

Structural Sensitivity of the Water-Gas Shift Reaction on Platinum Surfaces

Michail Stamatakis, Ying Chen and Dionisios G. Vlachos*
 University of Delaware, Newark, Delaware 19716
 *vlachos@udel.edu

Introduction

In view of recent economical and environmental pressures, the necessity of a paradigm shift in the production and utilization of energy has emerged [1]. In this shift, hydrogen is envisioned to play a central role, being regarded as a potential “fuel of the future” [2]. Hydrogen can be produced via the water-gas shift (WGS) reaction taking place during the catalytic reforming among others of oxygenated hydrocarbons derived from biomass [3].

Latest research has focused on the use of Pt as a catalyst for WGS, because it can break carbon-carbon bonds, carry out the WGS reaction, and is non-pyrophoric, thereby being suitable for portable applications. A number of experimental studies have thus elucidated the effect of the support on the achieved turnover frequency. However, the effect of metal surface structure on the activity remains unclear, since it is experimentally challenging to isolate metal structure sensitivity from the effect of the support. Motivated by this challenge, we present a first-principle theoretical study of the structure sensitivity of the WGS reaction on Pt surfaces, in order to identify the contribution of step and terrace sites on the overall reaction rate.

Materials and Methods

We employ a multiscale modeling approach that integrates density functional theory (DFT) calculations and kinetic Monte Carlo (KMC) simulation. Using DFT as implemented by the SIESTA software package we calculate the reaction barriers and enthalpies for the elementary steps of the WGS mechanism. The latter include adsorption-desorption events, water and hydroxyl decomposition, and the formation and decomposition of formyl, carboxyl and formate intermediates, occurring on terrace sites on Pt(111) and step sites on Pt(211). Transition state theory (TST) and statistical mechanics are employed to estimate pre-exponentials. In all DFT calculations the GGA-PBE functional is used. For Pt(111), 4 Pt layers (16 atoms) are modeled with a vacuum region of approximately 10 Å in height. The bottom 2 layers are kept fixed whereas the top 2 layers and adsorbates are relaxed. A p(2×2) unit cell and surface Monkhorst-Pack grids of 5×5×1 k-points in the surface Brillouin zone are used. For Pt(211), a repeated slab of twelve layers (24 atoms) is modeled, with the bottom 6 layers fixed. A p(2×1) unit cell is used with surface Monkhorst-Pack grids of 3×4×1 k-points.

We subsequently incorporate the DFT/TST-based rate constants into an in-house KMC framework that employs graph theoretical ideas to allow for the accurate simulation of complex elementary reaction steps. We perform simulations for three different Pt surfaces having different step-site densities: (111), (322) and (211), for a temperature range of 590-800 K and partial pressures of H₂O and CO equal to 0.10 bar and 0.05 bar, respectively. The simulated stochastic trajectories yield the activities as functions of temperature, the apparent activation energies and statistics for the events happening on steps or terrace sites.

Results and Discussion

Our simulations show that the WGS chemistry is indeed metal-structure sensitive, since the stepped surfaces exhibit much higher H₂ production rates than the Pt(111) surface (Figure 1A). Moreover, higher step densities result in higher activities in an extended temperature range. The apparent activation energies calculated from the Arrhenius graphs are 30.1, 16.8 and 33.5 kcal/mol for (111), (322) and (211) respectively, and are within the range of published experimental data, 13.9 ~ 27 kcal/mol [4].

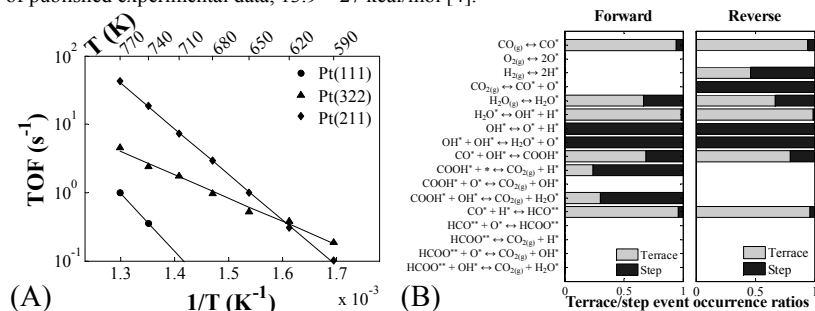


Figure 1. A) Arrhenius plots for the different Pt surfaces, B) statistical analysis of the occurrence of elementary reactions.

Statistical analysis of the occurrence of reaction events elucidates the structural sensitivity of different elementary steps of the WGS chemistry (Figure 1B). In particular, H₂O decomposition and HCO formation, occur primarily on terraces, whereas OH decomposition, OH-OH disproportionation and COOH decomposition require the involvement of step sites.

Significance

We have elucidated the contributions of different site types on the observed rate for the WGS reaction on Pt. It was shown that the higher activity observed on stepped surfaces is a result of synergistic effect between steps and terraces, as certain elementary steps occur preferentially on terraces whereas others on steps. This work is expected to give insights into the rational design and optimization of Pt catalysts for this chemistry.

References

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