THESIS ABSTRACT

Lewis acidic zeolites are silica-based, crystalline microporous materials containing tetravalent heteroatoms (M^{4+}=Ti, Sn, Zr, Hf) substituted in framework locations that are reported to catalyze a wide range of reactions involving oxygenates and hydrocarbons. The synthetic protocols used to prepare Lewis acid zeolites determine the structures of the active sites and the reaction pockets that confine them, which in turn influences reactivity, product selectivity, and stability. Specifically, aqueous-phase reactions of biomass-derived molecules, such as glucose isomerization, are sensitive to the hydrophobicity of confining environments, often leading to changes in turnover rates. As a result, precise evaluation of the structure and behavior of reaction environments and confined active sites among catalysts of varying provenance or treatment history requires quantitative descriptions of the active Lewis acid site densities, of the number of surface functional groups that determine the polarity of microporous confining environments, and of the kinetic behavior of these catalytic materials.

Methods for quantifying Lewis acid sites and silanol defects are developed here by analyzing infrared (IR) spectra collected after Lewis base (CD_3CN, pyridine) titrations of Lewis acidic zeolite surfaces and are compared to vapor-phase methanol and water adsorption isotherms. Additionally, *ex situ* (vapor-phase water flow) and *in situ* (aqueous-phase, 373 K, 0-50 wt% glucose) IR spectra are used to compare co-adsorbed water densities and structures within hydrophobic (low silanol density) and hydrophilic (high silanol density) confining environments on M-Beta zeolites. Under reaction conditions relevant for sugar conversion in aqueous media (353-398 K, 1-50 wt% glucose), hydrophilic reaction pockets stabilize liquid-like extended water structures within microporous environments while hydrophobic channels stabilize vapor-phase water at lower intraporous water densities. Higher aqueous-phase glucose isomerization rates

(368-383 K, 1-50 wt% glucose, per kinetically relevant active site) are observed on hydrophobic Ti-Beta (~6-12x, per Lewis acidic Ti) and Sn-Beta (~50x, per Lewis acidic Sn in open configuration) over their hydrophilic analogs. Higher turnover rates on hydrophobic M-Beda zeolites reflect the absence of an extended, hydrogen-bonded network of waters, which entropically destabilizes kinetically relevant hydride shift transition states by reducing flexibility in the primary solvation sphere. These findings suggest that catalyst design strategies which minimize the generation of silanol groups within confining reaction environments would lead to increases in turnover rates.

The methods derived herein can be applied to understanding the role of the confining environment and the associated co-adsorbed water on zeolitic materials of different topology and Lewis acid site identity. For example, the transient formation of silanol defects under aqueous-phase operating conditions is primarily responsible for the deactivation of Sn-Beta catalysts observed during aqueous-phase glucose isomerization. Further, quantifying the role of the confining environment geometry and hydrophobicity on aqueous-phase glucose isomerization rates can be used as guidance for catalyst design to increase reaction rates and selectivities toward specific isomerization products. These findings show that both the active site identity and its confining environment, which vary with zeolite topology and channel polarity, combine to influence reactivity, selectivity and stability for aqueous-phase glucose isomerization catalysis.