CO desorption from a catalytic surface: Elucidation of the role of steps by velocity-selected residence time measurements

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Kinetic modeling of desorption rates

For a first-order desorption kinetic assumption, the change of the number of adsorbed molecules, N_{ad}, per surface area is given by Eq. (S1):

$$\frac{\mathrm{d}N_{\mathrm{ad}}(t)}{\mathrm{d}t} = \Phi_i(t) - k_d(T_S)N_{\mathrm{ad}}(t) \tag{S1}$$

where $\Phi_i(t)$ is the time dependent flux of molecules approaching the surface, modeled by the sum of two Gaussian functions (Eq. (S2)) obtained from a measurement at $T_S = 973$ K:

$$\Phi_i(t) = A_1\mathrm{e}^{-(t-t_1)^2/w_1^2} + A_2\mathrm{e}^{-(t-t_2)^2/w_2^2} \tag{S2}$$

The number of molecules leaving the surface in a time interval $t \dots t + \mathrm{d}t$ is given by the number of adsorbed molecules, $N_{\mathrm{ad}}(t)$, at time t multiplied with the rate constant, k_d, for desorption. We obtain the analytical expression (Eq. (S3)) for $N_{\mathrm{ad}}(t)$ by integration of Eq. (S1) for $N_{\mathrm{ad}}(0) = 0$.

$$\begin{aligned} N_{\mathrm{ad}}(t) = \mathrm{e}^{-k_d t}\sqrt{\frac{\pi}{2}}\Bigg(& A_1\mathrm{e}^{k_d\, t_1+\frac{k_d^2 w_1^2}{2}}\, w_1 \mathrm{Erf}\left(\frac{t_1 + k_d w_1^2}{\sqrt{2}\, w_1}\right) \\ & - A_1\mathrm{e}^{k_d\, t_1+\frac{k_d^2 w_1^2}{2}}\, w_1 \mathrm{Erf}\left(\frac{-t + t_1 + k_d\, w_1^2}{\sqrt{2}\, w_1}\right) \\ & + A_2\mathrm{e}^{k_d\, t_2+\frac{k_d^2 w_2^2}{2}}\, w_2 \mathrm{Erf}\left(\frac{t_2 + k_d w_2^2}{\sqrt{2}\, w_2}\right) \\ & - A_2\mathrm{e}^{k_d t_2+\frac{k_d^2 w_2^2}{2}}\, w_2 \mathrm{Erf}\left(\frac{-t + t_2 + k_d w_2^2}{\sqrt{2}\, w_2}\right)\Bigg) \end{aligned} \tag{S3}$$

Since the sticking probability is not unity, we add a direct scattering contribution with zero residence time to the flux of molecules leaving the surface (Eq. (S4)). The two additional factors B_{DS} and B_{TD} are used to scale the model to the signal size observed in the experiment.

$$\Phi_d(t, T_S) = \underbrace{B_{\mathrm{DS}}\,\Phi_i(t)}_{\text{direct scattering}} + \underbrace{B_{\mathrm{TD}}\,k_d(T_S)\,N_{\mathrm{ad}}(t)}_{\text{desorption}} \tag{S4}$$

For the observation of bi-exponential desorption kinetics, Eq. (S4) changes to Eq. (S5):

$$\Phi_d(t, T_S) = \underbrace{B_{\mathrm{DS}}\Phi_i(t)}_{\text{direct scattering}} + \underbrace{B_{\mathrm{TD}}^{\mathrm{fast}} k_d^{\mathrm{fast}}(T_S) N_{\mathrm{ad}}^{(1)}(t)}_{\text{fast desorption}} + \underbrace{B_{\mathrm{TD}}^{\mathrm{slow}} k_d^{\mathrm{slow}}(T_S) N_{\mathrm{ad}}^{(2)}(t)}_{\text{slow desorption}} \tag{S5}$$

The model now contains two different rate constants, $k_d^{\mathrm{fast}}(T_S)$ and $k_d^{\mathrm{slow}}(T_S)$, as well as two different kinds of adsorbates, $N_{\mathrm{ad}}^{(1)}(t)$ and $N_{\mathrm{ad}}^{(2)}(t)$. Their time dependent population is given by Eq. (S6) and Eq. (S7), respectively:

$$\begin{aligned} &N_{\mathrm{ad}}^{(1)}(t) \\ &= \mathrm{e}^{-k_d^{\mathrm{fast}} t}\sqrt{\frac{\pi}{2}}\left(A_1 e^{k_d^{\mathrm{fast}}\, t_1 + \frac{\left(k_d^{\mathrm{fast}}\right)^2 w_1^2}{2}}\, w_1 \mathrm{Erf}\left(\frac{t_1 + k_d^{\mathrm{fast}} w_1^2}{\sqrt{2}\, w_1}\right)\right. \\ &- A_1 \mathrm{e}^{k_d^{\mathrm{fast}}\, t_1 + \frac{\left(k_d^{\mathrm{fast}}\right)^2 w_1^2}{2}}\, w_1 \mathrm{Erf}\left(\frac{-t + t_1 + k_d^{\mathrm{fast}}\, w_1^2}{\sqrt{2}\, w_1}\right) \\ &+ A_2 \mathrm{e}^{k_d^{\mathrm{fast}}\, t_2 + \frac{\left(k_d^{\mathrm{fast}}\right)^2 w_2^2}{2}}\, w_2 \mathrm{Erf}\left(\frac{t_2 + k_d^{\mathrm{fast}} w_2^2}{\sqrt{2}\, w_2}\right) \\ &\left.- A_2 \mathrm{e}^{k_d^{\mathrm{fast}} t_2 + \frac{\left(k_d^{\mathrm{fast}}\right)^2 w_2^2}{2}}\, w_2 \mathrm{Erf}\left(\frac{-t + t_2 + k_d^{\mathrm{fast}} w_2^2}{\sqrt{2}\, w_2}\right)\right) \end{aligned} \tag{S6}$$

$$\begin{aligned} &N_{\mathrm{ad}}^{(2)}(t) \\ &= \mathrm{e}^{-k_d^{\mathrm{slow}} t}\sqrt{\frac{\pi}{2}}\left(A_1 e^{k_d^{\mathrm{slow}}\, t_1 + \frac{\left(k_d^{\mathrm{slow}}\right)^2 w_1^2}{2}}\, w_1 \mathrm{Erf}\left(\frac{t_1 + k_d^{\mathrm{slow}} w_1^2}{\sqrt{2}\, w_1}\right)\right. \\ &- A_1 \mathrm{e}^{k_d^{\mathrm{slow}}\, t_1 + \frac{\left(k_d^{\mathrm{slow}}\right)^2 w_1^2}{2}}\, w_1 \mathrm{Erf}\left(\frac{-t + t_1 + k_d^{\mathrm{slow}}\, w_1^2}{\sqrt{2}\, w_1}\right) \\ &+ A_2 \mathrm{e}^{k_d^{\mathrm{slow}}\, t_2 + \frac{\left(k_d^{\mathrm{slow}}\right)^2 w_2^2}{2}}\, w_2 \mathrm{Erf}\left(\frac{t_2 + k_d^{\mathrm{slow}} w_2^2}{\sqrt{2}\, w_2}\right) \\ &\left.- A_2 \mathrm{e}^{k_d^{\mathrm{slow}} t_2 + \frac{\left(k_d^{\mathrm{slow}}\right)^2 w_2^2}{2}}\, w_2 \mathrm{Erf}\left(\frac{-t + t_2 + k_d^{\mathrm{slow}} w_2^2}{\sqrt{2}\, w_2}\right)\right) \end{aligned} \tag{S7}$$