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Ethylene versus ethane: A DFT-based selectivity descriptor for efficient catalyst screening

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ABSTRACT

The production of ethylene without its hydrogenation to ethane is a challenge for several catalytic processes. Here, we present a catalyst screening scheme, where the Gibbs free energy difference between the ethylene hydrogenation barrier and ethylene desorption energy is defined as a descriptor for ethylene selectivity. Using plane-wave, dispersion-corrected DFT calculations, we evaluated the descriptor values over the (111) facets of Pt, Pd, and Cu as well as a series of Pt- and Pd-based bimetallic alloys. Our predicted descriptor values indicate that the addition of a Group IB metal (Cu, Ag, or Au) to Pt or Pd improves ethylene selectivity. Ag induces the most significant improvement at 50% while Au has the strongest effect at 75% atomic composition. Pd-based alloys exhibit superior ethylene selectivity over their Pt-based counterparts. Our descriptor model offers an efficient method for the initial screening of catalysts with improved ethylene selectivity.

1. Introduction

Ethylene is an important building block in the modern chemical industry for the production of polyethylene and many other industrial chemical compounds. The production of ethylene without immediate hydrogenation to the less valuable product, ethane, remains a selectivity challenge for several chemical processes. The most studied example of such processes is the selective hydrogenation of acetylene to ethylene ($C_2H_2 + H_2 \rightarrow C_2H_4$). Industrially, catalytic hydrogenation is the preferred method for converting acetylene impurities in cracking product streams back to ethylene [1]. Pd-based catalysts are the most commonly used for this process [2]. Pure Pd typically over-hydrogenates acetylene to the undesirable product, ethane [3,4]. Alloying Pd with a second metal effectively improves its selectivity towards ethylene. Pd-Ag is one of the most widely used bimetallic alloy systems for acetylene hydrogenation [5–9]. Han et al. demonstrated using TiO_2-supported catalysts that when the Ag to Pd ratio reached 1:1 or above, the bimetallic catalyst became highly selective towards ethylene formation (>80%) [5]. Other promoter elements have also been studied, including Au [3,10,11], Cu [12,13], Ga [14,15], and Zn [16,17].

Another example of a catalytic process involving the selectivity issue between ethylene and ethane is the hydrodechlorination of 1,2-dichloroethane (1,2-DCA). This process is a promising treatment method for industrial 1,2-DCA wastes [18]. The hydrodechlorination of 1,2-DCA can proceed through either the ethylene path ($C_2H_4Cl_2 + H_2 \rightarrow C_2H_4 + 2HCl$) or the ethane path ($C_2H_4Cl_2 + 2H_2 \rightarrow C_2H_6 + 2HCl$). A series of transition-metal catalysts have been experimentally tested for this chemistry. Monometallic Group VIII metals such as Pt [19,20] and Pd [21–23] are active dechlorination catalysts, but they also hydrogenate ethylene and produce mostly ethane. On the other hand, Cu is highly selective towards ethylene formation despite its low dechlorination activity [19,24]. Bimetallic alloys, such as Pt-Cu [19,25–29], Pd-Ag [21,30–36], Pd-Cu [24,33], Pt-Ag [37], and Pt-Sn [20,38] have been shown as the best catalysts for 1,2-DCA hydrodechlorination in terms of both dechlorination activity and ethylene selectivity. Vadlamannati et al. showed that a Cu to Pt atomic ratio of 3:1 or above was required for an ethylene-selective Pt-Cu bimetallic catalyst [19]. Lambert and coworkers demonstrated that for a Pd-Ag or Pd-Cu hydrodechlorination catalyst to be selective towards ethylene formation, the Pd composition should be 33% or less [33].

Despite the availability of a large number of experimental studies, mechanistic insights into the origin of ethylene selectivity are still lacking, which hinders the rational catalyst design and improvement. In the literature, a few density functional theory (DFT) studies have been found for the selective hydrogenation of

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acetylene [39–45]. Most of these studies point to the competition between ethylene desorption and its hydrogenation as the key factor that determines catalyst selectivity. Liu demonstrated in the study of Pd-doped Ag nanoclusters that the surface ethylene formed from hydrogenation of acetylene can be further hydrogenated to ethane if contiguous Pd sites were present [42]. Zhang et al. performed detailed reaction kinetics analyses for acetylene hydrogenation on several Pd-doped Cu/CuO_x surfaces [45]. They showed that ethylene selectivity can be correlated with the Gibbs free energy of ethylene adsorption and its hydrogenation Gibbs free energy barrier. These DFT studies, however, focus on the detailed reaction mechanisms on specific catalytic surfaces. Performing comprehensive DFT analyses for a large number of candidate catalysts is time-consuming and thus not efficient for catalyst screening purposes. Studt et al. performed a DFT-based catalyst screening study for the selective hydrogenation of acetylene [46], where they used the heats of adsorption of ethylene and acetylene as the selectivity and activity descriptors, respectively. They further correlated both parameters with the heat of adsorption of a methyl group through scaling relations, which allowed them to investigate a large group of catalyst candidates based on a single thermochemical parameter. Their catalyst screening scheme, however, is potentially an oversimplification of the reaction system, since no reaction kinetics parameters was involved. For the selective dehydrogenation of ethane to ethylene, Hook and Celik proposed a model to predict catalyst selectivity using the energy difference between the ethylene dehydrogenation barrier and its desorption energy [47]. Their study focused on a specific set of Pt-based surface alloys. Also, temperature and entropy effects were not accounted in their model.

Here, we seek to provide a fundamentals-based selection scheme for hydrogenation/hydrodechlorination catalysts based on their ethylene product selectivity. We propose a descriptor-based model where the Gibbs free energy difference between the ethylene hydrogenation barrier and the ethylene desorption energy is defined as a descriptor for ethylene selectivity. Our descriptor model explicitly takes into account the reaction kinetics; moreover, the use of Gibbs free energy accounts for entropic effects which may become significant at elevated reaction temperatures. We present the DFT-derived ethylene selectivity descriptor values for a series of monometallic and bimetallic surfaces. Our method allows for efficient screening of candidate surfaces with reasonable accuracy for the design of highly selective hydrogenation/hydrodechlorination catalysts. In addition, our approach can be easily generalized and applied to other reaction systems which involve competition between the desorption and reaction of an intermediate product.

2. Methods

All the DFT calculations were performed using the Vienna *Ab-initio* Simulation Package (VASP) [48,49], a plane-wave total-energy code. The electron-ion interactions were described by the projector augmented-wave (PAW) potentials [50,51], and the exchange-correlation functional was described using the generalized gradient approximation (GGA-PBE) [52]. The electronic wave functions were expanded using plane waves with an energy cutoff of 400 eV. The dispersion interactions were accounted for by adding to the conventional Kohn-Sham DFT energy a correction term evaluated using the Tkatchenko-Scheffler method with self-consistent screening (TS + SCS) [53].

All the metal surfaces were modeled by three-atomic-layer slabs periodically repeated in a supercell geometry. Each slab consisted of a (4×4) unit cell, which corresponds to a surface coverage of 1/16 ML. Adsorption was allowed on only one side of the two exposed surfaces of each slab, and the electrostatic potential was adjusted accordingly [54,55]. The topmost layer and all the adsorbate atoms were fully relaxed; the bottom two layers of each slab were fixed at their truncated lattice position. In the vertical direction along the surface norm, any two successive slabs were separated by at least 12 Å of vacuum. The first Brillouin zone was sampled with a $(4 \times 4 \times 1)$ Monkhorst-Pack k-point mesh [56]. Convergence of the total energy with respect to the k-point set and energy cutoff was confirmed within 0.01 eV. A systematic error of 0.09–0.12 eV was observed when we increased the slab thickness from three to four layers (with the bottom two fixed), while the relative order of the energies remains unchanged (Table S1). Therefore, the three-layer surface model serves the purpose of ranking different surfaces with reasonable accuracy. Since the aim of our study is to provide a model for catalyst screening, we performed all the calculations on the three-layer slabs as a compromise for the computational cost. This allows for the sampling of a wide range of catalyst candidates within a short period of time. Our calculated lattice constant values of all the metals and metal alloys involved in this work are summarized in Table S2; in general, the calculated lattice constant values are in good agreement with the experimental ones.

The binding energies of individual surface adsorbates were defined with respect to their gas-phase energy using Eq. (1):

$$\mathrm{BE} = E_{\mathrm{tot}} - E_{\mathrm{slab}} - E_{\mathrm{gas}} \quad (1)$$

where BE stands for the binding energy of the adsorbate, E_{tot} for the total energy of the adsorbed species and the slab, E_{slab} for the total energy of the clean slab, and E_{gas} for the total energy of the adsorbate in the gas phase.

The transition states and activation energy barriers were identified using the climbing image nudged elastic band (CI-NEB) method [57] with seven interpolated images in addition to the initial and final states. The structures were relaxed until the maximum force on all images was smaller than 0.1 eV/Å. The transition states were confirmed by vibrational frequency analyses [58] yielding a single imaginary frequency along the reaction coordinate. Entropies and heat capacities of adsorbates and transition states were determined from the DFT-calculated vibrational frequencies; detailed procedures were described in previous publications [59,60].

3. Results and discussion

In this section, we first explain the definition of our ethylene selectivity descriptor. We then present the calculated descriptor values on a series of monometallic and selected bimetallic alloy surfaces and briefly explore the relationship between the kinetic and thermochemical parameters in our model. In the end, we discuss implications of our results as well as potential applications of this descriptor model.

To define the ethylene selectivity descriptor, we consider two possible reaction events when ethylene is formed on the surface along with an adsorbed hydrogen atom ($CH_2CH_2^* + H^*$; * denotes an adsorbed species or adsorption site): (1) desorption of both surface species to form gas-phase ethylene and hydrogen ($CH_2CH_2(g) + 1/2H_2(g)$), and (2) combination of both species to form $CH_3CH_2^*$ (ethylene hydrogenation: $CH_2CH_2^* + H^* \rightarrow CH_3CH_2^* + {}^*$) through a transition state ($[CH_2CH_2 + H]^*_{TS}$), which would ultimately lead to the formation of ethane through a subsequent hydrogenation step. The idea is illustrated graphically by the Gibbs free energy surface shown in Fig. 1. The desorption Gibbs free energy (ΔG_{des}) and hydrogenation Gibbs free energy barrier (ΔG_{TS}) are defined by Eqs. (2) and (3), respectively: