Analysis of the Effects of Adsorbate-Adsorbate Interactions for CO Methanation on Transition Metal Surfaces

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Introduction

Advances in electronic structure theory have enabled researchers to calculate adsorption energies and transition state barriers for reaction intermediates on transition metal surfaces with sufficient accuracy for estimating the kinetics of surface reactions [1]. Previous research has demonstrated the utility of this method for modeling a variety of chemical reactions. Using such an approach, several examples have been reported of the discovery of new catalyst materials for heterogeneous reactions [2,3].

This modeling technique, however, is based on a series of assumptions that may not be appropriate under all conditions. One such assumption that is commonly made is the mean field model, which describes reaction kinetics with fast diffusion and low coverages of reaction intermediates. Dissociation of strongly bonded molecules (e.g., N-N, O-O, C-O), however, typically takes place under conditions where the surfaces coverages of intermediates are relatively high. While one can generally state that reactant coverages of ~0.5 monolayers are associated with high rates, this may not be true for reactions where multiple surface intermediates interact with each other. The methanation of CO is potentially one such example of this. It has been reported that relatively high coverages of adsorbed CO are required along step sites in order to facilitate C-O bond breaking [4]. Interactions between adsorbed reaction intermediates may potentially have significant effects on their adsorption energies, and hence on reaction rates and selectivities. To test this hypothesis, we assumed a simple model for adsorbate-adsorbate interactions (similar to one described elsewhere [5]), and calculated the predicted shifts in methanation rates when such interactions are taken into account.

Materials and Methods

Adsorption energies for CO methanation reaction intermediates and transition states were calculated using density functional theory on the stepped (211) surfaces of Ag, Cu, Pd, Pt, Rh, and Ru with 1/4 to 1 monolayer coverages, and were scaled with the binding energies of carbon (ΔE_C) and oxygen (ΔE_O) [6]. Adsorbate-adsorbate interaction effects were modeled using a piecewise linear interaction model [5]. A microkinetic model was used that involved elementary reaction steps for the adsorption/dissociation of reaction products (CO, H2) and the hydrogenation/desorption of surface carbon/oxygen to CH4 and H2O. All reactions were treated as potentially rate-determining. Steady-state solutions of the microkinetic model were obtained for typical methanation conditions (T = 523 K, P = 1 bar, 1% CO in H2).

Results and Discussion

Theoretical activity volcanoes for CO methanation were obtained with and without interactions (Figure 1). The highest methanation rates were predicted for Ru, Co, and Ni, which is consistent with earlier theoretical and experimental studies [3]. As can be seen from Figure 1, the position of the maximum rate, as well as the rates of weak-binding metals, were essentially unchanged. The inclusion of interaction effects primarily resulted in an increase in the predicted rates for strong-binding metals. This was due to a reduction in surface poisoning by strongly bound reaction intermediates and an increase in the concentration of vacant (i.e., active) reaction sites. Importantly, the overall trends in the predicted rates for transition metal catalysts were not affected by the interactions between adsorbates at high coverages.

Significance

In general, the results support the use of the mean field model for determining qualitative trends in simple reaction schemes such as methanation. The method described here also improves the quantitative modeling of surface-catalyzed reactions. This becomes especially relevant for reactions where selectivity issues play a major role.

Figure 1. Theoretical turnover frequencies as a function of ΔE_C and ΔE_O with and without interaction effects (T = 523 K, P = 1 bar, 1% CO in H2). Carbon and oxygen binding energies for the (211) surfaces of selected transition metals are depicted.

References