



Editor's choice paper

Unraveling the mechanism of propanoic acid hydrodeoxygenation on palladium using deuterium kinetic isotope effects



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ABSTRACT

A combined experimental and computational kinetic isotope effect (KIE) study was performed for the catalytic hydrodeoxygenation (HDO) of deuterium-labeled propanoic acid (PAC-2, 2-D₂) over Pd catalyst. For the experimental study, the kinetics were measured in a plug flow reactor over a 5 wt% Pd/C catalyst at 200 °C and 1 atm under differential conversion using a reactor feed consisting of 1.2% PAC and 5% or 20% H₂, with balance helium. Different experimental KIE values for the high ($k_H/k_D = 1.13 \pm 0.04$) and low ($k_H/k_D = 1.62 \pm 0.05$) partial pressures of hydrogen were observed. Density functional theory calculations were performed to obtain the reaction parameters of the elementary steps involved in the HDO of PAC on Pd (1 1 1), and a microkinetic model was developed to estimate the KIE for the low hydrogen partial pressure case from first principles. The computed result ($k_H/k_D = 1.49$) is in good agreement with the experiment. In addition, the product distribution favored C₂H₆ and CO, suggesting decarbonylation (DCN) is the main reaction pathway. This provides strong evidence for the proposed mechanism for the formation of C₂H₆ on both Pd (1 1 1) and supported Pd nanoparticles presenting primarily that exposed crystal face.

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1. Introduction

An extensive amount of research has explored the catalytic performance for the hydrodeoxygenation (HDO) of biomass-derived carboxylic acids and acid esters [1,2]. Supported palladium is one of the most investigated catalysts in the area of catalytic hydrodeoxygenation of biomass-derived platform molecules [3–14]. For instance, early studies showed that supported palladium offers a strong activity and selectivity for the HDO of PAC [15–19]. While kinetic studies reveal overall reaction rates, reaction orders, and apparent activation barriers, they do not provide enough information for determining the fundamental elementary steps involved in the reaction mechanism [20,21]. For HDO reactions, the network of these underlying steps is complex and not yet fully understood.

In our previous DFT studies [22–24], the HDO of PAC was investigated over Pd (1 1 1) model surfaces. The elementary reaction

steps involved in the decarbonylation (DCN) and decarboxylation (DCX) were identified from first principles (Fig. 1). A microkinetic model was developed to determine the dominant pathway and rate-controlling steps under realistic reaction conditions of 200 °C and low, medium, and high partial pressures of hydrogen (0.001, 1 and 30 bar) in the presence and absence of solvents. Our results suggest that under gas phase reaction conditions, DCN is favored over the DCX, while in the presence of water, DCN and DCX mechanisms become essentially competitive [22]. This is in agreement with our experimental study of the gas-phase HDO of PAC over supported group VIII noble metals, where we found that on various metals the DCN pathway dominates [25].

Additionally, computations found that in all reaction environments, and at a low hydrogen partial pressure, dehydrogenation of the α -carbon in PAC is the primary rate-controlling step. With increasing hydrogen partial pressure, C–OH bond dissociation becomes the rate-controlling and the importance of C–H bond cleavage is diminished [22]. The dissociation of the C–OH bond is one of the key reactions in the DCN and was previously also identified as the rate-determining step for the HDO of acetic acid [26,27]. Our studies, however, clearly suggest that at all conditions, dehydrogenation steps of the α -carbon of the acid have at least some importance for the HDO of the acid to hydrocarbons. He and Wang,

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Davis and Barteau have also examined the deoxygenation of carboxylic acids over Pd [1,28,29]. They suggest that a carboxylate intermediate undergoes dehydrogenation, which is accompanied by C–O bond cleavage, resulting in CO and hydrocarbon formation by C–C bond cleavage. Similar work has been reported previously, such as the experimental work of Maier et al. on the gas-phase deoxygenation of octanoic acid [30] and recent computational work on the DCX of butanoic acid by Lamb et al. Their work suggested that dehydrogenation of the α -carbon occurs during DCN/DCX of aliphatic carboxylic acids over Pd [31].

The present study explores the deuterium kinetic isotope effect (KIE) [32–39] for the HDO of PAc in order to further confirm the importance of C–H bond cleavage in the reaction pathway. PAc substituted with deuterium at the α -carbon position ($\text{CH}_3\text{CD}_2\text{COOH}$) was deoxygenated over 5 wt% Pd/C catalyst and its reaction rate and TOF compared with that obtained from unlabeled PAc ($\text{CH}_3\text{CH}_2\text{COOH}$). From these data, experimental rate constant ratio ($k_{\text{H}}/k_{\text{D}}$) was determined under various hydrogen partial pressures. Density functional theory (DFT) calculations were performed for labeled PAc and its intermediates on Pd (1 1 1) to obtain the reaction parameters of all the elementary steps involved. The DFT-derived parameters were then implemented in a microkinetic model that allowed prediction of $k_{\text{H}}/k_{\text{D}}$ under the same conditions used for the experiments. The experimental and computational results are consistent with each other, and confirm the importance of C–H bond cleavage in governing the rates of HDO of PAc on Pd.

2. Experimental

2.1. Materials and catalyst characterization

The experimental conditions have been previously reported in detail and thus will only be discussed briefly [16]. Propanoic Acid ($\text{CH}_3\text{CH}_2\text{COOH}$, 99%) and propanoic acid-2, 2-d2 ($\text{CH}_3\text{CD}_2\text{COOH}$, 98%) were purchased from Alfa Aesar and Cambridge Isotope Laboratories, respectively, and used without further purification. The gases for the reactor studies were H_2 (UHP), He (UHP, 99.99%), Ar (UHP, 99.99%) and ethane (CP grade, 99.99%) supplied by Airgas National Welders. The 5 wt% Pd/C catalyst (CP-97, $S_{\text{BET}} = 615 \text{ m}^2/\text{g}$) was supplied by BASF and reduced *in-situ* at 350 °C. The dispersion (16.9%) and mean particle size (6.8 nm) of 5 wt% Pd/C was determined by pulsed hydrogen titration of oxygen pre-covered sites utilizing a Micromeritics 2920 AutoChem II Analyzer. Additionally, analysis based on Van Hardeveld and Hartog statistics [40] suggests that for a 6.8 nm particle size, 70–72% of exposed Pd faces correspond to Pd(1 1 1), whereas only 16–17% correspond to Pd(100), with the remaining sites made up from corners and edges (which were found to be essentially inactive) [25].

2.2. Reaction evaluation

The reaction experiments were performed in a single pass, packed bed, plug flow reactor system connected to a GC system (Supporting information, Scheme S1). The experiments were carried out under differential (<5%) conversion at 200 °C under atmospheric pressure. Two sets of experiments were conducted: (1) 1.2% PAc/20% H_2 /balance He and (2) 1.2% PAc/5% H_2 /balance He in a total flow of 50 sccm. This catalyst under these reaction conditions has previously been shown to be free of both external and internal mass transfer effects [16]. In addition, the carbon support was tested separately and found to exhibit no activity at these reaction conditions [16]. The reaction rate was determined based on the formation of product (which is proportional to the rate of acid disappearance) in μmol product formed/min \cdot g_{cat} . The turn over frequency (TOF) was determined based on the reaction rate

per active site in min^{-1} of the 5 wt% Pd/C catalyst. Unlabeled and labeled PAc were kept in separate vapor-liquid equilibrium (VLE) saturators (Supporting information, Scheme S1) and the concentrations of the both acids (e.g., labeled and unlabeled) in the gas feed were set equal prior to starting the reaction. Once the reaction with unlabeled PAc reached steady-state, the reactor feed was switched to the labeled PAc. This process was cycled until steady state reaction was attained for each species. In this way, the KIE can be determined as the ratio between the unlabeled and labeled TOF (i.e., $k_{\text{H}}/k_{\text{D}}$). Carbon mass balances closed to within 1% in all the experiments and the activity was stable (i.e., no deactivation was observed) over the entire course of the reaction time on stream.

Measurements of the isotopic composition of the products were conducted by mass spectroscopy. To ensure only the products were analyzed by MS, the PAc (unreacted) was condensed in a cold trap (–55 °C) (Supporting information, Scheme S1). This was verified by analyzing the gas effluent with gas chromatography to confirm only products such as C_2H_6 and CO were detected. The gas products were diluted with argon carrier gas (for a total of 50 sccm) before being sampled by a Stanford Research Systems Residual Gas Analyzer (RGA100) mass spectrometer with an electron multiplier. The detailed description of this apparatus and sampling procedure is included in the Supplemental information. The masses 29–31 were monitored to track various ethane species, while water, nitrogen, oxygen, hydrogen and argon were also monitored to rule out leakage. For the MS study the PAc conversion was increased (~10%) by adjusting the catalyst loading (0.9 g).

2.3. Computational methodology

All density functional theory calculations have been conducted with the Vienna Ab Initio Simulation Package (VASP) [41–43]. The Kohn–Sham valence states are expanded in a plane wave basis sets with an energy cut-off of up to 400 eV. The interaction between core electrons is described with the projector-augmented wave (PAW) [43,44] method. The exchange correlation energy is calculated within the generalized gradient approximation (GGA) using the functional form proposed by Perdew and Wang, which is known as Perdew–Wang 91 (PW91) [45–47]. Similar pseudopotentials were used for hydrogen and deuterium atoms with only the mass modified for deuterium atoms.

The lattice constant obtained from the optimization of the fcc-Pd bulk is 3.953 Å, which is in reasonable agreement with the experimental value of 3.891 Å. The surface Brillouin zone is sampled with $4 \times 4 \times 2$ Monkhorst-pack k -point grid. Pd (1 1 1) is modeled by a 4-layer slab with a (3×4) surface unit cell and the palladium layers separated by a 15 Å vacuum.

The bottom two layers were fixed to their bulk configuration during all calculations while the top two layers were free to relax in all directions. Adsorption energies of all intermediates were calculated at their most stable geometry by the following equation:

$$E_{\text{ads}} = E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate}}(\text{g}) \quad (1)$$

where $E_{\text{slab+adsorbate}}$ is the total energy of the adsorbed intermediate on the Pd slab, E_{slab} is the total energy of the Pd slab and $E_{\text{adsorbate}}(\text{g})$ is the total energy of the adsorbate in the gas phase.

Transition states were obtained from our previous DFT studies [22–24] on PAc and finally, vibrational frequency calculations have been performed to obtain the frequency modes for all labeled intermediates and transition state structures.

The zero-point energy correction for all the structures was taken into account by using the following equation:

$$(2) \Delta E_{\text{ZPE}} = \sum_i \frac{1}{2} h \nu_i \text{ where } h \text{ is the Plank constant and } \nu_i \text{ is the vibrational frequency of mode } i.$$

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