

Mechanistic studies of the synthesis and decomposition of ethanol on Rh catalysts

YongMan Choi and Ping Liu*

Department of Chemistry, Brookhaven National Laboratory, Upton, NY, 11973 (USA)

*pingliu3@bnl.gov

Introduction

The finite resources of fossil fuels along with environmental concerns have stimulated a broad intensive search for alternative energy sources. As a fuel, ethanol has several ideal properties: It is nontoxic and easy to store and transport; it can be produced from renewable sources; and it has a high energy density comparable to that of gasoline. However, ethanol applications in energy have been impeded due to the slow kinetics and low selectivity in relation to the ethanol oxidation and synthesis. Recently, Rh-based catalysts have been found to display a unique efficiency and selectivity in catalyzing both of the processes [1,2]. In particular, to the best of our knowledge, the mechanisms are still unclear due to the intrinsic complexity of catalytic reactions on the Rh-based catalysts [1,2]. What is the role of Rh in the ethanol chemistry? Is there any alternative to replace expensive Rh catalysts? In this study, we investigate the ethanol synthesis and decomposition on Rh(111) by means of density functional theory (DFT) calculations along with molecular dynamic (MD) simulations, which allow us to make insight into the reaction mechanisms.

Materials and Methods

Periodic density function theory (DFT) calculations with the projector-augmented wave (PAW) method were carried out for all calculations, as implemented in the Vienna *ab initio* simulation package (VASP) [3,4]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used. The kinetic energy cutoff for a plane wave basis set was 400 eV. We applied a Monkhorst-Pack mesh with sufficient enough *k*-points, allowing convergence to 0.01 eV of the total electronic energy. For the 2-D slab model calculations, Rh(111) surfaces comprised of three atomic layers were separated by a vacuum space equivalent to four layers (~23 Å) in the direction perpendicular to the surface. The reaction pathways of the synthesis/decomposition processes on Rh(111) were investigated using the nudged elastic band (NEB) method [5].

Results and Discussion

In order to examine optimum energy pathways, we mapped out the potential energy profiles for the ethanol synthesis and decomposition on Rh(111). Figure 1 shows a simplified potential energy diagram. In the case of the ethanol synthesis from CO and H₂, the reaction starts with CO hydrogenation. As shown in Figure 1, the COH* formation from CO* and H* is the rate-determining step, which display a relatively higher reaction barrier (TS1, 1.18 eV) than the other steps. The production of C* is indispensable to form a C-C bond. One of crucial steps producing carbon sources is the process forming H₂O and C* after overcoming TS3. It should be noted that a systematic calculation was carried out to find plausible pathways for the carbon-formation reactions, including CO* → C* + O* and COH* → C* + OH*, whose reaction barriers are approximately 3.20 eV and 2.80 eV, respectively. The C-C bond formation takes place *via* the reaction between C and CO species to produce the CCO

intermediate (TS4), which is followed by hydrogenation reactions to produce CH₃CH₂OH* with an exothermicity of 3.94 eV. For the ethanol decomposition, our MD simulations at 300 K clearly manifest that the C-C bond cleavage is the slowest step. Again CCO was identified as the precursor for breaking the C-C bond, and as shown in Figure 1, the barrier for the CCO decomposition into C and CO is only 0.49 eV. Our calculations agree well with experimental results, showing a complete decomposition of ethanol into C, CO and H₂ [6].

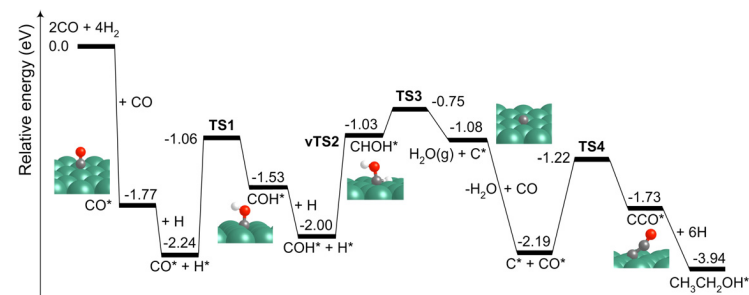


Figure 1. Potential energy profiles for simplified optimum reaction pathways for the ethanol synthesis and decomposition on Rh(111). “*” denotes a surface site.

Overall, the DFT/MD calculations demonstrate that Rh is capable of catalyzing the ethanol synthesis from CO and H₂, as well as the ethanol decomposition. CCO is an important intermediate, which is involved in both C-C bond formation and cleavage reactions.

Significance

The present mechanistic studies at the molecular level are imperative to gaining a fundamental understanding of the ethanol synthesis and decomposition on Rh catalysts and to providing important insight into rational design of better catalysts for production and utilization of ethanol.

Acknowledgement

This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-98CH10886 with the U.S. Department of Energy (Division of Chemical Sciences). This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References

1. Subramani, V. and Gangwal, S. K. *Energy & Fuels* 22, 814 (2008).
2. Idriss, H., *Platinum Met. Rev.* 48, 105 (2004).
3. Kresse, G. and Hafner, J. *Phys. Rev. B* 47, 558 (1993).
4. Kresse, G. and Furthmüller, J. *Phys. Rev. B* 54, 11169 (1996).
5. Henkelman, G., Uberuaga, B. P., and Jónsson, H. *J. Chem. Phys.* 113, 9901 (2000).
6. Vesselli, E., Baraldi A., Comelli G., Lizzit S., and Rosei R., *ChemPhysChem* 5, 1133 (2004).