MECHANISTIC INSIGHTS INTO AQUEOUS-PHASE DEHYDRATION OF 1-PROPANOL OVER H-ZSM-5 ZEOLITES

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Abstract

The effects of water on the dehydration of 1-propanol over H-ZSM-5 zeolite were investigated using density functional theory calculations. The aqueous environment significantly stabilizes the protonated propanol monomer over the transition state, leading to a higher activation barrier and a greater entropy gain for the rate-limiting step in the dehydration pathways. While it is less effective, the formation of propanol dimer also retards the dehydration activity in the similar way.

Keywords

Alcohol, Dehydration, Zeolite, Reaction mechanism, Density functional theory.

Introduction

Catalytic conversion of biomass-derived bio-oils to transportation fuels and value-added chemicals attracted significant interests for both industries and academia (Climent et al. 2014). As one of important reaction steps involved, selective dehydration of aliphatic alcohols, polyols, as well as phenols to hydrocarbons using solid acid catalysts such as metal oxides (Iglesia et al. 1997) and zeolites (Galadima and Muraza 2015). It is well known that HZSM-5 zeolite is active for vapor- and liquid-phase dehydration of mono-alcohols and polyols (Makarova et al. 1994). However, fundamental understanding of reaction mechanisms of alcohol dehydration is still lacking for H-ZSM-5 zeolites. On the other hand, the influence of water on the alcohol dehydration over Brønsted acid sites of zeolites is also found to be critical. In the present work, density functional theory calculations were used to study the dehydration mechanisms of propanol over H-ZSM-5 zeolites, In particular, the water effects on the dehydration activity will be addressed.

Methodology

Periodic density functional theory (DFT) calculations were carried out using the CP2K code (Goedecker et al. 1996, Perdew et al. 1996, VandeVondele et al. 2005). All calculations employed a mixed Gaussian and plane wave basis sets. The generalized gradient approximation exchange-correlation functional of Perdew, Burke, and Enzerhof (PBE) was used. The van der Waals (vdW) dispersion interactions between the adsorbate and the zeolite was included using the DFT-D3 scheme.(Grimme et al. 2010) Transition states of elementary steps in the dehydration and etherification reaction routes were located using the CI-NEB method (Henkelman et al. 2000). Both Gibbs free energy (ΔG) and enthalpy (ΔH) changes along reaction pathways were calculated using standard thermodynamic method (Psofogiannakis et al. 2006). A periodic three-dimensional H-ZSM-5 zeolite structure of $Si_{96}O_{192}$ with experimental lattice parameters of $20.022 \times 19.899 \times 13.383$ Å^3 was used. The unit cell of the H-ZSM-5 with Si/Al = 23 then was built by replacing four Si atoms with four Al atoms. The resulting negative charges were compensated by adding four H atoms at the oxygen atoms, which are close neighbors of Al atoms on the zeolite frame, yielding the active Brønsted acidic sites.

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Results and Discussion

DFT calculated energy diagram for 1-propanol dehydration on a periodic H-ZSM-5 zeolite via both E1 and E2 mechanisms is shown in Figure 1. The calculated adsorption energy of 1-propanol is -109 kJ mol^{-1}, which is slightly higher than our experimental measured heat of adsorption of -95 kJ mol^{-1} (Zhi et al. 2015). Upon adsorption, the protonation of the adsorbed propanol at the Brønsted acidic site is facile with a low activation barrier of 6 kJ mol^{-1}. The protonated propanol is then dissociated into water and the carbenium cation intermediate in the E1 mechanism. This step is endothermic (+30 kJ mol^{-1}) with an activation barrier of 138 kJ mol^{-1}. At the transition state, the C−O bond length is 248 pm. This indicates that the C-O bond is completely cleaved; suggesting that the rate-limiting step in the E1 mechanism pathway has a late transition state. The following deprotonation step forms propene with the activation barrier is 63 kJ mol^{-1}, which is significantly lower compared to the C-O bond scission barrier. For the E2 mechanism, the protonated propanol decomposes concertedly to propene and the hydronium (H_3O^+) with an activation barrier of 130 kJ mol^{-1}. The hydronium transfers the proton back to the zeolite forming water. The calculated activation energies for E1 and E2 type mechanisms in the absence and presence of explicit water molecules are very close, indicating that the prevalence of E1 or E2 mechanisms cannot be enthalpically discerned, while the calculated entropies suggest that the E1 mechanism is slightly favored.
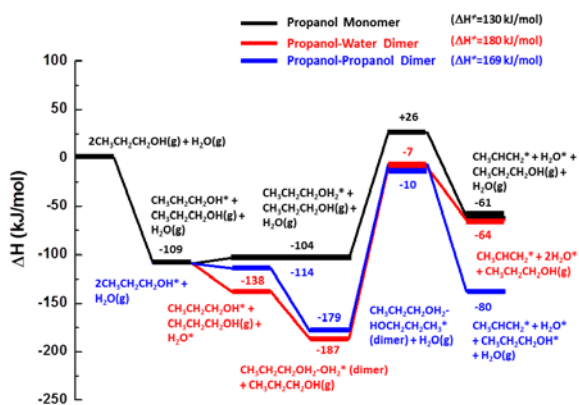

Figure 2. The formation of water-propanol and dimeric propanol on the propanol dehydration over H-ZSM-5 zeolite.

In the presence of water, the water-propanol formation shown in Figure 1 is thermodynamically favorable, gaining the energy of 78 kJ mol^{-1}, which is even more stable than the dimeric propanol complex. Our calculations show the formation of these polar complexes makes the water elimination via the C-O bond cleavage more difficult with the higher activation barriers of 180 and 169 kJ mol^{-1},

although the presence of water or second propanol also slightly stabilizes transition states (33 and 36 kJ mol^{-1}) via hydrogen-bonding interactions. Therefore, the unequivocal role of water and polar reactant molecules in inhibiting the propanol dehydration activity in H-ZSM-5 zeolite by stabilizing the ground state of the reactive intermediate much more effectively than the transition state.

Conclusions

The effects of water on the 1-propanol dehydration to propene over H-ZSM-5 zeolite were studied using DFT calculations. The inhibiting water effects on the propanol dehydration are majorly due to the different stabilization for the adsorbed reaction intermediate and the transition states for the rate-determine step. The presence of water stabilizes the protonated propanol intermediate better than the transition state for the C-O bond scission, resulting in the higher activation barrier for the rate-determining step in the dehydration pathways. The formation of dimeric propanol complex also retards the dehydration reactivity in the similar way.

References

Climent, M. J., et al. (2014). *Green Chem.,* 16, 516.
Galadima, A. and O. Muraza (2015). *J. Ind. Eng. Chem.,* 31, 1.
Goedecker, S., et al. (1996). *Phys. Rev. B,* 54, 1703.
Grimme, S., et al. (2010). *J. Chem. Phys.,* 132, 154104.
Henkelman, G., et al. (2000). *J. Chem. Phys.,* 113.
Iglesia, E., et al. (1997). *Catal. Today,* 38, 339.
Makarova, M. A., et al. (1994). *J. Catal.,* 149, 36.
Perdew, J. P., et al. (1996). *Phys. Rev. B,* 54, 16533.
Psofogiannakis, G., et al. (2006). *J. Phys. Chem. B,* 110, 24593.
VandeVondele, J., et al. (2005). *Comput. Phys. Commun.,* 167, 103.
Zhi, Y., et al. (2015). *J. Am. Chem. Soc.,* in press.