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, \( N_{\text{ad}} \), per surface area is given by Eq. (S1):

\[
\frac{dN_{\text{ad}}(t)}{dt} = \Phi_t(t) - k_d(T_S)N_{\text{ad}}(t) \tag{S1}
\]

where \( \Phi_t(t) \) 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:

\[
\Phi_t(t) = A_1e^{-(t-t_1)^2/\sigma_1^2} + A_2e^{-(t-t_2)^2/\sigma_2^2} \tag{S2}
\]

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

\[
N_{\text{ad}}(t) = e^{-k_d t} \sqrt{\frac{\pi}{2}} \left( A_1e^{k_d t_1 + k_d^2\sigma_1^2/2}w_1 \text{Erf} \left( \frac{t_1 + k_d w_1^2}{\sqrt{2} w_1} \right) - A_1e^{k_d t_1 + k_d^2\sigma_1^2/2}w_1 \text{Erf} \left( \frac{-t + t_1 + k_d w_1^2}{\sqrt{2} w_1} \right) + A_2e^{k_d t_2 + k_d^2\sigma_2^2/2}w_2 \text{Erf} \left( \frac{t_2 + k_d w_2^2}{\sqrt{2} w_2} \right) - A_2e^{k_d t_2 + k_d^2\sigma_2^2/2}w_2 \text{Erf} \left( \frac{-t + t_2 + k_d w_2^2}{\sqrt{2} w_2} \right) \right) \tag{S3}
\]
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.

$$\Phi_d(t, T_S) = \frac{B_{DS} \Phi_{d1}(t)}{\text{direct scattering}} + \frac{B_{TD} k_d(T_S) N_{ad}(t)}{\text{desorption}} \quad (S4)$$

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

$$\Phi_d(t, T_S) = \frac{B_{DS} \Phi_{d1}(t)}{\text{direct scattering}} + \frac{B_{TD} k_d^{\text{fast}}(T_S) N_{ad}^{(1)}(t)}{\text{fast desorption}} + \frac{B_{TD} k_d^{\text{slow}}(T_S) N_{ad}^{(2)}(t)}{\text{slow desorption}} \quad (S5)$$

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

$$N_{ad}^{(1)}(t) = e^{-k_d^{\text{fast}} t} \sqrt{\frac{\pi}{2}} A_1 e^{k_d^{\text{fast}} t_1 + \frac{(k_d^{\text{fast}})^2 w_1^2}{2}} w_1 \text{Erf}\left(\frac{t_1 + k_d^{\text{fast}} w_1^2}{\sqrt{2} w_1}\right) - A_1 e^{k_d^{\text{fast}} t_1 + \frac{(k_d^{\text{fast}})^2 w_1^2}{2}} w_1 \text{Erf}\left(-t + t_1 + k_d^{\text{fast}} w_1^2\right) + A_2 e^{k_d^{\text{fast}} t_2 + \frac{(k_d^{\text{fast}})^2 w_2^2}{2}} w_2 \text{Erf}\left(\frac{t_2 + k_d^{\text{fast}} w_2^2}{\sqrt{2} w_2}\right) - A_2 e^{k_d^{\text{fast}} t_2 + \frac{(k_d^{\text{fast}})^2 w_2^2}{2}} w_2 \text{Erf}\left(-t + t_2 + k_d^{\text{fast}} w_2^2\right) \quad (S6)$$

$$N_{ad}^{(2)}(t) = e^{-k_d^{\text{slow}} t} \sqrt{\frac{\pi}{2}} A_1 e^{k_d^{\text{slow}} t_1 + \frac{(k_d^{\text{slow}})^2 w_1^2}{2}} w_1 \text{Erf}\left(\frac{t_1 + k_d^{\text{slow}} w_1^2}{\sqrt{2} w_1}\right) - A_1 e^{k_d^{\text{slow}} t_1 + \frac{(k_d^{\text{slow}})^2 w_1^2}{2}} w_1 \text{Erf}\left(-t + t_1 + k_d^{\text{slow}} w_1^2\right) + A_2 e^{k_d^{\text{slow}} t_2 + \frac{(k_d^{\text{slow}})^2 w_2^2}{2}} w_2 \text{Erf}\left(\frac{t_2 + k_d^{\text{slow}} w_2^2}{\sqrt{2} w_2}\right) - A_2 e^{k_d^{\text{slow}} t_2 + \frac{(k_d^{\text{slow}})^2 w_2^2}{2}} w_2 \text{Erf}\left(-t + t_2 + k_d^{\text{slow}} w_2^2\right) \quad (S7)$$