

Mechanistic pathway in the electrochemical reduction of CO₂ on RuO₂

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Introduction

Electrochemical reduction of CO₂ has the potential to enable the storage of power from intermittent renewable energy sources as energy-dense chemical fuels[1]. Electrochemical reduction of CO₂ to methanol (CH₃OH) is very attractive because methanol as a liquid is conveniently used for energy storage and automotive applications [2], but unfortunately, methanol has not been observed as a major product in CO₂ reduction on pure metals [3,4]. By contrast, experiments on metal oxide catalysts, such as RuO₂ have demonstrated direct electrochemical reduction of CO₂ to methanol [5].

In the current study, we perform Density functional theory (DFT) calculations in conjunction with the computational hydrogen electrode (CHE) model to investigate the mechanism for CO₂ reduction and address why RuO₂ exhibits activity and selectivity towards methanol. To this end, we first identify the thermodynamically stable adsorbate phases of the surface as function of potential under reaction conditions. We find that at reducing potentials the RuO₂ surface is partially reduced and structures covered with CO exhibit high thermodynamic stability. Following this, we investigate the reaction mechanism for CO₂ reduction and compare the activity and selectivity for CO₂ reduction on RuO₂ (110) to that on Cu(211).

Materials and Methods

The total energies of adsorbates on RuO₂(110) are calculated with Density Functional Theory (DFT) using the grid-based projector-augmented wave method implemented in the GPAW code and integrated with the Atomic Simulation Environment (ASE). Calculations are performed using the RPBE exchange-correlation functional. The computational hydrogen electrode (CHE) model is used to calculate the free energy of adsorbates and reaction intermediates [6].

Results and Discussion

The most stable surface structure under reaction conditions are defined by examining relative stability of different adsorbates at various coverages. We find that 0.25 ML CO covered surface is particularly stable at mildly reducing conditions.

To get insight into the mechanism for CO₂ reduction on RuO₂ as well as activity and selectivity, we inspect several possible reaction intermediates and construct free energy diagrams corresponding to different reaction pathways. Figure 1 shows the lowest-energy pathway for the reduction of CO₂ to CH₃OH and CH₄ on RuO₂(110). As it can be seen, reduction of formate (OCHO*) to formic acid (HCOOH) is the thermodynamically most difficult step and becomes exergonic at potentials below -0.43 V vs. the reversible hydrogen electrode (RHE). The mechanism for CO₂ reduction on RuO₂ is different from that on Cu [4]:

1) methane and ethylene are the main reduction product through reduction of CO on Cu, while methanol is the main reaction product on RuO₂, 2) CO* is an intermediate in the reduction of CO₂ on Cu. However, it presents as a spectator rather than an intermediate the reduction of CO₂ on RuO₂, and 3) While formic acid is not reduced on Cu, it is an intermediate in the reduction of CO₂ on RuO₂.

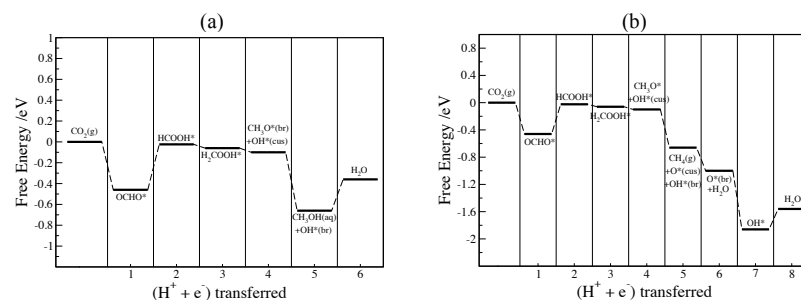


Figure 1. Free energy diagram for the lowest energy pathway in the reduction of CO₂ to: (a) CH₃OH(aq) and (b) CH₄(g) at 0 V (RHE) on 0.25 ML CO covered RuO₂(110) surface.

Our results indicate that HCOOH and methanol are the main reaction products of CO₂ reduction on the RuO₂(110) surface and that methanol is formed by reduction of adsorbed formate at relatively low overpotentials.

Significance

Using our understanding of CO₂ reduction mechanism on RuO₂, we suggest reduction of formic acid on RuO₂, which leads to methanol production at relatively low overpotentials. Moreover, this mechanism can be used as a tool to search for new active and selective catalysts for the electrochemical reduction of CO₂.

References

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