Adsorption and Activation of Methyl Acetate on Pd surfaces

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Introduction

Esters (ROCOR') are a class of organic molecules frequently encountered in industrial polymer synthesis and biomass feedstock processing. While the reactions of esters on transition metal catalysts, including decomposition, hydrogenolysis, and transesterification, has been extensively studied experimentally,[1-4] the mechanistic details, in particular the factors that influence the mode of activation, remain scarce. We are carrying out a systematic study of the interactions between simple esters and several transition metals to address the lack of this knowledge. In this contribution, we present the results of density functional theory (DFT) calculations performed to investigate the adsorption and activation of methyl acetate on different crystalline facets of palladium, an active hydrogenation catalyst.

Methods

Spin-polarized periodic DFT calculations are performed in the generalized gradient approximation (GGA-PBE).[5] The projector augmented wave method is used to describe core electrons,[6] and the Kohn-Sham valence states are expanded in a plane wave basis up to a kinetic energy of 400 eV. Geometry optimizations are converged to 0.03 eV/Å. The minimum-energy reaction pathways are calculated using the climbing-image nudged elastic band method.[7] Charge partition is analyzed with Bader charge analysis.[8]

Results and Discussion

The adsorption of methyl acetate and the various C-O and C-H bond scission steps are investigated on the flat Pd(111) and Pd(100) surfaces, the stepped Pd(533) surface, and kinked Pd sites. We find that molecular methyl acetate adsorbs weakly on all the Pd surfaces considered, regardless of the molecular orientation. Of the C-O bonds, the O-acetyl bond is the easiest to break, followed by the O-methyl bond and the carbonyl C=O bond. The scission of both the acetate and the methyl C–H bonds is a highly activated process on Pd, but the dehydrogenation of methyl acetate can lead to its isomerization to the enolate or enol form, which interacts strongly with the surface and opens up additional reaction channels at high temperature. Preliminary results indicate that the activation of methyl acetate is sensitive to the local structure of the Pd surface.

Significance

The results of our study begin to shed light on the molecular-level features of the Pd surface that control the activation of methyl acetate and are therefore likely of importance to the selective conversion of simple esters in general via heterogeneous catalysis.

References

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