ABSTRACT

Vega-Vila, Juan Carlos Ph.D., Purdue University, December 2019. Synthetic Strategies to Tailor Active and Defect Site Structures in Lewis Acid Zeolites for Sugar Isomerization Catalysis. Major Professor: Rajamani Gounder.

Lewis acid zeolites contain framework metal heteroatoms that catalyze sugar isomerization reactions at different turnover rates depending on the local coordination around metal centers and the polarity of their confining secondary environments. Post-synthetic modification routes that react metal precursors with framework vacancy defects in dealuminated Beta zeolites (Sn-Beta-PS-OH) are developed as an alternative synthetic strategy to the hydrothermal crystallization of Sn-Beta zeolites (Sn-Beta-HT-F). Post-synthetic routes provide the ability to systematically tailor the structural features of active and defect sites in Sn-zeolites, especially in composition ranges inaccessible to materials crystallized by hydrothermal routes (Si/Sn $<$ 100; $>$ 2 wt.% Sn), yet often result in incomplete or unselective Sn grafting within framework vacancy defects and form extraframework metal oxide domains and residual defect sites. The development of robust post-synthetic routes to prepare Sn-zeolites with intended active and defect structures has been limited by the dearth of characterization techniques to unambiguously detect and quantify such structures present in stannosilicate materials, and of mechanistic links between such structures and the turnover rates of catalytic reactions.

The presence of framework Sn centers that can expand its coordination shell from four- to six-coordinate structures, and small extraframework tin oxide domains that cannot, were unambiguously detected from diffuse reflectance UV-Visible spectra of stannosilicate materials measured after dehydration treatments (523 K, 0.5 h) to discern ligand-to-metal charge transfer bands for tetrahedrally-coordinated Sn het-

eroatoms (< 220 nm, > 4.1 eV) and those for tin oxide domains (> 230 nm, < 4.1 eV). Liquid-phase grafting of stannic chloride in dichloromethane reflux (333 K) enables preparing Sn-Beta zeolites with higher framework Sn content (Si/Sn = 30–144; 1.4–6.1 wt.% Sn) than grafting performed in isopropanol reflux (423 K, Si/Sn > 120; 1.6 wt.% Sn). This reflects competitive adsorption of isopropanol solvents with stannic chloride at framework vacancy defects during grafting procedures, consistent with infrared spectroscopy (IR) and temperature-programmed desorption (TPD) of dealuminated Beta samples after saturation with isopropanol at reflux temperatures (423 K), and not any limitations inherent to the structure of vacancy defects within dealuminated zeolite supports that would prevent reaction with metal precursors as often proposed.

This insight enabled preparing Sn-Beta zeolites with varying densities of residual defects, via dichloromethane-assisted grafting of stannic chloride to different extents, into dealuminated Beta supports of different initial Al content (Si/Al = 19–180) and mineralizing agent used for hydrothermal crystallization of the parent Al-Beta sample (e.g., fluoride or hydroxide). Preparation of low-defect Sn-Beta zeolites using post-synthetic routes (Sn-Beta-PS-F) first required the synthesis of parent Al-Beta zeolites in fluoride media to minimize residual siloxy defects (OSi^-) formed during crystallization, and dilute Al content (Si/Al > 100, < 0.6 Al (unit cell)$^{-1}$), to minimize the density of intrapore silanol groups formed after dealumination and high temperature oxidative treatment. The methanol packing density within microporous voids of Sn-Beta zeolites was assessed from relative volumetric uptakes at the point of micropore filling from single-component methanol (293 K) and nitrogen (77 K) adsorption isotherms, and decreased systematically among samples with increasing density of silanol groups. The total density of silanol groups within micropores and at external crystallite surface in Sn-Beta zeolites was quantified by H/D isotopic exchange during temperature-programmed surface reactions (500–873 K), and within microporous voids from IR spectra measured after saturation of microporous binding sites with CD_3CN (2275 cm^{-1}, 303 K). *In situ* IR spectra collected at low methanol

pressures (P/P0 < 0.2, 303 K) provide further evidence that methanol molecules arrange in localized clusters within Sn-Beta-PS-F, but form extended hydrogen-bonded networks within Sn-Beta-PS-OH.

Glucose-fructose isomerization rate constants (373 K) were used to probe the local coordination of Sn heteroatoms and the polarity of the secondary environment as influenced by silanol defects within microporous cavities. *Ex situ* pyridine titration of Sn-Beta-HT-F samples suppressed isomerization rates (per total Sn, 373 K) after only a subset of Sn sites were poisoned, which correspond to the number of open Sn sites quantified *ex situ* via CD_3CN IR (303 K), providing further evidence that open Sn sites are dominant active sites for glucose isomerization. First-order isomerization rate constants (373 K) decrease with increasing Sn content when normalized by total Sn density, and are invariant when normalized by the number of open Sn sites, because open Sn sites are grafted preferentially within Sn-Beta-PS-OH (Si/Sn = 30–144; 1.4–6.1 wt.% Sn) at low Sn densities. Isomerization rate constants (per open Sn, 373 K), however, are lower by ∼4x and ∼15x on Sn-Beta-PS-F (Si/Sn = 284; 0.7 wt.% Sn) and Sn-Beta-PS-OH, respectively, than on Sn-Beta-HT-F. Open Sn sites catalyze aqueous-phase glucose isomerization at higher turnover rates (373 K) when their microporous surroundings contain silanol defects present in low (hydrophobic) densities than high (hydrophilic) densities, which are characteristic of Sn-Beta-HT-F and Sn-Beta-PS-OH samples, respectively. This reflects reorganization of extended water networks, which are stabilized in high-defect, hydrophilic micropore environments, at kinetically relevant 1,2-hydride shift transition states that incurs entropic penalties that lower turnover rates. This thesis highlights the development of synthesis-structure-function relationships to guide the preparation of catalytic materials with intended active and defect site structures within confining reaction environments, the development of characterization techniques for the identification and quantification of such structures, and the influence of such structures on turnover rates of liquid-phase sugar isomerization.