

A First Principles Analysis of the Ensemble Effects in the Synthesis of Vinyl Acetate over Pd/Au Substrates

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Introduction

Vinyl acetate is used in the production of various polymers and copolymers used in the commercial production of different adhesives, laminate films and paints. The synthesis of vinyl acetate is typically carried out via the oxyacetylation of ethylene over Pd/Au supported over silica. It is well established that the introduction of Au has been shown to enhance both the activity as well as the selectivity of this chemistry [1]. There has been some debate, however, as to influence of Au and the ensemble size, Au composition, and structure sensitivity for this reaction [2,3]. Here, we examine surface ensemble effects on the selectivity and activity of this process. Density functional theory (DFT) calculations were performed for a number of elementary reaction steps involved in VA synthesis and ethylene combustion on the Pd 111 surface in addition to active sites (single Pd atom or Pd dimers) dispersed in the Pd/Au (100) surface identified by Goodman [3]. On the Pd/Au (100) surface, chemisorption predominantly takes place at the Pd sites; the Au regions tend to remain free. The Au regions separate the active sites such that they are less crowded by other adsorbates. On pure Pd, the surface is found to be covered with oxygen and acetate, which hinders adsorption, surface diffusion, and reaction of ethylene and acetate. Separated Pd atoms and dimers in the alloy serve as sites for adsorption and reaction. The dispersion of sites significantly improves the selectivity by shutting down active combustion and decomposition routes, while the introduction of Au into the surface improves the activity. It is still unclear, however, whether Pd monomers or dimers dispersed in Au are the most active ensembles.

Materials and Methods

DFT calculations were performed with the Vienna Ab-initio Simulation Program [4] (VASP) using a plane wave basis set with a cutoff of 396 eV and ultra-soft pseudopotentials. Unit cells consisted of four layers of nine atoms in a 3x3 arrangement, separated by 10 Å of vacuum. The Brillouin zone was sampled using a 6x6x1 mesh.

Results and Discussion

The synthesis of vinyl acetate is found to proceed by two mechanisms. In both pathways, oxygen acts as both a hydrogen scavenger and directly assists in some surface reactions. The first mechanism, which is similar to the one proposed by Samanos [1], involves direct coupling of ethylene and acetate to form an acetoxyethyl intermediate. The intermediate then undergoes hydride elimination, forming vinyl acetate. The DFT results indicate that the rate limiting step for this path appears to be the coupling reaction. The second mechanism, which is similar to the one proposed by Mosieev [5], proceeds by oxygen assisted dehydrogenation to form vinyl, followed by coupling of the vinyl to acetate to form vinyl acetate. DFT results indicate that either ethylene dehydrogenation or vinyl coupling with surface acetate are similar and may be rate determining, depending on the reaction conditions.

This path is favored at high oxygen partial pressure, while the first path appears to be favored at low oxygen partial pressure.

Significance

This work attempts to elucidate the reaction pathways involved in the catalytic gas phase synthesis of vinyl acetate monomer including the effects of surface ensembles present on Pd/Au bimetallic surfaces.

References

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