Computationally-Aided Catalyst Design for Steam Methane Reforming

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Introduction

Reforming of fossil fuels, in particular steam methane reforming (SMR), is responsible for most of the hydrogen produced worldwide today [1]. Experimental researchers are developing industrial membrane reactors capable of the *in situ* separation of the CO_2(g) and H_2(g) products of SMR. The CO_2(g) can be pumped underground for sequestration, while the H_2(g) can be used in automobiles, fuel cells, or industrial processes. Nickel is the preferred SMR catalyst because of its cost and availability; however, it is susceptible to deactivation via carbon formation [2]. Thus, the design of new SMR catalysts that are inexpensive but resistant to deactivation is of particular interest. To aid in this search for improved catalysts, we seek an improved understanding of the processes occurring on the catalyst surface.

Ni-catalyzed SMR has been studied in detail experimentally, resulting in macroscopic rate laws describing SMR kinetics, often following the assumption of rate-determining steps [3,4]. More recently, microkinetic modeling has been applied to investigate SMR and deactivation kinetics, providing additional information about rate-limiting steps [5,6]. However, the short-lived nature of the intermediates, the high temperature and pressure, and the complexities of the heterogeneous catalysis make experimental determination of microkinetic model parameters extremely challenging or even impossible. Fortunately, theoretical computations based on density functional theory (DFT) can tell us much about these difficult-to-measure processes occurring on the surface. Researchers have previously applied DFT to investigate Ni-catalyzed SMR [7,8]. However, unlike most previous studies, we combine statistical thermodynamics and first-order saddle point searches to more accurately compute the thermochemistry and rate coefficients for the many competing pathways on the catalyst surface.

Materials and Methods

Planewave DFT calculations are performed with the software package Dacapo [9], using the RPBE functional with spin polarization [10]. Planewave and density cutoffs of 340 eV are used, and the Brillouin zone is sampled by a (4,4,1) k-point Monkhorst-Pack grid. Statistical thermodynamics are applied to the DFT data to obtain thermochemical and kinetic parameters at industrially relevant temperatures and pressures. The binding energies of the possible surface intermediates that can be formed from the combination of one molecule of CH_4(g) and one of H_2O(g) are calculated. In addition, nudged elastic band studies and first-order saddle point searches are employed to find the transition state energies. Flux and sensitivity analyses are employed to investigate the SMR mechanism to obtain information about rate-limiting steps and gain chemical intuition about the relevant surface reactions, which are then used to guide the investigation of Ni-bimetallic catalysts, such as Ni/Ag.

Hydrotalcite-derived 12 wt% Ni catalyst is prepared by a co-precipitation method. A method using surface redox reaction between Ni and $AgNO_3$ has been developed to precisely control the surface alloy, making it possible to compare experimental kinetic data with DFT predictions. The kinetic study of steam methane reforming over Ni and Ni/Ag catalysts is performed in a fixed bed reactor at 1 bar.

Results and Discussion

The SMR thermochemistry and activation energies are combined in a microkinetic model. The dominant reforming pathways on the Ni terrace are found to be through the CH^* species' combination with either O^* or OH^* to form CHO^* and $CHOH^*$, respectively. In addition to CH_4(g) adsorption, the formation of the $CH_xO_y^*$ complex is found to be a sensitive step in the SMR mechanism. The $CH_xO_y^*$ complex readily dissociates to form the adsorbed products CO^* and H^*. H_2(g) sticking coefficient and desorption kinetic parameters are found to agree well with single-crystal Ni data. In addition, the thermochemistry of methane's dissociation products on the Ni terrace is found to agree with experimental observations [11].

The information gained from studying the Ni catalyst is applied to guide investigation of the Ni catalyst doped with 0.25 mL Ag. Analysis of the Ni/Ag surface at this Ag coverage has predicted a destabilization of key intermediates such as CH_3^*, CHO^*, and $CHOH^*$. As a result, we predict increases in the barriers of the key reactions forming these intermediates. When compared to pure Ni catalyst data in a fixed bed reactor, the Ni/Ag catalyst is found to inhibit the steam reforming reaction by means of increasing the activation energy approximately 40 kJ/mol, in agreement with the alloying effect predicted through quantum chemistry.

Significance

Quantum chemistry allows for the investigation of surface reactions and reaction intermediates that have proven highly difficult to study experimentally (at realistic temperatures and pressures). The combination of quantum chemistry with experimental investigation results in a powerful tool for studying heterogeneous catalysis, such as the search for new catalysts that are active to SMR and exhibit high resistance to deactivation through carbon formation.

References

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