Isopropylation of naphthalene over modified HMCM-41, HY and SAPO-5 catalysts [1]

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Abstract

The alkylation of naphthalene with isopropanol was carried out over modified MCM-41, HY and SAPO-5 catalysts. The catalysts were characterized by XRD, IR, sorption techniques and temperature programmed desorption of ammonia. The yields of 2-isopropylnaphthalene were 32.1, 47.2 and 52.6 wt.% at 74.7, 55.9 and 81.0% conversion over HMCM-41, CeMCM-41 and LaKY, respectively. The yields of 2,6-diisopropyl naphthalene were in the range of 8 to 35.3%. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Molecular sieves are widely used in the synthesis of speciality and fine chemicals [1–14]. Zeolites are used in the alkylation reactions due to their activity, selectivity, thermal stability, and reusability and eco-friendly nature. We have carried out alkylation of naphthalene with methanol over modified zeolites [14]. The yields of 2-methylnaphthalene and 2,6-dimethylnaphthalene were 42.7, 26.4 wt.% at 73.9% conversion over HY zeolite [14]. The dialkyl or diisopropylnaphthalene is useful in the synthesis of high temperature resistant polymers, liquid crystal polymers, and speciality polyesters. The iso-propylation of naphthalene over unmodified zeolites has been reported in the literature [15–22]. So far, there are very few reports for the alkylation of naphthalene over MCM-41, silicoaluminophosphate (SAPO) and Y molecular sieves. In this paper, we report the isopropylation of naphthalene over modified Y, MCM-41 and silicoaluminophosphate (SAPO-5) molecular sieves.

2. Experimental

MCM-41 and SAPO-5 were prepared in our laboratory as per the literature procedure [23,24]. HY (Si/Al = 2.5) catalyst was obtained from the PQ, USA. All the catalysts were modified using metal nitrate salts by wet impregnation method. In a 100-ml beaker, required amount of

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Table 1
Surface area and pore volume results of the various catalysts

Sl. no.	Catalyst	Pore volume (cm^3/g)	BET surface area (m^2/g)
1	HMCM-41	0.64	684
2	LaMCM-41 (5 wt.% La)	0.63	540
3	CeMCM-41 (5 wt.% Ce)	0.62	563
4	HY	0.30	419
5	LaKY (5 wt.% La, 3 wt.% K)	0.29	313
6	LaHY (5 wt.% La)	0.21	268
7	SAPO-5	0.27	127

corresponding metal nitrate salt was taken (La/Ce) (e.g., for 5 wt.% of lanthanum, 0.62 g of lanthanum nitrate was taken) and 30 ml of doubly distilled water was added and stirred to get uniform solution. To this solution, 4 g of meshed catalyst was added and stirred thoroughly at 30°C for 3 h. Then the catalyst was dried in an oven and calcined for 4 h at 400°C.

The similar procedure was repeated for stepwise promoted catalysts. Each ion was impregnated one after the other. Lanthanum/cerium was impregnated first followed by the modification with potassium.

All the catalysts were characterized by XRD and sorption techniques. The catalysts were crystalline before and after the reactions. The surface area and pore volume were estimated using a Sorptomatic 1900 (Carlo-Erba Instrument, Italy) unit. For ammonia, uptake is esti-

mated as equivalent of pulses of size 0.5 ml introduced over 0.1 g catalyst at 125°C after activation of catalyst in the flowing helium (30 ml/min) at 540°C for 1 h. After attainment saturation of ammonia uptake, the TPD was recorded at a heating rate of 10°C/min from 125 to 550°C. The chart speed was 0.2 cm/min. Helium flow was maintained at 30 ml/min.

The reactions were carried out in a fixed bed, tubular, down flow Pyrex reactor with 20 mm internal diameter. The amount of catalyst was 4 g with 18×30-mesh size. The reaction mixture of naphthalene and isopropanol (1:5 molar ratio) with required amount of benzene as solvent was fed using a calibrated syringe pump (SAGE Instruments, USA). The products were ice cooled and collected at the bottom at regular intervals of an hour using the required number of ice cooled traps. The products were analyzed

Table 2
Ammonia uptake of various catalysts

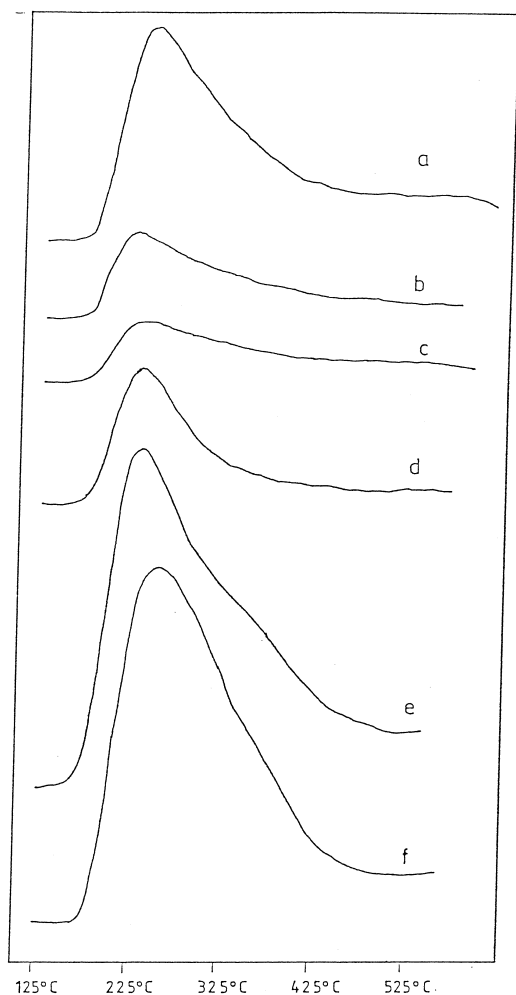| Sl. no.	Catalyst	Ammonia uptake (ml NH_3/0.1 g catalyst)	Acidity (meq of NH_3/g of catalyst)	Acidity (mmol/g of catalyst)
1	HMCM-41	0.37	3.7	0.16
2	LaMCM-41 (5 wt.% La)	0.51	5.1	0.23
3	CeMCM-41 (5 wt.% Ce)	0.53	5.3	0.24
4	HY	1.5	15.0	0.59
5	LaHY (5 wt.% La)	2.0	20.0	0.89
6	LaKY (5 wt.% La, 3 wt.% K)	0.84	8.4	0.38
7	SAPO-5	0.89	8.9	0.40

Fig. 1. Temperature programmed desorption of ammonia sorbed on (a) HMCM-41, (b) LaMCM-41, (c) CeMCM-41, (d) LaKY, (e) LaHY and (f) SAPO-5.

by gas chromatography using 20% SE-30 column of 2 m length fitted with FID. The analysis

was confirmed by GC–MS and NMR techniques.

3. Results and discussion

The catalysts were characterized by sorption studies. The surface area and pore volume of various catalysts is given in Table 1. In case of MCM-41, the surface area was decreased due to the presence of lanthanum ions which are present inside the pores. Similarly for Y zeolites surface area varied depending on pore volume occupied by the cations, cation distribution and the presence of mesopores, amorphous material. The ammonia uptake of the various modified molecular sieves is given in Table 2. The trend in total acidity at 125°C was LaHY > HY > SAPO-5 > LaKY > LaMCM-41 ~ CeMCM-41 > HMCM-41. The data indicate that lanthanum increased the acidity, while the addition of potassium decreased the acidity. The total acidity at 125°C corresponds to all strengths of acidic centres. On the other hand, area under the curve corresponds to the medium strong acidic centres showing desorption of ammonia in the range of 200–400°C and need not be the total acidity. Lanthanum being strong Lewis acidic centre and coordinates with ammonia and also generates Bronsted acidic centre by dissociating water molecule according to the equation:

$$[La(H_2O)]^{3+} \rightarrow [La(OH)]^{2+} + H^+$$
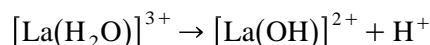
and therefore the sorption of ammonia increased. While potassium neutralizes the Bron-

Table 3
Reaction of naphthalene with isopropanol: variation of catalyst

Sl. no.	Catalyst	Conversion of naphthalene (wt.%)	TOS (h)	Yield (wt.%)			
				2-MIPN	2,7-DIPN	2,6-DIPN	Others
1	HMCM-41	74.7	5	32.1	7.1	35.3	–
2	CeMCM-41 (5 wt.% Ce)	55.9	4	47.1	Trace	8.8	–
3	LaMCM-41 (5 wt.% La)	31.2	2	30.8	Trace	0.2	0.2
4	LaY (5 wt.% La)	73.2	2	39.5	2.6	14.7	16.3
5	LaKY (5 wt.% La, 3 wt.% K)	81.0	3	52.6	Trace	28.3	0.1
6	SAPO-5	70.5	3	32.5	8.0	20.4	9.5

Naphthalene:isopropanol = 1:5 molar ratio, solvent: benzene (10 ml), reaction temperatue: 250°C, WHSV: 0.5/h, TOS: time on stream.
2,7-DIPN = 2,7-diisopropylnaphthalene, 2,6-DIPN = 2,6-diisopropylnaphthalene, others: polyalkylated naphthalenes.

Table 4
Reaction of naphthalene with isopropanol: variation of reaction temperature

Sl. no.	Reaction temperature (°C)	Conversion of of naphthalene (wt.%)	TOS (h)	Yield (wt.%)			
				2-MIPN	2,7-DIPN	2,6-DIPN	Others
1	200	57.5	5	29.3	8.2	12.3	0.5
2	250	74.7	5	32.1	7.1	35.3	–
3	300	69.8	1	39.7	6.9	22.6	0.5
4	350	33.1	3	26.3	0.4	2.6	3.6
5	400	24.6	1	15.1	1.2	5.2	3.0

Naphthalene:isopropanol = 1:5 molar ratio, solvent: benzene (10 ml), catalyst: HMCM-41, WHSV: 0.5/h, TOS: time on stream.
2,7-DIPN = 2,7-diisopropylnaphthalene, 2,6-DIPN = 2,6-diisopropylnaphthalene, others: polyalkylated naphthalenes.

sted acidic centre and therefore acidity was decreased in case of LaKY zeolite.

The temperature programmed desorption of ammonia over various modified molecular sieves is depicted in Fig. 1. If we approximately consider the area under peak corresponds to acidity, then the trend in the acidity is in the following order, LaHY ∼ SAPO-5 > HMCM-41 > LaKY > LaMCM-41 > CeMCM-41 (except for the SAPO-5 the trend is similar). All the molecular sieves are having the medium strong acidic centres showing the desorption of ammonia in the range of 200–400°C.

The reactions of naphthalene with isopropanol were carried out over various modified molecular sieves and the results are given in Table 3. The reaction was carried out at 250°C, 0.5/h weight hourly space velocity (WHSV), naphthalene:isopropanol = 1:5 molar ratio and

atmospheric pressure. The yields of 2-isopropylnaphthalene were 32.1, 47.1, 30.8, 39.5, 52.6 and 32.5 wt.% at 74.7, 55.9, 31.2, 73.2, 81.0 and 70.5% conversions over HMCM-41, LaKY and HSAPO-5 catalysts, respectively, as given in Table 3. The selectivity towards the alkylated products was generally more than 90%. HY was better catalyst compared to the catalysts given in Table 3, for the alkylation of naphthalene under present experimental conditions. The alkylation activity was enhanced due to the modification of HY by lanthanum. The extent of coking (deactivation) was reduced by addition of appropriate amount of potassium by optimizing the acidic centres. Song and Schmitz [16] were reported high selectivity for monoalkylated product (2-isopropylnaphthalene) over H-mordenite. It was also observed that 2-isopropylnaphthalene was formed pre-

Table 5
Reaction of naphthalene with isopropanol: variation of WHSV

Sl. no.	WHSV	Conversion of naphthalene (wt.%)	TOS (h)	Yield (wt.%)			
				2-MIPN	2,7-DIPN	2,6-DIPN	Others
1	0.25	76.8	1	25.7	5.5	15.4	30.1
2	0.5	74.7	5	32.1	7.1	35.3	–
3	0.75	69.0	2	32.3	5.9	25.1	2.6
4	1.0	76.2	1	36.3	7.3	30.6	1.9
5	1.25	70.8	2	36.7	5.6	25.2	3.2

Naphthalene:isopropanol = 1:5 molar ratio, solvent: benzene (10 ml), catalyst: HMCM-41, reaction temperature = 250°C, TOS: time on stream.
2,7-DIPN = 2,7-diisopropylnaphthalene, 2,6-DIPN = 2,6-diisopropylnaphthalene, others: polyalkylated naphthalenes.

Table 6
Reaction of naphthalene with isopropanol: variation of molar ratio of naphthalene to isopropanol

Sl. no.	Naphthalene: isopropanol	Conversion of naphthalene (wt.%)	TOS (h)	Yield (wt.%)			
				2-MIPN	2,7-DIPN	2,6-DIPN	Others
1	1:5	74.7	5	32.1	7.1	35.3	–
2	1:6	72.7	3	33.5	6.8	32.1	0.2
3	1:7	69.2	2	34.7	6.2	28.2	–
4	1:8	75.4	2	33.9	6.5	33.9	1.0
5	1:9	85.3	3	22.5	6.5	30.7	25.5
6	1:10	83.7	1	23.5	6.7	32.7	20.7

Reaction temperature: 250°C, solvent: benzene (10 ml), catalyst: HMCM-41, WHSV: 0.5/h, TOS: time on stream.
2,7-DIPN = 2,7-diisopropylnaphthalene, 2,6-DIPN = 2,6-diisopropylnaphthalene, others: polyalkylated naphthalenes.

dominantly compared to 1-isopropylnaphthalene [16]. They have carried out reaction in autoclave under pressure.

The effect of reaction temperature in this reaction was studied and results are given in Table 4. The reactions were carried out in the temperature range of 200–400°C, 0.5/h WHSV with naphthalene to isopropanol ratio = 1:5 mol over HMCM-41 molecular sieve. The yields of 2-isopropylnaphthalene were 29.3, 32.1, 39.7, 26.3 and 15.1 wt.% at 57.5, 74.7, 69.8, 33.1 and 24.6% conversions at 200, 250, 300, 350 and 400°C reaction temperature, respectively. The best yield was obtained in between 200 and 300°C. At high temperature (> 350°C), the con-

version and yield decreased due to the coking. The results of effect of WHSV are given in Table 5. The yields of 2-isopropylnaphthalene were 25.7, 32.1, 32.3, 36.3 and 36.7 at 76.8, 74.7, 69.0, 76.2 and 70.8% conversions at 0.25, 0.5, 0.75, 1.0 and 1.25 h^{-1}, respectively. It seems in case of HMCM-41, the reaction may not be diffusion controlled.

The results of the effect of molar ratio of the naphthalene to isopropanol are given in Table 6. The conversion of naphthalene was in the range of 72–85%. The molar ratio of naphthalene to isopropanol was varied from 1:5 to 1:10. The yields of 2-isopropylnaphthalene were in the range of 22–35 wt.%. At higher amount of

Table 7
Reaction of naphthalene with isopropanol: time on stream experiment

TOS (h)	Conversion of naphthalene (wt.%)	Yield (wt.%)			
		2-MIPN	2,7-DIPN	2,6-DIPN	Others
1	29.5	24.1	1.6	3.3	0.5
2	64.2	34.3	5.7	24.0	–
3	63.3	32.0	5.3	25.0	1.0
4	66.0	33.8	5.8	25.0	1.4
5	64.7	33.2	5.1	26.4	–
6	65.8	34.0	5.6	24.6	0.7
7	56.2	28.2	3.0	13.0	12.0
8	53.0	35.3	1.7	10.6	5.4
9	55.6	30.3	2.8	11.3	11.1
10 + 11	55.7	27.8	3.4	12.8	11.7
12 + 13	56.7	28.7	5.0	23.0	–
14	48.5	23.8	4.4	20.3	–
15	37.7	25.7	1.0	8.0	3.0

Reaction temperature: 250°C, solvent: benzene (10 ml), catalyst: HMCM-41, WHSV: 0.5/h, TOS: time on stream.
2,7-DIPN = 2,7-diisopropylnaphthalene, 2,6-DIPN = 2,6-diisopropylnaphthalene, others: polyalkylated naphthalenes.

isopropanol content in the reaction mixture, the yields of 2-isopropylnaphthalene were decreased by more than 10% due to the formation of higher (polyalkylated) alkylated naphthalenes. Song and Schmitz [16] have also observed trialkylated naphthalenes. The isopropylation of naphthalene was carried out for more than 15 h to study the effect of deactivation over HMCM-41 catalyst under typical experimental conditions and results are given in Table 7. Initially, for 9 h, the yield of 2-isopropylnaphthalene was 30–35 wt.% at 55 to 66% conversion. During 11–15 h, the yield of 2-isopropylnaphthalene was 24–29 wt.% at 38–57% conversion. The ratio of 2,6/2,7-diisopropylated naphthalene was reported to be in the range of 1.76–2.29 by Song and Schmitz [16]. On the other hand, in our studies, the ratio of 2,6/2,7-diisopropylated naphthalene was observed in the range of 6 to 18.

In the isopropylation of naphthalene, an optimum number acidic centres are required as was reported in the methylation of naphthalene and 1-naphthol [14,25]. The trend in the conversion of naphthalene was LaKY > HMCM-41 ~ LaY > SAPO-5 > CeMCM-41 > LaMCM-41. The trend in the ammonia TPD is similar to trend in the maximum alkylation activity observed.

The conclusions are as follows.

(1) LaKY is better catalyst for the synthesis of monoisopropylnaphthalene with respect to the yield and selectivity. The yields are better than those of reported in the literature.

(2) La^{3+} promotes the alkylation activity and K^+ optimizes the acidity and reduces the coking.

(3) HMCM-41 catalyst is better catalyst for the synthesis of diisopropylnaphthalene. The modification of HMCM-41 with the La^{3+}/Ce^{3+} reduced the formation of diisopropylnaphthalene. The process is continuous, eco-friendly and selective.

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