Selective Catalytic Synthesis of Branched C_4-C_7 Hydrocarbons by Low Temperature C_1 Homologation Reactions over Medium and Large Pore Acidic Zeolites

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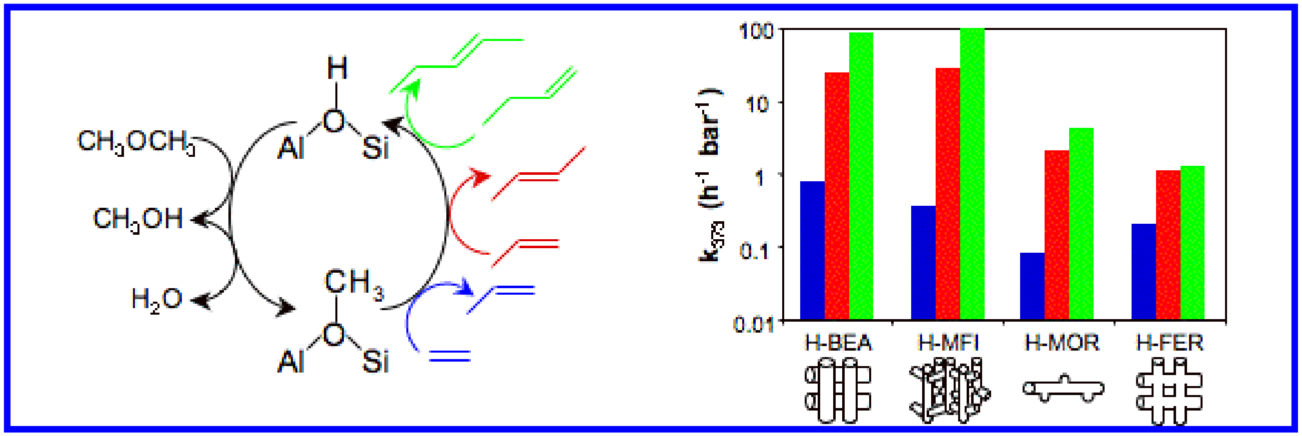
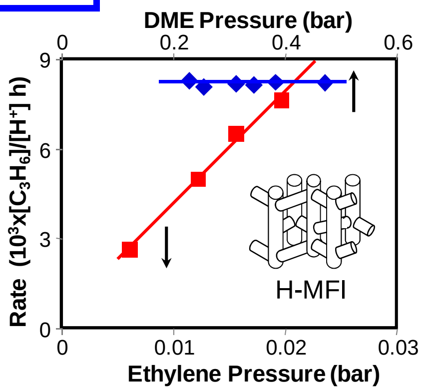
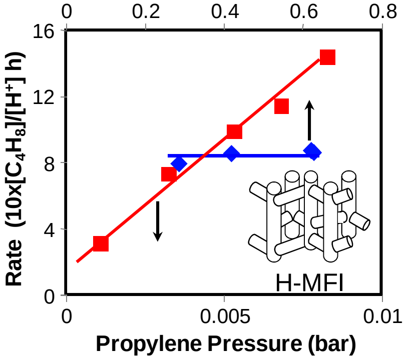


The conversion of methanol-to-hydrocarbons (MTH) over zeolite catalysts represents the final step in upgrading any gasifiable feedstock to gasoline-range hydrocarbons. CH_3* groups derived from methanol cannot be coupled directly into hydrocarbons at rates relevant for steady state MTH catalysis. Instead organic species, specifically olefins and arenes, contained inside the zeolite pore act as scaffolds for C-C bond formation. Speciation preferences in this dual olefin and arene methylation cycle determine catalytic rates and selectivity in MTH catalysis. Under low temperature and low conversion reaction conditions where the olefin methylation cycle can be selectively propagated, we report that the kinetics of olefin methylation are consistent with a mechanism involving a surface predominantly covered by CH_3* species that react with olefins ($C_2^=$ - $C_4^=$) in kinetically relevant elementary steps. A systematic decrease in activation barriers is noted with increasing substitution of the olefin consistent with the involvement of carbocationic transition states. Our data also show that FER, MFI, MOR, and BEA zeolites propagate the olefin methylation cycle to varying extents thereby explaining the marked diversity in selectivity and yield for C_1 homologation observed using different zeolites.





Kinetics and Mechanism of Olefin Methylation Reactions on Zeolites. Ian M. Hill, Saleh Al-Hashimi, and Aditya Bhan. Journal of Catalysis (2011) Accepted