

1. Overview. Analyses of reaction rates via proposed elementary steps and DFT calculations were used to determine mechanistic details and understand the effects of catalyst composition on reactivity for vinyl acetate (VA) formation.

2. Kinetic and isotopic studies. The VA rates on monometallic Pd were measured at regular intervals at a reference condition to track deactivation and normalize number of active sites for intermediate measurements at other conditions. Slight decrease in rates with increasing residence time was traced to the small concentrations of CO produced, which inhibits reactions by blocking active sites at some conditions. The effects of C_2H_4 , CH_3COOH , O_2 and CO pressure were included in elementary steps used to derive rate equations (Fig. 1). Figure 2 shows the effects of C_2H_4 , CH_3COOH , O_2 pressures on VA formation rates. The rates decreased monotonically with C_2H_4 pressures at low CH_3COOH and O_2 pressures (10, 2 kPa), suggesting that the reaction is inhibited by C_2H_4 in addition to the greater amounts of CO formed at higher C_2H_4 pressures. Higher CH_3COOH and O_2 pressures (18, 7 kPa), however, saturate surfaces with adsorbed acetates (see denominator term for CH_3COO^* in Fig. 1), leading to increase in VA rates with increasing C_2H_4 pressures at low C_2H_4 pressures (Fig. 2a). Thus, VA formation rates can exhibit positive or negative orders depending on coverages, which are captured well by the elementary steps. The rates increase with increasing CH_3COOH pressures at low pressures and level-off at high pressures where surfaces are covered with acetates (Fig. 2b). The rates increase linearly with O_2 pressures (Fig. 2c), suggesting the involvements of molecular O_2 in kinetically-relevant steps (Fig. 1). Dissociated O-atoms instead led to a half-order O_2 dependence in equations that did not describe the data accurately. The kinetic isotope effects derived from CH_3COOH/CH_3COOD and C_2H_4/C_2D_4 rate ratios (1.1 and 3.1, respectively) show that at typical conditions C-H activation is rate-limiting, and O-H activations occur rapidly.

The selectivity to VA on 1%Pd/SiO₂ was nearly independent of residence times, suggesting that secondary reactions do not contribute significantly to the selectivity, and therefore, it can be expressed as ratios of rates between desired VA formation rates and undesired parallel reactions to CO, CO₂ and minor CH₃CHO products. The rate ratios (selectivity, Fig. 3) were interpreted using elementary steps for ethylene or acetate combustion (near O₂^{*}) or decomposition (near *) at coverages identical to the ones that describe VA rates (Fig. 1,2). The VA selectivity increases with increasing C_2H_4 and CH_3COOH pressures (Fig. 3ab), consistent with the enhancement of coupling reactions when both reactants cover the surfaces. Higher C_2H_4 pressures at low CH_3COOH and O_2 pressures lead

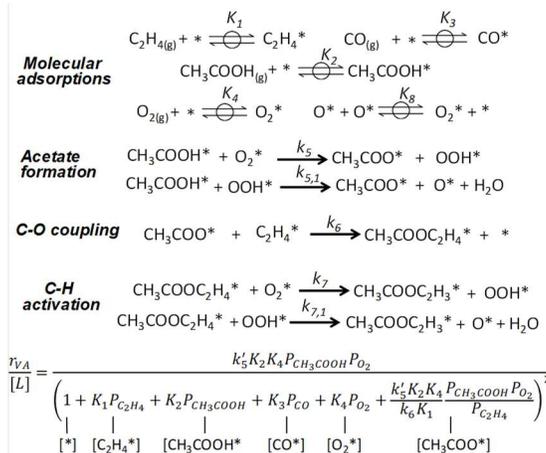


Figure 1. Proposed steps and rate equation.

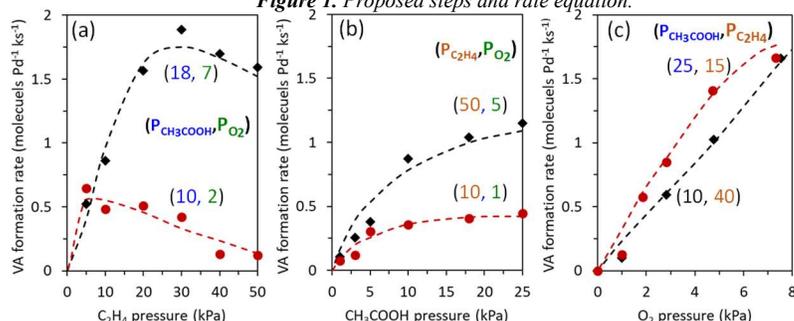


Figure 2. VA formation rates as a function of (a) C_2H_4 , (b) CH_3COOH and (c) O_2 pressure on 1wt.% Pd/SiO₂ catalysts (433 K, C_2H_4 and CH_3COOH conv. < 5%, O_2 conv. < 10%). Dashed curves show best fits to rate equations.

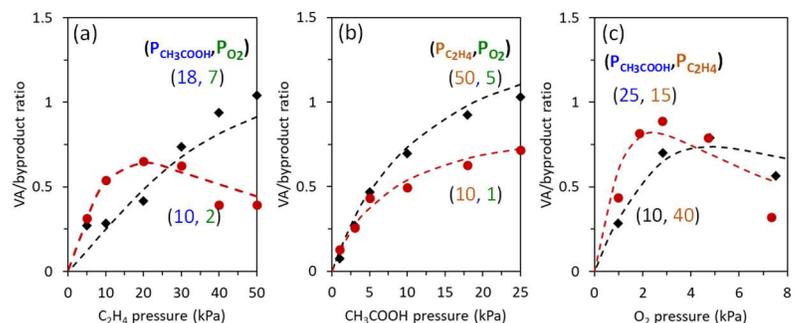


Figure 3. VA selectivity shown as a ratio of rates of formation of VA to that of undesired products (CO, CO₂ and CH₃CHO) as a function of (a) C_2H_4 , (b) CH_3COOH and (c) O_2 pressure on 1wt.% Pd/SiO₂ catalysts (433 K, C_2H_4 and CH_3COOH conversion < 5%). Dashed curves represent best fits to equation describing rate ratio.

Higher C_2H_4 pressures at low CH_3COOH and O_2 pressures lead

to lower selectivity due to increasing C₂H₄ coverage without concomitant increase in acetate coverage. Selectivities are lower at very low O₂ pressures because O₂ is required for OH dissociation to form acetates to maintain high acetate coverages (Fig. 1, denominator terms in rate equation). High O₂ pressures also lower the selectivity because of increased unselective combustion reactions, leading to maximum selectivity at intermediate O₂ pressures. The highest selectivity based on carbon moles in these results is near 75% (at rate ratios near 1 in Fig. 3). These data show that reaction orders and selectivity depend strongly on reaction conditions and coverages, and highest rates and selectivity may be achieved at different reactant pressures for the different catalysts. These data and comparisons with DFT and spectroscopy will form the basis of quantitative comparison with different compositions.

3. DFT calculations. Energies of reactive intermediates and transition states mediating acetate and VA formations at low and high acetate coverages were calculated using VASP program, PBE-D3BJ DFT functionals, projector augmented wave potentials and three-layer p-4×x Pd metal slabs. Figure 4 shows Gibbs free energies as a function of reaction coordinate near saturation coverage for the formation of sixth acetate species and subsequent ethylene adsorption and VA formation on starting surfaces with five bidentate acetates on 4×4 Pd slabs (ten out of sixteen surface atoms occupied). These data show that direct O-H activation by O₂ is more facile than unassisted O₂ dissociation at covered surfaces, and that the C-H activation step limits rates as its transition state has the highest energy along the reaction coordinate. IR spectra for different surface acetate coverages, molecular acetic acid and diacetate cluster were obtained to detect differences between peak positions and intensities among these species to help guide *in-situ* spectroscopy.

4. Composition effects. VA formation rates and selectivity were measured on fcc metals neighboring to Pd (Rh, Ir, Ni, Pt, Cu, Ag, Au) and the results were assessed using DFT derived binding strengths for acetate species and ethylene molecules. Based on Sabatier principle, binding strengths of species should be just right for optimum reactivity. DFT shows that all metals other than Pd bind either ethylene or acetate or both species either too strongly or too weakly, with no other metal has similar binding strengths as Pd, which is consistent with experimental VA formation rated on Pd being well over an order of magnitude higher than other metals. Bimetallic compositions such as PdCu and PtCu containing isolated Pd or Pt atoms showed slightly weaker ethylene binding strengths than Pd and similar acetate binding strengths, and these bimetallic compositions were more active and selective than monometallic counterparts at certain conditions. CO adsorption IR, XAFS and EDX measurements showed that Pd is atomically dispersed in PdCu bimetallic samples with low Pd concentrations. These combined experimental and DFT analyses have led to identification of promising bimetallic compositions that can be more active and selective than current Pd rich PdAu samples used in the industry, and detailed molecular-level understanding of structure-function relations for these compositions will be performed in future studies.

5. Impact of PRF funding

The PRF funding contributed significantly to education and training a graduate student (Zhaoru Zha) and a postdoctoral scholar (Leelavathi Annamalai) working on this project in the PI's lab. The two researchers collaborated on various aspects of the project involving synthesis, characterization, kinetic measurements and development of GC methods and calibrations. Zhaoru has successfully defended his thesis proposal the work done using the support from PRF and the forward plans. The funding was helpful in obtaining significant results that we plan to publish soon. The PI submitted proposals to federal agencies for future work on this project. This work was shown in three oral presentations at national meetings and one invited seminar.

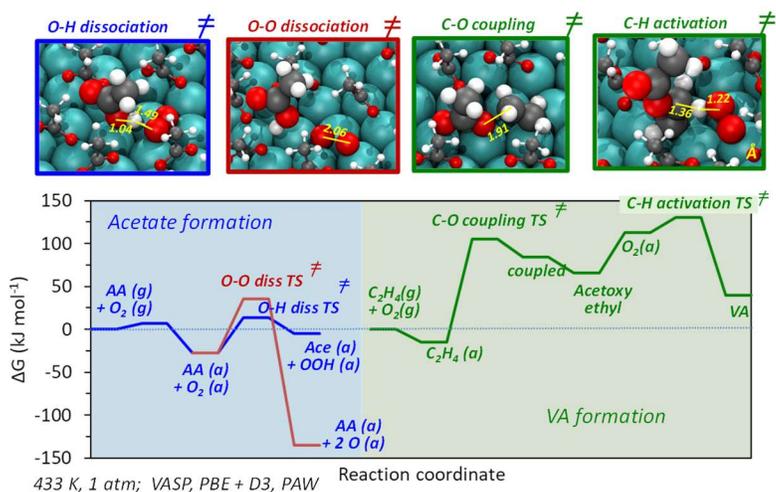


Figure 4. Gibbs free energies as a function of reaction coordinate at 433 K and 1 atm, using 3-layer 4×4 metal slab with five pre-adsorbed acetates.