Structure-reactivity relationship in glucose isomerization by Sn-BEA zeolite

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Introduction

- HMF is considered a key biorenewable platform molecule
- To efficiently convert glucose to HMF, it has to be isomerized to fructose prior to the dehydration reaction [1].
- Sn-BEA zeolite is a uniquely active catalyst for glucose isomerization [2].
- The origin of this unique reactivity is not clear yet.

Methods and Models

DFT calculations: VASP 5.2 GGA-PBE, DFT-D2 for vdW interactions; PAW for electron-ion interaction, \( E_{\text{cut}} = 400 \text{ eV} \), \( \Gamma \)-point.

Sn-BEA (64T atoms): Sn at T2 site [3,4]

Coordination and activation

- Glucopyranose ring-opening is structure-insensitive
- Increased coordination mobility of defect Sn-OH site is beneficial for the stabilization of O2H-deprotonated glucose intermediate
- Activation barriers as well as the TS and intermediate structures for the key O2H-deprotonation and H-shift steps over Sn(IV) and SnOH are similar

Coordination and activation requires O1H-coordination

Catalysis over extended SnOH' defect site

- H-bonding network induces one-step deprotonation/H-shift and stabilizes TS
- FF formation promoted
- Molecular recognition effect due to concert action of Sn center and silanol nest

Summary

- O1H-coordination of glucose to Sn is essential for the isomerization
- Lattice Sn(IV) and SnOH sites show similar reactivity
- Activity of SnOH can be enhanced in the presence of an extended lattice defect next to the Lewis acid sites: specific reaction environment at such site promotes glucose activation and its conversion to fructose [4]