

First-principles-based kinetic Monte Carlo simulation of the selective hydrogenation of acetylene over Pd(111)

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Abstract

The kinetics for the selective hydrogenation of acetylene over Pd(111) was investigated by using first-principles-based kinetic Monte Carlo simulations. Density functional theory (DFT) calculations were carried out to obtain intrinsic kinetic data for a Horiuti–Polanyi-type reaction mechanism involving the sequential hydrogenation of acetylene. The results were subsequently used to develop a detailed intrinsic kinetics database that includes the adsorption energies of the reactants, intermediates, and products, the reaction energies and activation barriers of the elementary steps in the proposed reaction mechanism. The DFT-calculated energies and activation barriers were initially performed at lower surface coverages, to probe the intrinsic surface chemistry. Subsequent calculations were carried out at higher coverages, to capture the influence of the local environment on the reaction kinetics, and used to parameterize coarse-grained models that describe adsorbate interactions. A van der Waals force field model and a modified bond order conservation model were subsequently used within the simulation to calculate the local *through-space* interactions and the lateral *through-surface* interactions occurring between coadsorbates, respectively, and to assess the influence of the local reaction environment. The intrinsic DFT-derived kinetic data and the coarse-grained reaction environment models were used together in a variable time step kinetic Monte Carlo simulation to track the molecular transformations involved in acetylene hydrogenation over the (111) surface of Pd. The kinetic Monte Carlo simulation method [E.W. Hansen, M. Neurock, Chem. Eng. Sci. 54 (1999) 3411; E.W. Hansen, M. Neurock, J. Catal. 196 (2000) 241; E.W. Hansen, M. Neurock, Surf. Sci. 464 (2000) 91; E.W. Hansen, M. Neurock, J. Phys. Chem. B 105 (2001) 9218] used herein explicitly treats the atomic surface structure, the effects of the local reaction environment, and the reaction conditions on the surface kinetics. The simulated apparent activation energy for acetylene hydrogenation was calculated as 8.0 ± 0.6 kcal/mol at $P_{\text{H}_2} = 100$ Torr and $P_{\text{C}_2\text{H}_2} = 100$ Torr over the temperature range of 300–500 K, in very good agreement with the value of 9.6 kcal/mol reported from experimental studies over well-defined Pd(111) surfaces [H. Molero, B.F. Bartlett, W.T. Tysoe, J. Catal. 181 (1999) 49]. The reaction orders were calculated as -0.52 ± 0.03 for acetylene and 1.16 ± 0.03 for hydrogen, which agree very well with the experimental reaction orders by Molero et al. [H. Molero, B.F. Bartlett, W.T. Tysoe, J. Catal. 181 (1999) 49] of -0.66 and 1.04 , respectively. A comparison of the simulations carried out assuming non-interacting adsorbates (hard sphere) and those that include lateral interactions between adsorbates showed that although the overall apparent activation energy was weakly sensitive to the presence of lateral interactions, the surface coverages and intrinsic rates changed considerably due to the presence of lateral interactions. The addition of lateral interactions between coadsorbates was found to be essential in simulating the correct overall selectivity behavior and appropriately predicting the apparent reaction orders with respect to hydrogen and acetylene.

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1. Introduction

The catalysts used in the polymerization of ethylene to polyethylene are quite sensitive to the amount of acetylene, which is typically within the range of 0.5–2 vol% in refined ethylene feedstocks [6–10]. These feedstocks must first be hydrogenated

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Scheme 1. Hydrogen addition reactions, where * denotes one empty surface site and the species identified with * denote an adsorbed intermediate.

to reduce the acetylene impurities to <5 ppm, to prevent the deactivation of olefin polymerization catalysts. The hydrogenation of acetylene from ethylene feeds is generally carried out in a fixed-bed reactor over supported Pd catalysts in two different types of processes known as front-end and tail-end processes [6,10,11], with the terms referring to the location of the hydrogenation reactor within the overall ethylene plant. In the front-end process, acetylene hydrogenation is carried out just before the methanation unit, whereby the feed contains acetylene together with fair amounts of hydrogen and light hydrocarbons. The partial pressure of hydrogen in the front-end process is typically much greater than that in the tail-end process. The higher pressures of hydrogen increase the rate of acetylene hydrogenation and limit the formation of carbon deposits. In the tail-end process, acetylene hydrogenation is carried out after the de-ethanizer unit, where the feed is typically ethylene rich [6,10,11]. Tail-end acetylene processes are typically run at significantly lower partial pressures of hydrogen, at which reactor runaway is not an issue. The lower partial pressures of hydrogen, however, can lead to the development of carbonaceous deposits and the formation of green oil, which can cover the catalyst and significantly lower the reaction rate [12].

It is now generally accepted that acetylene hydrogenation over Pd follows a sequential series of hydrogen addition reactions [13–17], such as those shown in Scheme 1. This is the classical Horiuti–Polanyi mechanism [18], which involves the sequential hydrogenation of acetylene and its subsequent hydrocarbon intermediates, thus resulting in the desired ethylene and undesired ethane products. These reactions tend to follow Langmuir–Hinshelwood rather than Eley–Rideal paths [13–16, 19].

The selective hydrogenation of acetylene reaction is typically carried out over supported Pd particles and is fairly selective, thus actively catalyzing acetylene hydrogenation while minimizing ethylene hydrogenation. The selectivity to acetylene hydrogenation was initially proposed to be the result of thermodynamic adsorption differences between acetylene and ethylene [20]. More recent explanations, however, suggest that mechanistic differences may control the differences in hydrogenation activities between acetylene and ethylene. These explanations are more consistent with the experimental observations that accompany ethylene hydrogenation as well as carbonaceous product formation [21–25]. They point to the dif-

ferences in the relative reaction rates of the elementary steps as being responsible for the overall selectivity of acetylene hydrogenation to ethylene. Therefore, the selectivity for acetylene hydrogenation depends not only on the surface coverage of the reaction intermediates, but also on the local reaction environment surrounding the active intermediates. In the case of acetylene, for example, acetylene will not form a well-defined overlayer when adsorbed at temperatures over 200 K in the presence of hydrogen [26]. This is thought to be due to changes in the sticking probability of acetylene in the presence of hydrogen. Furthermore, on heating, acetylene decomposes into ethynidyne, as seen by LEED [27]. Ethynidyne can subsequently decompose into carbonaceous deposits on further heating, as reported by Tysoe [28] and Kesmodel [29]. These observations on acetylene indicate that selectivity is controlled by the elementary steps involving the adsorption of acetylene as well as its different reaction paths. In addition, certain sequences of coupling pathways can lead to the formation of C₄ intermediates that can subsequently go on to form oligomers, which can deactivate the catalyst. *Mechanistic effects* appear to be important in determining the selectivity in acetylene hydrogenation. Mechanistic effects were also seen to be important in our earlier theoretical results [30,31] that specifically examined the relative rates for acetylene and ethylene hydrogenation. These studies indicated that vinyl was a key surface intermediate, because different surface intermediates can form from vinyl depending on the reaction environment around the vinyl species. Thus these studies strongly suggest that all of these reaction paths need to be included in the development of a detailed reaction mechanism and a rate model for the catalytic selective hydrogenation of acetylene.

Many of the analytical reaction rate models for acetylene hydrogenation developed over the past 30 years were reviewed by Bos and Westerterp [12,32], who compared the validity of these models under different experimental conditions. Nearly all of the models predict the reaction order for hydrogen to be between 1.0 and 1.5 and that for acetylene to be between 0.0 and –0.5 with respect to the overall rate of acetylene hydrogenation. But the rate constants used for the different rate models are typically only applicable at the reaction conditions under which they were regressed. The local surface coverage for different intermediates is typically ignored, and the rates are taken as some macroscopically averaged surface coverage at that reaction condition. Although the present kinetic rate models offer a good qualitative understanding of the kinetics for acetylene hydrogenation, they are nevertheless limited because they are empirical in nature and hold only under the condition for which they have been determined. They ignore the local composition and surface coverage, in addition the influence of heterogeneous (different) reaction sites.

Atomistic simulation can begin to overcome a number of the limitations of conventional deterministic models in that they can track molecular-level transformations and retain the specific atomic surface structure. This enables one to readily include different reactive surface sites based on differences in their atomic surface structure as well as the influence of the

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