



Professor

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*Mechanistic Insights into Acid Catalysis and Selective
Homologation of C₁ Species to Isobutane and 2,2,3-trimethylbutane*

The acid-catalyzed conversion of dimethyl ether (DME) to 2,2,3-trimethylbutane (triptane) and isobutane occurs with high selectivity on large pore acidic zeolites at modest temperatures (400-500 K) and DME pressures (60-250 kPa). Kinetic and isotopic methods are used to elucidate the mechanistic details of this chain growth which occurs via elementary steps mediated by carbenium ion transition states. The unusual product specificity reflects the formation of hydrocarbon chains with a linear C₄ backbone, which preferentially terminate via hydrogen transfer when tertiary carbons reside next to primary ones and exhibit low reactivity in β -scission and isomerization reactions. Rapid isomerization and β -scission of chains that grow beyond triptane form isobutyl species. These steps are general to acid catalysis and also occur on mesoporous acids; the effects of spatial constraints on selectivity provide rigorous insights into the role of solvation and of acid strength on acid-catalyzed methylation and hydride transfer steps. The presence of adamantane as a hydrogen transfer co-catalyst allows the co-homologation of light alkanes and DME to form larger and highly branched chains, while also avoiding the formation of unsaturated byproducts, which are required for hydrogen balance when alkanes form from pure DME reactants. Dihydrogen can also be used to satisfy this H-balance. In these systems, alkenes are hydrogenated with H₂ on Ga-sites in Ga-exchanged H-BEA, and the resulting alkanes are re-incorporated into homologation chains via adamantane-catalyzed hydrogen transfer on acid sites.

Monday, March 28, 2016

4:00 P.M.

2033 Young Hall