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A facile O-alkylation of 2-naphthol over zeolites Hβ, HY, and HZSM5 using dimethyl carbonate and methanol

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Abstract

Alkylation of 2-naphthol using dimethyl carbonate (DMC) and methanol (MeOH) as alkylating agents over zeolite Hβ, HY, and HZSM5 with different pore architecture is studied. The efficacies of the two alkylating agents are compared. The products of 2-naphthol (A) alkylation are 2-methoxynaphthalene (B), 1-methyl-2-naphthol (C), and 1-methyl-2-methoxynaphthalene (D). Zeolites β and Y are more active than ZSM5, and the selectivity toward 2-methoxynaphthalene (B) is always higher than C and D, irrespective of the zeolite type and conversion levels. DMC and MeOH are both equally effective methylating agents for the reaction, even though MeOH seems to have a slight edge over DMC with respect to C-alkylation. A mechanistic pathway for the formation of the products is suggested. The study also suggests that the active sites responsible for O-alkylation and C-alkylation are not necessarily the same and O-alkylation is more facile. The product formation is discussed from the point of view of zeolite pore structure and the presence of weak to moderate acid sites, which are mostly available within the pores. The mechanism of 2-naphthol alkylation on a zeolite surface involving Bronsted acid sites is the same for both alkylating agents, viz. DMC and MeOH. From the kinetic studies it is suggested that the reaction follows a Langmuir–Hinshelwood mechanistic pathway.

Keywords: 2-Naphthol; O-Alkylation; Zeolite; Hβ; HY; HZSM5; Kinetics; DMC; MeOH; Mechanism

1. Introduction

Alkylation of aromatics is an important reaction in organic chemistry widely used in the synthesis of petrochemicals, fine chemicals, pharmaceuticals, fragrances, dyes, and agrochemicals [1]. Conventionally Friedel–Crafts reactions are performed in the liquid phase using homogeneous acid catalysts like $AlCl_3$, BF_3, and H_2SO_4, often lacking selectivity toward the targeted product [2] and the corresponding industrial processes present severe environmental problems [3]. Alkylation reactions over solid acid catalysts have generated a lot of interest as alternatives for the conventional catalysts and are also being employed in several industrial processes [4–6]. Acidic zeolites such as HZSM5, HY, and Hβ have been shown to be effective catalysts for alkylation of aromatic compounds [7–20]. The main advantage of zeolite as an alkylating catalyst, in comparison with a non zeolitic catalyst, is that it can significantly influence the product selectivity due to its uniform microporous structure. For example, selective alkylation of naphthalene to 2,6-dialkylnaphthalenes has been reported over zeolite Y and mordenite catalysts [7,14]. Zeolites β and Y were found to be highly selective for 2,6-isopropylation of naphthalene as well as for tertiary butylation of naphthalene [8, 13,19]. Zeolite β gave selectively 2-tert-butylnaphthalene (2-TBN), whereas zeolite Y gave 2,6-di-TBN. In the methylation of naphthalene, ZSM5 was more selective toward 2-methylnaphthalene compared to H-mordenite and HY [20]. The product distribution thus depends to a large extent on the zeolite type and its pore architecture. Narayanan and coworkers [21–26] have carried out the alkylation of phenols and cresols with methanol over oxides and zeolites and studied the influence of acidity on conversion and selectivity of the alkylated products. They have discussed the differences between C- and O-alkylation as well as the competitive nature of both these alkylations and the conditions under which the formation of one or the other dominates. The selective formation of the alkylated products of phenol over various oxides, mixed oxides, and zeolites using methanol as

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the alkylating agent is also discussed. The formation of C-alkylated products, viz. *ortho*-cresol, 2,6-xylenol, has been reported in preference to anisole. Methanol has been found to be a reasonably good alkylating agent, which is always taken in excess. It has been suggested that the water formed during the reaction would also help creation of Bronsted hydroxyl groups over the catalysts [15]. The only problem, however, is that the excess water formed might poison the catalyst and also add to the problem of product separation. The present study focuses on the alkylation of 2-naphthol over zeolites with different structural features and on the selectivity preference for O-alkylation of 2-naphthol. The methylation of 2-naphthol assumes importance because one of the products namely 2-methoxy naphthalene is a starting material in the production of naproxen, a widely used non-steroidal anti-inflammatory drug [27]. Methylation is normally carried out using dimethyl sulphate or methyl halides, which are corrosive and toxic. Methanol (MeOH), an alternate methylating agent, is equally efficient and environmentally safe and also prolongs the catalyst life. There are only a few reports on the use of zeolites and mesoporous MCM materials for the methylation of 2-naphthol using methanol [28,29]; however, no information is available on the use of dimethyl carbonate (DMC) as an alkylating agent for this reaction. In recent times, dimethyl carbonate has emerged as another highly selective and efficient alkylating agent [30–34]. Dimethyl carbonate has been used for the esterification of benzoic acid and substituted benzoic acids [35,36]. Sreekumar et al. [37] have carried out studies on the comparative alkylation efficiencies of MeOH and DMC for aniline alkylation over Zn–Co–Fe terniaray spinel systems. It was observed that the alkylating agent influenced the selectivity patterns of the products.

Alkylation of aromatics over solid catalysts is known to occur either by the adsorption of both the aromatic and the alkylating agent molecules on the surface i.e., by a Langmuir–Hinshelwood (LH) mechanism or by the reaction of the adsorbed alkylating agent with aromatic molecules in gas phase, i.e., by a Eley–Rideal (ER) mechanism. There are contradicting reports on the alkylation mechanism over zeolites. Venuto [38] has strongly supported the operation of an ER-type mechanism for zeolite-catalyzed alkylation reactions. Corma et al. [39] have concluded from their investigation on the alkylation of benzene with propene over MCM-22 that an Eley–Rideal mechanism is followed. In contrast, Becker et al. [40] have earlier reported that this reaction proceeds through the Langmuir–Hinshelwood mechanism over H-mordenite catalysts. More recently Sridevi et al. [41] have shown that the alkylation of benzene with ethanol over modified 13X zeolite follows the LH pathway. Smiriniotis and Ruckenstein [42] have shown that the pore size of the zeolite plays an important role in the alkylation mechanism. The alkylation of bulky aromatic over small or medium pore zeolites obeys the LH mechanism whereas the alkylation of relatively small aromatics over large pore zeolites follows the ER mechanism.

In the present investigation a comparative performance of DMC and MeOH as alkylating agents for 2-naphthol alkylation over zeolites under varying experimental conditions is examined. The alkylation activities of the zeolites Hβ, HY, and HZSM5 are also compared. A kinetic study has been carried out to determine whether the LH pathway or the ER pathway is followed during this methylation over zeolites β and Y. This study is relevant since not much work has been published on the kinetics of 2-naphthol alkylation. Most of the kinetic studies reported are on alkylation of benzene and toluene. There are only a few reports on the kinetics of phenol alkylation. Here again there is a lot of argument supporting both LH and ER mechanisms under certain conditions of reaction, type of the reactant molecule, and the zeolite type. Therefore, based on the product formation as well as the kinetics of reaction, a mechanism for the methylation reaction over zeolites using DMC and MeOH is proposed.

2. Experimental

Zeolites β, Y, and ZSM5 were used in the alkylation of 2-naphthol by DMC and MeOH. Protonated forms of the zeolites Y and ZSM5 were obtained from Conteka, the Netherlands. The sodium form of zeolite β was obtained from United Catalysts India Limited and was converted to its protonated form following the ion-exchange procedure using aqueous 1 M NH_4NO_3 solution at 353 K for 12 h followed by calcination in air at 823 K. BET surface areas of the zeolite samples were measured on a Micromeritics Pulse Chemisorb 2700 instrument using N_2 as the adsorbate. Acidity of the zeolites was measured by stepwise temperature-programmed desorption (STPD) of ammonia on the same instrument, and by bracketing the temperature of desorption the relative strengths of acidity were arrived at. The details of acidity measurement have been described already by Narayanan and Deshpande [43]. The physicochemical properties of the zeolites used are given in Table 1. The alkylation reaction was carried out in a down-flow fixed-bed Pyrex glass reactor (length 30 cm, diameter 1.5 cm) at atmospheric pressure. A known weight of the zeolite powder (0.5–4.0 g) was introduced into the reactor and the zone (∼5 cm) above the catalyst bed packed with quartz grains served as a pre-

Table 1
Physicochemical properties of zeolites used

Zeolite (Si/Al)	BET surface area (m^2/g)	Acidity[a] (mmol/g) NH_3 Weak (A)	Medium (B)	Strong (C)	Pore dimension (Å)
Hβ (8)	434	1.03	2.3	4.50	5.5 × 5.5 7.6 × 6.4
HY (25)	730	1.51	1.70	0.99	7.4 × 7.4
HZSM5 (30)	400	1.89	1.16	3.05	5.3 × 5.6 5.1 × 5.8

[a] Estimated by STPD of NH_3 [43].

heater. The reactor was placed in a tubular furnace with a temperature control. A thermocouple placed close to the catalyst bed was used to measure the reaction temperature. The catalyst was activated in air flow (25 cm^3/min) at 723 K for 2 h before the start of the experiment. The reaction was carried out in the temperature range 473–673 K. The feed consisting of either 2-naphthol and DMC or 2-naphthol and MeOH with varying molar ratios between 0.1 and 0.25 was charged into the reactor using a motorized syringe pump (Braun Melsugun, Germany) at a predetermined rate along with N_2 (40 cm^3/min) as a carrier gas. The liquid products were collected at the bottom of the reactor for 1 h using a trap cooled in ice. Analyses of the products were done on a gas chromatograph (HP 6890, FID detector; column: HP-5, 15 m × 0.25 mm × 0.23 µm) and further product identification was done on a GC-MS (HP 5973 mass selective detector, column: HP-1MS 15 m × 0.25 mm × 0.25 µm). Apart from the unconverted reactant 2-naphthol (A), the products identified were 2-methoxynaphthalene (B), 1-methyl-2-naphthol (C), and 1-methyl-2-methoxynaphthalene (D). The conversion, yield, and selectivity were calculated based on the GC analyses. Selectivity of the product i (% selectivity of i) is expressed by

$$S_i = 100 \times \frac{\text{product formed } (i)}{\text{total products formed}}.$$

In the absence of a catalyst, the reaction did not proceed with either dimethyl carbonate or methanol, suggesting the involvement of an acidic site for the reaction as well as for the generation of alkyl groups, which would attack the hydroxyl group of 2-naphthol.

3. Results and discussion

3.1. Preliminary experiments

Alkylation of 2-naphthol was carried out over 1 g of zeolites Hβ and HY at 473 K at a given feed rate of 2 ml/h. The mole ratio of the feed mixture, i.e., 2-naphthol:alkylating agent was varied from 1:4 to 1:10. With increasing DMC/MeOH content the conversion increases from 43–47 to 64–75% over the zeolites (Table 2). There is not much of a difference in the conversion at high molar ratios of 1:8 and 1:10. Therefore we chose the feed mole ratio of 1:8 for most of the experiments. The excess alkylating agent also acts as a solvent for dissolving the solid 2-naphthol. Hβ was found to be generally more active than HY. The use of either DMC or MeOH as an alkylating agent did not affect the conversion to any great extent, especially at a high mole ratio of the feed. Table 3 gives a comparative performance of zeolites HZSM5, HY, and Hβ for the reaction. As can be seen HZSM5 is the least active with about 22–26% conversion of 2-naphthol for both MeOH and DMC as methylating agents. The conversion of 2-naphthol (A) over HY and Hβ is much higher than HZSM5 at around 64 and 75%, respectively. The selectivities of the products 2-methoxynaphthalene (B), 1-methyl-2-naphthol (C), and 1-methyl-2-methoxynaphthalene (D) are also compared in Table 3. It is clear that 2-methoxynaphthalene is preferentially formed on all the three zeolites and the selectivity varies between 68 and 96%. The selectivities for the other two products C and D are below 27%. It is interesting to note that the least active HZSM5 gives the highest selectivity for 2-mehoxynaphthalene (B) of 96% with 4% of 1-methyl-2-methoxynaphthalene (D). As the conversion increases on HY and Hβ there is a drop in the selectivity for 2-methoxynaphthalene. A cursory inspection of the conversion and selectivity patterns over HZSM5 with the other two zeolites gives an impression that the increase in conversion is accompanied by a decrease in the selectivity of 2-methoxynaphthalene and increase in 1-methyl-2-naphthol (C) and 1-methyl-2-methoxynaphthalene (D). However, a closer examination especially of the activities of HY and Hβ reveals that it is not so. For example, both HY with around 65% conversion and Hβ with around 75% conversion have more or less the same selectivity for B of 70 and 80% for MeOH and DMC as methylating agents, respectively. It might suggest that the zeolite type may be responsible for the differences in the conversion and the selectivity patterns. In order to understand the dependence of zeolite type on selectivity patterns, methylation reactions were carried out under certain experimental conditions so as to give a comparable conversion of 2-naphthol. In Table 4 the selectivity of 2-methoxynaphthalene (B), 1-methyl-2-naphthol (C), and 1-methyl-2-methoxynaphthalene (D) on the three zeolites Hβ, HY, and HZSM5 is compared un-

Table 2
Alkylation of 2-naphthol over zeolites: Effect of mole ratio

Catalyst	Alkylating agent	2-Naphthol:alkylating agent (molar ratio) 1:4	1:6	1:8	1:10
		Conversion of 2-naphthol (%)			
Hβ	DMC	47	74	75	75
	MeOH	43	65	73	73
HY	DMC	43	66	67	67
	MeOH	38	59	64	64

Temperature = 473 K, zeolite wt = 1.0 g, feed rate = 2 ml/h.

Table 3
Alkylation of 2-naphthol over zeolites: Effect of zeolite type

Catalyst	Alkylating agent	Conversion (%) A	Selectivity (%) B	C	D
Hβ	DMC	75	80	8	15
	MeOH	73	70	25	5
HY	DMC	67	79	7	14
	MeOH	64	68	26	6
HZSM5	DMC	26	95	–	5
	MeOH	22	96	–	4

2-Naphthol:alkylating agent = 1:8 (mol/mol), temperature = 473 K, zeolite wt = 1 g, feed rate = 2 ml/h. A, 2-naphthol; B, 2-methoxynaphthalene; C, 1-methyl-2-naphthol; D, 1-methyl-2-methoxynaphthalene.

Table 4
Alkylation of 2-naphthol over zeolites at comparable conversion of 2-naphthol

Catalyst	Alkylating agent	Conversion (%)	Selectivity (%)		
		A	B	C	D
Hβ	DMC	35	88	5	7
	MeOH	32	82	12	6
HY	DMC	29	88	6	6
	MeOH	27	80	15	5
HZSM5	DMC	26	95	–	5
	MeOH	22	96	–	4

2-Naphthol:alkylating agent = 1:8 (mol/mol); temperature = 473 K, zeolite wt = 1.0 g, feed rate Hβ and HY = 12 ml/h, HZSM5 = 2 ml/h. Please refer Table 3 for explanation of A, B, C, and D.

der a conversion level range of 22–35%. Under more or less the same conversion levels, the preferential formation of 2-methoxynaphthalene (B) on all these zeolites is between 80 and 96%. Even under these relatively low conversion levels Hβ and HY gave more of 1-methyl-2-naphthol (C) and 1-methyl-2-methoxynaphthalene (D) than HZSM5. For a comparison, Table 3 refers to the reaction carried out at low feed rate of 2 ml/h on all the catalysts and Table 4 refers to the reaction carried out on Hβ and HY at a much higher feed rate of 12 ml/h. At such a high feed rate the conversion is expected to be lowered. However, the selectivity for 2-methoxynaphthalene (B) over Hβ and HY is increased by around 5–10%. One also observes a corresponding decrease in the C-alkylated products, namely 1-methyl-2-naphthol (C) and 1-methyl-2-methoxynaphthalene (D). This might suggest that the conversion and selectivity depend on the zeolite type. HZSM5 with a relatively narrow pore aperture compared to Hβ and HY could not help the formation of C-alkylated products as is evidenced from the absence of 1-methyl-2-naphthol (C) and the presence of very little 1-methyl-2-methoxynaphthalene (D). In Hβ and HY one noted the formation of 1-methyl-2-naphthol (C), and 1-methyl-2-methoxynaphthalene (D), which can be attributed to the larger pore dimensions of these zeolites than those of HZSM5. For a given zeolite the selectivity of the products may be dependent on the contact time. This study also suggests that O-alkylation leading to 2-methoxynaphthalene is a facile reaction. There is not much of a difference in the alkylation efficacy of DMC and MeOH, though MeOH seems to have a slight edge over DMC with respect to C-alkylation.

3.2. *Effect of temperature*

The effect of temperature on 2-naphthol alkylation was studied over zeolites HY and Hβ in the temperature region of 473–673 K (Fig. 1). As temperature increases the conversion of 2-naphthol increases from ~75 to ~85% in the case of Hβ and from ~65 to ~80% in the case of HY. The yield of 2-methoxynaphthalene (B) decreased from ~70–80% to ~50–60%. The C-alkylated product 1-methyl-2-naphthol (C) on the other hand increased from 25 to 30% on both Hβ and HY with MeOH as the alkylating agent. However, DMC showed a lower C-alkylation on both Hβ and HY even though the selectivity increased from 5 to about 15%. The selectivity for 1-methyl-2-methoxynaphthalene (D) also increases with temperature on both the zeolites.

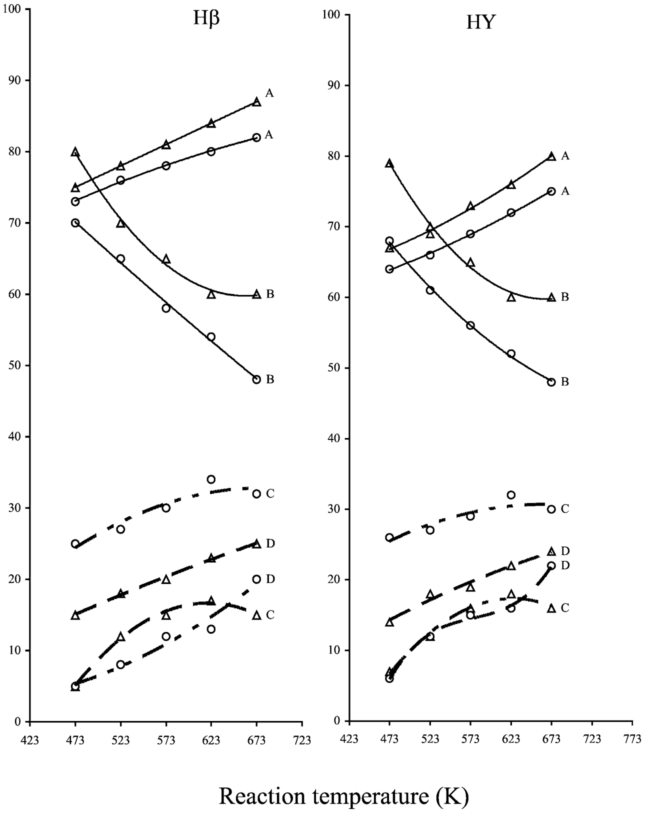


Fig. 1. Alkylation of 2-naphthol with DMC (△) and MeOH (○) over zeolites. Effect of temperature: 2-naphthol:alkylating agent = 1:8 (mol/mol), zeolite wt = 1 g, feed rate = 2 ml/h. Please refer Table 3 for explanation of A, B, C, and D.

3.3. *Time on stream*

The time on stream experiments for 2-naphthol methylation at 473 K were carried out over Hβ and HY using DMC and MeOH as the methylating agents (Figs. 2 and 3). The conversion stays fairly steady up to 4 h but then decreases gradually up to 8 h. The selectivity for the O-alkylated product (B) remained rather steady throughout the time on stream experiment. With time on stream only C-alkylation seems to have been affected beyond 4 h of operation and there is a tendency to increase with increase in conversion. In most of the cases 1-methyl-2-naphthol (C) is not much affected. There is not much of a difference between the alkylating agents with respect to conversion and selectivity. Both the zeolites Hβ and HY behave rather in the same manner with respect to 2-naphthol conversion and product selectivity patterns.

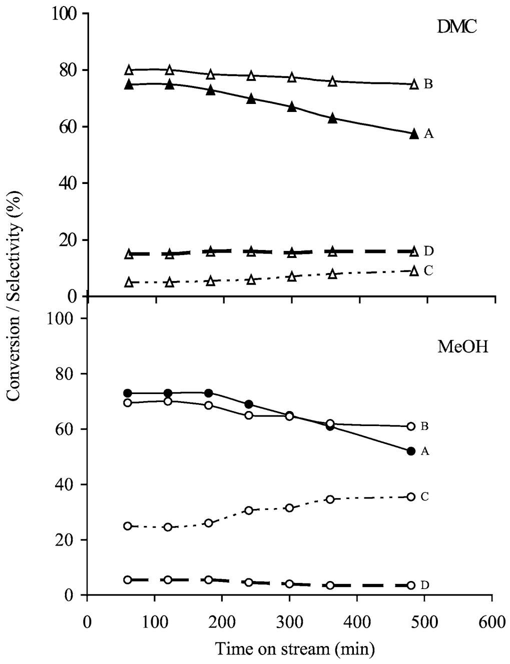


Fig. 2. Alkylation of 2-naphthol over Hβ. Effect of time on stream: 2-naphthol:alkylating agent = 1:8 (mol/mol), temperature = 473 K, zeolite wt = 1 g, feed rate = 2 ml/h. Please refer Table 3 for explanation of A, B, C, and D.

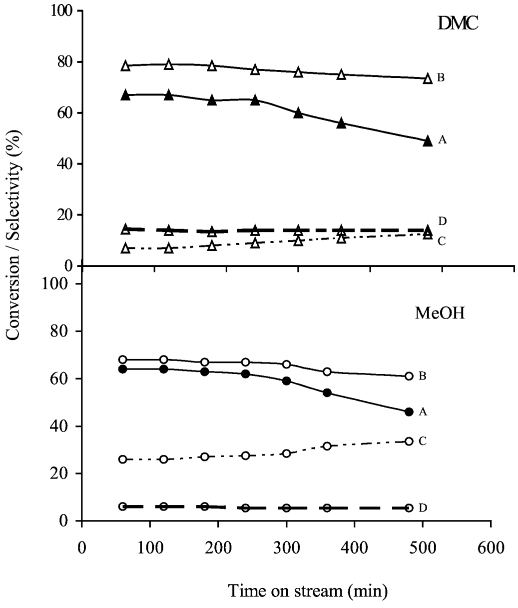


Fig. 3. Alkylation of 2-naphthol over HY. Effect of time on stream: 2-naphthol:alkylating agent = 1:8 (mol/mol), temperature = 473 K, zeolite wt = 1.0 g, feed rate = 2 ml/h. Please refer Table 3 for explanation of A, B, C and D.

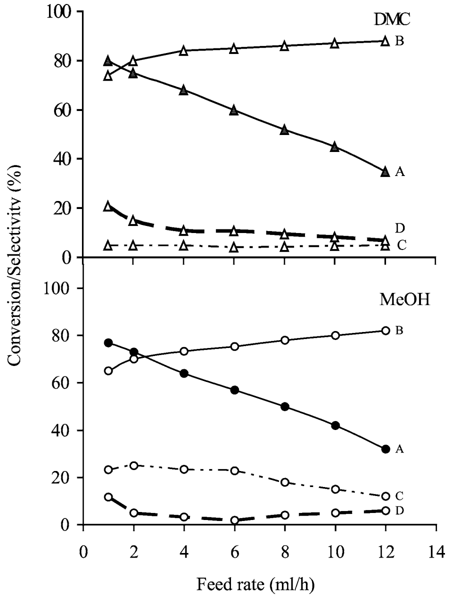


Fig. 4. Alkylation of 2-naphthol over zeolite Hβ. Effect of feed rate: 2-naphthol:alkylating agent = 1:8 (mol/mol), temperature = 473 K, zeolite wt = 1.0 g. Please refer Table 3 for explanation of A, B, C, and D.

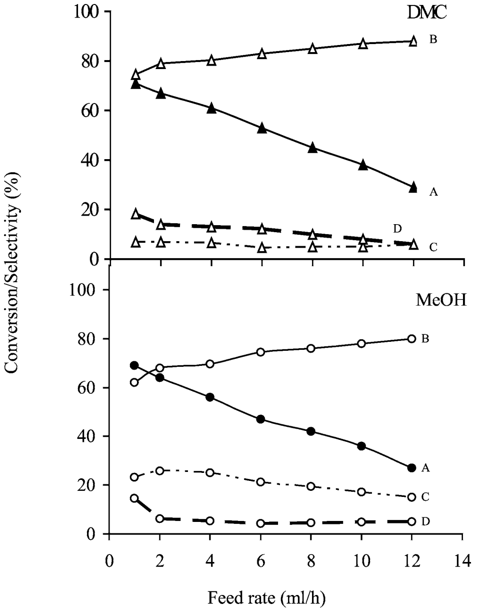


Fig. 5. Alkylation of 2-naphthol over zeolite HY. Effect of feed rate: 2-naphthol:alkylating agent = 1:8 (mol/mol), temperature = 473 K, zeolite wt = 1.0 g. Please refer Table 3 for explanation of A, B, C, and D.

3.4. Effect of feed rate

Alkylation of 2-naphthol over zeolites Hβ and HY was carried out at 473 K by changing the feed rate from 2 to 12 ml/h and keeping the catalyst weight at 1 g. As can be seen from Figs. 4 and 5, 2-naphthol conversion falls rather sharply with increasing feed rate on both Hβ and HY, irrespective of the alkylating agent. For example, in the case of Hβ the conversion fell from 75% to as low as 25%. However, the change in selectivity is not commensurate with the fall in conversion even though 2-methoxynaphthalene (B) selectivity tends to increase with increasing feed rate and a corresponding decrease in 2-naphthol conversion. Similarly the selectivity for C-alkylated products 1-methyl-2-naphthol (C) and 1-methyl-2-methoxynaphthalene (D) does not show any drastic variation; nevertheless, there is a decrease in se-

Table 5
Alkylation of 2-naphthol with DMC over Hβ and silylated-Hβ

Catalyst	Conversion (%)	Selectivity (%)		
	A	B	C	D
Hβ	75	80	8	15
Silylated Hβ	73	78	4	18

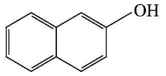
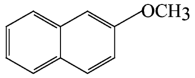
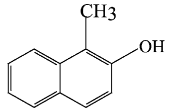
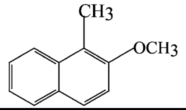
2-Naphthol:alkylating agent = 1:8 (mol/mol), temperature = 473 K, zeolite wt = 1.0 g, feed rate = 2 ml/h. Please refer Table 3 for explanation of A, B, C, and D.

lectivity with high feed rate. The study of feed rate effect on the zeolites reveals that O-alkylation is a facile and a preferred reaction over C-alkylation and it is not influenced much by the contact time of the feed.

From the foregoing studies on the effect of temperature, mole ratios of the reagents, and feed rate, the following observations are made. There is not much of a difference in the efficacies of DMC and MeOH as alkylating agents for this reaction. This is evident from the more or less same conversion levels of 2-naphthol for both alkylating agents at a given reaction condition over a zeolite. Therefore only the type of zeolite seems to be responsible for any difference in the conversion and especially the pore architecture may play a role. HZSM5, HY, and Hβ differ in the total acidity as well as the strength of acidity. The reaction requires only weak to moderate acidity, which is bound to be present in all the three zeolites studied. It has been suggested that for the esterification of aromatic carboxylic acids the active sites are available inside as well as outside the zeolite pores [36]. However more of these sites have been found to be available inside the pore than on the outside or near the pore mouth. 2-Naphthol alkylation reaction was carried out over silylated Hβ and it was compared with the nonsilylated Hβ. There was no appreciable difference in the conversion and selectivity patterns of the two as evident from Table 5, obviously supporting the argument that the active sites are mostly inside the pores of the zeolite for 2-naphthol alkylation. Therefore the differences in the conversion can possibly be explained on the basis of pore architecture. In Table 1, the pore dimensions of the three zeolites are given. In Table 6 the molecular dimensions of 2-naphthol and the methylated naphthols are given. HZSM5 has pore dimensions smaller than that of Hβ and HY. If the active sites are within the cavities of zeolites, as seems to be the case here, then pore architecture alone will decide the activity. HZSM5 shows much lower conversion compared to HY and Hβ (Table 3). The active sites within the pores are not easily available for the reactant or even if they are available the products formed with large molecular dimensions are not able to come out of the pores. Hβ and HY with wider pores than HZSM5 are more accessible to the reactants as well as to the products; naturally there is more conversion over these two zeolites.

Theoretically though O- and C-alkylation can take place, a more facile and preferential O-alkylation of 2-naphthol is observed under the conditions of experiments carried out. It is evident from the alkylation studies that irrespective of the conversion levels, O-alkylation of 2-naphthol takes place forming 2-methoxynaphthalene. Only high temperatures and high contact time seem to favor C-alkylation though to a small extent. Under severe conditions it is possible that C-alkylation can take place though to a limited extent either directly from 2-naphthol or via 2-methoxynaphthalene. Scheme 1 gives the plausible pathways for the product formation during 2-naphthol methylation.

Table 6
Molecular dimensions of 2-naphthol and the methylation products

Compound	Molecular structure	Molecular dimension dimension (Å)
A		6.9 × 4.8
B		8.8 × 4.8
C		6.9 × 5.5
D		8.8 × 5.5

3.5. Kinetics of 2-naphthol methylation

The methylation of 2-naphthol can take place by following either a Langmuir–Hinshelwood model or an Eley–Rideal model. The kinetics of these two mechanisms do vastly differ. For example, LH kinetics involves a reaction between the alkylating agent and the 2-naphthol, both of which are adsorbed on the catalyst surface. The rate of alkylation is given by

$$r_{\mathrm{A}} = \frac{k_{\mathrm{s}}' K_{\mathrm{N}} K_{\mathrm{A}} C_{\mathrm{A}}}{(1 + K_{\mathrm{A}} C_{\mathrm{A}} + K_{\mathrm{N}} C_{\mathrm{N}})^2}, \tag{1}$$

where $k_{\mathrm{s}}' = k_{\mathrm{s}}$ if adsorption of the alkylating agent is the controlling step, and $k_{\mathrm{s}}' = k_{\mathrm{s}} C_{\mathrm{N}}$ if the chemical reaction is the rate-limiting step [39,42].

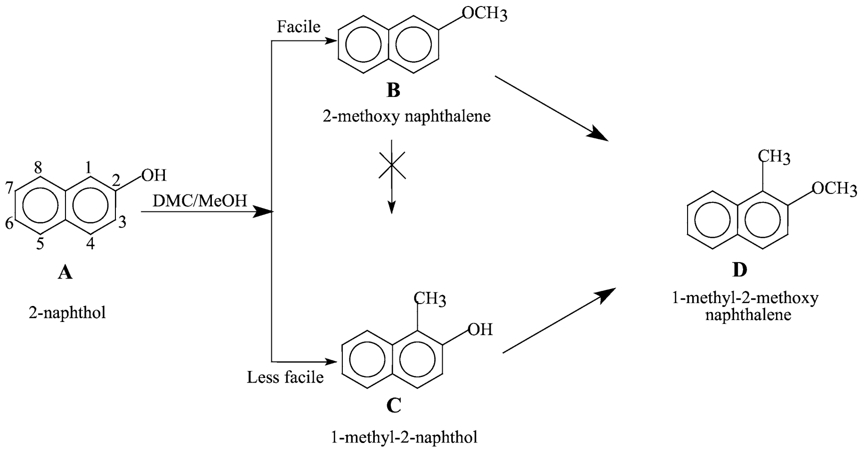
If the reaction follows the ER model where the adsorbed alkylating agent reacts with 2-naphthol in the gas phase, then the following Eqs. (2) and (3) are obtained depending on the competitive adsorption between 2-naphthol and the alkylating agent.

(a) Without competitive adsorption of 2-naphthol,

$$r_{\mathrm{A}} = \frac{k_{\mathrm{s}}' K_{\mathrm{A}} C_{\mathrm{A}}}{(1 + K_{\mathrm{A}} C_{\mathrm{A}})}. \tag{2}$$

(b) With competitive adsorption of 2-naphthol,

$$r_{\mathrm{A}} = \frac{k_{\mathrm{s}}' K_{\mathrm{A}} C_{\mathrm{A}}}{(1 + K_{\mathrm{A}} C_{\mathrm{A}} + K_{\mathrm{N}} C_{\mathrm{N}})}. \tag{3}$$



Scheme 1. Possible reaction pathway for the alkylation of 2-naphthol with DMC/MeOH.

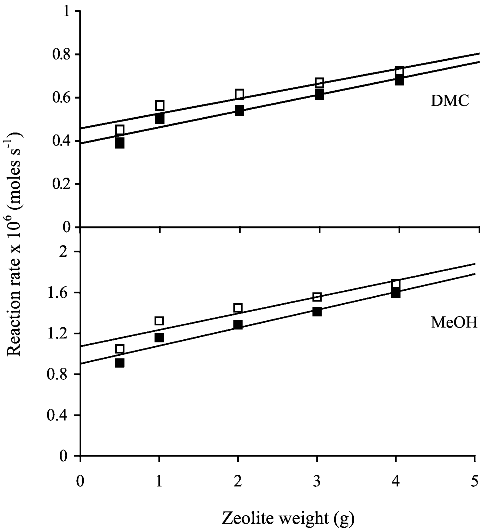


Fig. 6. Alkylation of 2-naphthol over zeolites Hβ (□) and HY (■). Effect of catalyst weight on reaction rate: 2-naphthol:alkylating agent = 1:8, temperature = 473 K, feed rate = 2 ml/h.

It is well known that the adsorption of the alkylating agent on the Bronsted acid sites is a relatively fast step [44,45]. The state of 2-naphthol when it reacts with the alkylating agent determines which one of these two mechanisms will be followed. It is not possible to determine whether a competitive adsorption of 2-naphthol takes place or not; however, it is safe to assume that 2-naphthol adsorption does take place on the acid sites of the zeolites.

In order to determine the mechanism of 2-naphthol methylation with DMC/MeOH, experiments were carried out varying the weight of the catalyst (0.5–4.0 g) and determining the rates of the corresponding reactions. A plot of the reaction rate vs the weight of zeolite catalyst is presented in Fig. 6. A linear relationship can be seen between the rate of reaction and the catalyst weight. This suggests that diffusion limitations are not dominant and the rate-determining step is the chemical reaction step. In all the experiments the concentration of DMC and MeOH was kept constant at a relatively high level when compared to the concentration of 2-naphthol. The alkylating agent to 2-naphthol molar ratio was varied by varying the 2-naphthol concentration. We can constant and Eqs. (1) and (3) will then become Eqs. (4) and (5), respectively,

$$r_A = \frac{A_1}{(A_2 + C_N K_N)^2} C_N, \tag{4}$$

and

$$r_A = \frac{A_1'}{(A_2 + C_N K_N)} C_N, \tag{5}$$

where $A_1 = k_s K_N C_A K_A$, $A_2 = 1 + C_A K_A$, $A_1' = k_s C_A K_A$.

The constants in the above equation can be obtained from the continuity equation for a fixed bed flow reactor

$$\int_0^W (\mathrm{d}W/F) = \int_0^{X_a} (\mathrm{d}x/r_A). \tag{6}$$

If 2-naphthol alkylation follows the LH mechanism, then a plot of rate of methylation versus 2-naphthol concentration must pass through a maximum according to Eq. (4) and is represented as

$$C_{N,\max} = (1 + C_A K_A)/K_N. \tag{7}$$

The maximum rate of alkylation is given by

$$r_{A,\max} = k_s C_A K_A/4(1 + C_A K_A). \tag{8}$$

If 2-naphthol alkylation proceeds through an ER mechanism, then the plot of rate of methylation vs concentration will not pass through a maximum as evident from Eq. (5).

The rates of methylation of 2-naphthol with MeOH and DMC over zeolites Hβ and HY at 473 K as a function of 2-naphthol concentration are presented in Figs. 7 and 8. The rate of alkylation of 2-naphthol with DMC passes through a broad maximum at CN $\approx 0.4 \times 10^{-3}$ mol/L and at CN $\approx 0.35 \times 10^{-3}$ mol/L with MeOH over both zeolites Hβ and HY. The values of the parameters in Eq. (1), determined by nonlinear square fitting, are given in Table 7. The goodness of the fit is relatively high in all cases and attempts to fit

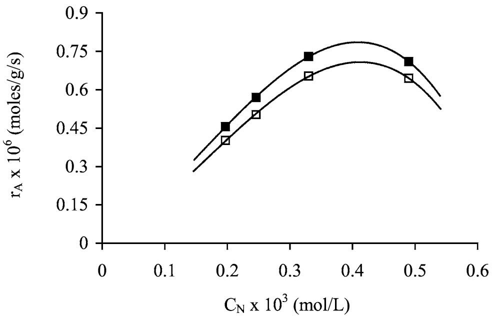


Fig. 7. Alkylation of 2-naphthol with DMC over zeolites Hβ (□) and HY (■). Effect of 2-naphthol concentration on the reaction rate: temperature = 473 K, Concn. of DMC (C_A) = 2.03 × 10^{-3} mol/L, zeolite wt = 1.0 g, Feed rate = 2 ml/h.

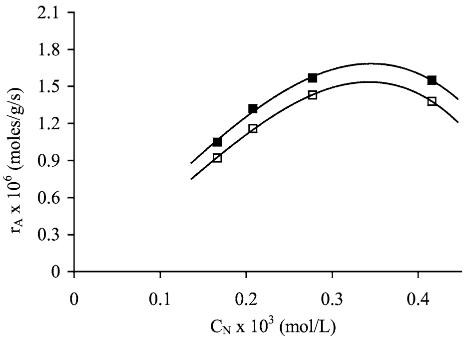


Fig. 8. Alkylation of 2-naphthol with MeOH over zeolites Hβ (□) and HY (■). Effect of 2-naphthol concentration on the reaction rate: temperature = 473 K, Concn. of MeOH (C_A) = 2.0 × 10^{-3} mol/L, zeolite wt = 1.0 g, feed rate = 2 ml/h.

Table 7
Kinetic data for the alkylation of 2-naphthol over zeolites Hβ and HY

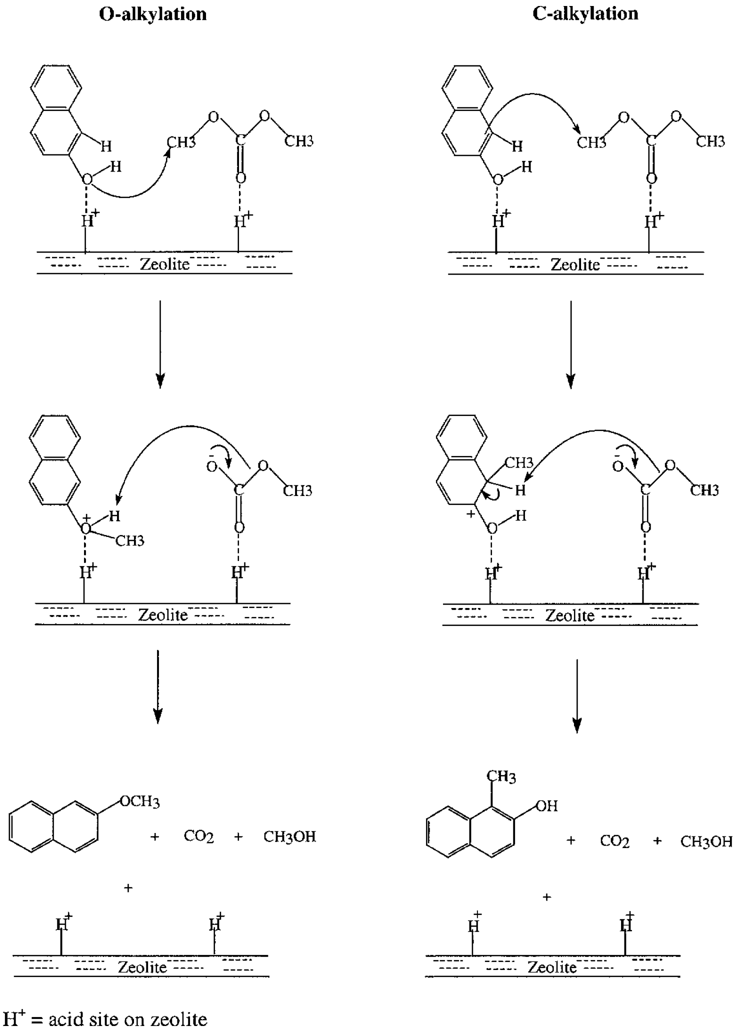
Catalyst	Alkylating agent	$k_S \times 10^6$ (mol/(g_{cat} s))	K_A (mol/L)	K_N (mol/L)	Goodness of fit (%)
Hβ	DMC	6.37	487.33	2468.78	90
HY	DMC	6.16	442.21	2213.00	89
Hβ	MeOH	19.23	261.2	2644.51	93
HY	MeOH	18.31	241.91	2488.34	91

the data to Eq. (5) corresponding to an ER mechanism were not satisfactory. This indicates that the 2-naphthol methylation reaction follows a Langmuir–Hinshelwood model over zeolites Hβ and HY, irrespective of whether MeOH or DMC is used as the methylating agent. The adsorption constant (K_A) for 2-naphthol as well as DMC and MeOH is greater over Hβ than over HY. K_A of DMC is greater than that of MeOH, indicating a stronger adsorption over the zeolites. The differences in the strength of adsorption may be responsible for the differences in the yield and selectivity.

4. Mechanism

It has been established that the methylation of 2-naphthol follows the LH pathway, irrespective of whether DMC or MeOH is used as an alkylating agent. Based on the studies, a possible pathway for the product formation is given in Scheme 1. The trends in the variation of selectivity and yield of the 2-methoxynaphthalene (B), 1-methyl-2-naphthol (C), and 1-methyl-2-methoxynaphthalene (D) suggest that D is formed by the methylation of B as well as C (Scheme 1). Alkylation of 2-methoxynaphthalene (B) with DMC and MeOH gave only 1-methyl-2-methoxynaphthalene (D). Therefore the transformation of B to C is ruled out. The yield of B is always higher than C and the contribution of B toward the formation of D is expected to be more than C. This study also suggests that the active sites responsible for O-alkylation and C-alkylation are not necessarily the same. The time on stream study suggests that the sites responsible for O-alkylation get deactivated faster than the sites responsible for C-alkylation.

As elucidated from this study, the mechanism of alkylation of 2-naphthol using MeOH/DMC over zeolites β and Y follows the Langmuir–Hinshelwood model. Santacesaria et al. [46] have studied the O- and C-alkylation of phenol and have tried to establish the types of sites responsible for the reaction. They have deduced that the alkylating agent after forming the carbo-cation on the acid site would be able to react with both O- and C-centers of phenol. The phenol molecule itself is activated on another adjacent active site in such a way that the alkylating agent could interact with both C- and O-centers of adsorbed phenol moiety. The selectivity depends on the energy of activation of the molecules, orientation of the reacting molecules, and proximity of the active sites. O- and C-alkylation can be facilitated if phenol is weakly adsorbed on the active site perpendicularly to the surface by H-bonding via its OH group [47]. Renken and co-workers [48–52] have extensively investigated the vapor-phase alkylation of catechol with MeOH over γ-alumina. They have observed that the O/C-alkylation product ratio decreases with increase in basicity of the alumina catalysts; in other words a decrease in the acidity favors C-alkylation. Beutel [53] has proposed a mechanism based on in situ spectroscopic studies for the alkylation of phenol with dimethyl carbonate, where the dimethyl carbonate is activated on the Lewis acid site by its carbonyl oxygen and phenol on an adjacent Lewis base site by H-bonding. Jyothi et al. [34] have also proposed a similar mechanism for the alkylation reaction of dimethyl carbonate making use of both the acid and the basic sites on the catalyst. According to Bal et al. [29] the mechanism for 2-naphthol methylation probably involves the formation of a transient 2-naphtholate species on the less acidic site. C-alkylation of the ring can occur when the activation of the 2-naphthol ring is relatively small. Taking all these facts into consideration mechanisms for the alkylation of 2-naphthol with DMC and MeOH over a zeolite are envisaged in Schemes 2 and 3, respectively. 2-Naphthol and the alkylating agent are adsorbed on adjacent protonic acid sites of the zeolite. CO_2 and methanol are the by-products when DMC is used as an alkylating agent (Scheme 2). Methanol being an alkylating agent is not ex-



Scheme 2. Possible reaction mechanism for the alkylation of 2-naphthol with DMC over zeolites.

pected to have any negative effect and will help alkylation. In the case of methanol as alkylating agent (Scheme 3) water is the only by-product and it will to some extent help maintain the Bronsted acidity [15]. It has been suggested earlier that the reaction requires only acid sites whose value of H_0 is smaller than −6.63 [54]. As the concentration and the number of the acid sites increase the conversion will also increase due to the adsorption of more 2-naphthol and the alkylating agent.

5. Conclusion

2-Naphthol methylation has been carried out over zeolites with a fairly good yield of 2-methoxynaphthalene. 1-Methyl-2-naphthol and 1-methyl-2-methoxynaphthalene are the other products formed during the reaction. Zeolites β and Y are more active for this reaction than zeolite ZSM5. This can be attributed to pore-size restriction in ZSM5. Medium acidic sites have been found to be the active centers for this reaction. Zeolite β, which has more moderate acid sites than zeolite Y, is also more active for this methylation. Selectivity is also high over Hβ when compared with HY. DMC and MeOH are both equally effective methylating agents for this reaction, though the selectivity towards 2-methoxynaphthalene is found to be higher in the case of DMC. From the kinetic study, it is concluded that this reaction follows a Langmuir–Hinshelwood pathway by the adsorption of both 2-naphthol and the alkylating molecule on the surface of the zeolite. The mechanism of alkylation is the same for both DMC and MeOH. The difference in the selectivity, however, could be attributed to the differences in the acid strengths of the zeolite and the activation of 2-naphthol as well as the alkylating molecule on the zeolite active center.

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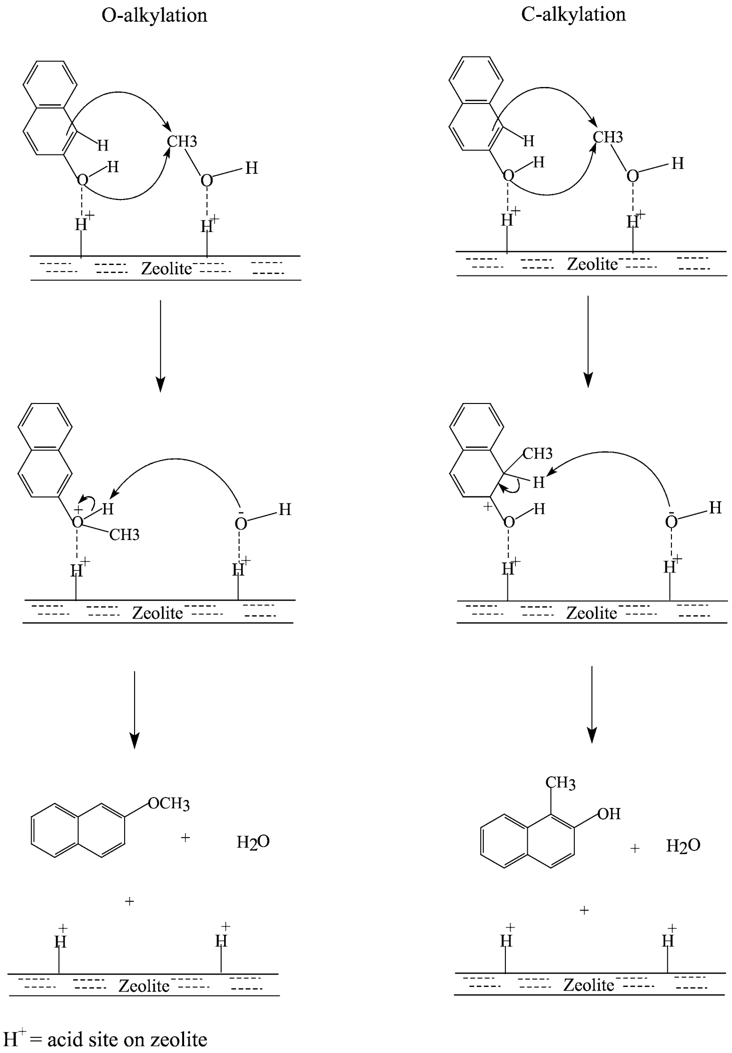

Scheme 3. Possible reaction mechanism for the alkylation of 2-naphthol with methanol over zeolites.

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