Homologation of Dimethyl Ether to Highly Branched Alkanes on Acidic Zeolites

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Introduction

Triptane (2,2,3-trimethylbutane), a valuable fuel additive because of its high octane number of 112, can be produced from methanol using homogeneous solutions of Zn and In halides[1-3] at ~473 K with nearly 50% triptane selectivity in the C_{5+} hydrocarbons.[3] Methanol homologation appears to involve carbocationic intermediates and alkene methylation rates that increase with degree of substitution.[1, 3] Triptane synthesis using ZnI_2 is selective, but poses practical challenges in separation and purification of products and in the use of corrosive and toxic halides. We report here the first successful synthesis of triptane via dimethyl ether (DME) or methanol homologation on halide-free zeolite catalysts.

Materials and Methods

H-zeolites were prepared by treating NH_4-FER (Si:Al=10:1; Zeolyst), NH_4-MOR (Si:Al=10:1; Zeolyst), NH_4-ZSM5 (Si:Al=15:1; Zeolyst), NH_4-USY (Si:Al=3:1; Engelhard), and NH_4-BEA (Si:Al=12.5:1; Zeolyst) in flowing dry air (1.7 cm^3 s^{-1} g^{-1}) at 773 K. Homologation rates and selectivities were measured in a plug-flow reactor using gaseous reactants at conversions less than 2% of DME. The reactor effluent was analyzed by on-line gas chromatography using flame ionization and thermal conductivity detection.

Results and Discussion

Selective conversion of DME to triptane and isobutane was achieved on acid zeolites at modest temperatures (400-500 K) and pressures (60-250 kPa). H-BEA showed the highest productivity, triptane selectivity, and stability among the zeolites tested (H-FER, H-MOR, H-ZSM5, H-USY, H-BEA). Homologation preferentially forms C_4 and C_7 alkanes (40% and 30% carbon selectivities, respectively) with isobutane accounting for 90% of C_4 hydrocarbons and triptane for 80% of C_7 products at 473 K and 60 kPa DME (Figure 1). Competitive reactions of ^{13}C-labeled DME with unlabeled alkenes (propene, trans-2-butene, isobutene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 2,3,3-trimethyl-1-butene) allowed rigorous assessments of the relative rates of methylation, hydrogen transfer, and isomerization and of the details of chain growth pathways during homologation. These data also demonstrated the basis for the remarkable specificity of these pathways for isobutane and triptane products. This triptane and isobutane specificity, previously unreported on solid acids, reflects a positional preference for methylation among growing chains, which leads to backbone structures that cannot change in length via cracking or isomerization (Figure 1). Homologation occurs via pathways involving the methylation of highly-substituted carbenium ions with methylation rates increasing as the degree of substitution in growing chains increases. Hydride transfer irreversibly terminates growing hydrocarbon chains as alkanes, and hydrogen abstraction terminates such chains reversibly as alkenes, which can readsorb and continue to grow. Methylation of triptane/triptene leads to C_8 and C_9 molecules that undergo rapid β-scission to form isobutene which causes the high selectivity to branched C_4 alkanes. These branched C_4 molecules can be reincorporated into homologation pathways, especially in the presence of a hydride transfer co-catalyst, such as adamantane.[4] High selectivity to triptane results because the ratio of methylation rate to hydrogen transfer rate is smaller for 2,2,3-trimethyl sec-butoxide intermediates than for the C_3-C_6 precursors to triptane. Thus, DME homologation produces triptane via pathways in which triptane is protected against further growth while its precursors are protected against backbone rearrangements that lead to products other than triptane. Co-homologation of DME with alkenes or alkanes also occurs with selective formation of isobutane and triptane. Chain termination to alkanes (via hydride transfer) can be reversed by the addition of catalytic amounts of adamantane to alkane-DME feeds.[4] Adamantane acts as hydrogenation-dehydrogenation co-catalyst and allows the efficient co-homologation of DME with typically unreactive and undervalued alkanes. These alkane co-homologation processes also eliminate the need for the concurrent formation of unsaturated molecules, such as hexamethyl benzene, to provide H-atoms required by stoichiometry in DME and DME-alkene conversion to alkanes.

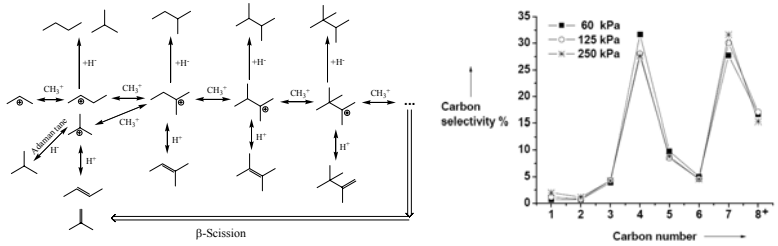

Figure 1. Schematic of reaction pathway for the homologation of dimethyl ether to branched alkanes (beginning at C_3 for simplicity) and carbon selectivity for homologation of dimethyl ether on H-BEA at 473 K and 60-250 kPa dimethyl ether (0.4 g H-BEA with Si:Al=12.5:1, space velocity of 0.7 cm^3 s^{-1} g^{-1}, DME conversion rate of 380 μmol C [s mol Al]$^{-1}$).

Significance

We provide evidence for the selective homologation of DME and its mixtures with alkanes or alkenes to branched alkanes on acid zeolites and the fundamental basis for the unprecedented selectivity observed for triptane and isobutane.

Acknowledgement

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