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:

$$\langle x^2 \rangle^{\frac{1}{2}} = \sqrt{4 \cdot D \cdot t} \tag{1}$$

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

$$D = D_0 \cdot \exp\left(\frac{-E_A}{k_B T}\right) \cdot (1 - \theta) \tag{2}$$

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

$$D_0 = \frac{1}{4} \cdot v_0 \cdot d^2 \tag{3}$$

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 θ is estimated to be 0.95. We then calcluate 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[1], 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 turnoverfrequency 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.

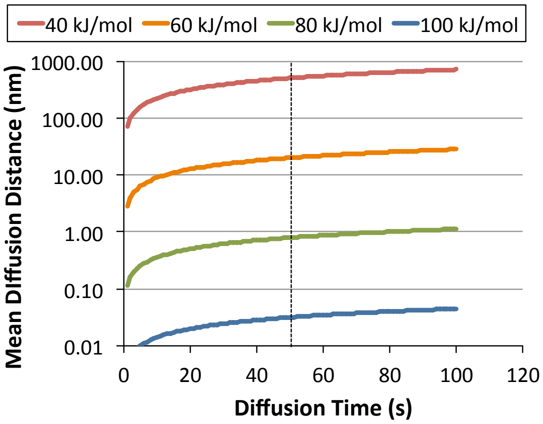

Fig. S1 Calculated root-mean-square diffusion distance versus time for a molecule adsorbed on a catalyst surface. The dashed vertical line at 50 s represents approximately one divided by the turnover frequency for C=O bond hydrogenation in these systems (see Fig. 9), which serves as an estimate of a reactant's lifetime on the catalyst surface.

References

1. Reutt-Robey, J.E., Doren, D.J., Chabal, Y.J. & Christman, S.B. Microscopic Co Diffusion on a Pt(111) Surface by Time-Resolved Infrared Spectroscopy. *Physical Review Letters* **61**, 2778-2781 (1988).