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Promotion catalytic role of ethanol on Brønsted acid for the sequential dehydration-etherification of fructose to 5-ethoxymethylfurfural

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ABSTRACT

The function of ethanol and Brønsted acid for the dehydration-etherification of fructose to 5-ethoxymethylfurfural (EMF) has been theoretically investigated at G4 level in ethanol solution. Initially, fructose prefers to dehydration other than etherification with ethanol in the presence of Brønsted acid. The proton H^+ should be solvated on ethanol other than fructose, resulting in $[C_2H_5OH_2]^+$ as the catalytically active species. Both protonation and $[C_2H_5OH_2]^+$ exhibit good catalytic performance, but ethanol does not. Furthermore, $[C_2H_5OH_2]^+$ displays better catalytic performance than protonation, which reflects the promotion catalytic role of C_2H_5OH on the proton H^+. The turnover frequency analysis shows that the SN2 nucleophilic substitution for the etherification of 5-hydroxymethylfurfural (HMF) to EMF is the rate-controlling step in the whole reaction catalyzed by $[C_2H_5OH_2]^+$. The catalytic performance of $[C_2H_5OH_2]^+$ stems from the positive charge of $—OH_2$ group, which assists both the H_2O release of fructose to HMF and the etherification of HMF to EMF. For the dehydration of fructose, the catalytic superiority of $[C_2H_5OH_2]^+$ to protonation comes from the shift of the intramolecular H-shift catalyzed by protonation to the intermolecular H-shift catalyzed by $[C_2H_5OH_2]^+$, which lowers the activation energy barrier for the H_2O release. The present study is useful for understanding the roles of ethanol and Brønsted acid in acid-catalyzed dehydration-etherification of carbohydrates to biofuel in ethanol solution.

1. Introduction

Facing the diminishing fossil reserves and environmental problems, selective transformation of biomass resource into fuels and bulk chemical with efficient catalysts are one of the major challenges [1–3]. Hexoses are the most abundant monosaccharide, as an important constitute of biomass, existing in nature [4]. Herein, glucose and fructose are economical and suitable to be used as the chemical feedstocks [4–6]. Currently, the catalytic transformation of hexoses into furans has received wide attention and exhibited great potential in the replacement of fuels and chemicals produced from fossil resources. Among, 5-ethoxymethylfurfural (EMF) is an excellent additive for diesel, owing to its positive results for significant reduction in soot (fine particulates) and reduction of the SO_x emission, together with a high energy density of 30.3 MJ L^{-1}, close to diesel (33.6 MJ L^{-1}), similar to regular gasoline (30.6 MJ L^{-1}), and higher than ethanol (23.5 MJ L^{-1}) [7].

Both homogeneous and heterogeneous catalysts with Brønsted acidic sites and/or Lewis acidic sites have been employed for the synthesis of EMF from 5-hydroxymethylfurfural (HMF) [8], or 5-chloromethylfurfural (CMF) [7], or carbohydrates [9–11]. Starting from HMF or CMF, the acid-catalyzed etherification usually gave high EMF yield [7,8,12]. However, synthesis of EMF from HMF or CMF is limited in the practical application due to the high cost of HMF and CMF. Much effort has been devoted to the synthesis of EMF from the cheap and renewable fructose through one-pot reaction [13]. The one-pot reaction strategy combines the dehydration of fructose into HMF and the followed etherification of HMF into EMF, which avoids the isolation and purification of HMF, saving time, energy, and solvent.

For the conversion of fructose into EMF in ethanol, various catalytic systems have been developed. Brønsted acid, such as H_2SO_4, has been used with an EMF yield of ca. 60%. However, using H_2SO_4 is limited by serious corrosion, safety concerns, and critical reaction conditions [14]. Heteropolyacids, such as $H_3PW_{12}O_{40}$ (HPW), have attracted considerable interest because of their well-defined structure Brønsted acid, possibility to modify their acid-base properties by changing their chemical composition, ability to accept

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and release electrons, and high proton mobility [15]. With HPW as catalyst, EMF has been obtained from fructose in a yield 64% [13,16]. Moreover, metal chlorides, containing $AlCl_3$, $FeCl_3$, and NH_4Cl were capable of successively catalyzing dehydration of fructose to HMF and etherification of HMF with ethanol to EMF [17–19]. However, these homogeneous catalysts are soluble in the solvent, which hurdles product purification and catalyst recycling.

From an economical and environmental point of view, catalytic sequential dehydration-etherification of fructose into EMF with heterogeneous catalysts was required to be developed. For example, the exchange of H^+ of HPW with different cations (e.g., K^+, Cs^+, and Ag^+) results in the formation of insoluble salts, which opens a strategy for the use of heteropolyacids as heterogeneous catalysts in sustainable chemistry [15]. Using solid acid can avoid the drawbacks associated with a strong Brønsted acid such as H_2SO_4. Furthermore, silica coated magnetic Fe_3O_4 nanoparticles [20], the immobilization of sulfonic acid on the surface of silica-encapsulated Fe_3O_4 nanoparticles [21], K-10 clay supported HPW [22], sulfonic acid functionalized catalysts, SO_3H-functionalized ionic liquids [9], silica supported sulfonic acid [23], a cellulose sulfuric acid [11], two different types of solid acid catalysts (Brønsted acid Amberlyst 131 and Lewis acid zeolite sn-BEA) [24], and methylimidazolebutylsulfate phosphotungstate ($[MIMBS]_3PW_{12}O_{40}$) were also successfully applied [25]. However, relatively low yields of EMF are always observed, which may be ascribed to the lack of highly efficient catalytic sites in selective etherification of HMF with ethanol as well as the low stability of EMF that can be further converted into ethyl levulinate. In this regard, new catalytic systems with good reactivity and suitable acidity or basicity need to be developed for the sequential reaction [26–29]. Unfortunately, how acid, especially Brønsted acid, exhibits the sequential dehydration-etherification catalytic performance of fructose into EMF remains little known.

To design more efficient catalysts, obtaining accurate information on the reaction mechanism is an important aspect to address the challenge. For the acid catalyzed conversion of fructose to HMF, Vlachos et al. suggested that an intramolecular hydride transfer is the rate-controlling step from a nine step reaction pathway with water [30]. Later, they proposed that the C1−C2 hydride transfer is actually rate-limiting [31]. Assary et al. suggested that the transformation of fructose in neutral media is unlikely because of the large activation energy [32]. In contrast, the computed potential energy surface is much more favorable for the transformation in acidic media [32]. Later, they proposed multiple reaction pathways for fructose to HMF conversion in aqueous acidic medium, including the protonated intermediates [33]. Experimentally, several intermediates and different reaction paths were identified in different solvents [34]. There are recent reports of kinetic studies conducted on the purported H^+ (hydrogen cation) homogeneously catalyzed dehydration of D-fructose to HMF in water [30,33,35]. It is apparent that these references emphasized on the reaction mechanism of acid directly interacting with fructose. Nevertheless, how acid interacts with ethanol holds elusive. In a homogeneous catalytic system of α/β-D-fructose/H_2SO_4/ethanol, the experimentally observed ethyl fructoside species are preferentially converted back to the D-fructose starting material rather than undergoing further hydrolysis to EMF [36]. Lately, we found that for the dehydration of fructose to HMF in DMSO solution with Brønsted acid, H^+ prefers to interact with DMSO other than fructose, forming $[DMSOH]^+$ as the catalytically active species, and the catalytic role of $[DMSOH]^+$ originates from the valence unsaturation of both S and O atoms, and the H-mediated effect of –SOH group [37]. Despite the plausible reaction pathways have been suggested to probe the reaction mechanism [38,39], and a clear understanding of the chemistry is lacking for the acid catalyzed dehydration-etherification of fructose into EMF in ethanol solution.

In this work, we report the catalytic mechanism for the fructose conversion to 5-ethoxymethylfurfural in ethanol solution in the absence and presence of Brønsted acid catalysts. The goals are as follows: (a) to confirm the stable tautomer forms of fructose, HMF, and EMF in ethanol solution, (b) to elucidate how the proton H^+ in Brønsted acid catalysts interacts with fructose and ethanol, (c) to ascertain the catalytic nature of ethanol and Brønsted acid for the sequential dehydration-etherification of fructose into EMF, (d) to gain a deep insight into the determining transition state (TDTS) and the determining intermediate (TDI) of the turnover frequency (TOF), and (e) to probe the catalytic performance of protonation, C_2H_5OH, and $[C_2H_5OH_2]^+$ species and the promotion catalytic effect of solvent on the proton H^+.

2. Computational details

A universal continuum solvation model based on solute electron density SMD was applied to simulate the solvent effect of ethanol [40], which arises from an integral-equation-formalism polarizable continuum model (IEF-PCM) [41] and short-range interactions. All calculations were performed in ethanol solvent using the highly accurate Gaussian-4 (G4) level of theory [42], because the G4 level of theory with SMD model has been successfully employed in the conversion of fructose in solution [32,37]. For the G4 methods, the geometries and zero-point energies (scaled by 0.9854) were calculated at the B3LYP/6-31G(2df,p) level, and frequencies and high level corrections were added to account for deficiencies at CCSD(T) level with an expanded polarization set for the large basis set in the energy calculations, including an average absolute deviation from experiment of about 3.5 $kJ\,mol^{-1}$ [42]. For the reaction pathway analysis, every transition structure has a unique imaginary frequency, and the connections between the transition states and corresponding intermediates were testified by means of intrinsic reaction coordinate (IRC) calculations [43,44]. The natural charges, dominant occupancies of natural bond orbitals were analyzed using the natural bond orbital (NBO) analysis [45,46]. Unless otherwise mentioned, the Gibbs free energy of formation (ΔG) is relative to the initial ground state reactants obtained at G4 level in ethanol solution under atmospheric pressure and experimental temperature (6.0 atm and 403 K) [13]. All calculations were performed with the Gaussian 09 program package [47].

The efficiency of the catalyst can be determined by the turnover frequency (TOF) of the catalytic cycle. Based on the transition state theory (TST), the TOF can be calculated by Eqs. (i) and (ii) [48–51], in which δE (the energetic span [52,53]) is defined as the energy difference between the summit and trough of the catalytic cycle.

$$\mathrm{TOF} = \frac{k_B T}{h} e^{-\frac{\delta E}{RT}} \tag{i}$$

$$\delta E = \begin{pmatrix} G_{TDTS} - G_{TDI} & \text{if TDTS appears after TDI} \\ G_{TDTS} - G_{TDI} + \Delta G_r & \text{if TDTS appears before TDI} \end{pmatrix} \tag{ii}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and h is the Planck constant. G_{TDTS} and G_{TDI} are the Gibbs free energies of the TOF determining transition state (TDTS) and the TOF determining intermediate (TDI), and ΔG_r is the global free energy of the whole cycle. The rate constants $k(T)$ have been evaluated according to conventional TST $k'(T)$, including tunneling correction $\kappa(T)$, as mentioned in our previous study [54].

3. Results and discussion

For fructose molecules, there are five main conformers in the gas phase, including β-D-fructofuranoses (Fruc-1), β-D-fructopyranoses