Supporting Information

for

Progress in Accurate Chemical Kinetic Modeling, Simulations, and Parameter Estimation for Heterogeneous Catalysis

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I. Model details and Parameter Estimates for Temperature Programmed Desorption of ethanal from CeO₂(111)

The model used for the temperature programmed desorption (TPD) of ethanal from CeO$_2$(111) involved two adsorption states ("State 1" and "State 2") each with coverage dependence for the activation energies for desorption. A single desorption state with coverage dependence was not sufficient to reproduce the observed data.

In the two adsorption states model, desorption from each state was described as following a first order desorption rate model with the rate constant of an Arrhenius form. The activation energies were taken to be a linear function of the total adsorbate coverage (with slope g_i) and the preexponential was taken to have a value independent of coverage. The relative coverages of the two states are denoted as θ_1 and θ_2, with the two states assumed to reside on the same type of sites (perhaps belonging to different conformations, for example, as noted in the main text). That is, $\theta_i = n_i/n_{sites}$, where n_i is the total number of adsorbates in state i and n_{sites} is the total number of sites. The following equations were used to simulate the rates (following standard TPD differential equations, with an introduction to these equations provided in reference [1]). θ_T is the total coverage of adsorbates in nominal monolayers (ML, based on normalization to the number of molecules desorbed up to 325 K), β is the heating rate in degrees K s^{-1}, and T_0 is the temperature at the start of the temperature ramp, and t is the time elapsed from the start of the temperature ramp. The total observed rate is r_T and includes contributions from baseline/background signals, r_b.

$$k_i = A_i e^{-\frac{E_{a,i}(\theta_T)}{RT}} \tag{S1}$$

$$\theta_T = \theta_1 + \theta_2 \tag{S2}$$

$$E_{a,i}(\theta_T) = E_{a,i}(0) - g_i * \theta_T * E_{a,i}(0) \tag{S3}$$

$$T = T_0 + \beta t \tag{S3}$$

$$r_i = \frac{d\theta_i}{dT} = -\theta_i \frac{A_i}{\beta} e^{-\frac{E_{a,i}(\theta_T)}{RT}} \tag{S3}$$

$$r_T = r_b + \sum_i r_i \tag{S3}$$

Other models (including other two state models or different functional forms for the activation energy) are possible: it is not claimed that this is the correct model, this model was used for example purposes to demonstrate the differences of Bayesian Parameter Estimation (BPE) and conventional parameter estimation (CPE) when using a particular model. For BPE and CPE an uncertainty of +/- .005 ML s^{-1} was assumed for the baseline of the desorption rate (that is, for possible sources of background signal etc.). For the Figures 10 and 11 in the main article text, the priors for the kinetic parameters were identical for the two states (as shown in Table S1) with all distributions described by normal distributions, and no assumptions for the ratio between the states.

Table S1: Prior and BPE Point Estimate Values (Corresponding to Figure 10c)

Variable	Mean (Prior Expected Value)	Uncertainty (Prior Distribution Standard Deviation)	BPE MAP
$E_{a,1}(0)$	41,500 J mol^{-1}	20,000 J mol^{-1}	56,032
$E_{a,2}(0)$	41,500 J mol^{-1}	20,000 J mol^{-1}	46,907
$Log_{10}(A_1/s^{-1})$	13.00	2.00	10.70
$log_{10}(A_2/s^{-1})$	13.00	2.00	7.36
g_1	0.10	0.10	0.18
g_2	0.10	0.10	0.31
n_1/n_2	N/A	N/A	0.833

It was also investigated what would happen during BPE if the more strongly bound state had a higher zero coverage activation energy, such that $<E_{a,1}(0)> = <E_{a,2}(0)> + 20,000$ J mol^{-1} (based on the position of the > 300 K shoulder and typical peak temperatures[1]). The simulated TPD spectrum using that BPE MAP was nearly the same as that in Figure 10c, and was not significantly closer to the observed data.

The CPE point estimate values corresponding to Figure 10b are provided in Table S2 and were obtained using the Nelder-Mead method.

Table S2: CPE Point Estimate Values (Corresponding to Figure 10b)

Variable	Mean (Prior Expected Value)	CPE Point Estimate (Based on Weighted Fit)
$E_{a,1}(0)$	41,500 J mol^{-1}	52,596 J mol^{-1}
$E_{a,2}(0)$	61,500 J mol^{-1}	3,520 J mol^{-1}
$log_{10}(A_1/s^{-1})$	13.00	10.02
$log_{10}(A_2/s^{-1})$	13.00	-0.67
g_1	0.10	0.19
g_2	0.10	-0.44
n_1/n_2	N/A	1.36

II. Additional Conceptual Explanation of Figure 11 from the Main Text

Figure 11 from the main text is reproduced below as Figure S1. Panel **a** corresponds to a two dimensional area of the parameter space for the first adsorbate state, A_1 vs. $E_{a,1}$; Panel **b** corresponds to a two dimensional area of the parameters space for the second adsorbate state, A_2 vs. $E_{a,2}$. The green and orange points near the centers of the corresponding shapes represent the final point estimates of parameters for CPE and for BPE, and are tabulated in the Supporting Information. Note that a "point estimate" refers to a vector of discrete values (one value for each kinetic parameter), thus the orange point in Panel A is the same point as the orange point in Panel B: these two points are the same point (they represent the same set of parameter values) with the two panels showing views from different angles in the parameter space hypercube. Isolines are shown to display the qualitative shape from the conventional parameter optimization objective function response surface (green) and the Bayesian a-posterior distribution (orange). The isolines are two dimensional slices holding all other variables constant: the orange regions surrounding the BPE point estimate thus represent two-dimensional slices from the HPD region located around the MAP, and the green areas similarly represent slices from a multidimensional peak in the CPE parameter hyperspace.
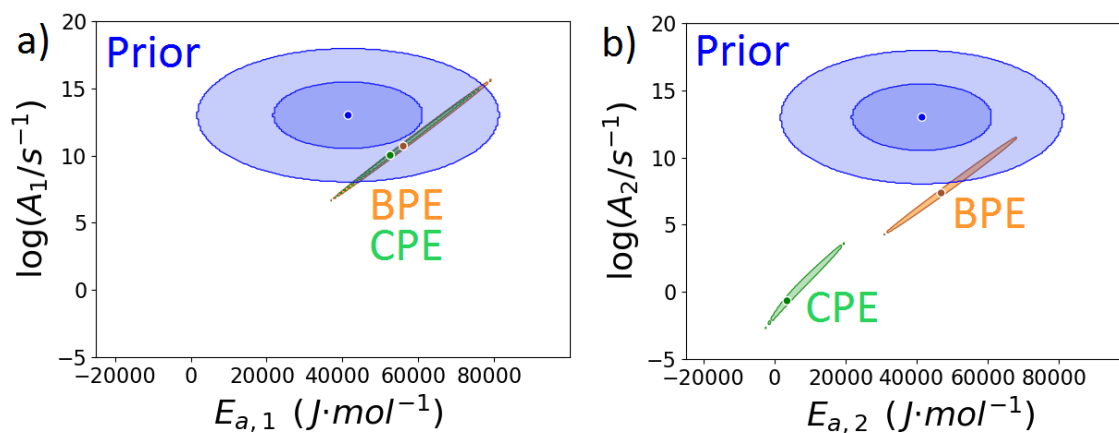

Figure S1. Plots of the point estimates and two dimensional slices (in the context of kinetic parameter estimates from the data in Figure 10) related to the Priors, BPE, and CPE for the parameter space for the first adsorbate state, A_1 vs. $E_{a,1}$ (Panel a) and for the second adsorbate state, A_2 vs. $E_{a,2}$ (Panel b). The vertical axes are log base 10. The shaded regions indicate the shapes associated with two dimensional slices of the response surface of the CPE and of the HPD region of the BPE. The regions associated with the priors are considered to be more physically realistic within the model's assumptions (based on existing knowledge), with the expectation of a 95% chance that the true values will fall within the outer blue ovals (if the model is correct).

References for Supporting Information:

1.   Masel, R. I., *Principles of Adsorption and Reaction on Solid Surfaces*. Wiley: New York, 1996; p xiv, 804.