HY zeolite catalyzes the *ortho*–methylation of 1–naphthol

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ABSTRACT

The selective *ortho*–alkylation of 1–naphthol with methanol is carried out over various commercially available acid solid catalysts under relatively mild reaction conditions (<300 ºC), in batch, and anhydrous zeolite HY shows the best catalytic activity. Removal of the strongly adsorbed water in the zeolite is key for the alkylation reaction. Mechanistic studies based on isotopically labelled experiments reveal the transformation of *O*–methylated 1–naphthol into the desired *ortho*–*C*–methylation product after intramolecular rearrangement of the methyl group. These results open the way to design a new synthesis of *ortho*–methyl 1–naphthol and, consequently, of vitamin K3, based on a commercially available, inexpensive and non–toxic solid catalyst such as HY zeolite.

Introduction

Vitamin K3 (menadione) is an important dietary component used as a drug to treat hypoprothrombinemia and also an intermediate in the synthesis of other vitamins, such as vitamin K4 [1,2]. A straightforward synthetic route for vitamin K3 consists of the *C*–methylation reaction of 1–naphthol **1** with methanol as an alkylating agent followed by the oxidation of 2–methyl–1–naphthol **2** (*ortho*–methyl 1–naphthol, Fig. 1) [1,2]. This alternative avoids the oxidation route of 2–methylnaphthalene with harsh oxidants [3,4]. However, in contrast to parent phenol, [5–10] the *ortho*–methylation of 1–naphthol **1** is a difficult process, which requires high reaction temperatures (typically >450 ºC) and shows low selectivity.

The direct methylation of 1–naphthol **1** with methanol in the gas phase gives mixtures of mono and polymethylated substrates [11]. The first systematic data for this reaction were obtained with Al_2O_3 catalysts, with a maximum yield of 37 % for *ortho*–methyl 1–naphthol **2** (at 350 °C) and a crude mixture containing nearly twenty by–products [12]. Fe_3O_4 has also been used as a catalyst with similar performance [6,13]. In general, the reported reaction conditions and yields for this reaction are far from a potential industrial application.

Zeolites are microporous, crystalline and negatively charged aluminosilicates, which host cations within their structure to balance the electronic density of the material [14]. These cations can be protons (Brønsted acid zeolites) or metal cations (Lewis acid or basic sites, depending on the metal employed) [15]. The pore size of some archetypical zeolites (i.e. zeolites X, Y or β) is ~7 Å, enough to allow the diffusion of the starting material **1** and the desired product *ortho*–methyl 1–naphthol **2** through the pores [16,17]. It is not in vain that the primary active component in the industrial catalyst for the Friedel–Crafts reaction is usually HY zeolite embedded in a porous silica–alumina active matrix and modified by adding several promoters. Thus, in principle, zeolites are candidates to catalyze the methylation reaction of 1–naphthol **1**. Cation–exchanged zeolites (i.e. La^{3+}–zeolite Y) have been described as catalysts for the alkylation reaction of 1–naphthol or naphthalene with methanol, but at high reaction temperatures (~400 ºC) and with low selectivity [11].

As said above, simple Brønsted zeolites such as HZSM–5, HY, and Hβ are excellent catalysts for the alkylation reaction of a variety of aromatic compounds despite not being reported yet as efficient catalysts for the methylation of 1–naphthol [18]. The pore architecture of the zeolite has a great influence on the product dispersion, [19] and despite the
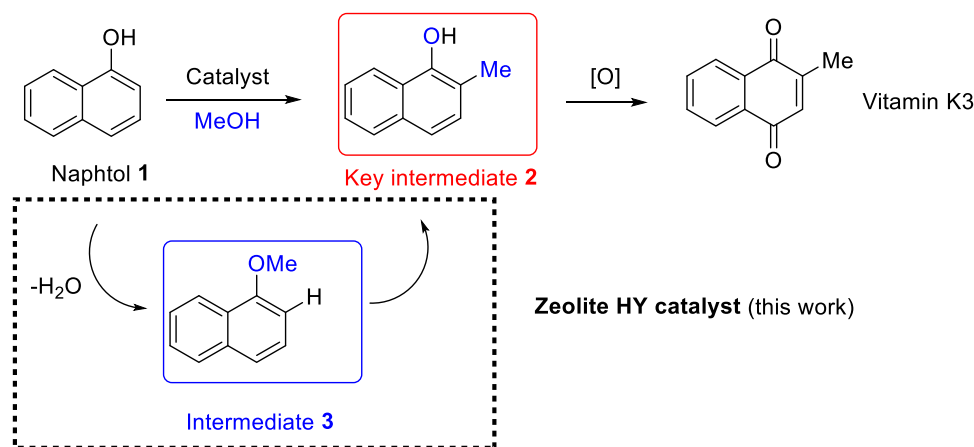
Fig. 1. A direct route to Vitamin K3.

zeolite–catalyzed methylation reaction is well–known with parent phenol, all previous attempts with zeolites as catalysts for the ring alkylation of 1–naphthols with alcohols have, on average, resulting in a complicated product mixture from which the separation of the individual compounds has proved to be difficult [20]. Besides, in clear contrast to phenol, the implementation of 1–naphthol **1** in a gas–phase methylation reaction, particularly in a continuous process, is much more complicated, since the boiling point of 1–naphthol is 100 ºC higher than phenol, further mismatching the high volatility of MeOH. Thus, a batch process for the methylation of **1** seems convenient from a practical point of view.

We show here that a robust, commercially available, non–toxic and inexpensive solid such as HY zeolite catalyzes the methylation of 1–naphthol **1** with MeOH after thoroughly dehydrating the solid. The previous removal of water is not innocent but absolutely necessary to activate the solid and generate *ortho–C*–alkylation product **2**, despite MeOH would displace water under reaction conditions. We also prove here that product **2** is obtained after acid–catalyzed rearrangement of the in–situ formed *O*–alkylation intermediate 1–methoxynaphthalene **3** (see Fig. 1), in a similar way to what occurs with parent phenol (from anisole to *ortho*–methyl phenol) [17,21–24] and with the necessary presence of an excess of MeOH, as corroborated by isotopically labelled experiments (vide infra). These results indicate that the mild synthesis of 1–methoxynaphthalene **3** under water–free reaction conditions is key to finally achieve the desired *ortho–C*–alkylation product **2** at lower reaction temperatures and with better selectivity, [25,26] in batch, by using a simple acid zeolite catalyst.

Materials and methods

General: Reagents (1–naphthol, ReagentPlus ≥99 % **1** and 1–methoxynapthalene, ≥98 % **3**) were obtained from commercial sources (Merck–Aldrich) and used without further purification otherwise indicated. H–USY zeolite (CBV–720, CBV–740, CBV–760, CBV–780) and H–Beta zeolite (CP–811) were purchased from Zeolyst. K–10 was purchased from Merck–Aldrich and TS–1 is also commercially available from different sources (ACS Material, LLD). H–Y refers to H–USY throughout the text (please note than H–Y is very unstable and rarely used in catalytic studies for organic synthesis, however, the literature seems to accept H–Y as notation, since, as said above, the real H–Y is not available). Gas chromatography (GC) and gas chromatography coupled to mass spectrometry (GC–MS) were carried out in gas chromatographs with 25 m capillary columns filled with 1 or 5 wt%

phenyl silicone (Shimadzu GC–2025, Agilent GC 6890N coupled with Agilent MS5973). ^{1}H– and ^{13}C–nuclear magnetic resonance (NMR) were measured in CDCl$_3$ at room temperature on a 400 MHz spectrometer (Bruker Ascend 400), respectively, using Me$_4$Si as the internal standard.

General reaction procedure: This experimental procedure aims to synthesize a compound by combining 1–naphthol **1** (2250 mg, 15 mmol) and methanol (1500 mg, 45 mmol) with a catalyst (750 mg, presumed 3 mmol based on a molar mass of 250 g/mol). Prior to employing the dry zeolites in the experimental procedures, a preliminary step involved subjecting them to an overnight drying process at a temperature of 300 °C. This procedure aimed to ensure the removal of any residual moisture, thereby optimizing the zeolite condition for subsequent use in the intended application. The mixture is reacted in a 20 mL stainless steel batch reactor under controlled conditions at 290–300 °C for 24 h at 500 rpm and a maximum pressure of 5 bar. Regular monitoring for observable changes is conducted. After completion of the reaction, the batch reactor was depressurized, cooled down to room temperature and then opened. Finally, AcOEt was added to dilute the reaction mixture, which was then centrifuged and analyzed by different analytical methods. Moreover, the filtration was carried out when some solid was present in the sample. The conversions and yields of products were estimated from the peak areas based on the internal standard technique using GC. GC–coupled mass spectrometry and NMR were used to identify the products, besides comparison with pure product samples. The experiments have been repeated several times with good reproducibility (±10 %). Isolated products could not be obtained, and selectivity is indicated in mol%.

Results and discussion

The reaction of 1–naphthol **1** with methanol was carried out at 295 ºC for 24 h, using various solids as a catalyst, and the results are shown in Table 1. The reaction mixture was analysed by gas chromatography (GC) and, in some cases, also by ^{1}H, ^{13}C nuclear magnetic resonance (NMR) and distortionless enhancement by polarization transfer (DEPT), in order to confirm the structure of the products. The latter are majorly either *C*–alkylation or *O*–alkylation products, i.e. the desired *ortho*–methyl 1–naphthol **2** and the by–product 4–methyl–1–naphthol **4**, and also 1–methoxynaphthalene **3**. Naphthalene, alkylated or not (products **5** and **6**), and the oxidized derivative 1–tetralone **7**, were also found as by–products of the reaction, coming from a dehydroxylation reaction (see ahead) [27].

Table 1

Results for the reaction of methylation of 1–naphthol **1** over different zeolites (mass ratio catalyst/1–naphthol=1/3) in a batch reactor at 295 ºC for 24 h. GC results, validated by ^{1}H, ^{13}C and DEPT NMR.

Entry	Catalyst	1:MeOH ratio	Conv (%)	Selec. 2 (%)	Selec. 3 (%)	Selec. 4 (%)	Selec. 5 (%)	Selec. 6 (%)	Selec. 7 (%)
1	No catalyst	1:3	–	–	–	–	–	–	–
2	Hβeta zeolite	1:3	–	–	–	–	–	–	–
3	Hβeta zeolite (dry)	1:3	14.2	13.63	67.3	10.8	1.1	–	1.9
4	HY zeolite	1:3	–	–	–	–	–	–	–
5	HY zeolite (dry)	1:3	82.3	11.6	26.7	2.4	31.8	9.7	4.0
6	HY zeolite (dry)	1:6	52.7	9.9	86.7	2.0	traces	–	1.1
7	LaNaY	1:3	20.6	5.3	76.0	1.6	1.8	–	15.6
8	Fe–K10	1:3	13.8	52.1	2.74	42.7	1.1	–	1.2
9	K10 zeolite	1:3	18.9	5.0	76.2	3.2	3.5	–	8.5
10	K10 zeolite (dry)	1:3	36.8	6.9	48.8	2.7	23.8	–	6.9
11	TS–1	1:3	–	–	–	–	–	–	–
12	TS–1 (dry)	1:3	11.1	5.2	65.4	1.8	10.4	5.8	2.8
13	Dealuminated HY zeolite (dry)	1:3	38.3	12.8	38.1	5.1	19.2	5.0	11.5
14	HY zeolite (dry) Si/Al 20	1:3	56.0	10.0	45.7	3.6	17.4	4.2	4.5
15	HY zeolite (dry) Si/Al 30	1:3	77.0	4.4	27.4	1.8	42.0	15.3	4.1
16	HY zeolite (dry) Si/Al 40	1:3	49.5	13.3	63.7	traces	7.3	1.8	2.5
17	Hierarchical HY 0.1 M HY	1:3	41.5	19.6	59.3	traces	12.0	2.7	6.3
18	Hierarchical HY 0.5 M HY	1:3	40.4	15.0	57.8	4.9	4.1	Traces	4.7

[a]The yield of products is calculated by measuring the amount of products obtained,and dividing this number by the theoretical amount that could be obtained after complete conversion, expressed as a percentage.
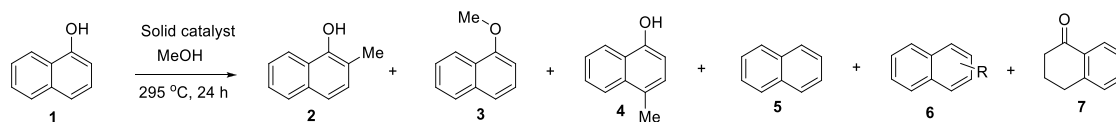
The methylation reaction does not proceed in the absence of a catalyst or with untreated Hβ zeolite as a catalyst (entries 1–2). However, a 15 % conversion is obtained when the Hβ zeolite is dehydrated at 250 ºC under vacuum for >4 h (entry 3), with a ~75 % selectivity to products **2** + **3**. The same effect occurs for the HY zeolite (entries 4–5): any conversion does not occur if the zeolite is not previously dehydrated, but a 41 % conversion of **1** is achieved after 24 h reaction time when the acid zeolite is dehydrated. A representative kinetic plot shows the evolution of the reaction products with time (Fig. S1 in Supplementary Material, SM). The higher conversion obtained with HY compared to Hβ zeolite cannot be ascribed to a different Si/Al ratio, higher surface or particle size of the crystal since both zeolites show a Si/Al of ~15, a surface area of ~600 g·m^{-2} and a particle size of 700 nm according to isotherm plots and X–ray diffraction analyses (Table S1 and Figs. S2–S4). The zeolite keeps its crystalline structure after reaction (Fig. S4). Field emission scanning electron microscopy (FESEM) and high–resolution transmission electron microscopy (HR–TEM) measurements of the zeolites, including electron dispersive X–ray (EDX) analysis and mapping of the sample, show a homogenous distribution of crystallite particles (Figs. S5–S7). Zeolite HY shows a good number of mesopores, according to the corresponding isotherm plots (Figs. S2 and S3, see also Table S1) and ^{27}Al NMR solid–state nuclear magnetic resonance experiments (^{27}Al ssNMR, Figs. S8), compared to H–Beta, which in principle allow a better diffusion of reactants and products (**1–3**) to interact with the acid sites of the zeolite. Importantly, pyridine titration (Figs. S9–S10) and temperature–programmed ammonia desorption (TPD, Figs. S11–S12) measurements show a higher number of strong Brønsted (but not Lewis) acid sites for the H–Y zeolite. Fig. 2 compares the Brønsted and acid Lewis sites in the different zeolites.

The dramatic change found in the zeolite catalytic activity depending on the presence or absence of strongly adsorbed water could be explained by better accessibility to the zeolite acid sites after water removal. However, Fourier transform infrared spectroscopy (FT–IR) experiments show that both MeOH and 1–naphthol **1** can compete for the acid sites even in the presence of water (Fig. S13, MeOH is a stronger nucleophile and Lewis base), which is in good agreement with the literature [28]. Thus, the beneficial effect of water removal could be related to the particular reactivity of the alcohols (1–naphthol **1** and the very same MeOH) within the acid zeolite pores in the absence of water. Indeed, an increase in the excess of MeOH during reaction, from 3 to 6 times with respect to **1**, resulted in a higher conversion of **1** (53 %) and higher selectivity to **2** + **3** (50 %, entry 6). This result is remarkable because it ranks among the best for a metal–free catalyst for this reaction when comprehensively compared with the solid catalysts reported in the literature for the methylation of 1–naphthol **1** with methanol (Table S3). A longer reaction time (48 h) increased the conversion up to 85 % but severely decreased the selectivity to form naphthalene derivatives as the main products of the reaction (Table S4).

Metal–supported catalysts, particularly some supported on zeolites, have been reported to be very active in the methylation of phenol and other related reactions [29,30]. Thus, at this point, we prepared some of the more active metal–supported solid catalysts reported so far for the methylation reaction of 1–naphthol (**1**) and phenol (see Table S3), and we tested them under our experimental reaction conditions (295 ºC, batch reactor). It can be seen that a LaNaY zeolite [3] only gives a 20.6 % conversion (entry 7), much lower than HY zeolite. It has been reported that the inclusion of La^{3+} in HY or NaY leads to a significant lattice deformation, similar to that caused by extra–framework Al species, [31] which readily impacts the catalytic performance and would explain the decrease in catalytic activity compared to the H$^+$ counterpart solid [32, 33]. A second very active reported catalyst for the methylation reaction of 1–naphthol **1** with MeOH is Fe–montmorillonite K10, thus we also
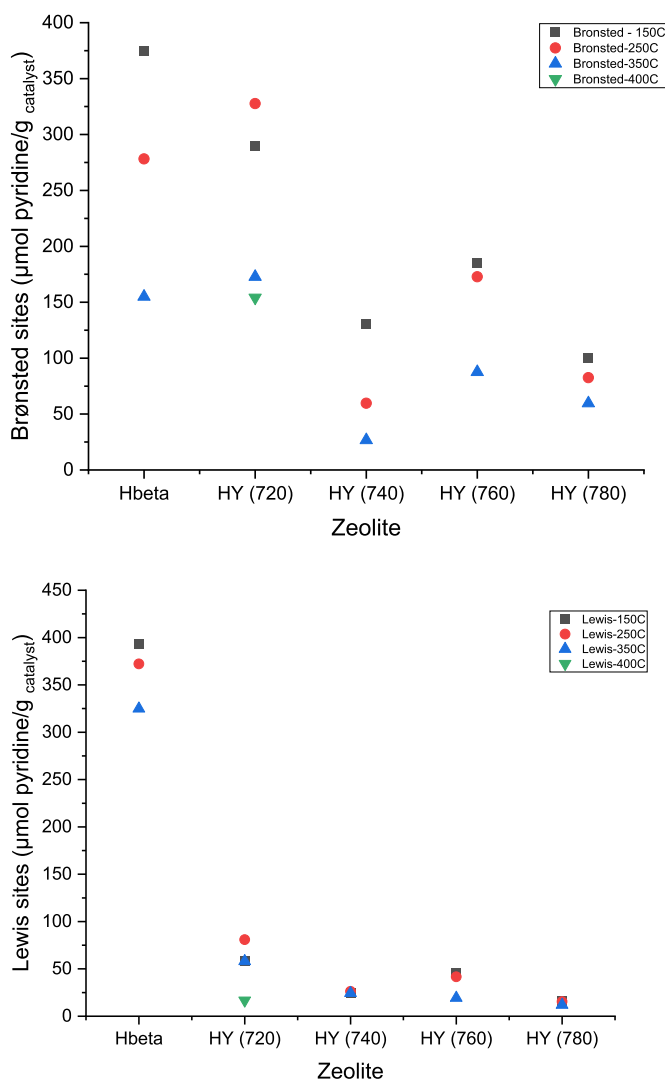
Fig. 2. Plot for the Brønsted (top) and acid Lewis sites (bottom) in the different catalytically active H–Beta and H–Y zeolites. The inset shows the desorption temperature for each acid site according to Table S2.

prepared and tested this solid catalyst (Fig. S14), following the reported procedure [34]. The result in Table 1 (entry 8) also showed a low conversion (13 %) and low selectivity to the desired products (<10 %) under our reaction conditions. In our hands, the reactions with reported catalysts worked in very low yield possibly because of a wrong synthesis of the materials, difficult to follow for us with the available literature. However, the conversion and selectivity to **3** increased to 19 % and 76 %, respectively, when just montmorillonite K10, free of iron, was used as a catalyst (entry 9). Remarkably, following the rationale found for H–Beta and HY zeolites, we repeated the reaction with dehydrated montmorillonite K10, and the conversion was twice (37%), with a respectable 50 % selectivity to **3** (entry 10). It is noteworthy here that this aluminosilicate does not have 3D channels and an extremely high inner surface; however, it still works as a catalyst for the reaction, although with lower catalytic activity than the HY zeolite.

In order to further validate the need of removing the strongly adsorbed water in the solid catalyst, a commercially available sample of titanium silicate (TS–1) was also tested. This microporous solid catalyst presents Ti^{4+} instead of Al^{3+} in the framework, thus having fewer Brønsted acid sites. Besides, the diameter pore size is ~5 Å, narrower than in Hβ and HY zeolites. Thus, in principle, the expected catalytic activity for the methylation of 1–naphthol **1** should be more restricted. Indeed, the conversion of **1** after dehydrating TS–1 was only 11 %,

however, with good selectivity to **3** (64 %, entry 12). But more importantly, any conversion was not observed if water was still present in the catalyst (entry 11), confirming the need to remove water for methylation of **1**. Please notice that most of the previous catalysts for this reaction contain metals, which cannot be heated at such high temperatures, otherwise the nature of the metal catalytic site will change or be destroyed. Therefore, the possibility of dehydrating the zeolite only arises from our approach here with bare acid zeolites as catalysts, without any metal supported, which gives as a consequence the zeolite dehydration.

The fact that the Brønsted and not the Lewis acid sites in the HY zeolite seem to be the catalytic active species during the reaction prompted us to prepare a dealuminated HY zeolite, where all the potential Al^{3+} Lewis sites in the solid are removed (see preparation details in the SI). The characterization of this new solid material by PXRD and FT–IR (Fig. S15), an isotherm plot (Fig. S16), HR–TEM (including EDX, Fig. S17) and pyridine absorption measurements (Fig. S18) confirms the stability of the HY zeolite after the removal of most of the Al^{3+} Lewis sites. The catalytic results for the dealuminated HY zeolite (entry 13 in Table 1) show a 38 % conversion, somewhat lower than the commercial HY zeolite after removing water. These results could indicate that some positive effect could be exerted by the Lewis sites during the catalysis, in any case minor compared to the Brønsted acid sites. Furthermore, we also tested other commercially available HY zeolites with increasing Si/Al ratios (20, 30 and 40, respectively), where the number of total Brønsted acid sites decrease but the acid strength increases. The evolution of the Brønsted acid strength and total Lewis sites in these HY zeolites is shown above in Fig. 2, and their corresponding characterization by isotherm plots and PXRD (Figs. S19–S24), HR–TEM visualization (Fig. S25) and also ^{27}Al ssNMR (Fig. S26) can be found in the SM. The catalytic results (entries 14–16 in Table 1) show that up to a 77 % conversion can be obtained (Si/Al= 30, entry 15), which further confirms that the catalytic activity comes from Brønsted acid sites in the zeolite. All the zeolites maintain their crystallinity after reaction (Fig. S27). These catalytic data showcase the complex relationship between Si/Al ratios and catalytic performance after water removal, highlighting the need for a finely balanced ratio to achieve the optimal catalytic activity and selectivity for the 1–naphthol **1** alkylation reaction.

Since the dried HY zeolite yielded 45 % of 1–methoxynaphthalene **3**, we also investigated the possible formation of **2** from **3**. The intramolecular rearrangement of the *O*–methyl to the *ortho C*–methyl is well–known for phenol from anisole (Table S5), [21–24] but this effect has been little investigated for 1–naphthol **1**. The results in Table 2 show that **3** is stable without a catalyst (entry 1) but mainly converts to starting 1–naphthol **1** when the zeolite is not dried or MeOH is not added (entries 2 and 3) [35]. However, when an excess of MeOH is added (entries 4 and 5), the conversion and the selectivity to **2** increase significantly. These results clearly indicate that the methylation reaction of **1** with MeOH to give **2** and **3** stays in equilibrium in the presence of the HY zeolite catalyst and that the removal of water helps to switch the equilibrium towards the desired product **2**.

Table 2
Results for the rearrangement reaction of 1–methoxynaphthalene **3** in the presence of HY zeolite catalyst. GC results, validated by ^1H, ^{13}C and DEPT NMR.

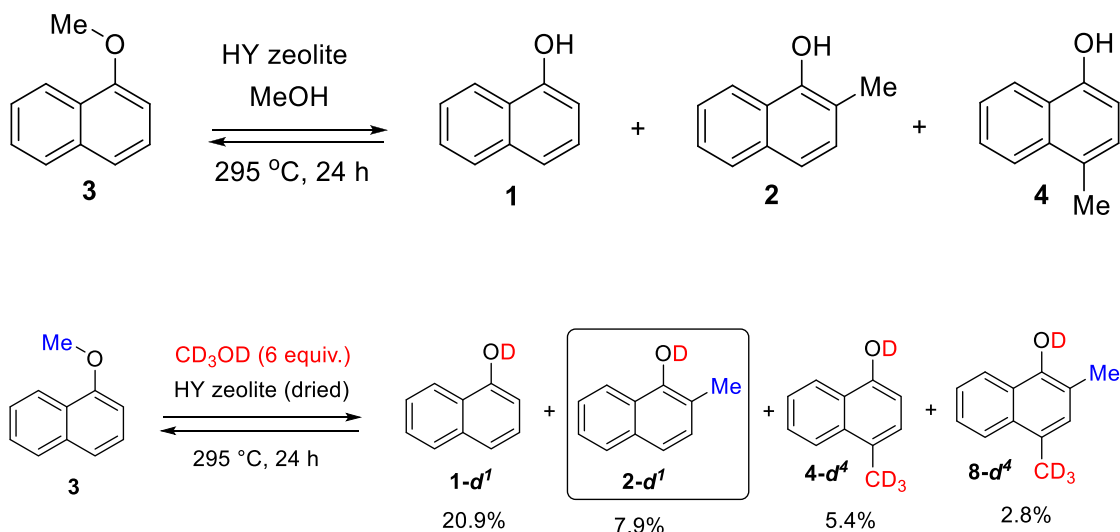| Entry	Catalyst	3:MeOH ratio	Conv (%)	Selec. 1 (%)	Select 2 (%)	Selec. 4 (%)
1	No catalyst	1:3	–	–	–	–
2	HY zeolite	1:3	46.7	30.1	10.3	–
3	HY zeolite (dry)	Just catalyst	57.3	19.3	8.6	5.0
4	HY zeolite (dry)	1:3	63.4	23.9	10.3	6.0
5	HY zeolite (dry)	1:6	76.0	25.3	26.4	17.7

Fig. 3. The reaction of 1–methoxynaphthalene **3** with deuterated methanol (D$_3$COD) under the optimised reaction conditions with dehydrated HY zeolite catalyst.

The mechanism for the transformation between **3** and **2** with the dehydrated HY zeolite as a catalyst, under optimised reaction conditions, was studied by reactivity studies with deuterated methanol (CD$_3$OD), and the results are shown in Fig. 3. Gas chromatography coupled with mass spectrometry (GC–MS) analysis shows the formation of deuterated products with different numbers of incorporated D atoms (from one to four D atoms, Fig. S28), and ^{1}H and ^{13}C NMR characterisation confirms products **2**–d^1 and **8**–d^4 as the *ortho*–methyl 1–naphthols formed. Remarkably, the ortho–methyl group is not deuterated in either case, unlike the *para*–methyl group, which unequivocally confirms that the formation of **2** from **3** occurs via intramolecular methyl rearrangement.

We then performed an additional experiment to confirm these results, after synthesizing the isotopically labelled compound **1d^4** (Fig. S29). After reaction with MeOH, we observe the formation of deuterated methoxynaphtol **3** (signal at 4.04 ppm, Fig. S30 top) and the methyl group in *para* position, deuterated product **4** [confirmed also by the corresponding ^{13}C signal at 21.2 ppm (Fig. S30, bottom)]. This result demonstrates that **2** appears after long times, since it is not observed in this experiment. Starting from **1**, we are able to form **3** and **4**, but **4** is not a product of **3**. In other words, a longer reaction time is needed to perform the intramolecular methyl rearrangement of **3**. We still maintain the deuterated position in *ortho*, confirming that this position is not involved in the direct intermolecular formation of **4**. At this point, we can only speculate that the necessary presence of MeOH during the reaction facilitates the methyl rearrangement, probably by some sort of bridging or H–assistance.

From the results above, one can say that water removal in the zeolite is essential to catalyze not only the methylation of 1–naphthol **1** with MeOH regardless of the catalyst structure, since a variety of dehydrated solids including H–beta and HY zeolites, montmorillonite K10 and TS–1, show the same effect, but also the intramolecular rearrangement reaction of 1–methoxynaphthalene **3** to the desired product **2**; that Brønsted acid sites are the catalytic active species in the zeolite, and that a balance between strength and number of acid sites, dictated by the zeolite Si/Al ratio, is necessary to achieve the optimal conversion and selectivity. It should be remarked here the convenience of using robust solid catalysts since dehydrating treatments imparted to metal–supported solids could, in many cases, deteriorate the catalytic metal site, while the removal of adsorbed water in HY zeolite is straightforward, without apparent erosion of the structure [36].

In early studies, it was clear that water partial pressure can have a significant impact on zeolite stability and, thus, catalytic efficiency [37,

38]. Thus, it is not surprising that the removal of water can lead to a better reactivity of alcohols **1** and MeOH inside the microporous acid solid catalyst. Besides, it has been reported that water can be easily replaced by MeOH [39], particularly in 7 Å channels [40]. The binding affinity of the first water molecule at a Brønsted site has been calculated to be about 50 kJ/mol for MFI framework zeolites and 34 kJ/mol for subsequent water molecules to form clusters. These water adsorption energies are easily surmountable for MeOH under our reaction conditions. Not only that, the water molecules can be replaced even by the nucleophilic 1–naphthol aromatic ring, activated by the electron donor OH group [41,42]. Besides, the water adsorption values significantly drop for the same Al–free framework, in this case, dealuminated HY, which explains the good result obtained after dealumination of the zeolite.

Finally, we further studied the possibility of using hierarchical zeolites, in order to further discard any shape selectivity issue, with just diffusion limitations operating during reaction [43–45]. For that, we synthesized different hierarchical zeolites with a simple treatment with NaOH (see SM for details). Significant weight loss was observed during the alkali treatment, leading to a practical limitation in the use of higher concentrations of NaOH. The higher NaOH concentrations (1.0 M and 1.5 M) resulted in a substantial decrease in the weight of the catalyst, making it challenging to obtain sufficient quantities for subsequent experiments. Consequently, for practical reasons, we chose to focus on 0.1 M and 0.5 M NaOH concentrations to investigate the hierarchical zeolites' effects. Furthermore, the decision to exclude the 1.0 M and 1.5 M HY samples was influenced by structural changes observed in the 0.5 M HY zeolite through the PXRD spectra (Fig. S31) [46,47]. The spectra indicated a discernible distortion in the zeolite framework at higher NaOH concentrations, suggesting potential damage to the crystalline structure. Given that preserving the zeolite structure is crucial for its catalytic activity, it was deemed imperative to exclude the 1.0 M and 1.5 M HY samples from the subsequent reactions [48].

In the case of the methylation reaction of 1–naphthol **1**, the hierarchical zeolite 0.1 M HY demonstrates notable results. This catalyst has a conversion rate of 41.5 % and a selectivity of 19.6 % towards product **2**. Also, a dominant selectivity of 59.3 % towards product **3** suggests a preferential reaction pathway. The hierarchical zeolite keeps the crystallinity after reaction (Fig. S32). In contrast, the 0.5 M HY zeolite, while maintaining a comparable conversion rate (40.4 %), exhibits altered selectivities. A decrease in selectivity towards product **2** (15.0 %) and an increase in selectivity towards side products **5** (12.0 %) and **7** (6.3 %) indicate variations in the reaction pathways compared to 0.1 M HY. The

observed outcomes highlight the delicate balance required in the preparation of hierarchical zeolites. While the destruction of the zeolite structure in 0.5 M HY may impact catalytic performance, [49] the results still point to the critical role of the hierarchical structure. This understanding informs the optimization of zeolite preparation methods for tailored catalytic applications. It acknowledges the intricate relationship between structural characteristics and catalytic performance.

Conclusions

Commercially available, non–toxic and inexpensive HY zeolite catalyzes, after dehydration of the zeolite, the methylation of 1–naphthol **1** to obtain *ortho*–methyl–1–naphthol **2** and 1–methoxynaphthalene **3**. The latter evolves to **2** under reaction conditions through an intramolecular methyl rearrangement, as unambiguously assessed with isotopically labelled experiments. However, the reaction system requires an excess of MeOH to be present, staying in an equilibrium state in which intermediate **3** reverts to **1**, limiting the conversion and yield. These results may help to find conditions for a potential industrial implementation applied to synthesising vitamin K3 since the catalyst is commercial and operates at temperatures <300 °C.

CRediT authorship contribution statement

Matea Bačić: Validation, Methodology, Investigation. **Maria Tejeda–Serrano:** Validation, Investigation. **Yongkun Zheng:** Formal analysis, Investigation, Methodology. **Judit Oliver–Meseguer:** Writing – original draft, Supervision, Methodology, Investigation. **Antonio Leyva–Pérez:** Writing – original draft, Supervision, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.apsadv.2024.100598.

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