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PAPER

Highly regioselective di-*tert*-amylation of naphthalene over reusable H-mordenite zeolite†

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Highly regioselective di-*tert*-amylation of naphthalene using different alcohols can be achieved over a H-mordenite (HM) zeolite. For example, the *tert*-amylation of naphthalene using *tert*-amyl alcohol in cyclohexane over HM (Si/Al = 10) zeolite has been optimised to give a 70% yield of 2,6-dialkyl-naphthalenes, of which 2,6-di-*tert*-amyl-naphthalene was produced in 46% yield along with 2-*tert*-amyl-6-*tert*-butyl-naphthalene (23%) and 2,6-di-*tert*-butyl-naphthalene (1%). This has been achieved by varying the reaction time, temperature, pressure and amounts of *tert*-amyl alcohol and zeolite. No 2,7-dialkyl-naphthalenes were seen under the conditions tried. The zeolites can be easily regenerated by heating and then reused.

Introduction

There is considerable interest in the use of zeolites to control alkylation of naphthalene,^{1–14} primarily as a result of the commercial importance of 2,6-dimethylnaphthalene (DMN), a precursor of naphthalene-2,6-dicarboxylic acid (NDA), which is needed for production of poly(ethylene naphthalate) (PEN). Current methods for the production of DMN are cumbersome and low yielding and require the separation of complex mixtures, including isomers,¹⁵ followed by extensive recycling in order to provide a reasonable quantity of product. Consequently, the utilisation of PEN is limited by the commercial availability and cost of DMN. A greener method for production of DMN or an alternative PEN precursor, involving fewer processes, higher yields of desired products, and less need for separation and recycling, is much needed.

A convenient process for preparation of DMN would be selective dimethylation of naphthalene. Unfortunately, in addition to the usual problems of polyalkylation, the β -positions of naphthalene are less reactive than the α -positions and there are 10 possible isomeric dimethylnaphthalenes, so simple double methylation of naphthalene is not easy to control to give the specific compound required. Mixtures of isomers are produced and require separation.¹⁶ Since the 2,6-disubstituted compounds are the most “linear” isomers, zeolites offer a possible way to favour such products.

It is well recognised that zeolites and other solid catalysts can play an important role in the development of greener organic

syntheses through their abilities to act as recyclable heterogeneous catalysts, support reagents, entrain by-products, avoid aqueous work-ups and enhance product selectivities.^{17–22} For example, we have shown that zeolites or other solids can have advantages in nitration,^{23–28} bromination,²⁹ chlorination,³⁰ methanesulfonylation³¹ and acylation^{32,33} as well as alkylation^{34,35} of aromatic compounds.

Indeed, a degree of β -selectivity in dimethylation of naphthalene has been achieved over zeolite HZSM-5, whereas non-selective methylation was seen over the larger pore H-mordenite (HM) and HY zeolites.³⁶ However, even using HZSM-5, a poor yield of the 2,6-isomer was obtained and the ratio of 2,6/2,7 isomers was approximately 1.

Since other 2,6-dialkyl-naphthalenes can in principle also be oxidised to NDA, attempts to gain greater control have been extended to the use of alternative alkylating agents. Isopropylation of naphthalene with propene,³⁷ isopropyl alcohol^{38–42} and isopropyl bromide⁴³ has been studied using a variety of zeolites and β , β -selectivities of over 75%, with a 2,6/2,7 ratio of approximately 2, have been reported using H-mordenite.⁴⁴ The best isopropylation procedure gave 2,6-di-isopropyl-naphthalene in 54% yield, along with 14% of 2,7-di-isopropyl-naphthalene, *i.e.* a 2,6/2,7 ratio of 4.⁴⁴ The best reported cyclohexylation makes use of HY zeolite, and results in the corresponding 2,6-dicyclohexyl-naphthalene in 19% yield, along with 17% of 2,7-dicyclohexyl-naphthalene, *i.e.* a 2,6/2,7 ratio of 1.1.⁴⁵ The same authors also reported *tert*-butylation to give a 23% yield of 2,6-di-*tert*-butyl-naphthalene, with around 4% of 2,7-di-*tert*-butyl-naphthalene, *i.e.* a 2,6/2,7 ratio of 5.9, with the added advantage of easy separation of the 2,6-isomer by crystallisation.^{46,47}

By studying the above reaction in more detail, we have previously shown that highly regioselective di-*tert*-butylation of naphthalene can be achieved over zeolite H-mordenite using *tert*-butyl alcohol as the alkylating agent under autoclave conditions.^{34,35} The process was a convenient, high yielding and

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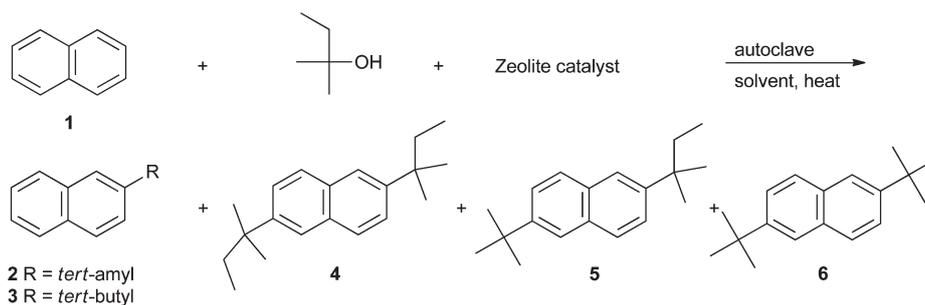
†CCDC 827589. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2gc16443d

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Table 1 Typical properties of the commercial zeolites^{2,50}

Zeolite	Product code	Si/Al ratio	Nominal cation form	Na ₂ O (wt%)	Pore volume ^a (Å ³)	Pore diameter (Å)	Surface area (m ² g ⁻¹)
HY	CBV 720	15	H	0.03	730	7.4 × 7.4	780
Hβ	CP 811E-150	75	NH ₄	0.05	150	6.6 × 7.7 & 5.5 × 5.6	720
HM	CBV 21A	10	NH ₄	0.08	150	6.5 × 7.0	500
HM	CBV 90A	45	H	0.05	150	6.5 × 7.0	500
HZSM-5	CBV 3024E	15	NH ₄	0.05	130	5.3 × 5.6 & 5.1 × 5.5	400

^a Pore volume was calculated using the formula: $= 4/3\pi(D_i/2)^3$, where D_i represents the maximum included sphere diameter (Å).⁵⁰

**Scheme 1** *tert*-Amylation of naphthalene (1) using *tert*-amyl alcohol over zeolite catalysts under autoclave conditions.

highly regioselective method for the synthesis of 2,6-di-*tert*-butylnaphthalene, which was produced in 60% yield, along with only 1% of 2,7-di-*tert*-butylnaphthalene, *i.e.* a 2,6/2,7 ratio of over 50.^{34,35} Although this method is easily the most selective yet discovered for the production of 2,6-dialkylnaphthalene, it may be difficult to oxidise the *tert*-butyl group to a carboxyl group.⁴⁸ Therefore, we were interested to see if a process could be devised that would give a 2,6-dialkylnaphthalene in which the alkyl groups could be cracked to an alkyl group that could be oxidised relatively easily to a carboxyl group.⁴⁹ We decided to undertake a study of dialkylation of naphthalene using various alcohols over different zeolites in a solvent under autoclave conditions similar to those used successfully in *tert*-butylation of naphthalene.^{34,35} We now report the details of such a study.

Results and discussion

We have shown previously that the best results obtained for the *tert*-butylation of naphthalene using *tert*-butyl alcohol under autoclave conditions involved the use of cyclohexane as a solvent and HM (Si/Al = 10) zeolite as a catalyst at 180 °C.^{34,35} Initially, a range of different commercial zeolites was screened for efficiency in the *tert*-amylation of naphthalene (1; 10 mmol) using *tert*-amyl alcohol under self generated pressure (50–150 psi) in cyclohexane, under conditions as close as possible to those used in the *tert*-butylation reactions.^{34,35} The properties of the zeolites used in this study are recorded in Table 1. The zeolites were calcined prior to use, which would have converted any ammonium forms into the corresponding proton forms. The major products of the *tert*-amylation reaction were 2-*tert*-amyl naphthalene (2), 2-*tert*-butyl naphthalene (3), 2,6-di-*tert*-amyl naphthalene (4), 2-*tert*-amyl-6-*tert*-butyl naphthalene (5), and 2,6-di-*tert*-butyl naphthalene (6) (Scheme 1) and the

yields obtained are given in Table 2. Several other minor peaks were seen in the gas chromatograph (GC), some of which were shown (by conducting an experiment in the absence of naphthalene) to arise from the decomposition of *tert*-amyl alcohol under the reaction conditions.

The results reported in Table 2 indicated that HY (Si/Al = 15) was not selective and produced various other alkylated naphthalenes. Zeolite HZSM-5 gave 2-*tert*-amyl naphthalene (2) in 13% yield along with 2-*tert*-butyl naphthalene (3; 1.5%) with low conversion (15%). No dialkylnaphthalenes were formed, presumably because the pores were too small to allow dialkylation to occur. The other zeolites tried were more reactive and more regioselective to produce 2,6-dialkylnaphthalenes 4–6. In the case of the HM zeolites no 2,7-dialkyl isomers were observed. Zeolite HM (Si/Al = 10) was found to be more reactive than zeolite HM (Si/Al = 45). With HM (Si/Al = 10), a naphthalene conversion of 83% and a 22.5% yield of 2,6-dialkyl products, of which 2,6-di-*tert*-amyl naphthalene 4 represented an overall 16% yield, were observed. 2-*tert*-Amyl naphthalene (2) was found to be the major product, produced in 60% yield, while, 2-*tert*-butyl naphthalene (3) was present in very low yield. Therefore, we undertook a more detailed study of the reaction with HM (Si/Al = 10) as activator in the hope of enhancing the conversion of 1 and 2 to 4.

Compounds 3, 5 and 6 were presumably obtained as a result of generation of *tert*-butyl carbocation through breakdown of *tert*-amyl cation produced from *tert*-amyl alcohol in the presence of acidic zeolite. *tert*-Amyl derivatives were produced in a similar way during reactions of naphthalene with *tert*-butanol,³⁴ indicating that interconversion of *tert*-butyl and *tert*-amyl cations occurs under the conditions (Scheme 2). However, the yields of *tert*-butyl derivatives in reactions involving *tert*-amyl alcohol were much greater than the yields of the corresponding *tert*-amyl compounds had been in reactions involving *tert*-butyl alcohol.

This presumably reflects easier diffusion of *tert*-butyl derivatives than *tert*-amyl ones within the zeolite pores, a phenomenon that may also be responsible for the greater 2,6-selectivity exhibited in reactions involving *tert*-amyl alcohol.

In order to test the effect of solvent in the reaction, reactions were carried out in several different solvents for 6 h at 180 °C in an autoclave. The results are recorded in Table 3.

With isopentane, dichloromethane and tetrachloroethene as the solvents, the reactions were significantly slower than the reactions carried out in other solvents. The yields of **4** and **5** were highest (16 and 6%, respectively) when the reaction was carried out in cyclohexane. It seemed that the best solvent was cyclohexane, which had already been used in the earlier study (Table 2).

Increased pressure could, in principle, enhance the rate of reaction through forcing hindered reactants into the pores of the zeolite. Our attention was therefore turned to an investigation of the effect of pressure on the reaction represented in Scheme 1. Several *tert*-amylation reactions of naphthalene (**1**; 10 mmol) were carried out using *tert*-amyl alcohol (20 mmol) over HM (Si/Al = 10; 4 g) in cyclohexane (50 mL) at 180 °C for 6 h under various initial external pressures (150–500 psi) of nitrogen gas in an autoclave. However, it was found that when the starting pressure was increased from 150 to 500 psi, the conversion and the yield of **4** decreased from 81 to 48% and from 12 to 3%, respectively. Compound **2** was the major product (31–58%) in all cases. The ratio of **4**:**5** appeared to diminish slightly at the higher pressures, but the yield of **6** was very low (0.5–1%) in all cases. Since applying additional pressure offered no yield

enhancement, it was decided to use only self-generated pressure for further reactions to try to improve the yield of **4**.

In order to gauge the effect of temperature, the reaction temperature was varied in 10 °C stages from 140 to 200 °C over 4.0 g of HM (Si/Al = 10). The results obtained are given in Table 4.

It was found that when the temperature was increased from 140 to 180 °C, the conversion increased from 5 to 81% and the yield of **4** increased from 0 to 12%. However, when the temperature was increased further to 200 °C, both conversion and yield of **4** were seen to fall, to 69 and 8%, respectively. In addition, the yield of **5** was seen to decrease when the yield of **4** decreased at the higher temperatures, but the yield of **6** seemed to increase. However, the maximum yields of **3** and **6** were only 3 and 1%, respectively. It is clear that **2** is still the major product in all cases. Therefore, it was decided to standardise the temperature at 180 °C for further reactions.

We next varied the quantity of HM (Si/Al = 10) in stages from 2 to 8 g under otherwise constant reaction conditions, without any externally applied pressure.

However, varying the amount of zeolite had no consistent effect on the conversion or on the yield of **4**. When the amount of the HM catalyst was 6 g, the conversion of naphthalene, the yield of **4** and the selectivity were all relatively high, but the lack of any trend implied that other factors (such as the efficiency of stirring mixtures containing large amounts of solid) might be equally significant and any increase in the yield of **4** would not justify the use of a large quantity of catalyst. Therefore, 4 g of catalyst was retained for further investigations.

To determine if there was any benefit to be gained by varying the amount of the reagent, the amount of *tert*-amyl alcohol was varied over 4.0 g of HM at 180 °C. The amount of *tert*-amyl

Table 2 *tert*-Amylation of naphthalene (**1**) using *tert*-amyl alcohol over various zeolites under autoclave conditions according to Scheme 1^a

Zeolite	Yields ^b (%)					
	1	2	3	4	5	6
HM (Si/Al = 10)	17	60	0.5	16	6	0.5
HM (Si/Al = 45)	53	31	2.5	8	3	0.5
Hβ (Si/Al = 75)	32	57	1.5	1	4	1.5
HY (Si/Al = 15) ^c	6	10	1	1	1	2
HZSM-5 (Si/Al = 15)	85	13	1.5	—	—	—

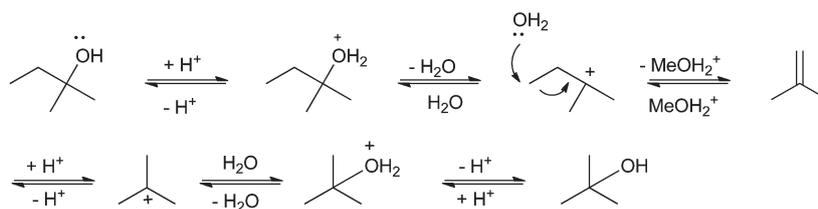
^a Autoclave reaction with stirring for 6 h under self generated pressure at 180 °C; zeolite catalyst (4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol) and *tert*-amyl alcohol (1.76 g; 20 mmol).

^b Determined by GC based on the response factors of **1**, **2** and **4**. It was assumed that the response factor of **3** is the same as for **2** and those of **5** and **6** are the same as for **4**. Numbers expressed as percentages have been rounded to the nearest whole number, except for yields below 3%, which have been rounded to the nearest 0.5%. ^c Various other alkylated naphthalenes were produced.

Table 3 Effect of solvent in the *tert*-amylation of naphthalene (**1**) using *tert*-amyl alcohol over HM (Si/Al = 10) under autoclave conditions according to Scheme 1^a

Solvent	Yields ^b (%)					
	1	2	3	4	5	6
Cyclohexane	17	60	0.5	16	6	0.5
Isopentane	95	3	2	—	—	—
Heptane	65	23	1.5	5	2	—
Dichloromethane	89	7	0.5	1	—	—
1,2-Dichloroethane	54	34	1	6	4	1
Tetrachloroethene	85	9	—	1	—	—

^a Autoclave reaction with stirring for 6 h under self generated pressure at 180 °C; HM (Si/Al = 10; 4.0 g), solvent (50 mL), naphthalene (1.28 g; 10 mmol) and *tert*-amyl alcohol (1.76 g; 20 mmol). ^b See footnote *b* to Table 2.



Scheme 2 Interconversion of *tert*-amyl and *tert*-butyl cations over zeolite.

Table 4 Varying the temperature in the *tert*-amylation of naphthalene (**1**) using *tert*-amyl alcohol over HM (Si/Al = 10) under autoclave conditions according to Scheme 1^a

<i>T</i> /°C	Yields ^b (%)					
	1	2	3	4	5	6
140	95	3	—	—	—	—
150	87	10	2	1	—	—
160	71	23	3	2	1	—
170	36	47	3	5	5	—
180	19	58	0.5	12	10	0.5
190	25	56	0.5	10	8	0.5
200	31	52	1.5	8	6	1

^a Autoclave reaction with stirring for 6 h under self generated pressure; HM (Si/Al = 10; 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol) and *tert*-amyl alcohol (1.76 g; 20 mmol). ^b See footnote *b* to Table 2.

Table 5 Varying the quantity of *tert*-amyl alcohol in the *tert*-amylation of naphthalene (**1**) over HM (Si/Al = 10; 4.0 g) according to Scheme 1^a

<i>tert</i> -Amyl alcohol (mmol)	Yields ^b (%)					
	1	2	3	4	5	6
20	30	52	2.5	9	5	1
40	16	51	1.5	19	11	1.5
60	21	50	3	14	8	1
80	40	49	0.5	7	3	0.5

^a Autoclave reaction with stirring for 6 h under self generated pressure at 180 °C; HM (Si/Al = 10, 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol) and *tert*-amyl alcohol. ^b See footnote *b* to Table 2.

alcohol was increased in stages from 20 to 80 mmol. The results obtained are given in Table 5.

It was found that increasing the amount of *tert*-amyl alcohol up to 40 mmol brought about increases in both the conversion and the yield of **4**, by 14 and 10%, respectively, perhaps because of the higher concentration of the alkylating agent. However, use of 60 and 80 mmol caused both the conversion and yield of **4** to fall successively, perhaps as a result of deactivation of acidic sites on the zeolite by interaction with the excess alcohol. However, it was interesting to note that the selectivity for production of **4** instead of **5** was somewhat greater in the presence of a larger quantity of the alcohol. Therefore, it was of interest to investigate the reactions in the presence of different quantities of alcohol over longer reaction periods, which would hopefully lead to higher conversions, while perhaps retaining the greater selectivity.

A series of experiments was conducted in which the duration of the reaction was varied from 1 to 12 h in cyclohexane (50 mL) while the quantity of *tert*-amyl alcohol was also varied (20 to 80 mmol for 10 mmol of **1**). Because of difficulties associated with representative sampling of heterogeneous reaction mixtures in an autoclave, a separate experiment was conducted for each data point, which could lead to some scattering in the results because of variations in stirring efficiency and other parameters. The results obtained are given in Table 6.

Table 6 shows that the reaction was faster with less *tert*-amyl alcohol (20 mmol) than with the larger quantities, especially

Table 6 Varying the reaction time and quantity of *tert*-amyl alcohol in the *tert*-amylation of naphthalene (**1**) over HM (Si/Al = 10; 4.0 g) according to Scheme 1^a

Time (h)	<i>tert</i> -Amyl alcohol (mmol)	Yields ^b (%)					
		1	2	3	4	5	6
1	20	43	47	—	6	3	—
3	20	34	52	0.5	9	4	0.5
6	20	16	60	0.5	16	6	1
12	20	25	55	0.5	13	6	0.5
6	40	22	54	0.5	15	8	0.5
12	40	29	55	0.5	10	5	0.5
24	40	16	52	0.5	19	11	1.5
1	80	100	—	—	—	—	—
3	80	90	8	—	1	—	—
4	80	67	31	—	2	—	—

^a Stirred autoclave reactions under self generated pressure at 180 °C; HM (Si/Al = 10, 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol) and *tert*-amyl alcohol. ^b See footnote *b* to Table 2.

80 mmol, which gave a low conversion (33%) and yield of **4** (2%) after 4 h. The general trend on increasing the reaction time was an increase in the conversion and yield of **4**, but increases were rather small after 6 h. Clearly, the majority of the reaction occurred within the first 6 to 12 h, at least when 20 or 40 mmol *tert*-amyl alcohol was used.

As the conversion and yield of **4** were not improved very much by increasing the amount of zeolite, an attempt was made at multistaging the reaction. After each stage, the old zeolite was removed; the product mixture was concentrated; and fresh zeolite, *tert*-amyl alcohol and cyclohexane were added. Several experiments were conducted in which the quantity of *tert*-amyl alcohol was 20 mmol for 10 mmol of **1** and the reaction time was 1 h in each experiment. The first stage was equivalent to the normal 4 g/10 mmol reaction. The resulting product mixture was reacted again with fresh zeolite, additional *tert*-amyl alcohol (20 mmol) and fresh solvent. Therefore, after two stages, HM (Si/Al = 10; 8 g) and *tert*-amyl alcohol (40 mmol) had been reacted with the naphthalene (10 mmol). This process was then repeated for third, fourth, fifth and sixth stages, such that catalyst (24 g) and *tert*-amyl alcohol (120 mmol) were used in total, although in principle these materials could be recycled. The results obtained are given in Table 7.

The results reported in Table 7 clearly indicated that both the conversion and yields of dialkyl naphthalenes **4–6** increased stage by stage. After the sixth stage, the yields of **4** and **5** were 35 and 20%, respectively, while the yield of **6** was 2%.

We have also attempted to vary the reaction time (6 or 12 h) in the multistaging *tert*-amylation of naphthalene (**1**) over HM (Si/Al = 10) in cyclohexane in an attempt to increase the yield of **4**. However, the yield of **4–6** obtained was only 49% after four stages (Table 8).

Our attention was next turned to studying the effect of reaction time and the quantity of *tert*-amyl alcohol in the multistaging *tert*-amylation of naphthalene. Two different sets of experiments were conducted in which the quantity of *tert*-amyl alcohol was varied (20 or 80 mmol for 10 mmol of **1**). The first stage was equivalent to the normal 4 g/10 mmol reaction. The resulting product mixture was reacted again with fresh zeolite, additional

Table 7 Multistaging *tert*-amylation of naphthalene (**1**) over HM (Si/Al = 10) in cyclohexane for 1 h according to Scheme 1^a

Stage	Yields ^b (%)					
	1	2	3	4	5	6
1	40	49	0.5	5	4	0.5
2	21	56	0.5	12	9	1
3	13	55	0.5	19	11	1
4	13	50	0.5	21	13	1
5	5	45	0.5	30	17	2
6	3	40	—	35	20	2

^a Each stage is a 1 h stirred autoclave reaction under self generated pressure at 180 °C; HM (Si/Al = 10; 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol), *tert*-amyl alcohol (1.76 g; 20 mmol). At the beginning of each stage, the old zeolite was removed by filtration and washed with acetone (20 mL); the combined filtrates were allowed to evaporate in air at atmospheric pressure for 6 h (to avoid losses of more volatile components such as naphthalene) before addition of fresh HM (Si/Al = 10; 4.0 g), fresh cyclohexane (50 mL) and fresh *tert*-amyl alcohol (1.76 g; 20 mmol). ^b See footnote *b* to Table 2.

Table 8 Multistaging *tert*-amylation of naphthalene (**1**) over HM (Si/Al = 10) in cyclohexane for different times according to Scheme 1^a

Stage	Time (h)	Yields ^b (%)					
		1	2	3	4	5	6
1	6	25	52	3	6	5	1
2	12	11	57	1.5	17	12	1.5
3	6	6	59	1	19	13	2
4	12	2	48	0.5	27	19	3

^a Each stage involved a stirred autoclave reaction under self-generated pressure at 180 °C; HM (Si/Al = 10; 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol, added at the first stage only), *tert*-amyl alcohol (1.76 g; 20 mmol) for the required time. At the beginning of each stage, the old zeolite was removed by filtration and washed with acetone (20 mL); the combined filtrates were allowed to evaporate in air at atmospheric pressure for 6 h before addition of fresh HM (Si/Al = 10; 4.0 g), fresh cyclohexane (50 mL) and fresh *tert*-amyl alcohol (1.76 g; 20 mmol). ^b See footnote *b* to Table 2.

tert-amyl alcohol (20 or 80 mmol) and fresh solvent. Therefore, after two stages, HM (Si/Al = 10; 8 g) and *tert*-amyl alcohol (40 or 160 mmol) had been reacted with the naphthalene (**1**; 10 mmol). This process was then repeated for third, fourth and fifth stages, such that zeolite (20 g) and *tert*-amyl alcohol (100 or 400 mmol) were used in total. The results obtained are given in Table 9.

The results reported in Table 9 clearly indicated that reactions with more alcohol proceeded more slowly than those with less. With 80 mmol of alcohol at each stage the maximum conversion after five stages was 90% and the combined yields of **4–6** were 42%, along with 47% of **2** and traces of **3**. Higher yields and conversions were obtained when 20 mmol of *tert*-amyl alcohol was used at each stage (combined yield of **4–6** was 70% after 5 stages), but the selectivity for production of **4** over **5** was better for reactions with 80 mmol of alcohol (after five stages the yield of **4** was up to 30%, with only 12% of **5** and virtually no **6**).

We therefore attempted the multistaging *tert*-amylation of naphthalene (10 mmol) in which *tert*-amyl alcohol (50 mL) was

Table 9 Multistaging *tert*-amylation of naphthalene (**1**) over HM (Si/Al = 10) in cyclohexane for 6 h according to Scheme 1^a

Stage	<i>tert</i> -Amyl alcohol (mmol)	Yields ^b (%)					
		1	2	3	4	5	6
1	20	22	58	2	10	6	2
2	20	11	55	1.5	18	13	1.5
3	20	4	41	1.5	31	20	1
4	20	—	36	1	38	24	1
5	20	—	28	1	46	23	1
1	80	66	31	1	2	—	—
2	80	37	47	1	11	4	0.5
3	80	25	46	3	16	7	0.5
4	80	20	52	2.5	17	7	0.5
5	80	10	47	0.5	30	12	—

^a Each stage was a 6 h stirred autoclave reaction under self-generated pressure at 180 °C; HM (Si/Al = 10; 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol, added at the first stage only), *tert*-amyl alcohol. At the beginning of each stage, the old zeolite was removed by filtration and washed with acetone (20 mL); the combined filtrates were allowed to evaporate in air at atmospheric pressure for 6 h before addition of fresh HM (Si/Al = 10; 4.0 g), fresh cyclohexane (50 mL) and fresh *tert*-amyl alcohol. ^b See footnote *b* to Table 2.

Table 10 Multistaging *tert*-amylation of naphthalene (**1**) over HM (Si/Al = 10) using *tert*-amyl alcohol (50 mL) for 24 h according to Scheme 1^a

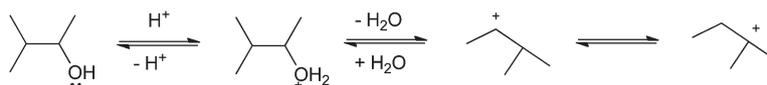
Stage	Yields ^b (%)					
	1	2	3	4	5	6
1	97	2	Traces	0.5	Traces	—
2	93	5	Traces	1	Traces	—
3	81	14	0.5	3	1	—
4	78	14	0.5	5	1	—
5	76	15	0.5	5	1	—
6	75	17	0.5	5	1	—

^a Each stage was a 24 h stirred autoclave reaction under self-generated pressure at 180 °C; HM (Si/Al = 10; 4.0 g), naphthalene (1.28 g; 10 mmol, added at the first stage only), *tert*-amyl alcohol (50 mL). At the beginning of each stage, the old zeolite was removed by filtration and washed with acetone (20 mL); the combined filtrates were allowed to evaporate in air at atmospheric pressure for 6 h before addition of fresh HM (Si/Al = 10; 4.0 g) and fresh *tert*-amyl alcohol (50 mL). ^b See footnote *b* to Table 2.

used as the solvent in order to improve the selectivity towards formation of **4** even further. The results obtained are given in Table 10.

It was found that using *tert*-amyl alcohol as the solvent resulted in a lower conversion (25%) even after 6 stages but the reaction was more selective towards formation of 2,6-di-*tert*-amyl-naphthalene (**4**), giving a **4** : **5** ratio of 5. Also, no 2,6-di-*tert*-butyl-naphthalene (**6**) was formed under the conditions tried.

The maximum yield of 2,6-dialkyl-naphthalenes obtained thus so far was in the region of 70% and it seemed likely that this would not be much improved under the kinds of conditions tried. Therefore, our attention was turned to study the alkylation of naphthalene using different alcohols under conditions similar to those used with *tert*-amyl alcohol to see if any benefits could be achieved.



Scheme 3 Generation of *tert*-amyl cation from 3-methyl-2-butanol over an acidic zeolite.

Alkylations of naphthalene (**1**; 10 mmol) were attempted at 180 °C, using 2,2-dimethyl-1-propanol, 2,3-dimethyl-2-butanol and 3-methyl-2-butanol (20 mmol in each case) over HM (Si/Al = 10, 4 g) in cyclohexane (50 mL) under conditions similar to those used for the reaction depicted in Scheme 1.

For the primary alcohol (2,2-dimethyl-1-propanol), it was not surprising that no products were observed under these conditions. With 2,3-dimethyl-2-butanol as an alkylating reagent, naphthalene conversion was 20%. The major products were mono-alkylated naphthalenes, namely 2-*tert*-amyl naphthalene (**2**; 0.5%) and 2-*tert*-butyl naphthalene (**3**; 5%) along with another mono-alkylated naphthalene, probably 2-(2,3-dimethyl-2-butyl)naphthalene (*ca.* 8%). Dialkylated naphthalenes were produced in low yields (*ca.* 0.5% each) as a mixture of 2,6-di-*tert*-amyl naphthalene (**4**), 2-*tert*-amyl-6-*tert*-butyl naphthalene (**5**) and 2,6-di-*tert*-butyl naphthalene (**6**) along with another dialkylated naphthalene, probably containing a (2,3-dimethyl-2-butyl) group.

With 3-methyl-2-butanol as alkylating reagent, a naphthalene conversion of 80% was achieved. The yield of 2-*tert*-amyl naphthalene (**2**) was 62%. 2,6-Di-*tert*-amyl naphthalene (**4**) and 2-*tert*-amyl-6-*tert*-butyl naphthalene (**5**) were also formed in 6 and 5% yields, respectively, along with traces of 2,6-di-*tert*-butyl naphthalene (**6**; 0.5%). The *tert*-amylated products were presumably formed due to generation of *tert*-amyl cation from 3-methyl-2-butanol over the acidic zeolite (Scheme 3), while the *tert*-butylated products would be produced due to the conversion of *tert*-amyl cation to *tert*-butyl cation over HM zeolite (Scheme 2).

In an attempt to increase the yield of 2,6-dialkyl naphthalenes from the reaction with 3-methyl-2-butanol, the reaction was carried out in multistage mode using naphthalene (**1**; 10 mmol), and for each stage the alcohol (20 mmol), HM (Si/Al = 10; 4 g) and cyclohexane (50 mL) at 180 °C for 6 h (Table 11).

The results reported in Table 11 showed that the conversion was 80% after the first stage and increased to 100% after the fourth stage. The yield of 2-*tert*-amyl naphthalene (**2**) was reduced from 62 to 45% after the fourth stage. The maximum yield of 2,6-dialkyl naphthalenes was 53%, of which the yield of **4** was 32%. Also, after the fourth stage, 2,6-dialkyl naphthalenes **5** and **6** were formed in 19 and 2% yields, respectively.

In order to check on the possibility of reuse of the zeolite, a single reaction of **1** (10 mmol) was carried out using *tert*-amyl alcohol (20 mmol), and the zeolite was recovered following extraction of the products and was then regenerated by heating overnight in air in an oven set at 550 °C. The regenerated zeolite was then reused in an identical reaction. This process was repeated several times with the same batch of zeolite. The yield and selectivity of each reaction are recorded in Table 12. It can be seen that the zeolite could be effectively recycled, while retaining substantial activity and selectivity even after six uses.

Table 11 Multistaging alkylation of naphthalene (**1**) using 3-methyl-2-butanol over HM (Si/Al = 10) in cyclohexane for 6 h^a

Stage	Yields ^b (%)					
	1	2	3	4	5	6
1	20	62	2.5	6	5	0.5
2	20	54	2.5	12	8	1
3	4	56	2	20	14	2
4	—	45	2	32	19	2

^a Each stage was a 6 h stirred autoclave reaction under self-generated pressure at 180 °C starting with naphthalene (1.28 g; 10 mmol); HM (Si/Al = 10; 4.0 g), cyclohexane (50 mL), and 3-methyl-2-butanol (1.76 g; 20 mmol). At the beginning of each new stage, the old catalyst was removed by filtration and washed with acetone (20 mL); the combined filtrates were allowed to evaporate in air at atmospheric pressure for 6 h before addition of fresh HM (Si/Al = 10; 4.0 g), fresh cyclohexane (50 mL) and fresh alcohol (1.76 g; 20 mmol). ^b See footnote *b* to Table 2.

Table 12 Efficiency of recycled calcined HM (Si/Al = 10) zeolite in *tert*-amylation of naphthalene (**1**) in cyclohexane according to Scheme 1^a

Run	Yields ^b (%)					
	1	2	3	4	5	6
1	22	58	2	10	6	2
2	21	59	2	9	5	3
3	20	59	2	10	6	2
4	21	57	3	11	5	2
5	20	58	2	10	5	2
6	23	57	2	9	4	3

^a Stirred autoclave reaction for 6 h under self generated pressure at 180 °C; HM (Si/Al = 10, 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol) and *tert*-amyl alcohol (1.76 g; 20 mmol). The reaction was scaled down after the first use of zeolite. ^b See footnote *b* to Table 2.

Conclusions

The autoclave reaction of *tert*-amyl alcohol with naphthalene at 180 °C in the presence of sufficient HM (Si/Al = 10) zeolite provides a convenient method for the synthesis of 2,6-dialkyl naphthalenes selectively in high yields, with no 2,7-isomers detected. However, in addition to 2,6-di-*tert*-amyl naphthalene, a significant quantity of 2-*tert*-amyl-6-*tert*-butyl naphthalene is also formed and is difficult to separate from the major product. Heating easily regenerates the zeolite, which can be reused to give results similar to those of a fresh sample.

The two major products of these reactions could both have commercial significance. 2-*tert*-Amyl naphthalene is a known lubricant,⁵¹ while 2,6-di-*tert*-amyl naphthalene, a novel compound, could, in principle, be cracked⁴⁹ to give DMN, a key

intermediate in the production of PEN. Current methods for production of DMN involve multiple steps (at least one of which is low yielding), difficult and tedious separations of isomers, and isomerisation/recycling of by-products. Therefore, the present method offers great potential for improving the “greenness” and commercial viability of the production of PEN, although it would probably need to be converted into a continuous process.

Experimental

Materials

Chemicals and solvents were purchased from Aldrich Chemical Company and used without further purification. H-Mordenite (HM; Si/Al = 10) zeolite was purchased from Zeolyst International and freshly calcined at 550 °C for a minimum of 6 h prior to use.

Analysis and characterization of the products

Product mixtures from the *tert*-amylation reactions of naphthalene were subjected to gas chromatography using a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a Zebron ZB-5 (5% phenyl–95% dimethylpolysiloxane), 0.32 mm ID 30 m length column. The GC conditions used for analysis were: 170 °C for 0.5 min, ramped to 300 °C at 4 °C min⁻¹. The injection temperature and detection temperature were each 295 °C. Hexadecane was used as a GC standard. The structure of the novel compound 2,6-di-*tert*-amyl-naphthalene (**4**) was confirmed by ¹H and ¹³C NMR spectra, mass spectral analysis and X-ray crystal structure (Fig. 1).

Melting points were determined by the open capillary method using a Gallenkamp melting point apparatus and are reported uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C measurements. Chemical shifts δ are reported in parts per million (ppm) relative to TMS and coupling constants *J* are in Hz. ¹³C multiplicities were revealed by DEPT signals. Assignments of signals are based on integration values, coupling patterns and expected chemical shift values. Mass spectra were recorded on a GCT premier-EI mass spectrometer.

The X-ray single-crystal diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K α (λ = 0.710 73 Å) radiation. The structure of **4** was solved by direct methods using SHELXS-96⁵² and refined with all data on *F*² full-matrix least squares using SHELXL-97.⁵³

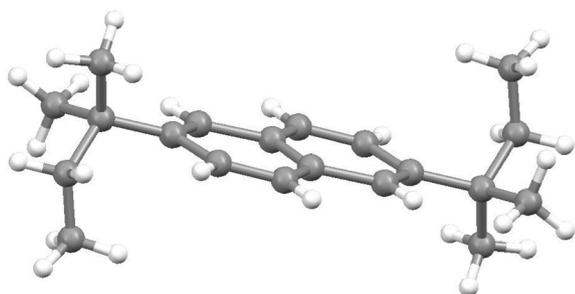


Fig. 1 X-Ray crystal structure for 2,6-di-*tert*-amyl-naphthalene (**4**).

Typical experimental procedure for the *tert*-amylation of naphthalene using *tert*-amyl alcohol over HM zeolite

Quantities are recorded in the footnotes to the appropriate tables. All reactions were carried out in a 100 ml Teflon-lined Parr autoclave, fitted with a thermocouple and gauge block assembly. To the Teflon liner of the autoclave were added a magnetic bar, naphthalene, *tert*-amyl alcohol and solvent. The mixture was allowed to stir until all naphthalene had dissolved (*ca.* 5 min) and then HM zeolite was added. The Teflon liner was transferred into the stainless steel autoclave, which was sealed and heated for the appropriate reaction time and temperature, with stirring, under self-generated pressure. In some experiments the system was artificially pressurised up to 500 psi with nitrogen gas prior to heating. After the given reaction time, the heating device was removed and the autoclave was allowed to cool to room temperature (*ca.* 2 h). The contents were removed and the apparatus was then washed thoroughly with acetone. The acetone washings were combined with the original contents and the catalyst was removed by filtration. The solid was thoroughly extracted with further acetone and the combined mother liquors were concentrated under reduced pressure. The product mixture was analysed by quantitative gas chromatography using hexadecane as the GC standard and the yields were calculated.

Preparation of a mixture of 2,6-dialkyl-naphthalenes by multistaging the reaction

A mixture of HM (Si/Al = 10; 4.0 g), cyclohexane (50 mL), naphthalene (1.28 g; 10 mmol, added at the first stage only) and *tert*-amyl alcohol (1.76 g; 20 mmol) was heated at 180 °C for 6 h in an autoclave. The mixture was allowed to cool to room temperature and the product mixture was concentrated (by allowing the volatile components to evaporate over 6 h) and fresh HM (Si/Al = 10; 4.0 g), fresh cyclohexane (50 mL) and fresh *tert*-amyl alcohol (1.76 g; 20 mmol) were added. The reaction was then allowed to proceed again under the same conditions. The crude product obtained after multistaging the reaction five times (Table 9) was a mixture of a white crystalline solid and an oily material (2.41 g), which were separated by filtration and the solid was washed with ethanol. The GC of oil and washing (0.70 g) indicated the presence of 2-*tert*-amyl-naphthalene (**2**) as the major component along with traces of the other compounds. The NMR analysis of the solid (1.71 g) showed the presence of 2,6-di-*tert*-amyl-naphthalene (**4**) along with 2-*tert*-amyl-6-*tert*-butyl-naphthalene (**5**) and 2,6-di-*tert*-butyl-naphthalene (**6**) in the ratio of *ca.* 12 : 5 : 1. Crystallisation of this solid (*ca.* 0.1 g) from ethanol provided colourless crystals of **4** that still contained a significant quantity of **5** but which could be analysed by X-ray crystallography to confirm the structure as **4** (Fig. 1).

GC MS Analytical data for the mixture of 2,6-dialkyl-naphthalenes 4–6

Yield: 1.71 g starting from naphthalene (1.28 g; 10 mmol). EI-MS (%) **4**: 268 (M⁺, 35), 253 (10), 239 (100), 224 (5), 210 (30), 195 (20), 167 (10), 141 (7), 128 (2), 71 (3); EI-MS (%) **5**: 254 (M⁺, 19), 239 (10), 225 (100), 210 (10), 195 (10), 181 (5), 167 (7), 141 (7), 128 (2), 57 (2); EI-MS (%) **6**: 240 (M⁺, 29),

225 (100), 218 (5), 210 (7), 195 (7), 179 (2), 165 (6), 152 (5), 141 (5), 129 (2), 115 (1), 91 (3), 77 (2), 57 (2).

Analytical data for 2,6-di-*tert*-amyl-naphthalene (4), deduced from the spectra of the mixture

^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, $J = 8.6$ Hz, 2 H, H-4 and H-8), 7.72 (d, $J = 1.7$ Hz, 2 H, H-1 and H-5), 7.52 (dd, $J = 1.7, 8.6$ Hz, 2 H, H-3 and H-7), 1.78 (q, $J = 7.5$ Hz, 4 H, 2 CH_2CH_3), 1.42 (s, 12 H, 4 CH_3), 0.73 (t, $J = 7.5$ Hz, 6 H, 2 CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 146.6 (s, C-2 and C-6), 131.9 (s, C-4a and C-8a), 127.9 (d, C-4 and C-8), 125.3 (d, C-3 and C-7), 124.0 (d, C-1 and C-5), 38.4 [s, $\text{C}(\text{CH}_3)_2$], 37.0 (t, CH_2CH_3), 29.0 [q, $\text{C}(\text{CH}_3)_2$], 9.6 (q, CH_2CH_3); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{28}$ [M^+]: 268.2191; found: 268.2184.

Crystal data for 4: colourless, $\text{C}_{20}\text{H}_{28}$, $T = 150(2)$ K, monoclinic, space group $P21/n$, $a = 6.7860(18)$ Å, $b = 12.584(2)$ Å, $c = 9.896(3)$ Å, $\alpha = 90^\circ$, $\beta = 94.038(8)^\circ$, $\gamma = 90^\circ$, 1413 reflections collected, 748 independent reflections, $R = 0.1100$, $wR = 0.2877$, $R(\text{int}) = 0.0949$. CCDC 827589.

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