Solid Lewis acids are used as catalysts in industry for a range of chemical transformations, including the epoxidation of propylene to propylene and the isomerization of glucose to fructose. The structures of active sites in these catalysts, defined by their primary coordination and secondary confining environments, varies with their synthetic provenance and leads to concomitant variation in their reactivity. Precise quantification of the numbers of various types of Lewis acid sites and of silanol defects present in Lewis acidic catalysts is necessary in order to normalize reaction rates prior to mechanistic interpretation of observed differences in reactivity among samples synthesized via different routes.

Lewis acid site titration and quantification methods are developed here, using chemisorption of Lewis basic titrants (carbon monoxide, deuterated acetonitrile, pyridine, ammonia, n-propylamine) followed by measurements of either transmission infrared spectra as a function of site coverage, or of mass spectra of titrants desorbed from sites during temperature programmed desorption. These characterization methods are applied to a variety of Lewis acidic metal centers (Sn, Ti, Zr) incorporated within a range of secondary environments in crystalline (Beta, CHA, and MFI zeolites) and amorphous siliceous oxides. These methods provide quantitative evidence that aqueous-phase glucose-to-fructose isomerization turnovers (1% w/w glucose, 373 K) occur exclusively over sites confined within zeolitic pores, and not at sites located within mesoporous or unconfined environments. Isomerization rate constants (373 K, per active Sn site) are an order of magnitude higher at open Sn sites confined within low-defect than within high-defect Sn-Beta zeolites, demonstrating that silanol defects influence isomerization turnover rates.

Moreover, these methods provide evidence that intramolecular and intermolecular Meerwein-Pondorff-Verley reduction and coupled Oppenauer oxidation (MPVO) reaction rates (per Sn) decrease with increasing extents of Sn incorporation in post-synthetically prepared Sn-Beta zeolites because less reactive Sn sites (i.e., closed Sn sites) are preferentially grafted as larger fractions of framework vacancies are healed. These titration techniques also demonstrate that decreases in first-order isomerization rate constants (373 K, per Sn) observed as low-defect Sn-Beta zeolites are exposed to hot liquid water (373 K) for longer times result from increases in their silanol defect density. Prevention of framework Si-O-Si bond hydrolysis in zeolite pores is therefore necessary to mitigate deactivation during catalysis in liquid water. This class of catalysts are stable over ~50 regeneration cycles (pure O_2, 823 K) in the gas phase after long-term exposure to gaseous H_2O at 673 K, however, and are used in industrial practice to catalyze gas-phase reactions with high selectivity, including the direct epoxidation of propylene with H_2 and O_2 over Au/titanosilicate MFI (Au/TS-1). Rigorous treatments of the kinetic inhibition by propylene oxide on epoxidation turnover rates (473 K) clarify the mechanistic origins of apparent reaction orders and provide further constraints on plausible epoxidation mechanisms. The active site characterization techniques developed here promise to aid in elucidating the active site requirements and mechanistic details of catalysis by Lewis acidic oxides, and in designing solid Lewis acid catalysts of diverse structure and composition for a variety of industrial applications.