Rational Design and Synthesis of Zeolite Acid Catalysts for Applications in Biomass Conversion

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The development of carbon efficient and economically viable biomass conversion technologies is crucial for the sustainable production of fuels and chemicals. Catalytic upgrading processes must remove oxygen and add hydrogen while targeting oxygen-containing functional groups. Catalysts must be water-tolerant, stable under hydrothermal conditions, and accessible for large organics. Zeolites are active and selective heterogeneous catalysts used in many industrial processes. Their microporous crystalline frameworks composed of tetrahedral silicate offer shape selectivity and high stability. Heteroatoms such as Sn or Al can be incorporated into these frameworks to create isolated Lewis and Brønsted acid sites.

This thesis uses synthesis, characterization, and reactivity studies to develop novel zeolite acid catalysts for upgrading biomass platform molecules. The first section focuses on designing hierarchical Brønsted acid zeolites to catalyze bulky molecules. Al-containing zeolite nanosheets of single-unit-cell thickness are synthesized using diquarternary ammonium surfactants. Characterization reveals high external surface area and mesoporosity and strong external acid sites. MFI nanosheets have higher stability and selectivity to larger olefins and aromatics in the conversion of propanal to hydrocarbons due to shorter diffusion path lengths compared to bulk MFI zeolite. MWW nanosheets have a three-fold increase in catalytic activity for the alkylation of benzene with benzyl alcohol compared to bulk MWW zeolite. Sn-containing MFI nanosheets are synthesized for the first time and are shown to have higher activity for the Baeyer-Villiger oxidation of bulky ketones than bulk Sn-MFI zeolite, and higher stability than mesoporous, amorphous Sn silicates. The second section focuses on studying and characterizing hydrophobic, water-tolerant Lewis acid zeolites. A detailed kinetics study compares transfer hydrogenation activity of Ti-, Sn-, Zr-, Hf-containing BEA zeolites with different hydrogen donors. A new characterization method using trimethylphosphine oxide probes and NMR is created to deduce structure-activity relationships. Finally, an integrated catalytic process is developed for the efficient production of γ-valerolactone from furfural through sequential transfer hydrogenation and hydrolysis reactions catalyzed by a mixture of Brønsted acid zeolite nanosheets and hydrophobic Lewis acid zeolites. Overall, this thesis demonstrates that a detailed understanding of the structure and active sites in zeolite acid catalysts can allow us to design more efficient catalytic processes.

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