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# Production of *p*-Cymene from Crude Sulphate Turpentine with Commercial Zeolite Catalyst Using a Continuous Fixed Bed Reactor

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**ABSTRACT:** Crude sulphate turpentine (CST), containing  $\alpha$ -pinene, 3-carene, other terpene isomers, and organic sulphur compounds, was used as feedstock in the production of cymenes with commercial zeolite catalysts. The catalysts used were not sensitive to sulphur, and the desulphurisation step was not needed prior to cymene synthesis. The experiments were performed in a continuous fixed bed reactor. Promising results were obtained after initial optimization at temperatures close to 300 °C with faujasite Y zeolite under 5 bar N<sub>2</sub> pressure. Cymenes were produced with 54% yields from model compound  $\alpha$ -pinene and with 28% yields from CST. The mechanistic route of the reaction can be divided into three steps: (1) ring opening, (2) rearrangement, and (3) dehydrogenation. The final step in the formation of *p*-cymene can occur via dehydrogenation or disproportion; here the effect of reaction conditions and catalyst plays a crucial role.

## INTRODUCTION

The petrochemical industry is strongly dependent on the depleting crude oil resources. Targeting 100% biobased chemicals and polymers as replacements for the crude oil derived equivalents is a hot topic in chemistry research. Terpenes, naturally occurring compounds that can be used as a renewable feedstocks, have a high potential in this field.<sup>1</sup> Terpenes can be modified by isomerisation, oxidation, esterification, carbonylation, and (de)hydrogenation reactions to access valuable chemical products.<sup>2</sup> Monoaromatic compounds produced from terpenes are valuable for petrochemical industry.<sup>2,3</sup> Of these, *p*-cymene is of particular importance as it has potential use in the synthesis of terephthalic acid<sup>4</sup> and already established main uses in *p*-cresol production.<sup>5</sup> *p*-Cymene has also uses as a solvent for dyes and varnishes, as a heat transfer medium, as the intermediate for the production of pesticides, fungicides, flavours, and pharmaceuticals.<sup>6</sup> Industrially *p*-cymene is produced by Friedel–Crafts alkylation of benzene or toluene with propylene or 2-propanol, and hazardous acid catalysts such as AlCl<sub>3</sub> or HF are used as catalysts in the process.<sup>5,6</sup> Due to the involvement of highly toxic substances, this process is becoming a restricted method by environmental legislation.<sup>7–11</sup>

The production of *p*-cymene from terpenes has emerged as an environmentally benign alternative.<sup>12</sup> Several heterogeneous and homogeneous catalysts have been used for the conversion of monoterpenes and terpene mixtures to monoaromatics. Special attention has been given to the production of *p*-cymene from  $\alpha$ -pinene and limonene over various metal catalysts such as Pd/C,<sup>13</sup> Pd/Al<sub>2</sub>O<sub>3</sub>,<sup>13</sup> Pd/Si,<sup>7,14,15</sup> Pd–Ce/zeolite,<sup>7,16,17</sup> Pd/zeolite,<sup>18</sup> Pt/C, Cu/Cr<sub>2</sub>O<sub>3</sub>, and ZnO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub>.<sup>19</sup> In addition silica–alumina supports,<sup>20</sup> modified clays,<sup>21</sup> and Pd nano-cluster<sup>22</sup> catalysts have been used. There are also examples of catalyst-free aromatization reactions.<sup>23</sup> A wide temperature range (150–500 °C) has been used in the aromatizations. It is known that, as high temperature is advantageous for *p*-cymene

formation, too high temperature (>400 °C) enhances the thermal cracking of the products.<sup>11</sup>

However, using pure  $\alpha$ -pinene or limonene for the production of *p*-cymene is limited due to their high market price in comparison with toluene and propylene. Especially limonene has high demand as it is emerging as a biodegradable solvent.<sup>21</sup> Crude sulphate turpentine (CST) is a cheap byproduct of Kraft pulping process of pine wood.<sup>12</sup> Crude sulfur turpentine contains mainly monoterpenes  $\alpha$ -pinene and 3-carene (Table 1, Scheme 1, this work), and it can be used as a starting material for the production of monoaromatics.

Table 1. CST composition (this work)

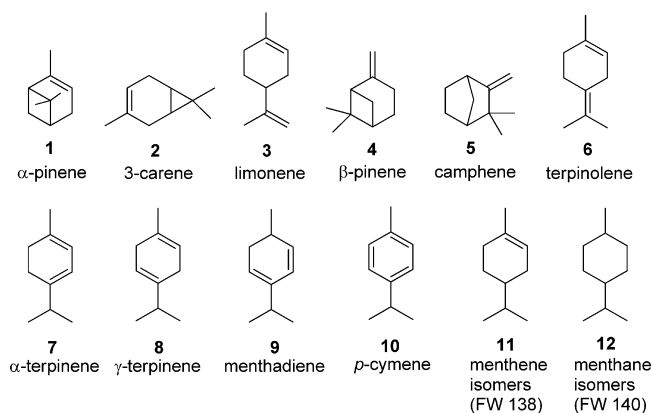
CST component	wt %
$\alpha$ -pinene	65
3-carene	24
<i>p</i> -cymene	0.46
<i>R</i> -(+)-limonene	2.0
other terpene isomers (FW 136)	7.4
terpene dimers (FW 204)	0.83
other compounds	0.29

The literature on the aromatization of CST is very scarce. This can be partly due to the chemical composition of CST as it also contains sulphur compounds in high concentrations (methyl mercaptan 0.2–5 wt %, dimethyl sulfide 1–12 wt %, and dimethyl disulfide 0–1.3 wt %).<sup>24</sup> The Pd catalysts traditionally used for  $\alpha$ -pinene aromatization are sensitive to sulphur and are therefore not suitable for CST aromatization. A similar conclusion can be drawn with several other metal

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Scheme 1. Terpene structures



catalysts. There are some examples in the literature on using zeolites for the isomerization and aromatization of pure  $\alpha$ -pinene and 3-carene.<sup>25,26</sup> The development of sulphur-tolerant catalyst systems for the production of biobased chemicals is vital for the emerging bioeconomy, as various biobased feedstocks, such as CST and crude tall oil, are rich in sulphur.

In this work, the potential of zeolite catalysts for aromatics production from CST was studied. Besides a good acidic platform, zeolites offer shape selectivity for the aromatization. In preliminary experiments,  $\alpha$ -pinene was used as a model compound for CST. Three different zeolite catalysts (Molecular Sieve 13X (FAU X), Mordenite (MOR), Faujasite Y (FAU Y)) were compared at 300 °C. The most promising catalyst, FAU Y, was chosen for further experiments with CST.<sup>27–29</sup>

## EXPERIMENTAL SECTION

CST was supplied by Stora Enso (Finland) and used as received. Other reagents and catalysts were obtained from commercial sources; (–)  $\alpha$ -pinene (Fluka, 98% (mixture of enantiomers) and 99% (GC grade)), *R*-(+)-limonene (97%, Sigma-Aldrich), *p*-cymene (Sigma-Aldrich, 99%, GC grade), 13X (Faujasite X, Union Carbide), Mordenite (Zeolyst), and Faujasite Y (Zeolyst). The main characteristics of the catalysts used are shown in Table 2.

A continuous tubular fixed bed reactor was used in the aromatization experiments (Figure 1). The catalyst bed was fixed with quartz wool (0.8 g) inside the reactor. Each experiment was run for 6 h to achieve a steady state. A pressure test was carried out with 5.5 bar ( $N_2$ ) followed by catalyst pretreatment at 500 °C (2 h) under vacuum for removal of moisture. The reactor pressure (5 bar  $N_2$ ) and catalyst bed temperature were adjusted prior the feed. The terpene feed was set to 10 g/h. The WHSV was between 1.5 and 6 L/h. The feed was preheated in the feed line to 160 °C, which is near the boiling point of monoterpenes. The product flow was cooled down after the reactor, and the liquid sample was collected in a cold trap for GC-MS analysis.

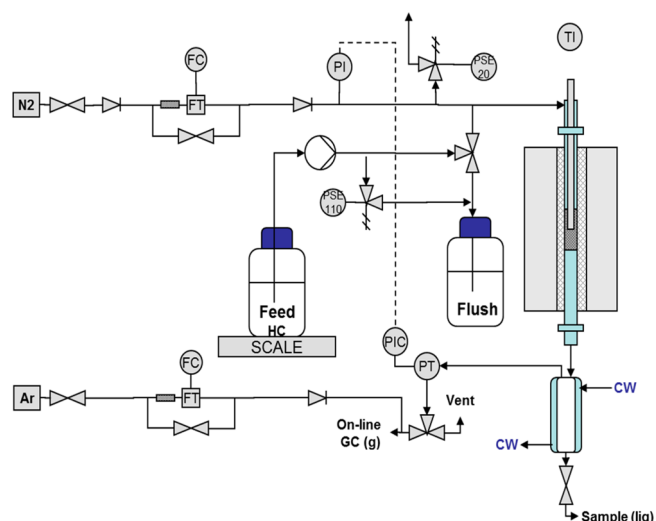


Figure 1. A schematic picture of the reactor equipment.

The analysis of the liquid samples and the feed CST was performed by GC-MS instrument trace GC ultra gas chromatograph, trace DSQ mass spectrometer (Thermo Finnigan, USA) column: HP-1MS dimensions 30 m  $\times$  0.25 mm, 0.25  $\mu$ m film thickness. Oven temperature program: 35 °C/hold 3 min/15 °C min<sup>–1</sup>/60 °C/hold 0 min/3 °C min<sup>–1</sup>/130 °C/hold 0 min/25 °C min<sup>–1</sup>/300 °C/hold 8 min. Carrier gas He, constant flow 1.3 mL/min; injection volume 1  $\mu$ L, split 1:30; mass spectrometer scan range *m/z* 35–600.

The results were calculated using external calibration method. *p*-cymene and  $\alpha$ -pinene were calculated quantitatively. Terpenes and aromatics were calculated semiquantitatively with the responses of  $\alpha$ -pinene and *p*-cymene, respectively. The uncertainty of the measurements was  $\pm 15\%$  for *p*-cymene and  $\alpha$ -pinene and  $\pm 30\%$  for semiquantitatively calculated compounds. The analysis results were confirmed with GC-FID and GC-MS. All of the calculated results are based on the analysed organic fraction. The results calculated in Tables 3 and 4 are from 4 to 6 h samples on-stream. Selectivity is calculated as moles of component in the product divided by reacted amount of feed components  $\alpha$ -pinene and 3-carene. Conversion is calculated for  $\alpha$ -pinene and 3-carene as reacted molar amount divided by molar amount in the feed.

## PROPERTIES OF THE ZEOLITES

All zeolites, FAU Y, FAU X, and MOR, are large pore zeolites having pore size  $>7.4$  Å (Table 2). FAU Y and FAU X have crystalline structures formed by spherical super cages of 14 Å diameter interconnected tetrahedrally through smaller openings of 7.4 Å.<sup>30</sup> MOR consists of two pore channels: an elliptical 12-membered ring (MR) channel (6.7 Å  $\times$  7.0 Å) which runs parallel to the *c*-axis and a 8 MR side pocket (3.4 Å  $\times$  4.8 Å) that runs in the *b*-axis direction.<sup>31</sup>

Table 2. Main characteristics of the catalysts used

catalyst	zeolite type	manufacturer	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	Na <sub>2</sub> O (wt %) <sup>a</sup>	BET (m <sup>2</sup> /g)	pore size (Å)
CBV600	Faujasite Y (FAU Y)	Zeolyst	5.2	0.2	660	7.44 <sup>b</sup>
CBV21A	Mordenite (MOR)	Zeolyst	20	0.08	500	7.0 $\times$ 6.7 <sup>c</sup>
13X	Faujasite X (FAU X)	Union Carbide	2.5 $\pm$ 0.5	9.56	412	7.4 <sup>b</sup>

<sup>a</sup>Value obtained from the manufacturer. <sup>b</sup>See ref 30. <sup>c</sup>See ref 31.

Table 3. Calculated Si/Al ratios and percentages of different Al species of the studied zeolite catalysts

sample	type	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	amount (%)			
			Al(IV) <sub>FR</sub>	Al(V) <sub>NFR</sub>	Al(VI) <sub>NFR</sub>	Al <sub>FR</sub> /Al <sub>NFR</sub>
MOR	Mordenite	15.7	34.6	38.6	26.8	0.346
FAU Y	Faujasite Y	8.4	37.9	8.4	53.7	0.379
FAU X	Faujasite X	1.4	96.9	0.1	3.0	0.969

<sup>a</sup>Calculated based on the integrals seen from the <sup>29</sup>Si MAS NMR spectra.

Table 4. Quantitative hydroxyl group amounts (acid OH, ALOH, and SiOH) and the total amount of H in each sample as calculated from the <sup>1</sup>H MAS NMR spectra

sample	type	amount (μmol/g)				total amount of H
		acid OH	ALOH	SiOH	residual template	
MOR	Mordenite	n.m	n.m	n.m	n.m	11580
FAU Y	Faujasite Y	450	262	489	1388	2589
FAU X	Faujasite X	68	73	46	1785	1972

#### Acidity of the Zeolites: Analysis with Solid-State NMR.

All NMR measurements were carried out at 293 K using Agilent narrow-bore 600 MHz (14.1T) NMR spectrometer equipped with a 3.2 mm HXY MAS probe. For the <sup>1</sup>H NMR experiments, the samples were dehydrated at 673 K for 4 h under dry nitrogen gas flow at atmospheric pressure. In the <sup>1</sup>H MAS NMR experiments, 128 transients were acquired using a 2.85 μs pulse (π/2), 30 s recycle delay, and a MAS rate of 20 kHz. After dehydration the samples were loaded inside a glovebox into 3.2 mm zirconia rotors. For the quantitative OH group determination, a full rotor of Q8M8 (octakis-(trimethylsiloxy)silesquioxane), Chymos GmbH, CAS No. 51777-38-9) was used as an external quantitation standard. In all cases a background signal, run under identical conditions with an empty rotor, was subtracted from the spectra. The amount of OH groups (μmol/g) in each sample was determined by comparing the experimental spectral area to that of external standard and normalizing by weight (spin counting).<sup>32</sup> <sup>27</sup>Al and <sup>29</sup>Si MAS NMR experiments were carried out on the samples without drying. In the <sup>27</sup>Al MAS NMR experiments, 4000 transients were acquired using a 1.0 μs pulse (π/12), 2 s recycle delay, and MAS rate of 20 kHz. In the <sup>29</sup>Si MAS NMR experiments, 20000 transients were acquired using 3.0 μs pulse (π/4), 10 s recycle delay, and MAS rate of 10 kHz.

The <sup>29</sup>Si MAS NMR spectra of the studied zeolites are shown in Figure 2 (left). <sup>29</sup>Si MAS NMR was used to measure and characterize the Si/Al ratio for the framework.<sup>33</sup> In the <sup>29</sup>Si NMR spectra of FAU Y and FAU X zeolites, relative intensities of the sharp resonances reflect directly the numbers and occupancies of the crystallographically inequivalent T-sites in the asymmetric unit of the unit cell. In the case of MOR zeolite, the shift dispersion is limited and acts mainly as an additional line-broadening mechanism in the spectrum. The calculated Si/Al ratios are depicted in Table 3.

The <sup>27</sup>Al MAS NMR of zeolites FAU Y, MOR, and FAU X are shown in Figure 2 (right). In the <sup>27</sup>Al NMR spectra, three different types of Al species were assigned according to their distinct isotropic chemical shift range: four-coordinated framework aluminum (Al(IV)<sub>FR</sub>) around 75–50 ppm, 5-coordinated nonframework aluminum (Al(V)<sub>NFR</sub>) around 30–40 ppm, and six-coordinated nonframework aluminum (Al(VI)<sub>NFR</sub>) around 20–0 ppm.<sup>34</sup> Table 3 shows the ratio of different

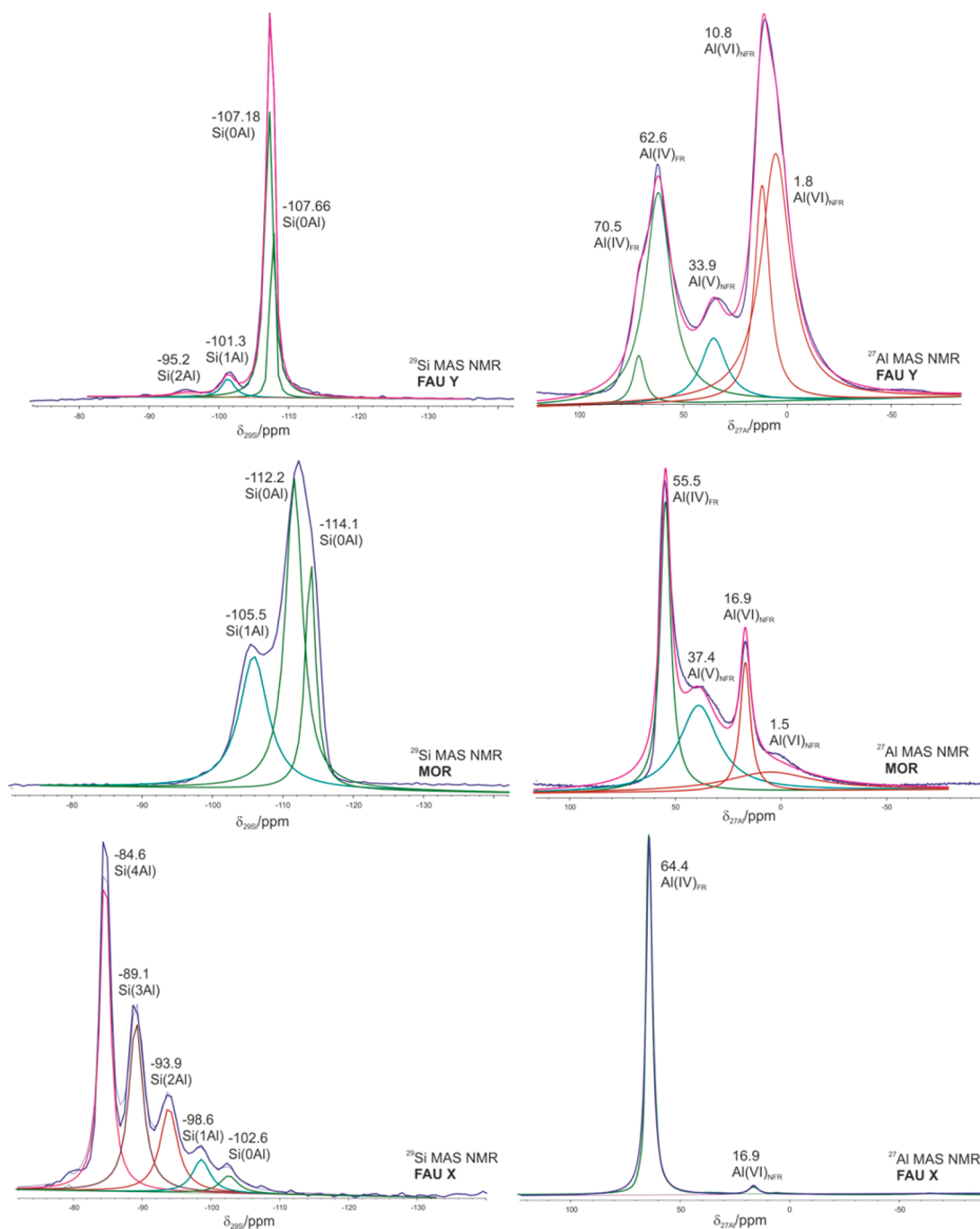
Al sites as determined from the peak area. The results indicate that in zeolite FAU Y only 38% of the total amount of aluminum in the catalyst is located in the framework, whereas in zeolite FAU X aluminum is mainly located in the catalyst framework (97%).

In this study, <sup>1</sup>H MAS NMR was used to measure quantitatively Brønsted acid sites (see beginning of this chapter) of the zeolites. The results are shown in Table 4. According to the results, the FAU Y zeolite (Si/Al 8.4) shows a Brønsted acidity of 450 μmol/g and the FAU X zeolite (Si/Al 1.4) only 70 μmol/g. This lower acidity of the FAU X zeolite (Si/Al 1.4) may be explained by the high amount of Na<sub>2</sub>O (9.56 wt %) present in the structure, where most of the Na is not removed during the dehydration procedure, respectively. Also, a broad and very intense signal in the <sup>1</sup>H MAS NMR spectra (Figure 3) at chemical shift around 7–8 ppm was observed and tentatively assigned to originate from residual template indicating the presence of hydrocarbons on the catalyst surface. To verify the possibility of residual water, <sup>1</sup>H MAS NMR spectrum of the hydrated zeolite FAU Y was measured, where the chemical shift of the residual water was at 6.5 ppm. In fact, the intense signal around 7–8 ppm was dominating the <sup>1</sup>H MAS NMR spectrum of the MOR zeolite so much that we were not able to carry out acid site calculations for the catalyst due to the measured very high number of total amount of H in the sample (Table 4).

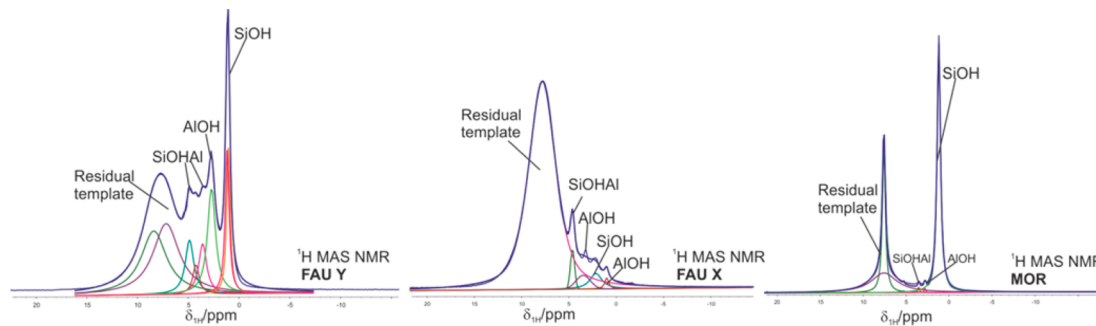
## RESULTS AND DISCUSSION

The three zeolites (Table 2) were tested for the aromatization of model compound α-pinene. The zeolites were tested at 300 °C under vacuum (Table 5). Although all three catalysts gave high conversions at 300 °C, FAU Y gave clearly higher selectivity to cymenes (34%) than MOR (17%) or FAU X (3.9%). The FAU X mostly yielded terpene isomers (78%). FAU Y was selected for further study. Also, different reaction temperatures were tested under vacuum but at 200 °C or below, the catalysts were mainly active for isomerization. The catalysts were tested without pretreatment, but it was discovered that the pretreatment is essential for the catalyst selectivity towards the desired aromatization.

The three zeolites are large pore zeolites having pore size >7.0 Å. The desired product *p*-cymene has a smaller kinetic diameter compared to isomers *o*- and *m*-cymene. The shape selectivity resembles the much-studied xylene isomer case. *p*-Xylene has critical diameter of 6.7 Å (molecule size), similar to benzene and toluene.<sup>27</sup> *p*-Xylene isomers *o*- and *m*-xylene have higher critical diameters of 7.4 Å.<sup>27</sup> For cymenes we have a similar case. *p*-Cymene has a similar structure compared to *p*-xylene, and *o*- and *m*-cymenes have structures compared to *o*- and *m*-xylenes. *p*-Cymene has a kinetic diameter of 6.31 Å calculated from the molecular weight using eq 1,<sup>27</sup> where σ is the kinetic diameter and *M<sub>w</sub>* is the *p*-cymene molecular weight. This indicates that *p*-cymene can form in all studied zeolites,



**Figure 2.**  $^{29}\text{Si}$  MAS NMR (left) and  $^{27}\text{Al}$  MAS NMR (right) of the three studied catalysts (FAU Y, MOR, and FAU X) with chemical shifts and signal assignments.



**Figure 3.**  $^1\text{H}$  MAS NMR spectra of the three studied catalysts (FAU Y, FAU X, and MOR) with signal assignments.



Table 5. Comparing catalyst activity with  $\alpha$ -pinene<sup>a</sup>

exp. no.	catalyst	conv. (%)	selectivity (%) <sup>b</sup>						
			terpene isomers <sup>c</sup>	cymenes				menthenes	menthanes
			(MW 136)	<i>o</i>	<i>m</i>	<i>p</i>	total	(MW 138)	(MW 140)
1	FAU X	86	78	0	0	3.9	3.9	5.1	0
2	MOR	98	50	1.1	10	16	17	20	0
3	FAU Y	100	0	1.4	9.3	23	34	15	16

<sup>a</sup>Reaction conditions: Catalysts were calcinated at 500 °C at vacuum prior to use, catalyst loading 6 g, *T* = 300 °C, vacuum (200 mbar),  $\alpha$ -pinene feed flow rate = 10 g/h. <sup>b</sup>Selectivity is defined in the Experimental Section. <sup>c</sup>Terpene isomers (MW 136) include all terpene isomers with this mass excluding the feed components  $\alpha$ -pinene and limonene.

Table 6. CST aromatisation experiments<sup>a</sup>

exp. no.	<i>T</i> (°C)	FAU Y catalyst loading (g)	<i>N</i> <sub>2</sub> flow (mL/min)	selectivity (%) <sup>b</sup>								
				conv. (%)		terpene isomers <sup>c</sup>	cymenes				menthenes	menthanes
				$\alpha$ -pin	3-car	(MW 136)	<i>o</i>	<i>m</i>	<i>p</i>	total	(MW 138)	(MW 140)
4	350		35	48	38	12	0	0	0.57	0.57	0	0
5	200	3	35	98	85	37	0	0.33	1.4	1.73	0.76	0
6	300	3	35	100	100	14	0	6.5	17	23.5	16	5.6
7	380	3	35	100	100	0	0.9	7.5	12	20	2.2	20
8	300	1.5	35	95	84	32	0.20	2.2	7.3	9.7	7.2	0.53
9	350	1.5	35	98	98	2.4	0.37	6.8	18	25	9.6	6.3
10	400	1.5	35	100	99	0.30	0.45	6.1	12	19	6.2	4.8
11	300	1.5	70	100	98	11	0.31	7.7	20	28	16	3.8
12	350	1.5	70	94	82	34	0.21	2.6	7.2	10	6.3	0.53
13	300	3	70	100	98	9.8	0.35	7.3	18	25	12	2.9
14	350	3	70	100	100	0	0.46	6.7	14	21	5.4	10

<sup>a</sup>Reaction conditions: Catalyst FAU Y, catalyst was calcinated at 500 °C at vacuum prior to use, pressure 5 bar *N*<sub>2</sub>, CST feed flow rate = 10 g/h.

<sup>b</sup>Selectivity is defined in the Experimental Section. <sup>c</sup>Terpene isomers (MW 136) include all terpene isomers with this mass, excluding the feed components  $\alpha$ -pinene, 3-carene, and limonene.

and the differences in the product distribution are caused by differences in acidity.

$$\sigma = 1.234(M_w)^{1/3} \quad (1)$$

Zeolites possess several types of acid sites, which participate in the reactions and affect the reactivity. Whereas framework Al species are always part of the bridging SiOHAl groups (i.e., Brönstedt acid sites), the nonframework aluminum species may occur as Al<sup>3+</sup>, Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub><sup>+</sup>, AlOOH, Al(OH)<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>.<sup>35</sup> Of these, Al<sup>3+</sup>, Al(OH)<sup>2+</sup>, and Al(OH)<sub>2</sub><sup>+</sup> may act as a Lewis acid sites, which may directly initiate the hydrocarbon conversion via hydride abstraction.<sup>36</sup>

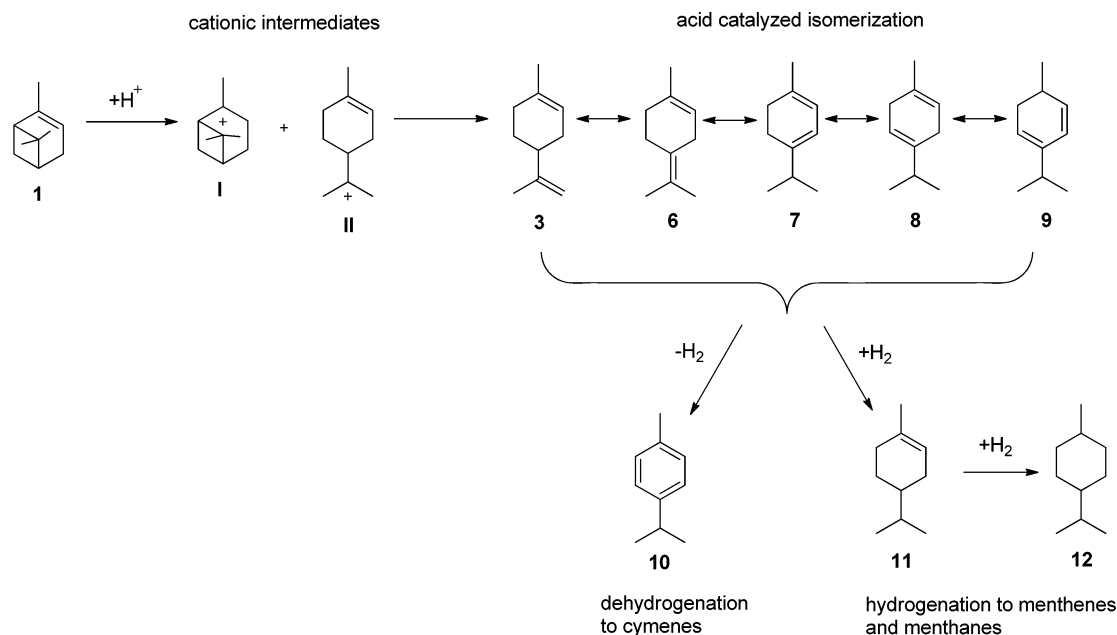
It has been observed that, if only Lewis acid sites are present, no catalytic activity is observed in  $\alpha$ -pinene isomerization and dehydrogenation. In addition also pure Brönstead acidity leads to low overall activity. The highest catalytic activity was achieved with catalyst having both Brönstead and Lewis acid sites.<sup>37,38</sup> In addition it has been shown that the transformation of monoterpenes occur by combination of acid catalysis and electron transfer.<sup>39</sup> On the contrary to monoterpenes, Narbeshuber et al. (1997) concluded that there is two parallel mechanisms of dehydrogenation of light alkanes occurring. The main mechanism is represented by monomolecular protolytic dehydrogenation. These sites produce the constant steady state dehydrogenation activity. In addition at the initial stages of the reaction extra framework aluminum moieties can participate in high dehydrogenation activity. They speculated that these sites are later blocked by the reaction product hydrogen.<sup>40</sup>

According to the results in Table 5, FAU X shows only high isomerization activity to terpene isomers and very weak dehydrogenation activity to cymenes. The low amount of Brönstead and Lewis sites in FAU X (Table 4) and the lower acidity of Brönstead sites is probably the main reason for the low activity towards cymene production but for high isomerization activity.<sup>41</sup>

FAU Y has a higher amount of Brönsted acid and Lewis acid sites compared FAU X (Table 4) and a higher concentration of acidic sites but of lower acidity compared to mordenite.<sup>28</sup> FAU Y shows the highest activity to cymenes, and thus the amount and strength of acidic sites in FAU Y seems to be optimum from the tested zeolites. Significantly higher amount of Lewis sites increases the dehydrogenation activity compared FAU X.

In addition it has to be stated that the reaction conditions (temperature, WHSV, gas flow) have major effect on the product distribution, as can be seen for FAU Y in Table 5. In addition to the cymene formation, isomerization reactions greatly depend on reaction conditions.

Compared to MOR, FAU Y has a lower acidity but a higher concentration of protonic sites.<sup>28</sup> Unfortunately, due to the impurity in MOR, the activity and acidity measurements are not entirely comparable to other zeolites. However, it can be generally concluded that the amount of acidic sites is comparable to FAU Y. The major difference is in the amount of nonframework Al(V) and Al(VI) species. Based on the Si/Al ratio, mordenite should have the strongest acidic sites. However, the impurity can affect the amount and strength of acidic sites. In addition, mordenite has two types of pore

Scheme 2. Mechanism of acid catalyzed  $\alpha$ -pinene isomerization, dehydrogenation, and hydrogenation

channels, and the smaller of these ( $3.4 \text{ \AA} \times 4.8 \text{ \AA}$ ) is not capable to occupy the reactant or product molecules. This decreases the available reactive space and can have effect on MOR activity.

Experiments with the model compound  $\alpha$ -pinene were carried on to test the effect of carrier gases and catalyst structure. The aromatization of  $\alpha$ -pinene has been studied extensively in the literature as discussed in the Introduction. In the presence of air, FAU Y was quickly deactivated by coke. Although the presence of  $\text{O}_2$  favored the dehydrogenation/hydrogenation ratio, a noticeable deactivation of FAU Y was observed as decreased conversion of  $\alpha$ -pinene. When  $\text{N}_2$  was used as carrier gas (35 mL/min), the selectivity to cymenes was dramatically improved, the total yield being 54% (*p*-cymene 44%, *m*-cymene 9.3%, *o*-cymene 0.7%), and 100% conversion was obtained. The nitrogen flush is likely to facilitate the selectivity by removing some of the hydrogen released in the catalyst bed. The dehydrogenation/hydrogenation ratio clearly increases when nitrogen flush is applied. Using powdered FAU Y did not improve the selectivity to the desired cymenes (data not shown).

The aromatization of CST was tested (Table 6) by varying the temperature (200–400 °C), catalyst loading (1.5 and 3 g), and nitrogen flow (35 mL/min and 70 mL/min). Also thermal reactions were studied in catalyst-free reaction conditions (Table 6, Experiment 4). In the catalyst-free experiment at 300 °C (Experiment 4), conversions remained low, and main products were terpene isomers. At 200 °C with 3 g of FAU Y (Experiment 5), high conversions were obtained, but the main products were again terpene isomers. It seems that 200 °C is sufficient enough temperature for the isomerization but not high enough for the dehydrogenation step to take place. A temperature of 300 °C gives a higher selectivity to cymenes with 3 g of catalyst (Experiment 6). With half the amount of catalyst (1.5 g), a higher temperature of 350 °C is needed to obtain comparable selectivities (Experiment 9), and with 1.5 g of catalyst at 300 °C, the selectivity to cymenes was rather low (Experiment 8). The highest selectivities to cymenes (up to 28%, Experiment 11) were obtained at 300 °C with half of the

original catalyst amount (1.5 g) but with an increased  $\text{N}_2$  flow rate from 35 mL/min to 70 mL/min. When the catalyst amount was increased at temperature of 300 °C (1.5 g  $\rightarrow$  3.0 g) at an increased  $\text{N}_2$  flow rate (70 mL/min), the selectivity to desired cymenes decreased slightly, and the selectivity to menthenes and menthanes increases. Temperatures higher than this caused undesired hydrogenation and cracking.

Besides the products listed in Tables 3 and 4, the reaction conditions used in these experiments also gave various byproducts. In the catalytic reaction conditions camphene is formed, which further reacts to cyclopentenenes. Cracking increases with increasing temperatures, giving coke and other aromatics besides cymenes, including toluene and tetramethylbenzene. Also, xylenes form at higher temperatures. Dimerization of terpenes was observed as well.

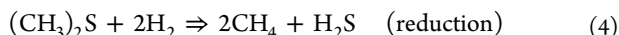
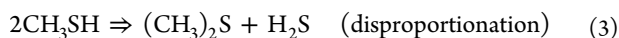
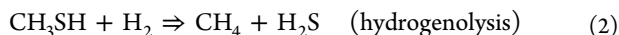
## DISCUSSION OF THE REACTION MECHANISM

Several reaction steps are required for the aromatization of  $\alpha$ -pinene and 3-carene to cymenes (Scheme 2). In the presence of an acid catalyst, cationic intermediates are likely to form (for example I and II), further reacting to the terpene isomers.<sup>26</sup> In Scheme 2 only the *p*-isomers are presented, but also *o*/*m*-isomers are forming. This isomerization can also take place by thermal reactions, as was concluded from Experiment 4 (Table 6). However, the conversion of  $\alpha$ -pinene and 3-carene to the terpene isomers is clearly higher in the presence of an acid catalyst, and therefore it is likely the acid catalyzed isomerizations are dominating under the reaction conditions.

After the isomerization, rearrangement of the monoterpene isomers can take place, catalyzed by acid.

The monocyclic terpenes can undergo dehydrogenation to cymenes. As remarked with Experiment 5, 200 °C was not a high enough temperature for the dehydrogenation to take place, but higher temperatures are required. Also in non-catalytic conditions (Experiment 4), no cymenes are formed; this shows that the dehydrogenation requires the acid catalyst. As one mole of hydrogen is forming in the dehydrogenation step, this hydrogen will to react further. There are several acceptors for the hydrogen. Terpenes can disproportionate by

accepting the hydrogen and become reduced to menthenes (FW 138). Menthenes can further accept a mole of hydrogen to give menthanes (FW 140). The organic sulphur compounds in the feed can also act as hydrogen acceptors as they can undergo hydrogenolysis, disproportionation, and reduction (eqs 2–4).



Equations 2–4 show possible reactions with methyl mercaptan and dimethyl sulfide.

By reacting with the hydrogen, the sulphur compounds may increase the selectivity towards cymenes. Oxygen would be a good hydrogen acceptor,<sup>23</sup> but as mentioned earlier, the presence of O<sub>2</sub> resulted in coke formation and deactivation of catalyst. Using N<sub>2</sub> flush seems to somewhat reduce the hydrogenation of terpenes by flushing away the forming H<sub>2</sub>. The importance of the N<sub>2</sub> flow is shown by the fact that the catalyst amount can be reduced by half when the N<sub>2</sub> flow is doubled and the desired cymene selectivity is increased. On the contrary, when the catalyst amount is increased at increased N<sub>2</sub> flow, a reduction in the desired cymene yield is observed due to increased hydrogenation reaction.

## CONCLUSIONS

The suitability of commercial zeolites for aromatization of  $\alpha$ -pinene and CST was studied. From the tested zeolites, FAU Y gave the best selectivity to cymenes. After initial optimization with  $\alpha$ -pinene, complete conversions were obtained with  $\alpha$ -pinene, giving over 54% selectivities to cymenes. Complete conversions were also obtained with CST with 28% selectivities. The major cymene isomer was in each experiment the desired *p*-cymene; *m*-cymene was also often obtained but with only very small amounts of *o*-cymene.

These results are promising, as they indicate that no noble metal catalysts may be needed in the production of biobased aromatic compounds from terpenes. The development of sulphur-tolerant catalyst systems is of vital importance to the bioeconomy, as sulphur-containing feedstocks such as CST or crude tall oil could be directly used for catalytic transformations to produce biobased chemical products. As this report describes the initial optimization studies, further work of the conditions and scope of these transformations is ongoing in our laboratory.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- Gallezot, P. *Catal. Today* **2007**, 121, 76–91.
- Swift, K. A. D. *Top. Catal.* **2004**, 27, 143–155.
- Mäki-Arvela, P.; Holmbom, B.; Salmi, T.; Murzin, D. Y. *Catal. Rev.* **2007**, 49, 197–340.
- Berti, C.; Binassi, E.; Colonna, M.; Fiorini, M.; Kannan, G.; Karanam, S.; Mazzacurati, M.; Odeh, I.; Vannini, M. WO/2010/2010078328, 2010; CAS abstract number 2010:847387.
- Fiege, H. In *Ullmann's encyclopedia of industrial chemistry*; Wiley-VCH: Weinheim, 2012; Vol. 10, Cresols and xlenols, pp 419–460.
- Eggersdorfer, M. In *Ullmann's encyclopedia of industrial chemistry*; Wiley-VCH: Weinheim, 2012; Vol. 36, Terpenes, pp 29–45.
- Buhl, D.; Weyrich, P. A.; Sachtler, W. M. H.; Hölderich, W. F. *Appl. Catal. A: Gen.* **1998**, 171, 1–11.
- Roberge, D. M.; Buhl, D.; Niederer, J. P. M.; Hölderich, W. F. *Appl. Catal. A: Gen.* **2001**, 215, 111–124.
- Wadaani, F. A.; Kozhevnikova, E. F.; Kozhevnikov, I. V. *Appl. Catal. A: Gen.* **2009**, 363, 153–156.
- Binitha, N. N.; Sugunan, S. *Catal. Commun.* **2007**, 8, 1793–1797.
- Golets, M.; Ajaikumar, S.; Mohln, M.; Wärnå, J.; Rakesh, S.; Mikkola, J.-M. *J. Catal.* **2013**, 307, 303–315.
- Räsänen, J.; Penttinen, T.; Harlin, A.; Kaila, R. WO/2011/2011151526 A1, 2011; CAS abstract number 2011:1582420.
- Grau, R. J.; Zgolicz, P. D.; Gutierrez, C.; Taher, H. A. *J. Mol. Catal. A: Chem.* **1999**, 148, 203–214.
- Buhl, D.; Roberge, D. M.; Hölderich, W. F. *Appl. Catal. A: Gen.* **1999**, 188, 287–299.
- Lesage, P.; Candy, J. P.; Hirigoyen, C.; Humblot, F.; Basset, J. M. *J. Mol. Catal. A: Chem.* **1996**, 112, 431–435.
- Weyrich, P. A.; Trevino, H.; Hölderich, W. F.; Sachtler, W. M. H. *Appl. Catal. A: Gen.* **1997**, 163, 31–44.
- Weyrich, P. A.; Hölderich, W. F. *Appl. Catal. A: General* **1997**, 158, 145–162.
- Roberge, D. M.; Buhl, D.; Niederer, J. P. M.; Hölderich, W. F. *Appl. Catal. A: Gen.* **2001**, 215, 111–124.
- Al-Wadaani, F.; Kozhenikova, E. F.; Kozhenikov, I. V. *Appl. Catal. A: Gen.* **2009**, 363, 153–156.
- Martín-Luengo, M. A.; Yates, M.; Martínez Domingo, M. J.; Casal, B.; Iglesias, M.; Esteban, M.; Ruiz-Hitzky, E. *Appl. Catal. B: Environ.* **2008**, 81, 218–224.
- Martín-Luengo, M. A.; Yates, M.; Saez Rojo, E.; Huerta Arribas, D.; Aguilar, D.; Ruiz, E. *Appl. Catal. A: Gen.* **2010**, 387, 141–146.
- Zhao, C.; Gan, W.; Fan, X.; Cai, Z.; Dyson, P. J.; Kou, Y. *J. Catal.* **2008**, 254, 244–250.
- Asikainen, M.; Jauhiainen, O.; Aaltonen, O.; Harlin, A. *Green Chem.* **2013**, 15, 3230–3235.
- Weyerhaeuser Crude Sulphate Turpentine Material Safety Data Sheet 2010.
- Eswaramoorthy, M.; Krishnasamy, V. *Indian J. Chem.* **2001**, 40A, 264–269.
- Özkan, F.; Gündüz, G.; Akpolat, O.; Beşin, N.; Murzin, D. Y. *Chem. Eng. J.* **2003**, 91, 257–269.
- Jae, J.; Tompsett, G. A.; Foster, A. J.; Hammond, K. D.; Auerbach, S. M.; Lobo, R. F.; Huber, G. W. *J. Catal.* **2011**, 279, 257–268, DOI: 10.1016/j.jcat.2011.01.019.
- Cejka, J.; Wichterlova, B. *Catal. Rev.* **2014**, 44, 375–421, DOI: 10.1081/CR-120005741.
- Roelofsen, D. P. *Molecular sieve zeolites – properties and applications in organic synthesis*. Doctoral Thesis, Technical University of Delft, 1972.
- Meier, W. M.; Olsen, D. H. *Atlas of zeolite structure types*; Butterworths: London, 1992.
- van Laak, A. N. C. *Post-Synthesis modifications on zeolites for improved accessibility and catalytic performance*. Doctoral thesis, University of Utrecht, 2011.
- Jiang, Y.; Huang, J.; Dai, W.; Hunger, M. *Solid State Nucl. Magn. Reson.* **2011**, 39, 116–141.
- Klinowski, J. *Chem. Rev.* **1991**, 91, 1459–1479.
- Huang, J.; van Vegten, N.; Jiang, Y.; Hunger, M.; Baiker, A. *Angew. Chem., Int. Ed.* **2010**, 41, 7776.
- Martens, J. A.; Souvris, W.; van Rhijn, W.; Jacobs, P. A. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H.,



Weitkamp, J., Eds.; Wiley-VCH: Weinheim, Germany, 1997; Vol. 1, pp 324–365.

(36) Sommer, J.; Jost, R.; Hachoumy, M. *Catal. Today* **1997**, 38, 309–319.

(37) Rachwalik, R.; Olejniczak, Z.; Jiao, J.; Huang, J.; Hunger, M.; Sulikowski, B. *J. Catal.* **2007**, 252, 161–170.

(38) Selvaraj, M.; Pandurangan, A.; Seshadri, K. S.; Sinha, P. K.; Lal, K. B. *Appl. Catal. A: Gen.* **2003**, 242, 347–364.

(39) Stratakis, M.; Stavroulakis, M.; Sofikiti, N. *J. Phys. Org. Chem.* **2003**, 16, 16–20.

(40) Narbeshuber, T. F.; Brait, A.; Kulathuyier, S.; Lercher, A. J. *Catal.* **1997**, 172, 127–136.

(41) Atkinson, D.; Curthoys, G. *J. Phys. Chem.* **1990**, 84, 1358–1360.