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Computational study of electrochemical CO₂ reduction at transition metal electrodes

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Abstract

A detailed understanding of the mechanism of electrochemical reduction of CO₂ to form hydrocarbons can help design improved catalysts for this important reaction. Density functional theory calculations were used here to model the various elementary steps in this reaction on transition metal surfaces, in particular Cu(111) and Pt(111). The minimum energy paths for sequential protonation by either Tafel or Heyrovsky mechanism were calculated using the nudged elastic band method for applied potentials comparable to those used in experimental studies, ranging from -0.7 V to -1.7 V. A detailed mechanism for CO₂ reduction on Cu(111) has been identified where the highest activation energy is 0.5 eV at -1.3 V vs. RHE. On Pt(111), a different mechanism is found to be optimal but it involves a higher barrier, 0.7 eV at -1.0 V vs. RHE. Hydrogen production is then a faster reaction with activation energy of only 0.3 eV on Pt(111) at the same potential, while on Cu(111) hydrogen production has an activation energy of 0.9 eV at -1.3 V. These results are consistent with experimental findings where copper electrodes are found to lead to relatively high yield of CH₄ while H₂ forms almost exclusively at platinum electrodes.

Keywords: Density functional theory, Electrocatalysis, Electrochemical reduction of carbon dioxide, Nudged elastic band

1 Introduction

The increasing energy demand, global climate change and foreseeable reduction in fossil fuel availability has sparked interest in the development of ways to produce synthetic fuel. One option is the conversion of CO₂ to methane or methanol. The latter is already produced commercially at a factory in Iceland in a two-step process, where hydrogen is first generated by electrolysis of water and

subsequently reacted with CO₂ [1]. Extensive, pioneering work on electrochemical reduction of CO₂ using pure transition metal catalysts has been carried out by Hori and coworkers [2, 3, 4]. They found significant yield of hydrocarbons formed at copper electrodes, with methane being the major product. The Faradaic yield for hydrocarbons was given as 72.3% while the yield for H₂ is 20.5%. In other words, copper both reduces CO₂ to form hydrocarbons and also reduces protons to form H₂. However, no other metal electrode was found to produce a significant yield of hydrocarbons. Hydrogen formed almost exclusively on many transition metals, such as Ti, Fe, Ni, and Pt, while the reduction of CO₂ terminated with CO desorption at Au and Ag electrodes. An important challenge is to identify the detailed mechanism of CO₂ reduction on Cu electrodes and explain why this reaction does not occur on other transition metals such as Pt. The reduction at Cu electrodes requires rather high overpotential and it would be advantageous to identify an improved electrochemical catalyst with a reduced overpotential. A detailed understanding of the mechanism could help design such an improved catalyst. By gaining a deeper understanding of the mechanism of CO₂ reduction on Cu, we hope to shed more light on the uniqueness of Cu as an efficient electro-catalyst for CO₂ reduction and, thereby, possibly contribute to the development of even better electro-catalyst for this reaction.

Significant progress has been made on the theoretical modeling of this reaction. Calculations based on density functional theory (DFT) have identified various possible reaction pathways for CO₂ reduction, in particular electrochemical reduction, and provided estimates of the electrical potential needed. Peterson and co-workers estimated the onset potential for various reduction products based on the free energy of intermediates on a stepped Cu surface [5]. The effect of applied voltage was modeled by adding neU for each electron added, where e is the charge of the electron and U is the applied potential [6]. We will refer to this as the thermochemical model. The onset potential is then estimated as the voltage needed for all the elementary steps in the mechanism not to increase the free energy. This is, however, only a rough estimate since the activation energy (i.e. transition state energy) is not included in the thermochemical model. Nevertheless, the calculated onset potentials turned out to be in good agreement with the measurements of Hori and co-workers for reduction at Cu electrodes [5]. The model, however, does not explain why other metal electrodes such as Pt do not form hydrocarbons but rather evolve H₂ gas, as discussed below. A more detailed study of the reaction mechanism is, therefore, needed.

Experimental studies [2, 7, 8, 9], as well as DFT calculations by Peterson and co-workers [5, 10, 11], have provided information about reaction paths for the formation of methane (CH₄) and ethylene (C₂H₄) on Cu. The reduction could proceed through various paths and an important issue is whether *CO is reduced to form *CHO or *COH. The thermochemical model predicts *CO to be reduced to *CHO on Cu(111) and to *COH on Pt(111), based on the relative stability of the two species, but this does not take activation energy into account.

Recently, Nie et al. estimated the activation energy for electrochemical CO₂ reduction to methane on Cu(111) [12]. There it was concluded that the rate-limiting step is the reduction of *COH to form *C with an activation barrier of only 0.4 eV at -1.15 V vs. RHE on the Cu(111). It should be noted that the electrochemical model used by Nie et al. is quite different from the one used in this study. Nie et al. include only one physisorbed water molecule to represent the water phase and only one H-atom was adsorbed on the metal surface. The barrier was calculated for a so-called H-shuttling mechanism where the H atom is first transferred to the water molecule, creating a hydronium ion, and then a proton is transferred to the *COH molecule, forming *C adatom and a water molecule that desorbs from the surface. The calculated value of the activation energy was actually 1.02 eV, but they use a model based on the Butler-Volmer formalism to extrapolate this value to the desired potential, -1.15 V vs. RHE in this case, which gave activation energy of 0.4 eV. The calculations presented here are more detailed and involve a more realistic model for the electrochemical system.

In the present study, a detailed mechanism of CO₂ reduction on Cu(111) and Pt(111) surfaces has been determined by calculating the activation energy for the key elementary steps as a function of applied voltage. In order to fully account for the reaction kinetics, calculations of the mechanism of

CO₂ on Cu(111) surface were carried out including evaluation of minimum energy paths (MEPs). Our results for electrochemical reduction of CO₂ to methane on Cu(111) surface have identified pathways with sufficiently low activation barriers to be active under the conditions used in the experimental measurements. Similar calculations for the Pt(111) surface show why Pt is not an active electrocatalyst for the reduction of CO₂. Both the Tafel mechanism and the Heyrovsky mechanism were studied.

2 Methodology

In order to model the water-solid interface as a function of electrode potential, a bilayer of water molecules was added to the surface and additional H-atoms inserted in the layer to form solvated protons and additional electrons at the electrode [13]. By changing the number of H- atoms added, the electrostatic potential of the double layer was tuned and chosen to be close to the experimental conditions in measurements of Pt and Cu electrodes by Hori et al. [2]. Slabs of three layers with (111) surfaces were used in this work. Adding more layers changed the calculated results by less than 0.1 eV. Calculations of the free energy of the various molecules adsorbed on the surface were carried out using the harmonic approximation and experimental estimates of the entropy of gas phase species. The DFT calculations made use of the RPBE functional and the Vienna Ab-initio Simulation Package (VASP). The application of an external electrical potential, U , affects the free energy of the intermediates of the reduction path in such a way that a contribution of $\Delta G = -eU$ gets added whenever one H^+ and one e^- react to add an H-atom to the admolecule. A calculated rise in the free energy at an elementary step involving reaction of 0.8 eV can therefore be eliminated by applying an electrical potential of -0.8 V. Assuming that a reaction path becomes active when no elementary step involves an increase in the free energy (neglecting the rise in free energy at transition states), the onset potential can be estimated from the largest free energy increase in an elementary step in the reaction path [6]. The most endothermic elementary step determines the onset potential within this thermochemical model.

In order to go beyond the thermochemical model, the MEPs of the elementary steps were calculated using the climbing image nudged elastic band (CI-NEB) method [14, 15]. The highest energy along the MEP corresponds to a first order saddle point on the energy surface and gives an estimate of the activation energy for the elementary step. A calculation of the frequency of vibrational modes at the initial state and at the saddle point can then be used to estimate the transition rate in harmonic transition state theory. For the reduction of each intermediate, both the Tafel mechanism, where a H-atom gets added to the admolecule, and the Heyrovsky mechanism, where a proton gets added directly from the water phase, was studied.

3 Results

The thermochemical model was used to estimate the onset potential for CO₂ reduction on various FCC(111) transition metal surfaces, including Cu, Pt, Ni, Rh, Ir, Pd, Ag and Au. From the calculated binding energy of the various intermediates on the surface the onset potential was estimated as described above. The results are shown in Fig. 1. For Cu(111), the onset potential turned out to have a large magnitude, -0.8 V, while the onset potential for the Pt(111) surface was found to have much smaller magnitude, -0.3 V. From these estimates alone, one would conclude that Pt(111) is a better electrocatalyst for CO₂ reduction than Cu(111), contrary to experimental findings. Analogous calculations for the other metals, Ni, Rh, Ir, Pd, Ag and Au, gave intermediate values for the onset potential, as shown in Fig. 1.

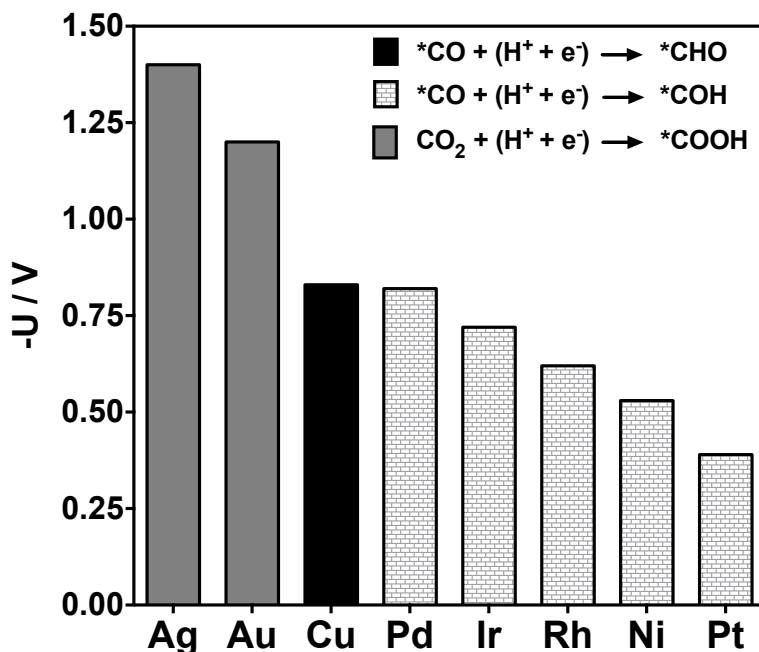


Figure 1: Calculated onset potential for the reduction of CO₂ to form methane or methanol using only the estimated free energy of the intermediates but neglecting activation energy. The legend indicates which elementary step has the largest rise in free energy and, thereby, determines the onset potential. Of the metal surfaces studied here, the smallest magnitude of the onset potential is predicted for Pt(111), significantly smaller than that for Cu(111), but experimental studies have reported significant methane formation only at copper electrodes, while hydrogen forms at platinum electrodes.

The MEP calculations of various possible reaction paths have revealed that the optimal mechanism for CO₂ reduction to methane on Cu(111) involves the formation of hydroxymethylidyne (COH) as a proton is added to adsorbed CO. These findings are consistent with recent experimental results of Schouten et al. [9]. By calculating the MEPs between local minima, a consistent picture is obtained and the trends between different metals can be explained. A sequence of elementary steps at the Cu(111) electrode, either involving Heyrovsky or Tafel mechanism, has been identified where the overall activation energy is low, around 0.5 eV at a voltage of -1.3 V, see Fig. 2.

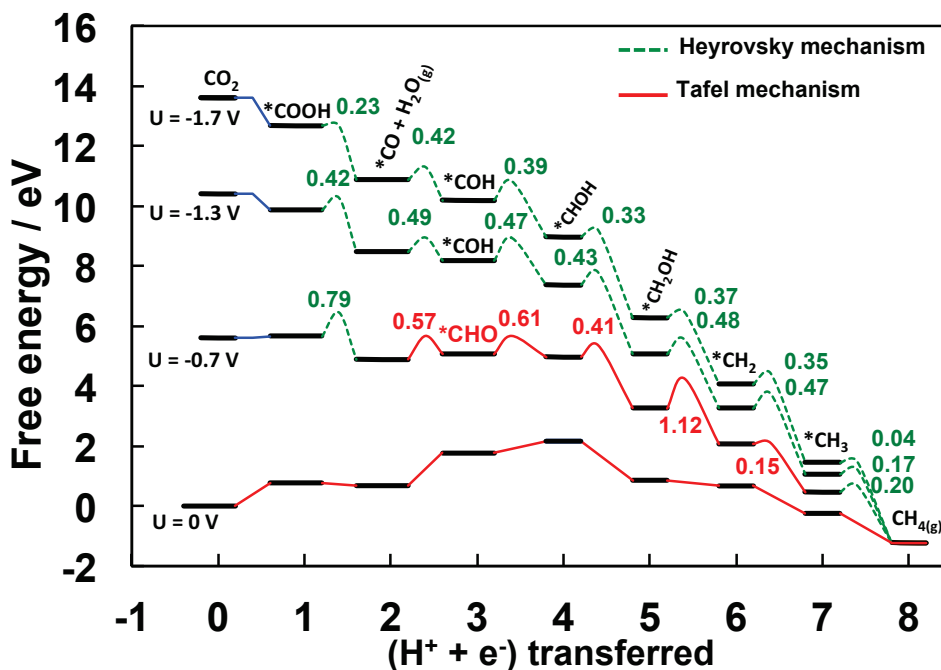


Figure 2: Free energy diagram for the electrochemical reduction of CO₂ to CH₄ on Cu(111) surface at 300 K as a function of applied voltage. Each step along the horizontal axis represents the transfer of a proton and an electron to the ad molecule. Minimum energy paths between local minima corresponding to the various possible intermediates were calculated for both Heyrovsky and Tafel mechanisms. The values of the lowest activation energy found are indicated next to the energy maxima.

The experiments of Hori et al. [3] used a large applied potential, of -1.44 V but it has been shown that hydrocarbons can already be formed at around -0.7 to -0.9 V vs. RHE on Cu electrodes [7]. Hydrogen evolution is a competing reaction and it is also important to calculate the MEPs for that reaction for comparison. The activation energy for hydrogen evolution reaction (HER) on Cu(111) under the same conditions is calculated to be significantly higher, 0.9 eV showing that CO₂ reduction can take place without the protons being consumed by H₂ formation. At the Pt(111) electrode, the opposite is found, i.e. a high activation energy for CO₂ reduction, 0.7 eV, but a low activation energy for H₂ formation, 0.3 eV at -1.0 V vs. RHR. These results help explain why CO₂ can be reduced at copper electrodes to form hydrocarbons while platinum electrodes mainly form hydrogen gas.

3.1 Discussion

The goal of this study was to gain better understanding of electrochemical reduction of CO₂ on copper electrodes and obtain an explanation for failed attempts to electrochemically reduce CO₂ on platinum electrodes. We have simulated conditions in the experiments by constructing a model of a double layer and evaluating the MEPs for both Tafel and Heyrovsky mechanisms. The activation energy for a range of possible elementary steps has been evaluated as well as the free energy of intermediates. From the free energy of intermediates alone, the thermochemical model, one would conclude that Pt(111) is the best electrocatalyst in a group of metals that includes Cu, Pt, Ni, Rh, Ir, Pd, Ag and Au. This is in stark contrast with experimental observation since no reduction products

from CO₂ have been observed at platinum electrodes. The overpotential for Cu(111) is predicted to be among the highest in this group of metals, and yet a significant yield of hydrocarbons can be obtained in experiments with copper electrodes. This discrepancy is removed when the activation energy for the various elementary steps is also calculated. The reduction of CO₂ has a significantly lower activation energy on Cu(111) than on Pt(111). The formation of H₂, however, has a significantly larger activation energy on Cu(111) than on Pt(111). This explains why CO₂ can be electrochemically reduced on Cu electrodes but only hydrogen forms on Pt electrodes. A detailed understanding of the mechanism of electrochemical CO₂ reduction on Cu can help optimize the process further, both to reduce the overpotential and to improve selectivity.

3.2 Conclusion

In conclusion, our DFT calculations of the activation energy for the various elementary steps have shown that the reduction of CO is the key step for the selective production of methane by CO₂ electroreduction on Cu(111) surface. The dominant path involves reduction of *CO to form *COH, which ultimately leads to the formation of methane. This reaction path is different from what is obtained solely from the reaction free energies in the thermochemical model. Also, it is important to include the effect of the aqueous environment, which stabilizes COH formation. Our proposed reaction path is able to explain experimental data on CO₂, CO, and CH₂O reduction on Cu electrodes. Other factors affecting the reaction rate such as coverage effects and surface structure, in particular the presence of step edges need to be explored in future studies. The results of our calculations contribute to an improved understanding of CO₂ electroreduction on Cu surfaces by providing estimates of the activation energy for the elementary steps. It could help design improved catalysts for CO₂ (photo)-electroreduction. For example, an important aspect is the relative activation energy for the formation of *COH and *CHO since the former intermediate leads to formation of methane while the latter leads to formation of formaldehyde, which then leaves the surface and is not reduced further.

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