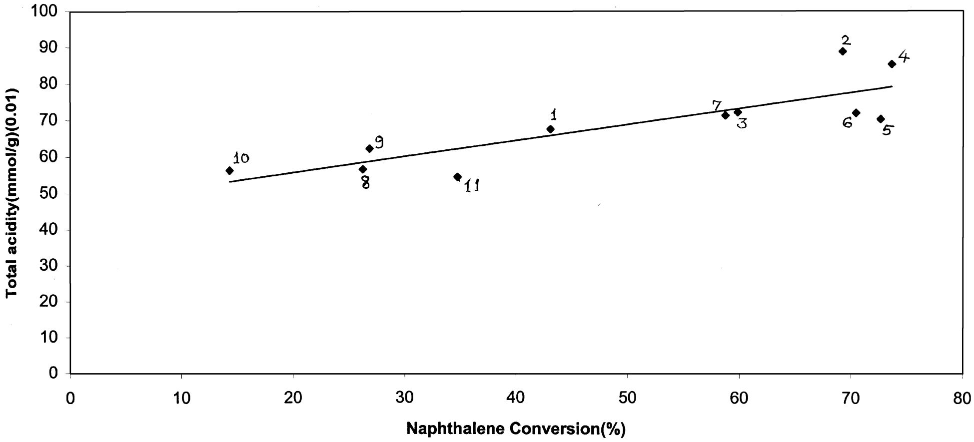

Fig. 4. Ethylation activity and acidity correlation (scatter plot). (1) HY, (2) CeHY, (3) LaHY, (4) CeMgHY, (5)LaMgHY, (6) CeKY, (7) LaKY, (8) HMCM-41, (9)CeMCM-41, (10) LaMCM-41, (11) SAPO-5.

naphthalene (TEN) was 49.7%, 40.3% and 6.8%, respectively.

Vapor phase ethylation of naphthalene over CeMgY was carried out at various reaction temperatures and the results are presented in Table 2. At 250°C after 1 h on stream, the naphthalene conversion was 73.6% and the selectivity towards MEN was 49.7%. This observation also indicates that Brönsted acidic centers are responsible for the formation of the carbocation which is required for this reaction. At higher reaction temperatures (see Table 2), the selectivity of MENs was higher compared to DEN which is due to the dealkylation of the DEN at a higher reaction temperature [24]. The dealkylation was also observed in the case of mono and binuclear aromatic alkylation reactions.

Ethylation of naphthalene was carried out at 0.25–1.25 h^{-1} WHSV over the CeMgY catalyst at 250°C. The best WHSV value for this reaction was 0.5 h^{-1}. The results of the variation of WHSV are presented in Table 3. As the WHSV is increased, the conversion of naphthalene was decreased. This may be due to the deactivation of the catalyst by the coking.

The vapor phase ethylation of naphthalene was carried out using various molar ratios of naphthalene to ethanol in the feed composition. The results of these reactions are given in Table 4. As

Table 2
Ethylation of naphthalene: variation of reaction temperature

S. no.	Reaction temperature (°C)	TOS (h)	Conversion (wt.%)	Liquid product selectivity (%)			
				$\sum$MEN	$\sum$DEN	$\sum$TEN	Others
(1)	200	4	53.3	73.0	21.1	4.5	1.4
(2)	250	1	73.6	49.7	40.3	6.8	3.2
		4	57.2	49.7	31.3	13.9	5.1
(3)	300	1	67.3	62.4	21.2	3.6	12.8
		4	54.0	53.6	27.8	11.9	6.7
(4)	350	4	45.2	53.5	28.1	13.0	5.4
(5)	400	2	37.6	52.6	30.2	14.4	2.8
		4	11.6	79.5	18.1	–	2.4

Catalyst: CeMgY(3.86 wt.% Ce, 1.81 wt.% Mg) (4 g), WHSV: 0.5 h^{-1}, feed composition: naphthalene (3g) + ethanol (7.0 g) (1:5 molar ratio), $\sum$MEN; sum total of (1-, 2-)monoethylatednaphthalenes, $\sum$DEN; sum total of (2,6-, 2,7-)diethylatednaphthalenes, $\sum$TEN; sum total of triethylatednaphthalenes, others; polyethylatednaphthalenes.

Table 3
Ethylation of naphthalene: variation of WHSV

S. no.	WHSV (h^{-1})	TOS (h)	Conversion (wt.%)	Liquid product selectivity (%)			
				$\sum$MEN	$\sum$DEN	$\sum$TEN	Others
(1)	0.25	3	62.4	47.1	32.7	11.1	9.1
		4	64.9	45.7	30.9	13.7	9.7
(2)	0.50	1	73.6	49.7	40.3	6.8	3.2
		4	57.2	49.7	31.3	13.9	5.1
(3)	0.75	2	58.0	50.8	30.2	13.5	5.5
		4	50.0	55.4	27.3	14.0	3.3
(4)	1.00	3	41.9	56.7	25.6	11.5	6.2
		4	25.9	70.0	20.0	5.6	4.4
(5)	1.25	2	37.9	52.5	29.6	9.6	8.3
		4	41.2	58.0	26.4	11.0	4.6

Catalyst: CeMgY(3.86 wt.% Ce, 1.81 wt.% Mg) (4 g), reaction temperature: 250°C, feed composition: naphthalene (3g) + ethanol (7.0 g) (1:5 molar ratio), $\sum$MEN; sum total of (1-, 2-)monoethylatednaphthalenes, $\sum$DEN; sum total of (2,6-, 2,7-)diethylatednaphthalenes, $\sum$TEN; sum total of triethylatednaphthalenes, others; polyethylatednaphthalenes.

Table 4
Ethylation of naphthalene: variation of molar ratio of feed

S. no.	Feed molar ratio (naphthalene:EtOH)	TOS (h)	Conversion (wt.%)	Liquid product selectivity (%)			
				$\sum$MEN	$\sum$DEN	$\sum$TEN	Others
(1)	1:5	1	73.6	49.7	40.3	6.8	3.2
		4	57.2	49.7	31.3	13.9	5.1
(2)	1:6	2	72.6	38.0	32.8	14.8	14.4
		4	62.3	41.3	30.3	15.5	12.9
(3)	1:7	2	70.9	41.9	35.0	13.3	9.8
		4	71.2	39.0	31.2	18.1	11.7
(4)	1:8	2	74.3	39.2	34.1	18.9	7.8
		4	68.5	42.1	32.5	19.3	6.1
(5)	1:9	2	69.4	38.9	29.4	18.7	13.0
		4	71.0	35.9	32.7	25.4	6.0

Catalyst: CeMgY(3.86 wt.% Ce, 1.81 wt.% Mg) (4 g), reaction temperature: 250°C, $\sum$MEN; sum total of (1-, 2-)monoethylatednaphthalenes, $\sum$DEN; sum total of (2,6-, 2,7-)diethylatednaphthalenes, $\sum$TEN; sum total of triethylatednaphthalenes, others; polyethylatednaphthalenes.

the amount of ethanol in the feed composition was increased, the conversion of naphthalene was decreased due to the formation of the polyethylated compounds, which resulted in the formation of coke, but at fourth hour time on stream the conversion is increased, despite the deactivation of the catalyst by coking during the initial hours. This is due to the development of a new reaction process involving trans-alkylation between polyethylatednaphthalenes which were entrapped in pores and naphthalenes followed by the former compounds [25,26]. Time on stream experiment was also carried out for this reaction over CeMgY at a reaction temperature of 250°C, 0.5 h^{-1} WHSV and 1:5 molar ratio of naphthalene to ethanol for 6 h. As the reaction time is increased, activity of the

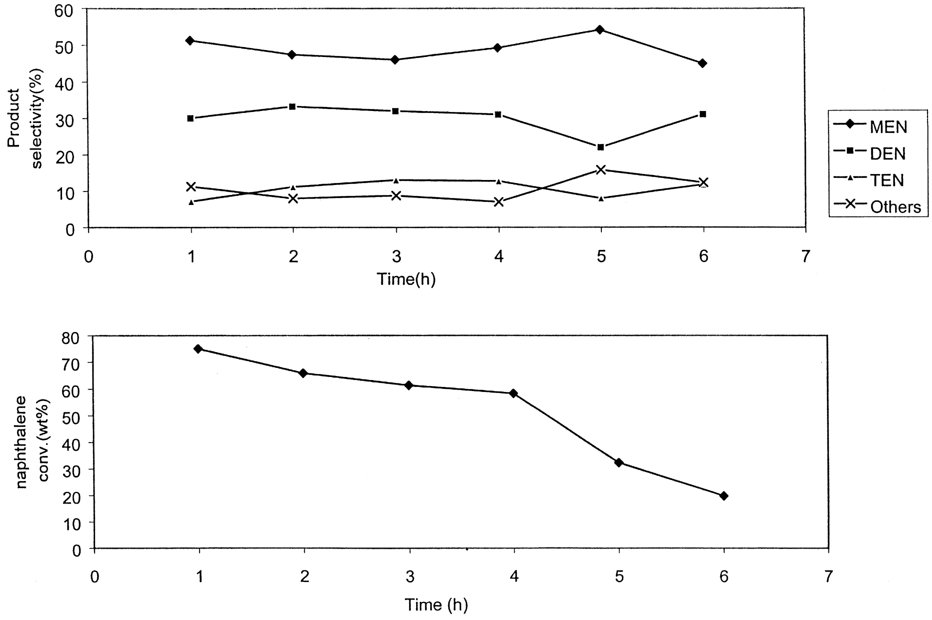

Fig. 5. TOS graph (scatter plot for 6 h).

catalyst was decreased resulting in a decrease in the conversion of naphthalene. The time on stream results are shown in Fig. 5.

4. Conclusions

From this study, the following conclusions can be made. Among the catalysts tested for this reaction, CeMgY was found to be the best catalyst for the selectivity of DEN at a reaction temperature of 250°C and 0.5 h^{-1} WHSV. Weak, medium strength Brönsted acidic centers were required for the ethylation of naphthalene in the vapor phase. The HY catalyst was modified with a rare earth metal cation either with Ce^{+3} or La^{+3} to increase alkylation activity and thermal stability. Further modification with alkaline earth metal cation optimizes the acidity to reduce the coking.

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