Efficient search for acetic acid synthesis pathway based on the bond disconnection process on Rh surface and Rh/metal oxide interface

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Significance and Relevance

This study revealed that the Rh/*t*-ZrO_2 (101) interface promotes efficient acetic acid (CH_3COOH) synthesis by forming acetyl (CH_3CO) intermediate from Rh-bound CH_3 and CO. The C-O bond elongation occurs as Rh-CO interacts with Zr cations, significantly lowering the activation energy for the coupling between CO and CH_3 to 0.73 eV. These findings explain the experimentally observed C-O bond weakening and increased production of C_2 oxygenates on Rh-Zr oxide catalysts. By identifying this CO structure at the Rh-ZrO_2 interface, the study establishes a rational design framework for engineering catalytic interfaces to enhance acetic acid synthesis from syngas.

Preferred and 2nd choice for the topic:
Fundamental advances in understanding catalysis / CO_2 utilization and recycling
Preferred presentation: Poster

Introduction and Motivations

The structure of active sites for acetic acid production from C1 molecules, such as CO and CO_2, using rhodium-supported catalysts remains unclear. This study created Rh monometallic and Rh/metal oxide interface models to investigate the acetic acid synthesis pathways in each model.

Materials and Methods

All calculations for structural optimization were conducted using Matlantis (v.3.0.0), a general-purpose atomic simulator that performs calculations based on the PreFerred Potential (PFP), one of the neural network potentials (NNPs).[4] The convergence threshold of structure optimization was set to be 10^{-5} eV. The adsorption energy E_{ad} of each adsorbate on the catalyst surface model was calculated by the following equation (1).

$$E_{\mathrm{ad}} = E(\mathrm{adsorbate/surface}) - E(\mathrm{surface}) - E(\mathrm{adsorbate}) \quad (1)$$

Where *E*(adsorbate/surface) and *E*(surface) are the total energy of the surface slab model with and without adsorbates, respectively. The *E*(adsorbate) is the total energy of each adsorbate, which was calculated with an adsorbate existing in a 20 Å cubic box. The Climbing Image Nudged Elastic Band (CI-NEB) method was performed to calculate the energy of the transition state during the bond disconnection process of the adsorbate.[5] The convergence threshold was set to be 0.005 eV, the number of images to 13, and the force constant to 0.05 eV $Å^{-1}$. Here, the activation energy $E_{a(c)}$ of the bond connection process was calculated from the following equation (2). E_{TS}, E_{FS} denote the energy of the transitional state and final state, respectively.

$$E_{\mathrm{a(c)}} = E_{\mathrm{TS}} - E_{\mathrm{FS}} \quad (2)$$

Results and Discussion

The reaction pathways involving processes characterized by smaller activation energies, $E_{a(c)}$ were thoroughly investigated based on the comprehensive analysis of the disconnection process. It was determined that at the Rh/*t*-ZrO_2(101) interface, the synthesis of acetic acid can proceed favorably on the point of kinetics through the formation of the acetyl structure (CH_3CO) from the interaction between Rh-CH_3 and Rh-CO species. This significant and intriguing finding is illustrated in Figure 1. Figure 1 (a) presents the detailed calculation model of the Rh/*t*-ZrO_2(101) interface, and (b) shows the energy diagram that was proposed by this investigation. Figures 1 (c) through (g) correspond to the visualized structures that were observed during the acetic acid synthesis pathway proposed in this study. As illustrated in Figure 1 (g), Rh-CO interacts with the Zr cations in the zirconia support *via* the oxygen atom in the adsorbed CO, which will be referred to henceforth as the CO_s structure (s means "support"). Notably, during this interaction, the length of the C-O bond is significantly elongated, leading to a substantial reduction in the activation energy of the CO insertion into CH_3 to 0.73 eV. These noteworthy and important results can provide a comprehensive explanation for the experimentally observed development of IR band structure that is originated from C-O stretching, particularly with the weakened C-O bond, and they also correlate closely with the increased production of C_2 oxygenates, including ethanol, acetaldehyde, and acetic acid, on catalysts that consist of both Rh and Zr oxides. Given these discussions, it is expected that the CO_s structure at the interface between Rh and ZrO_2 will play a crucial role in enhancing the efficiency of acetic acid synthesis from C_1 molecules, such as CO and CO_2, contributing significantly to future research in this area.

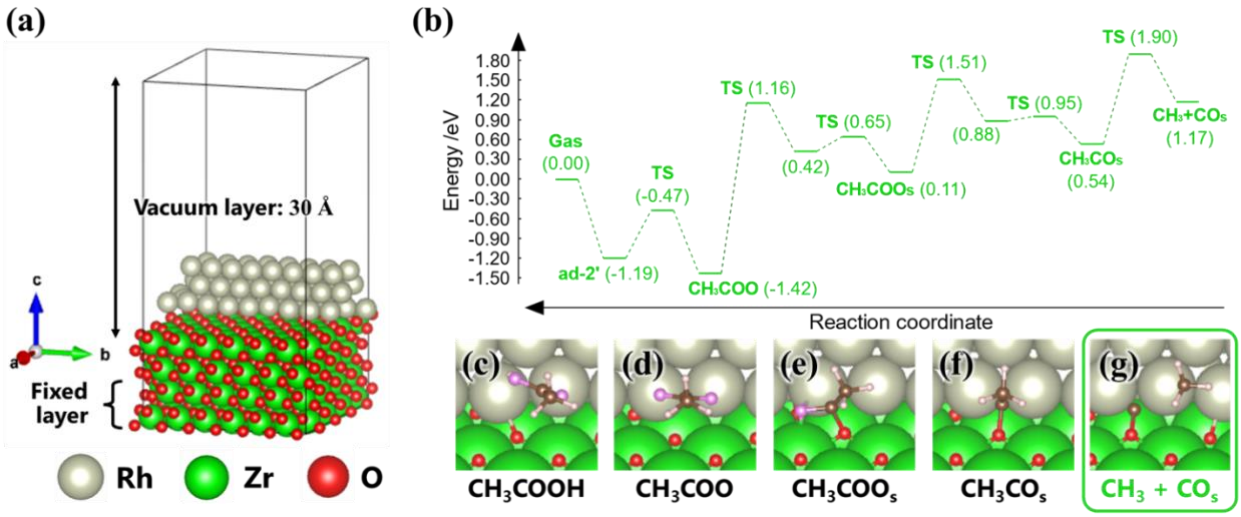

Figure 1 Rh/*t*-ZrO_2(101) model and energy diagram of acetic acid synthesis pathway.

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