

Formaldehyde Activation and Dissociation on Defective Co-doped CeO₂(111): First-Principles Calculations

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May 5, 2020

Abstract

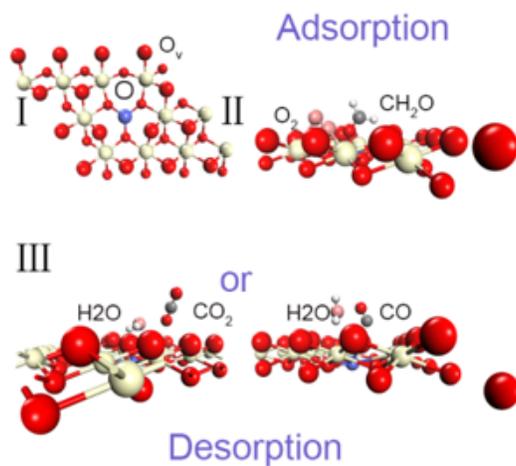
DFT+U calculations have been utilized to explore theoretically three potential pathways of HCHO oxidation on Co-doped CeO₂(111) with O-vacancy herein. To begin with possible adsorption configurations and resultant adsorption strengths of HCHO on Co-doped CeO₂(111) are presented, we conclude that HCHO adsorbed Co-doped CeO₂(111) has the kinetic stability order of $E_{\text{ads}(\text{Co-O-bridge})} > E_{\text{ads}(\text{O-top})} > E_{\text{ads}(\text{Ce-top-II})} > E_{\text{ads}(\text{Ce-O-bridge})} > E_{\text{ads}(\text{Ce-top-I})} > E_{\text{ads}(\text{Co-top})}$ with different adsorption locations. O-vacancy has further constructed artificially at the surface rather than subsurface to stimulate the catalytic activity of Co-doped CeO₂(111) because of surficial lower O-vacancy formation energy compared to the subsurface. Based on Langmuir-Hinshelwood mechanism in which O₂ and HCHO are both co-adsorbed on the reduced ceria surface, three resultant individual reaction products, resulting from different pathways of HCHO oxidation on Co-doped CeO₂(111) with O-vacancy, are identified in detail within the frame of transition state theory. It shows that, at Co-O bridge site, HCHO is oxidized to carbonate species with reactive energy barriers of TS1 of 0.71 and TS2 of 0.36 eV; at O top site, HCHO oxidized to CO need to overcome barriers of TS1 of 0.55 and TS2 of 0.06 eV; while at Ce-O bridge site, HCHO to CO₂ is the most difficult to proceed because of its highest energy barriers of TS1 of 0.96 and TS2 of 2.14 eV. We thus predict that the reaction pathway of HCHO to CO proceeds with the lowest overall barrier on defective Co-doped CeO₂(111). These findings provide clear insight into further exploration in formaldehyde activation processes.

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In this work, we studied the co-adsorption behavior of CH_2O and O_2 on the defective Co-doped $\text{CeO}_2(111)$ using the first-principles calculations. By determining the adsorption location and dynamic potential energy changes, we can elucidate that catalytic oxidation HCHO reaction on the defective Co-doped $\text{CeO}_2(111)$ reduced the C-H bond cleavage energy barrier, which makes Co-doped $\text{CeO}_2(111)$ promising for practical applications as an excellent electrocatalyst candidate for catalytic oxidation.