

Local Connectivity and Confining Environments of Sn-Sites in Sn-Chabazites Are Distinguishable Using DNP-NMR

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Chabazite molecular sieves with isomorphously substituted framework Sn heteroatoms (Sn-CHA) constitute model stannosilicate zeolites comprising a single crystallographically unique tetrahedral-site (T-site). The predominant incorporation of isolated Sn sites within framework positions was assessed from UV-Visible absorption edge energies (>4.1 eV), four-coordinate Sn centers measured after dehydration by X-ray absorption spectroscopy (XAS) and ¹¹⁹Sn dynamic nuclear polarization nuclear magnetic resonance (DNP NMR), and Lewis acid site fractions of nearly unity quantified by ammonia and acetonitrile titration. Aqueous-phase glucose-fructose isomerization turnover rates on Sn-CHA (per extracrystalline framework site) were similar to rates on an amorphous stannosilicate, while intermolecular Meerwein-Ponndorf-Verley propionaldehyde reduction and Oppenauer ethanol oxidation (MPVO) reactions confirm that Sn sites confined within micropores behave as Lewis acids capable of catalyzing intermolecular hydride shift steps.

The increased sensitivity afforded by DNP NMR enabled performing 2D ¹¹⁹Sn cross polarization magic angle turning (CPMAT) NMR experiments, which allows the detection of different sites having the same isotropic chemical shift but different chemical shift anisotropy (CSA) parameters, an unexpected result considering the presence of single T-site in CHA framework. By using pyridine as a probe molecule, which is too large to enter the pore of CHA framework, the Sn sites within mesoporous voids and at extracrystalline surfaces can be selectively detected by IR and ¹⁵N/¹¹⁹Sn DNP enhanced NMR. Experimentally measured ¹¹⁹Sn NMR CSA parameters were compared to values estimated using density functional theory (DFT), supporting the presence of defect-open and closed Sn sites in dehydrated samples, which evolves into hydrated defect-open and hydrolyzed-open sites respectively upon hydration. These findings highlight the characterization of local structures of active sites in Sn zeolites enabled by DNP NMR with the aid of DFT calculations, and the crucial role of the confining environment in zeolitic porous framework in Lewis acid promoted reactions.