Synthesis and Catalytic Structure Activity Relations of Hydrophobic Zeolites with Isolated Framework Metals that act as Water Tolerant Lewis Acids

By

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Abstract

Pure-silica zeolites containing a small amount of tetravalent heteroatoms with open coordination sites have emerged as highly active, water-tolerant solid Lewis acids for many important C-C bond forming and hydride transfer reactions involving activation of carbonyl groups. The catalytic activity of these materials is critically dependent on the successful incorporation of the metal center into the zeolite framework. However, synchrotron-based techniques and solid-state nuclear magnetic resonance (ssNMR) of samples enriched with $^{119}$Sn isotopes are the only reliable methods to verify framework incorporation. The research presented in this thesis highlights several novel characterization methods to facilitate molecular level understanding of catalyst sites in porous materials and the effects of promoter application on reactivity.

One characterization method applies dynamic nuclear polarization (DNP) NMR to study zeolites containing ~2 wt% of natural abundance tin without the need for $^{119}$Sn isotopic enrichment. DNP can greatly improve sensitivity by transferring the larger polarization of electron spins, such as those found in stable exogenous radical compounds, to nuclear spins. In order to avoid adsorption of this exogenous component on Lewis acid sites, this approach utilizes a sequential transfer of spin polarization from a bulky radical to tetrachloroethane solvent and then to the target nuclei. The 75x signal enhancement allowed for characterization of natural-abundance $^{119}$Sn-Beta in <24 h. By contrast, without DNP no $^{119}$Sn resonances appeared after 10 days of continuous analysis.

Another approach to characterize substituted zeolites involves solid-state NMR of pyridine adsorbed on the Lewis acid framework metals (Ti, Hf, Zr, Nb, Ta and Sn). This method permits the indirect analysis of NMR-inactive or quadrupolar nuclei even in the presence of solvents. Pyridine $^{15}$N chemical shift can resolve the identity of and provide a continuous acidity scale for different heteroatoms in Beta zeolites including the Brønsted acid heteroatoms, B, Ga, and Al. Experimental data showed a linear correlation of $^{15}$N chemical shift with Mulliken electronegativity of the metal. Furthermore, single pulse NMR offered the ability to quantify framework site concentration in the presence of extra-framework oxides. $^{15}$N pyridine chemical shift complements adsorption equilibrium data and enables catalyst selection to optimize reactant binding.
The second half of this thesis focuses on kinetic and mechanistic studies on sodium tetraborate promoted Sn-Beta in water. This system cooperatively catalyzed the epimerization of aldoses via an intramolecular 1,2 carbon shift mechanism as opposed to the intramolecular hydride shift observed in the absence of borate. A full factorial experimental design demonstrated the catalytic consequences of varying key reaction parameters such as pH, borate loading and reaction time. Reactivity data revealed that isomerization occurs under acidic conditions, epimerization dominates under neutral conditions, and drastic inhibition of both epimerization and isomerization rates results under basic conditions. The predominance of epimerization over isomerization products with substoichiometric borate suggested that borate could function pseudo-catalytically by potentially influencing the Sn active site directly. These findings motivated a detailed mechanistic study in which NMR correlation experiments and REDOR proximity measurements performed on all six singly $^{13}$C labeled glucose molecules led to a proposed glucose-borate-Sn complex geometry confined inside the zeolite pore. Subsequent analyses involving deuterium isotope tracers and competitive kinetic isotope effects showed that the epimerization of aldoses did not proceed through enolization or a retro-Aldol sequence. Directed removal of substrate functionality then led to a proposed Bilik-type reaction mechanism involving borate and Sn.

This body of work demonstrated the first application of DNP NMR to a zeolite and presented reactivity studies for one catalytic pair. Additionally, this thesis involved the synthesis of a wide variety of heteroatom-substituted zeolites including a novel Hf-Beta zeolite and indicated that solution redox chemistry could promote framework Sn incorporation. In general, Lewis acids catalyze many industrially relevant reactions and the ability to perform Lewis acid catalysis heterogeneously and in the presence of water holds great potential. The capacity to tailor Lewis acid sites through promoter incorporation furthermore enables novel catalytic reactions.

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