Complex reaction networks in the conversion of ethylene to ethylidyne on flat and stepped Pd

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Introduction

Adsorption and conversion of ethylene on flat and stepped Pd surfaces have been studied with the aim to understand the complex chemistry of small organic molecules on Pd. These processes are crucial to understand the experimental observations of the presence of a C subsurface layer in the active Pd catalysts [1]. Our results provide a view on the complex chemistry of olefins on the surface where several competitive processes take place simultaneously and where a hierarchy among different bond activations can be established.

Materials and Methods

Density functional theory calculations were carried out with the DACAPO [2] code, where Kohn-Sham equations are solved self-consistently using the revised Perdew-Burke-Ernzerhof generalized gradient correction [3] and Vanderbilt ultrasoft pseudopotentials [4]. We modeled the flat Pd(111) surface with a four-layer slab and a (3x2) unit cell and the stepped Pd(211) surface with a four-layer slab and a (2x1) unit cell. The transition states for the reactions were determined by applying the nudged elastic and adaptive nudged elastic methods.

Results and Discussion

Fig. 1 presents the calculated potential energy diagram for ethylene conversion to ethylidyne (CCH_3) on Pd(111) and Pd(211) surfaces. Our results show how under low coverage ethylene and its derivatives hydrogenation-dehydrogenation reactions are the most likely processes on both surfaces. This differs from Ni for which a more pronounced step effect in terms of the selectivity for activation of C-H and C-C processes is observed [5]. According to our calculations isomerization processes are energetically very costly and thus are not likely to take place under relevant operation conditions.

The most favorable reaction pathway from ethylene to ethylidyne goes via the formation of vinyl and ethylidene on both surfaces. In general, step sites strengthen the adsorption. Also the transition state energies are mainly lower on the step than on the terrace sites, thus the reaction proceeds more effectively on steps. From our reaction profiles, the first C-H bond breaking (from ethylene to vinyl) is the rate-limiting step of the dissociation process on both surfaces, and the zero-point energy corrected barriers agree very well with the measured value.

Dehydrogenation steps of the ethylene related structures are found to follow a Brønstead-Evans-Polanyi type of relationship with reaction energy. Considering the challenges in determining the transition states for hydrogenation and dehydrogenation reactions, this kind of relation is most useful to estimate activation barriers when reaction energy is known.

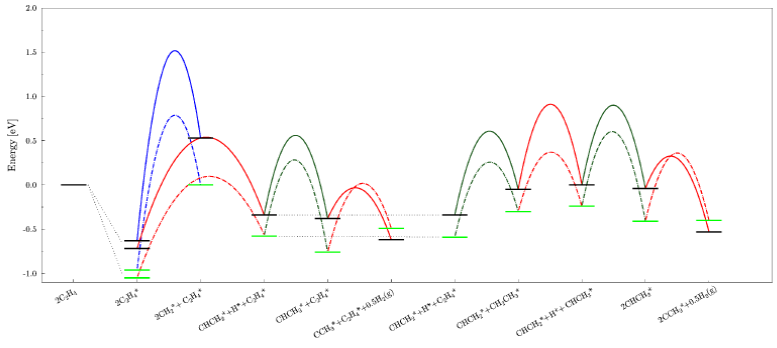

Figure 1 Potential energy diagram for ethylene decomposition on Pd(111) and Pd(211) surfaces . Black (green) lines represent the adsorption energies of the different hydrocarbon species on Pd(111) (Pd(211)). Transition state energies for C-C bond breaking, dehydrogenation and hydrogenation are illustrated in blue, red and green lines,respectively. The solid (dashed) line refers to the flat (stepped) surface.

Significance

Understanding the complex chemistry of small organic molecules on Pd is of fundamental importance to understand processes like, for instance, selective hydrogenation, steam reforming, polymerization on the atomic level.

References

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