

# Selective Homologation Routes to 2,2,3-Trimethylbutane on Solid Acids\*\*

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2,2,3-Trimethylbutane (triptane) is a valuable fuel additive with a research octane number of 112. It can be produced with high selectivity from methanol (or dimethyl ether (DME)) using solutions of Zn<sup>[1-4]</sup> or In<sup>[5,6]</sup> halides at approximately 473 K, via steps that seem to involve carbocationic intermediates.<sup>[2,3,5,6]</sup> Inhibition by H<sub>2</sub>O formed by methanol dehydration, however, limits reactions to a few methanol turnovers (ca. 4) and only around one triptane molecule formed per ZnI<sub>2</sub>.<sup>[2]</sup> Acid-catalyzed homologation of methanol/DME also occurs on zeolites<sup>[7-10]</sup> but at higher temperatures (> 573 K) and forms alkanes, alkenes, and arenes in near-equilibrium isomer distributions, as well as unreactive carbon-containing deposits that cause catalytic deactivation.<sup>[11]</sup>

We report herein the first selective catalytic conversion of DME to triptane on halide-free catalysts, specifically on crystalline solid acids, at much lower reaction temperatures (453–493 K) and higher DME pressures (60–250 kPa) than in established methanol/DME to hydrocarbon processes. Low temperatures avoid intervening skeletal isomerization and  $\beta$ -scission of triptyl chains or their precursors. These processes would otherwise occur before the methylation events that form the C<sub>7</sub> chains containing the triptane backbone, which desorb irreversibly as triptane. High DME pressures ensure that methylation occurs at sufficient rates to form C<sub>7</sub> chains before smaller alkanes form irreversibly by hydrogen transfer. These requirements apply also to other methylating agents (e.g. CH<sub>3</sub>X; X = OH, Cl, ...), but we use DME because its H<sub>2</sub>O/CH<sub>2</sub> ratio (0.5) is smaller than for CH<sub>3</sub>OH (1.0) and H<sub>2</sub>O inhibits methylation on Brønsted acids.<sup>[12]</sup> The DME vapor pressure (ca. 15 MPa) is also higher

than for CH<sub>3</sub>OH (ca. 4 MPa) at the reaction temperatures (ca. 470 K) allowing higher pressures of the methylating reagent.

Ferrierite (H-FER), Mordenite (H-MOR), ZSM-5 (H-MFI), Y (H-FAU; USY), and Beta (H-BEA) zeolites<sup>[13]</sup> were tested in their acid form (473 K; 60 kPa DME) in a reactor with plug-flow hydrodynamics. Triptyl (triptane and triptene (2,3,3-trimethylbutene)) formation rates (per Al, as surrogate for the number of acidic protons) and selectivities are shown in Table 1. H-BEA and H-FAU gave higher selectivities to C<sub>7</sub> among products and to triptyls within the C<sub>7</sub> fraction. H-MFI gave approximately 10% triptyls in C<sub>7</sub> and small-pore H-FER

**Table 1:** DME homologation rates (per Al site) and selectivities.<sup>[a]</sup>

Catalyst	H-FER	H-MOR	H-MFI	H-FAU	H-BEA
channel size <sup>[17]</sup> [nm]	0.42×0.54* 0.35×0.48*	0.65×0.70* 0.34×0.48* 0.26×0.57*	0.51×0.55*** 0.53×0.56***	0.74×0.74***	0.66×0.67** 0.56×0.56*
Si/Al ratio	10	10	15	3	12.5
selectivity ([%] C <sub>7</sub> in products)	< 0.01	2.6	5.2	7.6	21
selectivity ([%] triptyl in C <sub>7</sub> fraction)	< 0.01	59	11	46	72
product formation rate [ $\mu\text{mol C (s mol Al)}^{-1}$ ]	15	73	610	860	740
triptyl formation rate [ $\mu\text{mol (s mol Al)}^{-1}$ ]	< 0.01	0.16	0.49	4.3	16

[a] 60 kPa DME, 473 K, after ca. 4.8 ks on stream, 0.25 g catalyst, 0.20 cm<sup>3</sup> s<sup>-1</sup> total flow rate. The number of asterisks indicates the dimensionality of each channel. Methanol is in equilibrium with DME, so it is not included as a product in reported rates or selectivities.

catalysts formed only trace amounts of triptane and of hydrocarbons in general. Large 1D channels in H-MOR (0.65×0.7 nm) gave lower rates of triptyl formation than H-FAU or H-BEA, possibly because the H-FAU and H-BEA contain larger cages and intersections that stabilize bulky transition states required to form triptyl chains. The triptane to 2,3-dimethylpentane ratios observed are much greater (> 10 on H-BEA) than equilibrium values (0.1 at 473 K<sup>[14]</sup>).

H-BEA gave the highest triptyl formation rates, selectivities, and cumulative DME turnovers (> 10 C atoms per Al in zeolite after ca. 20 ks), as well as the most stable rates among zeolites tested (Supporting Information). As a result, we report herein the effects of reaction temperature (453–493 K; 250 kPa DME) and pressure (60–250 kPa DME; 473 K) on H-BEA. Triptyl formation and deactivation rates increased with temperature (Table 2). Deactivation occurs by formation of unsaturated residues (e.g., alkylated aromatics<sup>[11]</sup>), which provide the hydrogen atoms required to form alkanes from DME. Triptyl and C<sub>7</sub> selectivities decreased with increasing temperature, because of a preferential increase in isomer-

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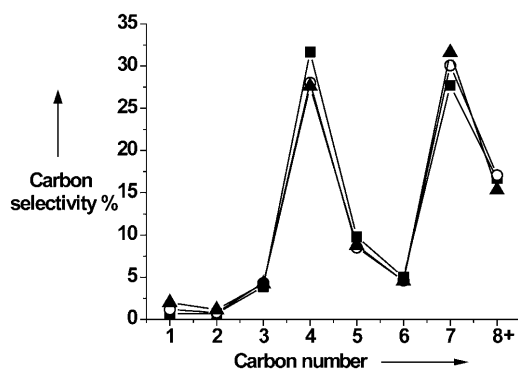
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**Table 2:** Triptyl formation rates, first-order deactivation constants of product formation rates ( $k_d$ ), and selectivities.<sup>[a]</sup>

T [K]	Triptyl formation rate [ $\mu\text{mol}(\text{s}\cdot\text{mol Al})^{-1}$ ]	$k_d$ [ $\text{ks}^{-1}$ ]	$C_7$ in products [%]	Triptyls in $C_7$ [%]
453	2.3	0.0027	33	88
473	3.8	0.0056	29	81
493	5.0	0.0093	26	75

[a] 1.6 g H-BEA; Si/Al = 12.5;  $0.28 \text{ cm}^3 \text{ s}^{-1}$  total flow rate, time on stream ca. 100 ks.


**Figure 1.** DME pressure effects (60 kPa (■), 125 kPa (○), and 250 kPa (▲)) on chain size of the hydrocarbon products (473 K, 0.4 g H-BEA; Si/Al = 12.5,  $0.28 \text{ cm}^3 \text{ s}^{-1}$  total flow rate, at DME conversion rates of  $380 \mu\text{mol carbon}(\text{s mol Al})^{-1}$ )

ization rates of triptyl species and their precursors before methylation. Triptyl and  $C_7$  selectivities increased with DME pressure (Figure 1) as a result of a concomitant increase in methylation rates.

$C_4$  (ca. 30%, ca. 90% isobutyls in  $C_4$  fraction) and  $C_7$  (ca. 30%, ca. 80% triptyls in  $C_7$  fraction) hydrocarbons are the predominant products formed on H-BEA (Figure 1). The preferential formation of  $C_4$  and  $C_7$  chains reflects:

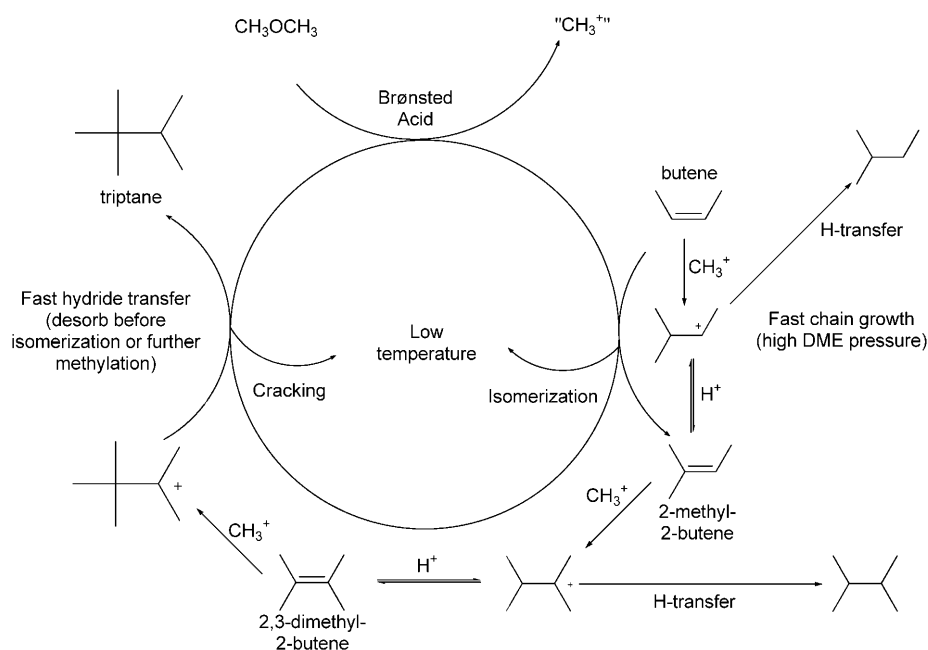
- selective addition of methyl groups at less-substituted C atoms in alkenes to form more-stable cations at transition states
- smaller methylation-to-hydrogen-transfer rate ratios (denoted as  $\chi$ ) for triptyl and *tert*-butyl chains than for triptyl precursors ( $\chi < 1$  for triptyl and *tert*-butyl chains; but  $\chi > 2$  for other chains)<sup>[15]</sup>
- negligible isomerization events that change the backbone length of triptyl chains and their precursors<sup>[15]</sup>

d) rapid  $\beta$ -scission of  $C_{8+}$  chains to form *tert*-butyl chains that tend to desorb as isobutane.<sup>[15]</sup>

The methylation position, the  $\chi$  for various chain lengths, slow isomerization, and facile cracking account for the unprecedented triptane selectivities reported herein on solid acids. These features have not been previously detected for methanol/DME conversion because these chemistries have been practiced at lower pressures and higher temperatures, which favor low  $\chi$  values, fast isomerization, and  $\beta$ -scission and concomitant equilibration of backbone structures and chain lengths.

In the pathways shown in Scheme 1, triptyls form via sequential methylation of propene, *n*-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene, each one of which represents the preferred methylation product of the smaller alkenes. These pathways (Scheme 1) are consistent with reactions of  $^{13}\text{C}$ -DME mixtures with unlabeled alkenes; the detailed results are reported elsewhere.<sup>[15]</sup> Methylation of  $C_3H_6$  does not form isobutane or isobutene, because addition at secondary carbons requires primary carbenium ions at transition states. The addition of  $C_3H_6$  to DME reactants (1:30 molar ratio) increased the rate of formation of linear  $C_4$  products by a factor of 7.5, but that for branched  $C_4$  hydrocarbons by only 1.5 (Table 3 part a). We therefore conclude that the primary products of propene methylation are linear  $C_4$  species, as previously proposed.<sup>[15,16]</sup>

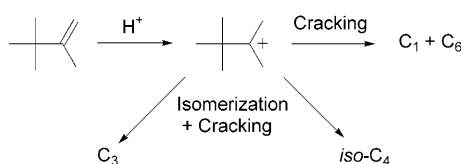
The addition of triptene to DME (1:20 molar ratio) selectively increased formation rates of branched  $C_4$  hydrocarbons much more than those for linear  $C_4$  products (Table 3 b), consistent with  $\beta$ -scission of larger hydrocarbons as the preferred route to isobutane. Triptyl chains do not readily crack to give isobutyl units, because  $\beta$ -scission of their


**Scheme 1.** DME homologation pathways for triptane synthesis. Alkoxide intermediates (alkoxy anions are omitted) are shown as their most stable carbenium ion, because of their cationic character at transition states. " $\text{CH}_3^+$ " represents methylating species and chain growth is started at  $C_4$  species for brevity.

**Table 3:** Effect of a) propene and b) triptene addition to DME on H-BEA.<sup>[a]</sup>

a)	Formation rate [ $\mu\text{mol (s mol Al)}^{-1}$ ]	
	60 kPa DME	60 kPa DME + 2 kPa propene
branched C <sub>4</sub>	31	47
linear C <sub>4</sub>	3.3	25
triptyls	15	19
b)	Formation rate [ $\mu\text{mol (s mol Al)}^{-1}$ ]	
	60 kPa DME	60 kPa DME + 3 kPa triptene
branched C <sub>4</sub>	29	77
linear C <sub>4</sub>	2.8	4.5
C <sub>3</sub>	3.6	3.7

[a] 473 K, 0.15 g H-BEA (Si/Al = 12.5), 0.28 cm<sup>3</sup> s<sup>-1</sup> total flow rate. Branched and linear C<sub>4</sub> formation rates are given as an upper and lower bound, respectively, because isobutene and 1-butene could not be separated chromatographically; thus, hydrocarbons reported as branched C<sub>4</sub> include 1-butene.



**Scheme 2.**  $\beta$ -Scission pathways of triptyl cations.

tertiary carbenium ions forms C<sub>1</sub> and C<sub>6</sub> chains (Scheme 2; triptyl chains can also be cracked by placing the positive charge on the primary carbon, but this is energetically unfavorable relative to the tertiary carbon, as shown). Isobutyl units form from triptyl chains only after: 1) their isomerization to 2,4-dimethyl-C<sub>5</sub>, or 2-methyl-C<sub>6</sub> or 2) their methylation to C<sub>8+</sub> chains. Skeletal isomerization products were not detected when <sup>12</sup>C-alkenes were added to <sup>13</sup>C-DME,<sup>[15]</sup> C<sub>3</sub> products, expected from  $\beta$ -scission of 2,4-dimethyl-C<sub>5</sub> or 2-methyl-C<sub>6</sub> chains, were present only in trace amounts (Table 3b). Thus, methylation of triptene to C<sub>8+</sub> chains provides facile  $\beta$ -scission routes to form isobutenes, via deprotonation of *tert*-butyl chains, which can methylate to triptane, or isobutane, by rapid hydrogen transfer to such *tert*-butyl chains.

These data show that triptane can be selectively produced through homologation reactions on halide-free acid zeolites at comparatively low temperatures (453–473 K); the proposed pathways are consistent with methylation, isomerization, and scission selectivities typical of carbenium-ion transition states. Three-dimensional large-pore zeolites, and specifically H-BEA, gave unprecedented triptyl selectivities within the C<sub>7</sub> products and stable reaction rates. High selectivities to isobutyl and triptyl species reflect the different relative rates of methylation, hydrogen transfer, isomerization, and  $\beta$ -scission for the various hydrocarbon chain structures formed by methylation. This remarkable specificity has not been detected previously on solid acids and provides a new and selective route for the synthesis of high-octane isoalkanes.

## Experimental Section

NH<sub>4</sub>-FER (Si/Al = 10; Zeolyst), NH<sub>4</sub>-MOR (Si/Al = 10; Zeolyst), NH<sub>4</sub>-ZSM5 (Si/Al = 15; Zeolyst), NH<sub>4</sub>-USY (Si/Al = 3; Engelhard), and NH<sub>4</sub>-BEA (Si/Al = 12.5; Zeolyst) were treated in flowing dry air (ca. 2.5 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>; zero grade, Praxair) by increasing the temperature to 773 K at 0.17 K s<sup>-1</sup> and holding at this temperature for 10 h to convert them into their acid forms.

Homologation rates and selectivities for DME and DME-alkene reactants were measured in a quartz plug-flow reactor (12.5 mm outside diameter (OD)) containing zeolites (0.15–0.25 g, 180–250  $\mu\text{m}$  aggregates) held on a porous quartz disc. Pressure and temperature effects were measured using a stainless steel tube (9.5 mm OD) with three thermocouples aligned along its center and catalysts (0.4–1.6 g, 180–250  $\mu\text{m}$  aggregates) held with quartz wool. Temperatures were kept constant using a Watlow controller (Series 989) and a resistively heated furnace. Catalysts were treated in dry air (0.83 cm<sup>3</sup> s<sup>-1</sup>; zero grade, Praxair) for 2 h at 773 K (at 0.17 K s<sup>-1</sup>) and cooled to reaction temperatures in flowing He (0.83 cm<sup>3</sup> s<sup>-1</sup>; UHP, Praxair) before introducing DME (99.5%, Matheson) with Ar (99.999%, Praxair), and with propene (99%, Sigma Aldrich) or 2,3,3-trimethylbutene (98%, Sigma Aldrich; by saturation with liquid at ambient temperature) for co-feed experiments. The reactor effluent was sampled through lines kept at 423 K into a gas chromatograph (Agilent 6890), equipped with a siloxane capillary column (HP-1, 50 m  $\times$  0.32 mm  $\times$  1.05  $\mu\text{m}$ ) and a flame ionization detector.

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