

STRUCTURAL AND KINETIC CHARACTERIZATION OF LEWIS ACID ZEOLITES FOR SUGAR ISOMERIZATION CATALYSIS

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Abstract

Framework Lewis acidic Sn sites in Beta zeolites (Sn-Beta) were quantified using five Lewis base titrants (pyridine, deuterated acetonitrile, carbon monoxide, n-propylamine, ammonia). Integrated molar extinction coefficients were determined for IR peaks of pyridine bound to Lewis acidic Sn sites and of deuterated acetonitrile (CD₃CN) bound to open and closed Sn sites. Temperature programmed desorption of n-propylamine (NPA) and ammonia counted equivalent numbers of Lewis acid sites as did pyridine and CD₃CN for low-defect and high Sn content samples (Si/Sn <175), but overestimated the number of Lewis acid sites on high-defect samples. Pyridine titration of active sites in Sn-Beta prior to aqueous-phase glucose isomerization (1% w/w, 373 K) gave quantitative agreement with the number of open Sn sites quantified *ex situ* by CD₃CN. Initial glucose-fructose isomerization turnover rates (per active site, 373 K) measured as a function of aqueous glucose concentration (0-50% (w/w)) were 10-50x higher for low-defect than for high-defect zeolites, apparently reflecting more effective stabilization of isomerization transition states in low-defect micropores devoid of bulk water during catalysis.

Keywords

Acetonitrile, Glucose Isomerization, Lewis Acid Zeolite

Introduction

Tetravalent metal heteroatoms (M⁴⁺ = Hf⁴⁺, Sn⁴⁺, Ti⁴⁺, Zr⁴⁺) in pure-silica zeolites behave as Lewis acid centers that catalyze intramolecular and intermolecular oxidation and reduction reactions (e.g., Meerwein-Ponndorf-Verley reductions, Oppenauer oxidations, and Baeyer-Villager oxidations) including the isomerization of glucose to fructose, sorbose, and mannose (Gounder, 2014). Experiment and theory provide evidence that partially-hydrolyzed “open” sites ((SiO)₃Sn(OH)) with neighboring silanol groups, rather than fully-coordinated “closed” sites ((SiO)₄Sn), are the predominant active sites for glucose-fructose isomerization (Bermejo-Deval et al., 2014, Rai et al., 2013, Li et al., 2014). Several direct and post-synthetic

methods to prepare M-Beta zeolites have been reported (Dapsens et al., 2015) and result in different densities of open metal sites and residual silanol defects, necessitating the development of methods to count active sites (open Sn) to rigorously compare the reactivity of materials that differ in origin or treatment history. First-order rate constants of aqueous glucose-fructose isomerization (per total M, 373 K) are 10-30x higher for low-defect Ti-Beta synthesized in fluoride media than high-defect Ti-Beta synthesized in hydroxide media (Gounder and Davis, 2013), which likely reflect either different densities of active metal sites or of silanol groups.

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Results

The crystal topologies of zeolites synthesized directly and by post-synthetic grafting of metal (Sn, Ti) precursors into dealuminated zeolites were confirmed with powder X-ray diffraction and N₂ micropore volumes (77 K). Diffuse reflectance UV-visible (DRUV) spectra measured on dehydrated M-Beta (He, 523 K) showed bands centered at ~205-220 nm and edge energies >4.1 eV, indicating that metal atoms were incorporated into predominantly tetrahedral framework positions (Blasco et al., 1998, Roy et al., 2013, Ross-Medgaarden et al., 2009). Controlled doses of Lewis base titrants (pyridine, CD₃CN) were admitted into a quartz transmission IR cell containing self-supporting zeolite wafers. IR peak areas for pyridine bound to Lewis acidic Sn sites (1450 cm⁻¹) at low pyridine coverage (<0.2 pyridine/Sn) for three different Sn-Beta samples were used to determine an integrated molar extinction coefficient (E) for IR peaks of pyridine bound to Lewis acidic Sn sites (1.42 ± 0.30 cm² μmol⁻¹). This E value was used to quantify the number of Lewis acid sites on M-Beta zeolites from spectra collected at saturation coverages. The numbers of Lewis acid sites on three Sn-Beta samples were used to fit molar extinction coefficients of IR peaks of CD₃CN bound to open (2316 cm⁻¹) and closed (2308 cm⁻¹) Sn sites to be 2.04 ± 0.43 cm² μmol⁻¹ and 1.04 ± 0.22 cm² μmol⁻¹, respectively. The number of Lewis acid sites estimated using IR-based methods (pyridine, CD₃CN), and temperature-programmed desorption (TPD) of n-propylamine and ammonia agreed quantitatively for four different low-defect Sn-Beta samples synthesized hydrothermally with Si/Sn <175, while NPA binding to silanol defects resulted in overestimation of the number of Lewis acid sites present on high-defect Sn-Beta samples. IR spectra were also used to determine an E value of 0.74 ± 0.16 cm² μmol⁻¹ for IR peaks of CD₃CN adsorbed on silanol defects (2275 cm⁻¹) which were present in ~100x larger densities in post-synthetic than in hydrothermally-synthesized Sn and Ti-Beta zeolites.

Isotopic labeling studies with aqueous glucose-D2 reactants (373 K) confirmed that fructose was produced via an intramolecular 1,2-hydride shift on all samples. Glucose-D2 reactants were used to determine H/D KIE values of ~1.7-2.1 for all samples and glucose concentrations studied, as expected for kinetically-limited isomerization turnover rates (Gounder and Davis, 2013). Pyridine titration of two hydrothermally-synthesized Sn-Beta samples prior to measurement of initial reaction rates estimated numbers of active sites that were approximately equal to the number of open sites counted *ex-situ* using CD₃CN IR. Apparent first order rate constants (per active site, 373 K), measured under low glucose surface coverages, were higher by 50x and 13x for low-defect Sn and Ti Beta zeolites, respectively, than their high-defect analogues. Apparent zero order rate constants, measured at high glucose surface coverages, were 30x higher for low-defect than high-defect Ti-Beta. We use a mechanism-

derived rate expression to conclude that the predominant difference in glucose isomerization rate constants between low and high defect Ti-Beta zeolites reflect lower free energies of intramolecular 1,2-hydride shift transition states within low-defect M-Beta zeolites.

Conclusions

The number of Lewis acid sites present in Sn-Beta zeolites were counted using five different Lewis base titrants, and the number of open sites counted using *ex-situ* CD₃CN IR agreed quantitatively with the number of active sites present during aqueous glucose-fructose isomerization determined from pyridine titration prior to reaction. First-order rate constants (per active site, 373 K) were 50x and 13x higher for low-defect Sn and Ti-Beta zeolites than for the corresponding high-defect materials. Zero-order rate constants, measured at high glucose coverage, were 30x higher on low-defect than high defect Ti-Beta zeolites, likely due to increased stability of the transition state in low-defect pores free of bulk water.

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