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The origin of selectivity in the conversion of glucose to fructose and mannose in Sn-BEA and Na-exchanged Sn-BEA zeolites

Sha Li^{a,b}, Tyler Josephson^{a,b}, Dionisios G. Vlachos^{a,b} and Stavros Caratzoulas^{a,*}

^aCatalysis Center for Energy Innovation, University of Delaware, Newark, DE 19716, USA

^bDepartment of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

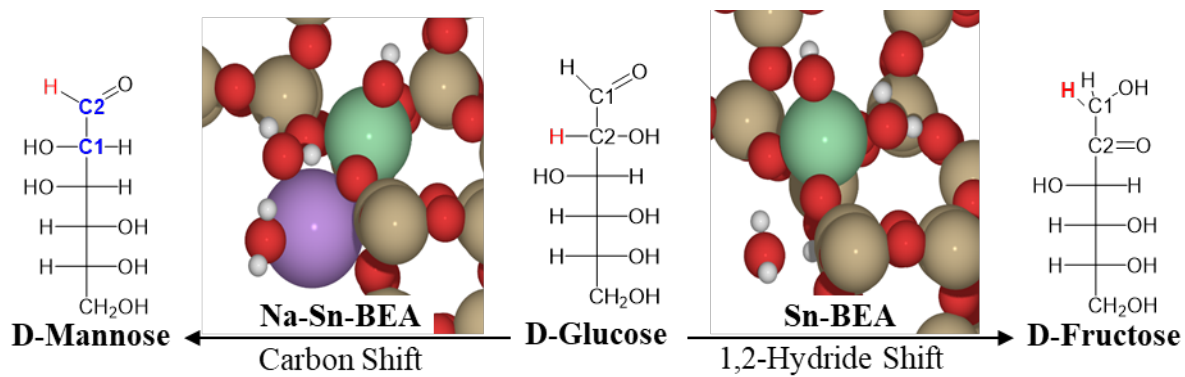
Corresponding Author

*E-mail: cstavros@udel.edu

ABSTRACT

We investigate the isomerization and epimerization of glucose to fructose and mannose in Sn-BEA and Na-exchanged Sn-BEA using density-functional theory calculations on periodic BEA crystals. We compare reaction pathways both in the absence and presence of water molecules in the vicinity of the active site and find that water effectively determines the selectivity in Na-Sn-BEA. We identify two competing epimerization pathways, one involving direct 1,2-carbon shift and the other involving 1,2-hydride shift via fructose. In Sn-BEA, the isomerization to fructose is the kinetically dominant pathway, while mannose is formed via the indirect 1,2-hydride shift epimerization pathway. In Na-Sn-BEA, the kinetically dominant pathway is epimerization to mannose via the direct 1,2-carbon shift pathway (Bilik mechanism) only in the presence of water solvent in the vicinity of the active site, whereas isomerization is preferred in the absence of water. We argue that polar water molecules that coordinate around the Na cation screen strong electrostatic interactions between Na⁺ and the glucose backbone that are responsible for the strong inhibition of the 1,2-carbon shift mechanism in the absence of water. In Sn-BEA, the presence of water does not influence the selectivity. Our calculations resolve for the first time the role of water and Na cations in the catalytic activity of Sn-BEA, and rationalize the experimental data.

Graphical abstract



Keywords: glucose isomerization; glucose epimerization; Sn-BEA zeolite; Na-exchanged Sn-BEA zeolite; periodic density-functional theory

1. Introduction

The chemical industry depends dominantly on fossil resources, depletion of which is foreseen in the near future. Therefore, establishing new, green chemistry protocols to convert renewable biomass-derived feedstocks to chemicals that are compatible with the existing infrastructure is highly desirable.[1-3] Valorization of the most abundant monosaccharide building block, glucose (GLU), to prospective platform molecules such as 5-hydroxymethylfurfural (HMF) is an important step in the transition towards a sustainable chemical industry. However, the direct transformation of GLU to HMF is challenging as it suffers from low selectivity.[4, 5] In comparison, conversion of fructose (FRU) to HMF can be carried out with much higher yield under mild reaction conditions.[6-8] Catalytic GLU-to-FRU isomerization is therefore an essential step in the successful valorization of glucose to platform molecules.

Following the first demonstration of the catalytic efficiency of the tin-containing zeolite with BEA topology (Sn-BEA) for oxidation of ketones to lactones by Corma *et al.*, [9, 10] Sn-BEA has shown its promise in catalyzing several reactions, including the Meerwein-Ponndorf-Verley (MPV) reduction of aldehydes and ketones,[11, 12] C-C coupling,[13, 14] Diels-Alder cycloaddition,[15] as well as glucose-fructose isomerization.[16-20] Apart from its outstanding activity and selectivity to the desired isomerization product from glucose, Sn-BEA is stable in aqueous acidic media, enabling the one-pot transformation of glucose to HMF.[21] These advantages of Sn-BEA in catalyzing glucose isomerization have spurred a number of experimental[16-19, 22-24] and computational studies[22, 25-29] which aim to characterize the active site as well as the reaction mechanism.

Two types of active sites may be found in Sn-BEA[30]: the unhydrolyzed, “closed” sites ($\text{Sn}(\text{OSi})_4$), where Sn is bonded to four O-Si groups; and the hydrolyzed, “open” sites ($(\text{SiO})_3\text{Sn}(\text{OH})$), consisting of a hydroxylated metal center and an adjacent silanol group (SiOH), the presence of which has been corroborated by IR spectroscopy.[31] [24] It has been demonstrated that the open sites of Sn-BEA are more active than the closed ones.[18, 22, 23, 28] Glucose epimerization to mannose (MAN) occurs in nearly every investigation of glucose conversion and competes with the isomerization reaction. Bermejo-Deval *et al.*[19] have recently reported that, upon Na-exchanging the silanol proton of the Sn-BEA open site, the selectivity tilts in favor of mannose. Despite a number of computational studies[25-29] of the catalytic pathways of glucose

isomerization to fructose in Sn-BEA, an explanation for the selectivity change upon Na exchange is yet to be provided.

To review briefly what is known, formally and following the fast opening of the pyranose ring, isomerization of GLU to FRU entails deletion of the H atom of O2H and addition of an H atom to the O1 oxygen atom. Mechanistically, the Lewis-acid catalyzed isomerization follows 1,2-hydride shift (1,2-HS) from C2 to C1. The 1,2-HS is activated by a prior donation of the O2H proton to the basic SnOH of the active site, which results in the formation of a water ligand. After the 1,2-HS, the water ligand donates a proton back to the O1 atom of the product. (We should also note that Li *et al.*[28] have proposed a mechanism that utilizes a framework oxygen instead of the SnOH of the open site.) Kinetic isotope effect experiments and computational studies have established that the 1,2-HS is the rate-limiting step.[18, 32, 33] The 1,2-HS is the only isomerization mechanism both in Sn-BEA and in Na-Sn-BEA. Computations and isotope labelling experiments have revealed that there are two distinct mechanistic pathways to epimerization, *viz.* mannose formation.[19, 25] The preferred epimerization pathway seems to depend on the catalyst. The pathway favored by Sn-BEA goes through a FRU intermediate and it involves 1,2-HS from C1 to C2, anti-periplanar to the 1,2-HS that converts GLU into FRU; we will be referring to this epimerization mechanism as “anti-1,2-HS”. (The reader is reminded that, upon FRU formation, there are two H atoms on the C1 carbon. The H atom that migrates from C1 to C2 to form MAN is the one that was trans to the H of C2 that shifted during isomerization.) In Na-Sn-BEA, the epimerization does not proceed through FRU, but rather via a more direct route, a 1,2-carbon shift (1,2-CS) of the C3 carbon atom from C2 to C1. In this case, the CS is the rate-limiting step, according to calculations and kinetic isotope effect experiments.[19, 25, 26]

Christianson *et al.*[25] and Rai *et al.*[26] explored the reaction pathways with computational methods using both cluster and embedded cluster ONIOM models. However, they did not capture the attendant selectivity shift upon Na exchange, probably—as we will see—due to the absence of solvent molecules (water) in the vicinity of the active site. Additionally, the open site models used in those studies do not seem to be faithful representations of the Sn-BEA open site, as it transpires from a recent study by Josephson *et al.*[34] By comparing the relative energies of 144 distinct open site structures, Josephson *et al.*[34] showed that the most stable configuration of the Sn-BEA open site features the SiOH group opposite the SnOH group and facing away from rather than toward the SnOH (the latter being the case in the models of Christianson *et al.*[25] and

Rai *et al*[26]). All these ‘facing-away’ configurations have the hydroxyl of the SiOH group farther away from the SnOH group than the rest of the explored configurations. The ‘facing-away’ configurations are thermodynamically more stable, *regardless* of the substitution T site. In this work, we adopt the most stable configuration of the Sn-BEA open site found by Josephson *et al*. [34]

As water is the solvent of choice for monosaccharides, because of poor solubility in organic solvents, it is critical to maintain the hydrophobic nature of the zeolite matrix in Sn-BEA, to prevent deactivation of the active sites from contact with bulk water.[35, 36] Spectroscopic studies also suggest that water changes the coordination geometry of the Sn center, from tetrahedral in the calcined catalyst, to octahedral during reaction on account of two water ligands around the metal center.[37-40] These findings imply the modification on the active site structure by water solvent, which is an important factor to consider in mechanistic studies. In a study that combined in situ ^{13}C NMR spectroscopy and DFT calculations, the competitive adsorption between sugar and water molecules on the active site of Sn-BEA has recently been suggested as the reason for the sluggish isomerization of the sugar in hydrated versus dehydrated Sn-BEA samples; that study, however, did not include the calculation of transition states.[41] Solvent participation in the chemical transformations taking place at the active site and product distribution changes with different solvents are also being investigated,[42] but the latter are outside the scope of the present study.

In this work, we present periodic-density functional theory (p-DFT) studies of the isomerization and epimerization of glucose in Sn-BEA. In particular, we investigate how the water solvent and Na cations influence the selectivity to fructose or mannose. For the first time, our results provide qualitative agreement with the experimentally observed change in selectivity, from 1,2-HS in Sn-BEA to 1,2-CS in Na-exchanged Sn-BEA. We also show that in Sn-BEA, the anti-1,2-HS mechanism through fructose and *not* the direct 1,2-CS mechanism is the preferred pathway to MAN, in complete agreement with experimental observations by Davis and co-workers.[19]

2. Methods

All DFT calculations were performed using VASP. The interaction between electrons and ions was modelled with the projected augmented wave (PAW) method[43, 44] with an energy cut-off of 400 eV. A larger cut-off of 600 eV proved unnecessary; for example, the binding energy of glucose changes by less than 0.01 eV. Standard GGA PBE potentials were used for all elements

except Sn, whose semicore *d*-electrons were treated explicitly. The DFT-D3 method[45] was used to describe dispersion interactions. The first Brillouin zone was sampled at the Γ -point. Full structure optimizations were performed with fixed cell parameters using a conjugate gradient algorithm. Convergence was assumed to be reached when the forces on all atoms became less than 0.05 eV/Å. The climbing image nudged elastic band method (NEB)[46, 47] was used to locate minimum energy paths and transition states.

The optimized parameters of the tetragonal BEA unit cell were $a=b=12.632$ Å and $c=26.186$ Å. In the case of Sn-BEA, the exact location of Sn in the framework is still a matter of debate as it is difficult to ascertain and also dependent on the synthesis method.[24, 31,

34, 48, 49]. In a recent study, Wolf *et al.* concluded that Sn-BEA zeolites prepared via different synthetic protocols possess different physicochemical properties and distributions of Sn(IV) species. Characterization via DNP ^{119}Sn solid-state NMR was performed to better discriminate between structurally different framework Sn(IV) sites. While the ^{119}Sn -NMR spectra observed for Sn-BEA zeolites from similar postsynthetic protocols showed minor variations, ^{119}Sn -NMR spectra of hydrothermal Sn-BEA varied quite significantly. As-synthesized hydrothermal Sn-BEA zeolites predominantly consist of closed framework sites most likely in T5, T6, and/or T7 positions, although a small amount of defect-open sites can be present, depending on the exact synthesis procedure used. On the other hand, postsynthetic materials prepared via solid-state ion-exchange exhibited closed T5, T8 sites and a significant higher amount of hydrolyzed and T9 open sites.[50] In the present work, we have opted for the T9 lattice position (Fig. 1), which was recently proposed by Josephson *et al.*[34] as the thermodynamically preferred *open* site. (We use the Newsam nomenclature for the labelling of the crystallographic lattice sites.[51]) At the open site,

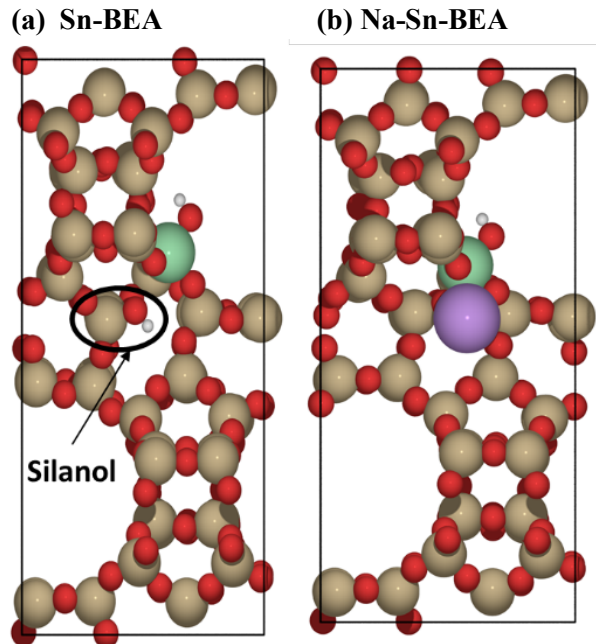


Fig. 1. DFT optimized structures of (a) Sn-BEA open site and (b) Na-exchanged Sn-BEA open site. The silanol O atom is 3.2 Å away from the Sn center, compared with the covalent Sn-O bond lengths of *ca.* 1.9 Å. (Si, O, Sn, H and Na atoms are represented by brown, red, green, white and purple spheres, respectively.)

Sn is tetrahedrally coordinated to three bridge oxygen atoms (brO), forming a $(\text{SiO})_3\text{Sn}(\text{OH})$ center; the silanol OH resides relatively far from the Sn center, with a $\text{Sn}\cdots\text{O}$ distance of 3.2 Å. Based on experimental findings,[19, 52] the Na-exchanged BEA was modelled by replacing the silanol proton of the open site with a Na cation (Fig. 1). Interestingly, upon Na-exchange, the silanol O is pulled closer to the Sn metal center, to a distance similar to the formal Sn-O bond lengths (2.1 Å vs. 2.0 Å). Two explicit water molecules were also included in our simulations to account for the influence of water on the geometry of the active center and on the substrate-catalyst interactions. More than 20 different arrangements for the two water molecules near the active center were tested and the most stable configuration was adopted for the calculations reported herein. In the following, we will be referring to the systems with water as ‘Sn-BEA+2H₂O’ and ‘Na-Sn-BEA+2H₂O’. We note that calculations with a larger number of water molecules proved quite challenging to converge.

3. Results and discussion

In this study we investigate all three pathways reviewed above, with and without explicit water molecules at the active site. As prior experimental and computational work have established that the hydride shift, in the isomerization case, and the carbon shift, in the epimerization case, are the rate-controlling steps, in the main text we focus on the steps that control selectivity and do not concern ourselves with the fast deprotonation and protonation steps. The full energy profiles, however, can be found in the Supporting Information (Fig. S1-S4).

3.1. Isomerization and epimerization in Sn-BEA

In Sn-BEA, the pre-activated GLU (*viz.*, deprotonated GLU; Fig. 2(a)) prefers a O1,O2- κ^2 bidentate coordination to the Sn center (see image in Fig. S5, Supporting Information). This is a stable intermediate, with energy -1.16 eV relative to the gas phase. The subsequent 1,2-HS is an exothermic step (by -0.46 eV), with an activation energy of 0.76 eV. The anti-1,2-HS is practically thermoneutral and requires 0.83 eV of activation energy, more than the activation energy (0.37 eV, Fig. S1, Supporting Information) required for the Sn water ligand to donate a proton back to O1. Therefore, FRU formation is kinetically favored along this pathway. In comparison, the 1,2-CS needs to overcome a barrier of 0.97 eV, which is 0.21 eV higher than the 1,2-HS, making the

direct epimerization pathway less favorable by two orders of magnitude at reaction conditions (atmospheric pressure and temperature around 363 K).

In the presence of two water molecules in the vicinity of the active site, the (O1,O2- κ^2 -GLU)Sn coordination is still preferred (Fig. 2(b) and image in Fig. S6, Supporting Information), like the solvent-free case. The deprotonated intermediate is further stabilized by 0.64 eV (Table S1, Supporting Information) on account of hydrogen bonds with the solvent. Solvent water does not change the coordination mode of the active Sn center, still being octahedral. With two solvent water molecules present, the energy gap between the 1,2-HS and 1,2-CS pathways opens further, from 0.21 eV (without water) to 0.35 eV, making the direct epimerization pathway less favorable by five orders of magnitude. The anti-1,2-HS is affected very little by the presence of the water molecules: the barrier drops by a mere 0.07 eV.

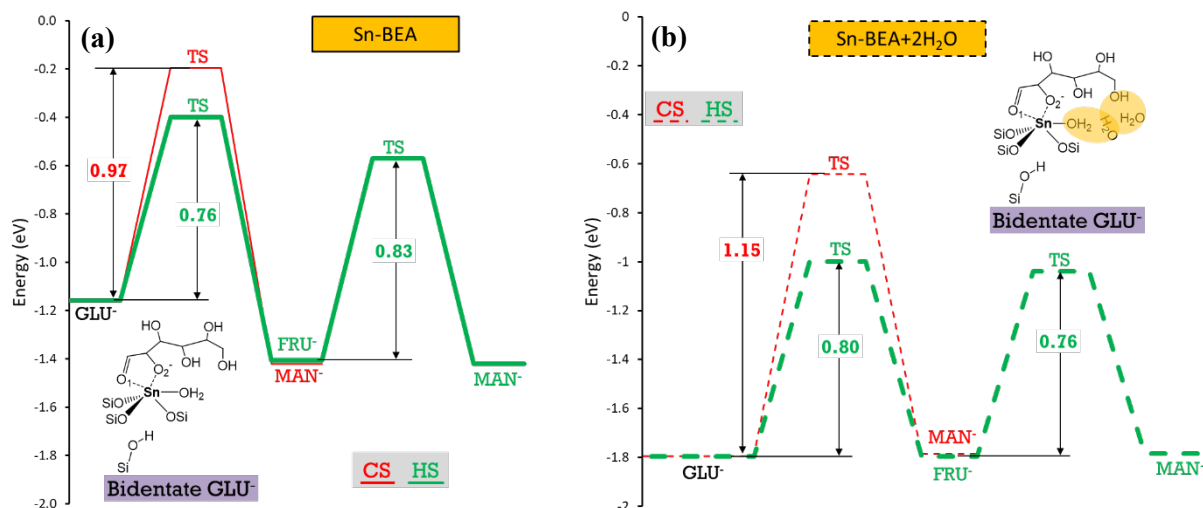


Fig. 2. Potential energy profiles for glucose isomerization and epimerization in Sn-BEA without (a) and with (b) water present at the active site.

The greater destabilization of the 1,2-CS transition state with water in the pore can be readily explained. In the presence of water molecules, the sugar molecule OH groups participate in a network of hydrogen bonds (Fig. S6, Supporting Information). This is evident from the stabilization of the deprotonated GLU intermediate by 0.64 eV in the presence of two water molecules. As the 1,2-CS of the C3 atom of the sugar entails movement of the C3-C6 segment of the backbone, the energy cost increases substantially because the surrounding water molecules have to rearrange as well, and this disrupts the hydrogen-bond network. In contrast, both the 1,2-

HS and anti-1,2-HS steps remain unaffected, for the most part, because the H migration has a negligible impact on the conformation of the bound substrate molecule.

We should note that in the course of these transformations, the silanol group of the open site is only a spectator and that the Sn center remains in an octahedral geometry throughout.

3.2. Isomerization and epimerization in Na-Sn-BEA

In Na-Sn-BEA, Sn is pentacoordinated to four bridge oxygen atoms and one OH group. During reaction, the glucose molecule O2- η^1 coordinates to the Sn atom, which assumes octahedral geometry (Fig. 3(a) and S7, Supporting Information). In addition, the GLU O1 atom (formyl group) participates in a hydrogen bond with the Sn water ligand, while more critically the O3H group is coordinated to the Na cation. The 1,2-HS energy barrier is 0.99 eV, that is 0.23 eV higher than in Sn-BEA. Interestingly, re-protonation of the substrate occurs concurrently with the 1,2-HS. This concerted mechanism is tightly intertwined with the monodentate O2- η^1 binding geometry and the aforementioned hydrogen bond between the formyl O1 atom and the Sn water ligand: the hydride transfer is accompanied by charge transfer from O2 to O1 and as a result the latter readily abstracts a proton from the Sn water ligand, regenerating the SnOH group of the open site.[53]

Although GLU prefers an O2- η^1 binding geometry in Na-Sn-BEA, we find that, in the course of the 1,2-CS, it passes through a metastable state in which it is O1,O2- κ^2 coordinated to Sn before it reaches a transition state of the same bidentate geometry (Fig. 3(a)). The corresponding energy barrier is 1.29 eV, that is 0.30 eV higher than the 1,2-HS, predicting that the isomerization is the preferred pathway, contrary to experimental evidence.[19]

The energy profiles change when we add two water molecules to the system. Not unexpectedly, the polar water molecules prefer to coordinate around Na⁺. Similarly to the solvent-free case, the 1,2-HS follows the concerted mechanism, with a comparable barrier of 0.93 eV. The 1,2-CS again goes through the bidentate O1,O2- κ^2 transition state (Fig. 3(b)) by overcoming an energy barrier of 0.90 eV, which is 0.03 eV lower than the 1,2-HS—and 0.4 eV lower than the 1,2-CS barrier in the solvent-free calculation. Quite remarkably, the transition state of the competing anti-1,2-HS pathway to MAN lies higher than both the 1,2-HS and the 1,2-CS transition states, by ca. 0.2 eV. Thus, our calculations predict that not only MAN formation is preferred in Na-Sn-BEA, but also that it proceeds via the direct 1,2-CS pathway, in agreement with experiment.

The effect of water on the energetics of the 1,2-CS can be explained as follows. As we noted earlier, in the absence of water, the Na cation coordinates the O3H of the sugar molecule. This has a severe effect on the migration of the C3 atom, as the system has to work against the strong electrostatic attraction between Na and the hydroxyl group on C3. This force, however, is screened when water is present because the polar water molecules prefer to be around the cation.

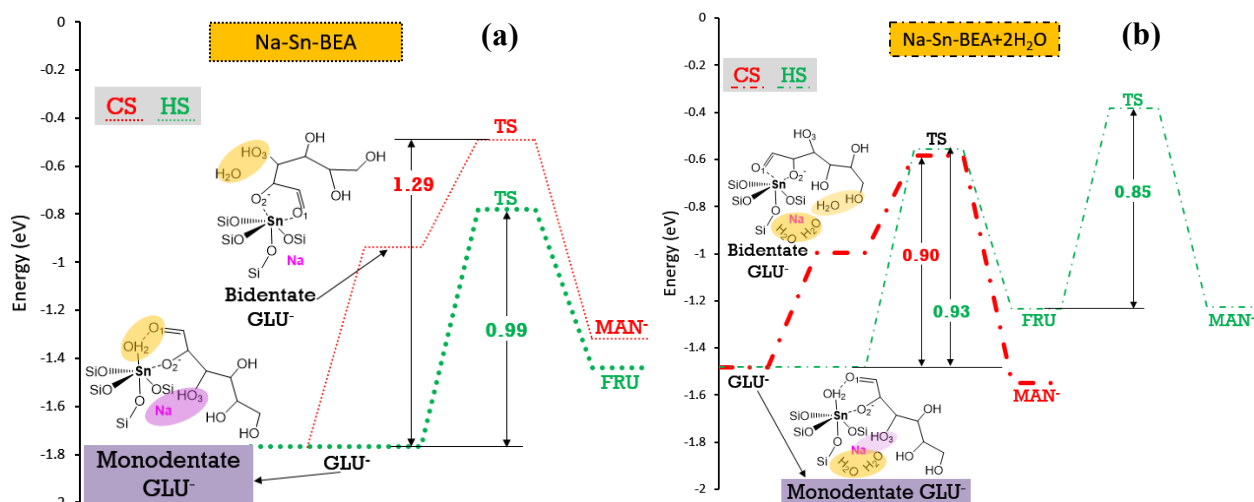


Fig. 3. Potential energy profiles for glucose isomerization and epimerization in Na-Sn-BEA without (a) and with (b) water present.

4. Conclusions

We have investigated the isomerization and epimerization of glucose to fructose and mannose in Sn-BEA and in Na-exchanged Sn-BEA. We have compared reaction pathways both in the absence and presence of water molecules in the vicinity of the active site. We have found that water not only influences the energetics of an individual pathway, but also effectively determines the selectivity, especially in Na-Sn-BEA. In Sn-BEA, the calculations predict the correct selectivity trends—*isomerization preferred to epimerization*—as well as the preferred epimerization pathway—*through fructose by anti-1,2-hydride shift*—between two competing ones. The presence of water at the active site of Sn-BEA is *not* critical to these predictions. But by adding water we see a wider energy gap between the 1,2-HS pathway that leads to fructose and the 1,2-CS pathway that leads to mannose, making the latter increasingly less favorable on account of the extensive solvent re-organization that it entails. Water is however critical to Na-Sn-BEA. Without it, the calculations incorrectly predict preference for the isomerization reaction instead of the epimerization via 1,2-CS. The high energy barrier along the 1,2-CS pathway is due to the Na

cation exerting an attractive force on the backbone of the sugar molecule. Water, on the other hand, prefers to “solvate” the cation and this screens the strong electrostatic interaction between the cation and the hydroxyl groups of the sugar. As a result, the 1,2-CS energy barrier drops by about 0.4 eV, making the epimerization reaction more favorable than the isomerization. Our calculations resolve for the first time the role of water and Na cations in the catalytic activity of Sn-BEA, and rationalize the experimental data.

Acknowledgments

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