

Progress Report 2018

PRF# 57869-DNI5

Project Title: Kinetic and Theoretical Study of Vinyl Acetate Synthesis on Palladium Based Bimetallic Catalysts

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1. Overview

The goal of this project is to better understand kinetic and mechanistic details of the formation of vinyl acetate by acetoxidation of ethylene ($C_2H_4 + CH_3COOH + \frac{1}{2} O_2 \rightarrow CH_3COOC_2H_3 + H_2O$) on Pd catalyst and the effect of the second element in bimetallic systems such as PdCu. These studies involve combinations of kinetic and spectroscopic experiments with DFT calculations. To date we have performed kinetic measurements on Pd/SiO₂ and PdCu/SiO₂ with Pd/Cu atomic ratios ranging from 0.003 to 2 prepared using different methods. The results show significant differences between kinetics for catalysts with low Pd/Cu ratios and for monometallic Pd. More detailed studies to probe these differences are planned. Preliminary reactivity measurements on other catalyst including PdAu, PdCu, PdCuKoAc, Pt, PdNi were also performed to explore more promising catalyst systems. DFT calculations were used to probe energetics of elementary steps at different acetate coverages and how they change for neighboring elements of Pd and Cu in the periodic table.

2. Experimental results

The VA synthesis occurs at complex conditions involving surfaces highly covered with adsorbates. Pd metal has been shown in the literature to convert to small inactive trimer clusters of Pd(OAc)₂, which causes a decrease in reaction rates with time on stream. These effects were eliminated from rate measurements in kinetic studies by measuring rates at a reference condition at regular intervals and using these rates to estimate changes in the number of active sites. The rates decrease significantly with increase in ethylene conversion, suggesting that a product formed in the reaction inhibits the reaction. Experiments involving addition of CO and H₂O to reactants and comparison with the quantities of these products formed during reaction suggest that most of the inhibition effects can be accounted by blocking of active sites by adsorbed CO (Fig. 1a). The rates at low conversion exhibit a near-zero or negative order-dependence on ethylene pressure, a Langmuir-type dependence on acetic acid pressure and nearly linear dependence of O₂. These trends represent combination of true reaction orders and inhibition by different extents of CO formed in these conditions. Selectivity to VA improves with acetic acid pressure and ethylene pressure, consistent with high coverages required to suppress combustion of reactants. The selectivity first increases with O₂ pressures at low pressures and then decreases, which corresponds to CO formation in low O₂ and CO₂ formation at high O₂ pressures. We are developing kinetic models that can accurately capture these trends.

PdCu systems with low Pd/Cu ratios differ significantly from monometallic Pd. These systems exhibit higher rates and VA selectivity than Pd at low O₂ pressures (compared to the difference between the two catalysts at high O₂), and produce an order of magnitude smaller CO than Pd at same condition and ethylene conversion. They also exhibit significant differences if ethylene and acetic acid pressure effects (Fig. 1b), which, based on preliminary kinetic models, are consistent with stronger acetate binding and lower CO production.

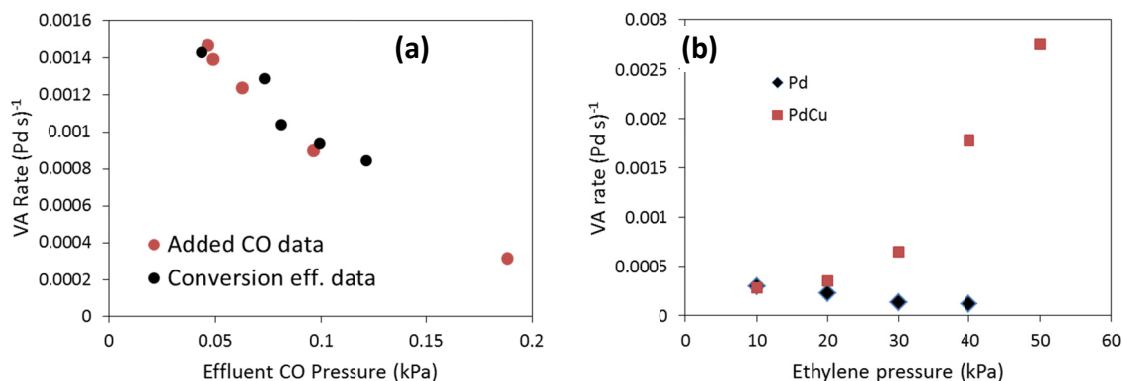


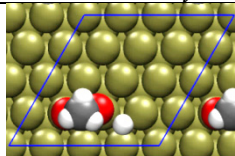
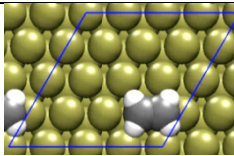
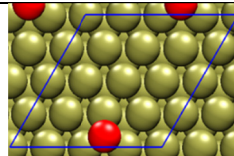
Figure 1. VA formation rate (a) as a function of CO pressure for CO formed via conversion of reactants and CO added with reactants on 1wt.%Pd/SiO₂, and (b) as a function of ethylene pressure on 1%Pd/SiO₂ and on 1:4 physical mixtures by weight of 1wt.%Pd/SiO₂ and 5wt.%Cu/SiO₂.

The kinetic details of PdCu co-impregnated systems are similar to physical mixtures of Pd/SiO₂ and Cu/SiO₂ samples, suggesting that either (i) Pd and Cu components can act cooperatively at a distance or (ii) dynamic re-structuring forms PdCu interfaces during reaction as shown for PdAu systems for this reaction. CO adsorption FTIR studies for Pd atop and bridge peaks appear to be consistent with formation of Pd atoms in Cu particles formed during reaction. More detailed studies involving XAFS measurements are underway.

3. Computational results

Some of the results of density functional theory calculations performed to examine effect of catalysts composition and energies of relevant intermediates and transition states are shown in shown in Table 1 and Figure 2.

Table 1. Adsorption energies at 1/16 monolayer.

Catalyst ((111) surface of fcc metals)	 Acetic acid adsorption energy (kJ/mol)	 Ethylene adsorption energy (kJ/mol)	 Fcc site 1/2 O ₂ adsorption energy (kJ/mol)
Pd	-124	-79	-145
Pt	-121	-87	-142
Rh	-165	-86	-195
Ir	-160	-91	-178
Cu	-116	-20	-177
Ni	-154	-60	-214

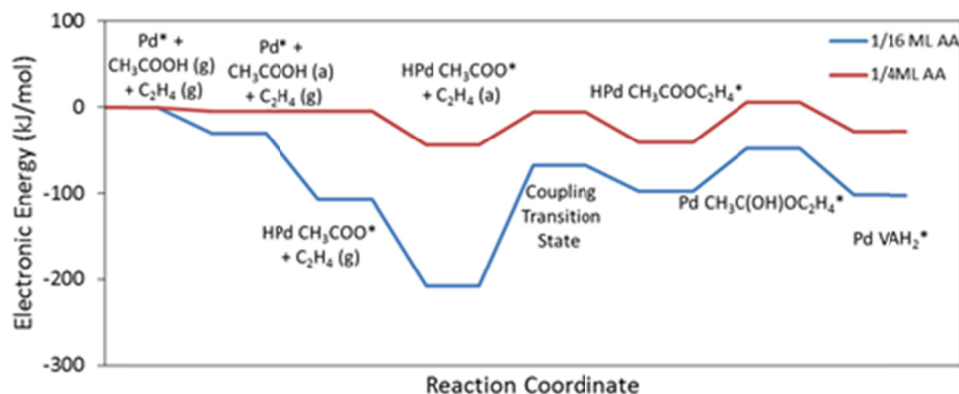


Figure 2. Effect of acetic acid (AA) coverage on energies for ethylene and acetic acid coupling on Pd surface.

4. 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 is on track to propose a PhD thesis based on the work done and the forward plans. Leela, plans pursue other research opportunities after finishing in 2019. The funding was helpful in obtaining significant results that we plan to publish soon and the PI plans to seek NSF CAREER or DOE funding for future work on this project. A talk on this topic at 2018 AIChE national meeting is scheduled and a couple of submissions for talks are planned in near future.