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Alkylation of 1-naphthol with methanol over modified zeolites[1]

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Abstract

The reaction of 1-naphthol with methanol was carried out over various modified zeolites, such as MgLaY. Various products were obtained in the reaction via C-alkylation, O-alkylation, rearrangement. The HY catalyst was modified by various elements/promoters to enhance the alkylation activity. LaY catalyst was further modified by basic metals, such as Mg, to reduce the acidity or deactivation.

Keywords: Alkylation; 2-Methyl-1-naphthol; 1-Naphthol; Methanol; Zeolites

1. Introduction

Zeolites have been used for the synthesis of specialty and fine chemicals [1–7]. Vitamin K_3 has been synthesized via two routes: (1) the oxidation of 2-methylnaphthalene; (2) the oxidation of 2-methyl-1-naphthol. The synthesis of 2-methyl-1-naphthol was carried out over alumina using 1-naphthol and methanol [8]. The selectivity was lower owing to various parallel reactions resulting in methoxynaphthalene and other mono- and di-methyl isomers. Grabowska et al. reported the synthesis of 2-methyl-1-naphthol from 1-naphthol and methanol over a modified iron oxide catalyst [9] with high yield and selectivity. In this paper, we report on the synthesis of 2-methyl-1-naphthol over various modified Y zeolites.

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2. Experimental

HY zeolite ($SiO_2/Al_2O_3 = 5.2$) was obtained from PQ Corporation USA. The zeolite was modified by stepwise impregnation using lanthanum nitrate and sodium, magnesium or calcium salts in water at pH ~ 4. The mixture was stirred for 4–6 h and dried in an oven. The catalyst was calcined at 400°C for about 4 h before the catalytic reactions. HY zeolite was activated before modification at 450°C for 10 h. The effect of the calcination before modification was studied and the reaction of naphthalene with methanol over various modified Y zeolites was reported elsewhere [10]. The modified zeolites were crystalline.

The reaction was carried out using a tubular, down-flow, Pyrex reactor with 20 mm internal diameter. The feed consisting of 1-naphthol and methanol was fed using a syringe pump (Sage Instruments). The products were ice-cooled and collected at the bottom using the required number

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of traps. The product was analysed by gas chromatography using a 30% SE-30 column. The analysis was confirmed by gc-ms.

3. Results and discussion

The reaction of 1-naphthol with methanol were carried out over various modified Y zeolite catalysts. The reaction was carried out at 300°C, 0.5 h^{-1} weight hourly space velocity (WHSV), a 1-napththol:methanol = 1:3 molar ratio and at atmospheric pressure. The yields of 2-methyl-1-naphthol were 52.0 wt%, 53.3 wt% and 58.4 wt% at 77.8%, 88.8% and 88.0% conversion over the zeolites NaLaY, CaLaY and MgLaY respectively, as given in Table 1. HY zeolite calcined at 450°C for 10 h was modified by lanthanum to enhance the alkylation activity and thermal stability. The catalyst was further modified by an alkali metal to reduce the acidity and deactivation. The percentages of lanthanum, magnesium, etc. were optimized in the reaction of naphthalene with methanol [10]. LaMgY was the best catalyst. The yields of 2-methyl-1-naphthol were 20.2 wt%, 10.3 wt%, 20.2 wt% and 16.5 wt% at 60.7%, 41.9%, 60.7% and 57.4% conversions over the zeolites CrLaY, FeLaY, CoLaY and NiLaY respectively. The reactions were carried out at 300°C, 0.5 h^{-1} WHSV, a 1-naphthol:methanol = 1:3 molar ratio, and the results are given in Table 1. By-products like 1-methoxynaphthalene, naphthalene and

Table 1
Reaction of 1-naphthol with methanol for modified zeolites: variation of the catalyst

Sample no.	Catalyst	Time on stream (h)	1-Naphthol conversion (%)	Yield (wt%)				
				2-Methyl-1-naphthol	1-Methoxy-naphthalene	Naphthalene	2-Methyl-naphthalene	Other products
1	NaLaY (3 wt% Na, 5 wt% La)	1	77.8	52.0	6.8	8.4	4.9	9.1
2	CaLaY (3 wt% Ca, 5 wt% La)	1	88.8	53.3	7.3	4.9	8.7	14.3
3	CaLaY (3 wt% Ca, 5 wt% La)	4	66.9	57.0	1.9	3.4	0.5	4.1
4	MgLaY (3 wt% Mg, 5 wt% La)	1	88.0	58.4	10.4	6.7	5.3	7.2
5	LaY (5 wt% La)	1	78.9	34.0	22.7	—	—	22.2
6	CrLaY (3 wt% Cr, 5 wt% La)	3	60.7	20.2	28.0	3.8	—	8.7
7	FeLaY (3 wt% Fe, 5 wt% La)	2	41.9	10.3	15.0	7.5	—	9.1
8	CoLaY (3 wt% Co, 5 wt% La)	3	60.7	20.2	28.0	3.8	—	8.7
9	NiLaY (3 wt% Ni, 5 wt% La)	2	57.4	16.5	22.6	4.0	—	14.3

Reaction temperature 300°C; atmospheric pressure; 1-naphthol:methanol = 1:3 molar ratio; WHSV = 0.5 h^{-1}.

Table 2
Reaction of 1-naphthol with methanol over MgLaY zeolite: effect of reaction temperature

Sample no.	Reaction temperature (°C)	Time on stream (h)	1-Naphthol conversion (%)	Yield (wt%)				
				2-Methyl-1-naphthol	1-Methoxy-naphthalene	Naphthalene	2-Methyl-naphthalene	Other products
1	250	1	58.7	25.1	24.8	—	—	8.8
		4	34.0	12.6	20.3	—	—	1.1
2	300	1	88.0	58.4	10.4	6.7	5.3	7.2
3	350	2	59.4	22.4	14.3	4.2	2.4	16.1
		4	30.4	16.2	6.1	—	—	8.1
4	400	3	49.1	36.7	7.7	—	—	4.7
		4	53.5	25.5	7.8	—	—	20.2

1-Naphthol:methanol = 1:3 molar ratio; atmospheric pressure; WHSV = 0.5 h^{-1}.

Table 3
Reaction of 1-naphthol with methanol over MgLaY zeolite: effect of WHSV

Sample no.	WHSV (h^{-1})	Time on stream (h)	1-Naphthol conversion (%)	Yield (wt%)				
				2-Methyl-1-naphthol	1-Methoxy-naphthalene	Naphthalene	2-Methyl-naphthalene	Other products
1	0.25	4	71.1	38.1	5.6	1.6	2.3	23.5
2	0.50	1	88.0	58.4	10.4	6.7	5.3	7.2
3	0.75	4	37.0	21.8	3.0	—	—	12.2
4	1.0	(3+4)	29.6	13.4	2.1	—	—	14.1

Reaction temperature 300°C; atmospheric pressure; 1-naphthol:methanol = 1:3 molar ratio.

Table 4
Reaction of 1-naphthol with methanol over MgLaY zeolite: effect of mole ratio

Sample no.	1-Naphthol:methanol mole ratio	Time on stream (h)	1-Naphthol conversion (%)	Yield (wt%)				
				2-Methyl-1-naphthol	1-Methoxy-naphthalene	Naphthalene	2-Methyl-naphthalene	Other products
1	1:1	3	51.7	23.2	1.7	—	—	26.8
2	1:2	2	56.2	23.7	4.3	2.3	1.4	24.5
3	1:3	1	88.0	58.4	10.4	6.7	5.3	7.2
4	1:4	4	58.6	37.6	5.5	1.7	1.4	12.4

Reaction temperature 300°C; atmospheric pressure; WHSV = 0.5 h^{-1}.

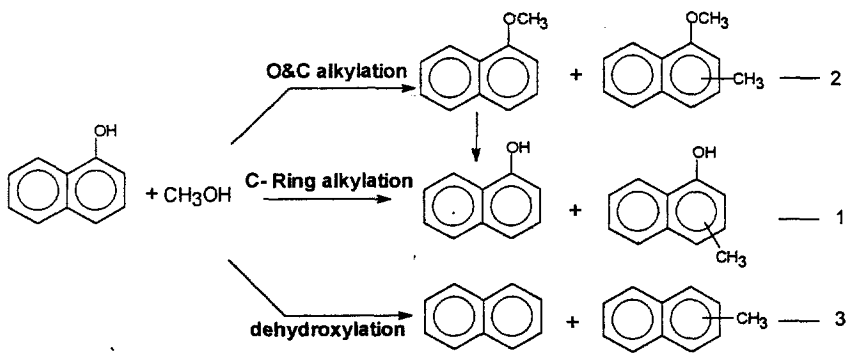

Fig. 1. The various reaction routes of 1-naphthol with methanol.

alkylated naphthalenes were observed. Owing to the presence of transition metal ions, other products, like naphthalene and substituted naphthalene, were observed due to the dehydroxylation activity of the cation.

The effect of the reaction temperature in the reaction of 1-naphthol with methanol over MgLaY zeolite, and the yields of 2-methyl-1-naphthol were 25.1 wt%, 62.6 wt%, 22.4 wt% and 36.7 wt% at 58.7%, 82.6%, 59.4% and 49.1% conversion at 250°C, 300°C, 350°C, and 450°C of 1-naphthol with methanol as given in Table 2. The yields of 2-methyl-1-naphthol were 38.1 wt%, 58.4 wt%, 21.8 wt% and 13.4 wt% at conversions of 71.1%, 88.0%, 37.0% and 29.6% based on 1-naphthol at 0.25 h^{-1} WHSV, 0.50 h^{-1} WHSV, 0.75 h^{-1} WHSV and 1.0 h^{-1} WHSV respectively, as given in Table 3. The reaction was carried out at 300°C,

Table 5
Cyclohexanol conversion over modified Y zeolites

Sample no.	Catalyst	Reaction temperature (°C)	Time on stream (h)	Cyclohexanol conversion (wt%)	Yield (wt%)		
					Cyclohexane	Cyclohexanone	Other products
1	LaMgY	180	2	21.3	18.5	0.4	2.4
			4	21.0	18.0	0.4	2.6
2	LaMgY	300	(1+2)	78.8	72.1	1.2	5.5
			4	59.2	56.4	1.5	1.3
3	LaY	180	2	95.4	82.9	3.5	9.0
			4	80.1	77.1	1.3	1.7
4	LaFeY	180	2	92.2	72.3	9.7	10.2
			4	58.2	44.0	5.8	8.4
5	LaFeY	300	2	87.6	57.6	0.5	29.5
			4	77.1	62.3	2.5	12.3
6	LaNiY	180	2	96.2	54.5	2.6	39.1
			4	64.8	13.0	13.3	38.5
7	LaNiY	300	2	92.0	72.2	0.4	19.4
			4	73.3	55.5	1.8	16.0
8	LaCrY	180	2	95.3	58.5	5.4	31.4
			4	84.2	68.4	7.0	8.8

WHSV = 0.5 h^{-1}.

0.5 h^{-1} WHSV, at atmospheric pressure. The percentage conversion of 1-naphthol and the yield of 2-methyl-1-naphthol decreased with increasing WHSV from 0.5 h^{-1} to 1.0 h^{-1}. This probably indicates that the reaction is diffusion controlled.

The effect of the molar ratio of 1-naphthol to methanol was studied and the results are shown in Table 4. The yields of 2-methyl-1-naphthol were 23.2 wt%, 23.7 wt%, 58.4 wt% and 37.6 wt% at 51.7%, 56.2%, 88.0% and 58.6% conversions of 1-naphthol at 1:1, 1:2, 1:3 and 1:4 molar ratios of 1-naphthol to methanol respectively. A reaction scheme is given in Fig. 1. It is proposed that the general trend is $k_1 > k_2 > k_3$. At lower reaction temperatures more 1-methoxy naphthalene is formed in the reaction, for which weak or medium acidic centres are required. The formation of naphthalene from naphthol via dehydroxylation by cracking was due to strong acidic centres at high temperatures.

Cyclohexanol [11,12] was also converted and the results are given Table 5. In the literature, this test reaction has been used to evaluate the acidity and activity of catalysts [11,12]. The formation of cyclohexene indicates the trend in the acidity of various catalysts. At a reaction temperature of 180°C the trend in the acidity was LaY > FeLaY > NiLaY > MgLaY zeolites. Approximately, the trend holds good in the alkylation. MgLaY showed a high activity, indicating that an optimum number of acidic centres are required. Thus, in the 1-naphthol alkylation, precalcined Y zeolite modified by La^{3+} and Mg^{2+} is the best catalyst among the catalysts considered in our study.

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