An Ab-Initio Study of CO Hydrogenation on Rh Surfaces

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Introduction

Ethanol can be used as a fuel additive as well as an alternative energy source. While a good deal of research efforts are devoted to the biochemical synthesis of this product, long chain hydrocarbons or oxygenates can also be obtained via catalytic conversion of syngas (CO and H_2). Experimental studies for CO hydrogenation on Rhodium(Rh)/SiO_2 and Rh promoted with Fe and Mn exhibit selective conversion towards oxygenated products such as ethanol [1,2]. This selectivity towards ethanol is generally attributed to the ability of Rh to promote both CO dissociation and CO insertion mechanisms [3-5]. Since syngas to ethanol conversion includes both elementary dissociation and association reactions linked together via a complex reaction network, multiple pathways exist with different rate determining steps along different routes. In this study, we have carried out comprehensive density functional calculations to elucidate the mechanisms responsible for the activity and ethanol selectivity on Rh surfaces. The conclusions from this investigation can be used to improve existing catalysts and screen new materials via rational catalyst design.

Methods

Self-consistent density functional calculations were performed within Vienna ab initio simulation package (VASP) for flat and stepped Rh surfaces modeled by (111) and (211) surfaces respectively. The (111) metal surface was modeled as a three-layered slab for (2x2) unit cell while the (211) metal surface was modeled as an eight-layered slab for (2x1) unit cell. A vacuum layer of 10 Å was introduced to eliminate interactions between neighboring unit cells. We used a 4x4x1 Monkhorst-Pack k-point mesh and 400 eV as the cut-off energy for plane wave basis sets for adsorption calculations on both the flat and stepped Rh surfaces.

Results and Discussion

Herein, we report the first-principles based energetic pathways from syngas to methane and ethanol on both flat Rh(111) and stepped Rh(211) surfaces. We have considered the lowest binding energy states and preferred reaction paths for 63 intermediates including the reactants, CO and H_2 and species with stoichiometric ratio of C_2H_6O and lower values. The binding energy trends for the adsorbed species indicate stronger binding on the step edges of Rh(211) surface due to the presence of under-coordinated metal atoms. The reaction route mapping from syngas to products provides insight into the intermediates involved in the formation of both C_1 and C_2 products, their relative abundance on the flat and stepped surfaces and indications about the product distribution trends. CO dissociation is determined to be energetically uphill by 1.6 eV and 1 eV on Rh(111) and Rh(211) surfaces respectively. The atomic products of CO dissociation bind more strongly on steps suggesting preferential CO dissociation in agreement with experimental observations[6]. An alternative pathway to CH_x formation via CO hydrogenation is considered on both surfaces and is found to be energetically feasible. Methane formation proceeds via CH_x hydrogenation and is exothermic on flat as well as stepped surfaces as compared to ethanol formation. We have also examined hydrogenation and CO insertion mechanism to ethanol formation in this study. The lowest energy pathway to ethanol as shown in Figure 1 includes acyl (CH_3CO) and ethoxy (C_2H_5O) intermediates, which have been observed experimentally in IR studies [7]. We proceed with the identification of key reactions for ethanol formation on Rh surface through microkinetic modeling by including reaction kinetics data along with the thermodynamically favorable routes.

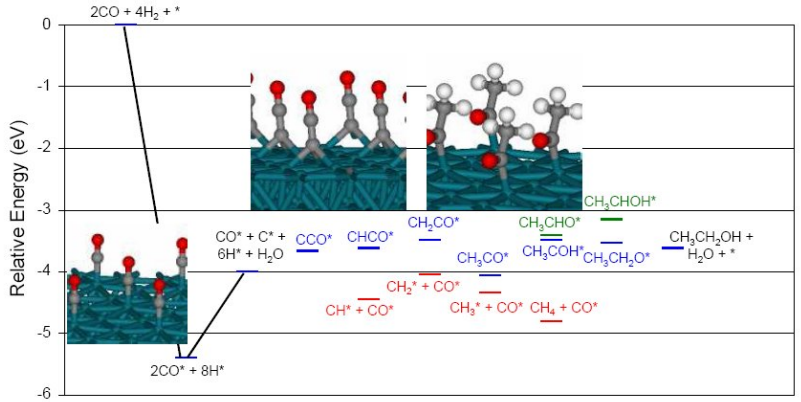

Figure 1. Lowest energy pathways from syngas to methane and ethanol on flat Rh(111) surface. The data points represent the lowest binding energies for the intermediates and infinitely separated co-adsorbed species.

Significance

We have mapped out all the possible intermediates involved in CO hydrogenation to methane and ethanol on both flat and stepped Rh surfaces in this comprehensive study and deduced the lowest energy pathways to the products. These thermodynamic paths indicate the probable reaction intermediates, provide an understanding of initiation steps responsible for catalyst activity and highlight key reactions for oxygenate formation. We can therefore, use this study as a baseline to screen potential catalysts for ethanol production from syngas.

References

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