

Synthesis and Study of Zeolites with Lewis Acid and Base Sites for the Cooperative Activation of Organic Oxygenates

by

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ABSTRACT

Zeolites containing Sn, Ti, Zr, or Hf heteroatoms are versatile catalysts for the activation and conversion of oxygenated molecules owing to the unique Lewis acid character of their tetrahedral metal sites. Through fluoride-mediated synthesis, hydrophobic Lewis acid zeolites can behave as water-tolerant catalysts, which has resulted in a recent surge of experimental and computational studies in the field of biomass conversion. However, many open questions still surround these materials, especially relating to the nature of their active sites. This thesis reports on studies that aim to understand the reactivity, deactivation, and active site speciation for Lewis acid zeolites.

First, Hf-, Zr- and Sn-Beta zeolites are shown to effectively catalyze the coupled transfer hydrogenation and etherification of 5-(hydroxymethyl)-furfural with primary and secondary alcohols into 2,5-bis(alkoxymethyl) furans, thus making it possible to generate renewable fuel additives without the use of external hydrogen sources or precious metals. Continuous flow experiments reveal nonuniform changes in the relative deactivation rates of the transfer hydrogenation and etherification reactions. ^{119}Sn and ^{29}Si magic-angle spinning nuclear magnetic resonance (NMR) studies show that this deactivation can be attributed to changes in the local environment of the metal sites. Next, Lewis acid zeolites are shown to catalyze the cross-aldol condensation of aromatic aldehydes with acetone under mild reaction conditions with near quantitative yields. NMR studies with isotopically labeled molecules confirm that acid-base pairs in the Si-O-M framework ensemble promote soft enolization through α -proton abstraction. These Lewis acidic zeolites maintain activity in the presence of water and, unlike traditional base catalysts, in acidic solutions, enabling synthesis of unsaturated dicarboxylic acid esters via aldol condensation of keto esters. Finally, Lewis acid zeolite active sites are characterized by adsorbing trimethylphosphine oxide (TMPO) and recording quantitative ^{31}P solid-state NMR spectra of the TMPO probe molecule. The ^{31}P spectra provide active site concentrations that can be correlated to catalytic activity. Overall, the method developed can be used to characterize and quantify the active sites of low-defect Lewis acidic zeolites regardless of heteroatom identity.

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