**Crotonaldehyde Hydrogenation on Platinum–Titanium Oxide and Platinum–Cerium Oxide Catalysts: Selective C=O Bond Hydrogen Requires Platinum Sites Beyond the Oxide–Metal Interface**

Supporting Information

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**Root-Mean-Squared Distance for Surface Diffusion**

The following equation is used to estimate the root-mean-square (rms) distance for the diffusion of a reaction intermediate on a catalyst surface:

\[ \langle x^2 \rangle^{1/2} = \sqrt{4 \cdot D \cdot t} \]  

(1)

where \( \langle x^2 \rangle^{1/2} \) is the rms distance, \( D \) is the diffusion coefficient, and \( t \) is the time the molecule is allowed to diffuse. In this equation, \( D \) is given by

\[ D = D_0 \cdot \exp \left( \frac{-E_A}{k_BT} \right) \cdot (1 - \theta) \]  

(2)

where \( E_A \) is the activation barrier to surface hopping, \( k_B \) is the Boltzmann constant, \( T \) is the catalyst temperature, and \( \theta \) is the relative coverage of the catalyst surface during reaction. In this equation \( D_0 \) is given by

\[ D_0 = \frac{1}{4} \cdot v_0 \cdot d^2 \]  

(3)

where \( v_0 \) is the hopping frequency and \( d \) is the distance between adjacent surface sites of the adsorbate.

Here we seek only to estimate these parameters to obtain a sense of possible rms diffusion distances for the crotyl-oxy intermediate on a Pt surface. Consequently, to obtain Fig. 1S, we estimate that \( v_0 \) is equal to \( 10^{12} \) Hz or 1/ps, \( d \) is estimated as 0.2 nm based on the approximate length of a Pt–Pt bond in an fcc lattice, and \( \theta \) is estimated to be 0.95. We then calculate the rms distance, \( \langle x^2 \rangle^{1/2} \), as a function of time for a range of surface hopping barriers, \( E_A \).

Although we do not know that exact activation energy for surface hopping of a crotyl-oxy intermediate, for reference we note that \( E_A \) is 18.4 kJ/mol for CO on Pt, significantly lower than the hopping barriers considered here. As seen in Fig. 1S below, for a hopping barrier of 60 kJ/mol and a residence time given by the turnover frequency for crotonaldehyde hydrogenation, the rms distance is predicted to be on the order of 10 nm. Although this is only a crude approximation, it provides a sense for the distances that reaction intermediates may travel on the catalyst surface during a turnover event.
Fig. S1 Calculated root-mean-square diffusion distance versus time for a molecule adsorbed on a catalyst surface. The dashed vertical line at 50 s represents approximately one divided by the turnover frequency for C=O bond hydrogenation in these systems (see Fig. 9), which serves as an estimate of a reactant’s lifetime on the catalyst surface.

References