

A first-principles study of ethylene transformation on M(111) (M = Pd, Pt, Ni, and Rh)

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Introduction

The chemistry of olefinic hydrocarbons on group VIII metal surfaces is important for the petrochemical and polymer industries. Ethylene is a prototypical system for studying reactions of alkenes [1]. As a first step towards understanding the reactions of unsaturated hydrocarbons on metal surfaces, we studied the evolution of ethylene on the metal Pd using a density functional method and slab models. We report the thermodynamics and kinetics of the C-C and C-H bond scission as well as the H-shift reactions of a series of species derived from ethylene on Pd(111) surface. In addition, we explored computationally the thermodynamics of a model decomposition of ethylene, $C_2H_4 \rightarrow C_2H_3 \rightarrow C_2H_2 \rightarrow C_2H \rightarrow C_2 \rightarrow 2C$, on the (111) surfaces of the four group VIII metals, Pt, Pd, Ni, and Rh.

Computational Methods

The DFT calculations were carried out with a plane-wave based method using the gradient-corrected PW91 exchange-correlation functional. The interaction between atomic cores and electrons was described by the projector augmented wave method. A $5 \times 5 \times 1$ k grid and an energy cutoff of 400 eV were used throughout. The surface was modeled with four-layer slabs and a (3×3) surface unit cell. Neighboring slabs were separated by a vacuum spacing of at least 10 Å. Transition states were located with the nudged elastic band method.

Results and Discussion

Figure 1 summarizes the calculated reaction heats on Pd(111) (values in bold), assuming infinitely separated product fragments, and the corresponding energy barriers (values in italics). The direct H-shift generally has a high barrier; the results for H-shift reactions refer to a process of two steps in which an H atom first dissociates onto the surface, and then recombines with the newly formed species (the barrier for the slowest step is indicated). From Figure 1 one notes that the C-C bond scission of ethylene is disfavored due to a notably higher barrier than that for the C-H scission. Instead, dehydrogenation to vinyl or H-shift to ethylidene will likely occur. Vinyl may further dehydrogenate to either acetylene or vinylidene. Alternatively, vinyl can change into ethylidyne via a H-shift. Ethylidyne is expected to lose one H atom and to form ethylidyne. As for ethylene, the C-C cleavage of both vinyl and ethylidyne is unfavorable. Transformation of ethylidyne to methyl and carbon black is also predicted to be unlikely, based on the large endothermicity, 116 kJ/mol. According to the calculated barrier, formation of acetylene is likely through the dehydrogenation of vinyl. Note that for acetylene the C-H and C-C bond breaking barriers are comparable; thus this species may be the precursor of C-C bond scission. Further dehydrogenation of acetylene leads to acetylidene; the latter

needs to overcome barriers of ~ 160 kJ/mol to form C_2 or CH and carbon black. Previously C_2 [2], C_2H_2 [3], C_2H_3 and C_2H_4 [4] were suggested as precursors of C-C bond breaking in ethane hydrogenolysis on group VIII metal surfaces. Our results show that C_2H_2 is very likely the precursor on Pd(111). With the unity bond index quadratic exponential potential (UBI-QEP) approach, Zeigarnik et al. [5] estimated the barriers and reaction heats of C-C bond scission for a series of moieties on Pd(111). The UBI-QEP barriers for the decomposition of CH_2CH_2 , CH_3CH , and $CHCH$ are relatively close (within 30 kJ/mol) to our first-principles results, whereas those for CH_2CH and especially CHC are remarkably lower, by 70 and 152 kJ/mol, respectively, than the present values. In addition, the heats of reaction from the UBI-QEP method differ significantly from our first-principles results.

We calculated dehydrogenation steps to become more exothermic in the order $Pt < Pd < Rh < Ni$. Dehydrogenation of CH_2CH_2 and CH_3CH may occur significantly easier than that of $CHCH$ and CHC . At variance with the dehydrogenation, the decomposition of C_2 species becomes thermodynamically more favorable in the order $Ni < Rh < Pd < Pt$. Thus ethylene dehydrogenation will occur easiest on Ni(111).

Significance

We systematically investigated ethylene transformations on (111) surfaces of various group VIII metal, to foster understanding of reforming and conversion process of hydrocarbons.

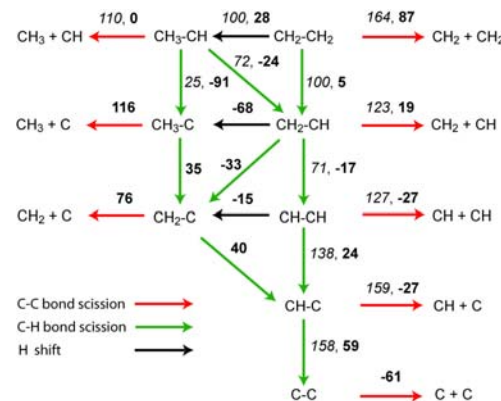


Figure 1. Transformation pathways of ethylene on Pd(111). Values in bold and italics represent heats of reactions and reaction barriers, respectively.

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