Mechanistic and microkinetic analysis of CO_2 hydrogenation on ceria: Electronic Supplementary Information

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1 Reaction Equilibrium and Rate Equations

For the COOH route, we can write the set of equilibrium and rate expressions as follows (based on Figure 1):

$$
\begin{aligned}
\theta_{CO_2^*} &= K_1 P_{CO_2} \theta_* \\
\theta_{H^*} &= \sqrt{K_{21} P_{H_2}}\, \theta_* \\
r_2 &= k_{f,2} \theta_{CO_2^*} \theta_{H^*} - k_{r,2} \theta_{COOH^*} \theta_* \\
r_3 &= k_{f,3} \theta_{COOH^*} \theta_* - k_{r,3} \theta_{CO^*} \theta_{OH^*} \\
r_7 &= k_{f,7} \theta_{CO^*} \theta_{H^*} - k_{r,7} \theta_{HCO^*} \theta_* \\
r_8 &= k_{f,8} \theta_{HCO^*} \theta_{H^*} - k_{r,8} \theta_{HCOH^*} \theta_* \\
r_9 &= k_{f,9} \theta_{HCOH^*} \theta_{H^*} - k_{r,9} \theta_{H_2COH^*} \theta_* \\
r_{10} &= k_{f,10} \theta_{H_2COH^*} \theta_{H^*} - k_{r,10} \theta_{H_3COH^*} \theta_* \\
r_{19} &= k_{f,19} \theta_{H^*} \theta_{OH^*} - k_{r,19} \theta_{H_2O^*} \theta_* \\
\theta_{CH_3OH^*} &= \frac{P_{CH_3OH} \theta_*}{K_{18}} \\
\theta_{H^*} &= \frac{P_{H_2O} \theta_*}{K_{20}}
\end{aligned}
$$

Since r_9 is the rate-limiting step, all other reaction steps are assumed to follow the pseudo steady state hypothesis. Thus, we can write $r_2 = r_3 = r_7 = r_8 = r_{10} = r_{19} = 0$ and $K_i = \frac{k_{f,i}}{k_{r,i}}$.

From the mass conservation law, we can write:

$$
\theta_{CO_2^*} + \theta_{H^*} + \theta_{COOH^*} + \theta_{CO^*} + \theta_{OH^*} + \theta_{HCO^*} + \theta_{HCOH^*} + \theta_{H_2COH^*} + \theta_{H_3COH^*} + \theta_{H_2O^*} + \theta_* = 1
$$

According to the equations above, we thus derive:

$$
\begin{aligned}
\theta_* = {} & 1/\Big(1 + K_1 P_{CO_2} + \sqrt{K_{21} P_{H_2}} + K_1 K_2 P_{CO_2} \sqrt{K_{21} P_{H_2}} + K_1 K_2 K_3 P_{CO_2} \sqrt{K_{21} P_{H_2}} \\
& + \frac{K_{18} P_{CH_3OH}}{K_{10} \sqrt{K_{21} P_{H_2}}} + \frac{K_{18} P_{CH_3OH}}{K_{21} K_8 K_9 K_{10} \sqrt{K_{21} P_{H_2}}} + \frac{K_{18} P_{CH_3OH}}{K_{21} K_9 K_{10} P_{H_2}} \\
& + \frac{K_{18} P_{CH_3OH}}{(K_{21})^2 K_7 K_8 K_9 K_{10} K_{19} \left(P_{H_2}\right)^2} + \frac{P_{CH_3OH}}{K_{18}} + \frac{P_{H_2O}}{K_{20}}\Big)
\end{aligned}
$$

Thus, we can calculate the TOF of the COOH route, based on the rate-limiting step:

$$
r_9 = k_{f,9} \left(K_1 K_2 K_3 P_{CO_2} \sqrt{K_{21} P_{H_2}}\right) \sqrt{K_{21} P_{H_2}}\, \theta_* - k_{r,9} \left\{ \frac{P_{CH_3OH} \theta_*}{\left[(K_{21})^2 K_7 K_8 K_9 K_{10} K_{19} \left(P_{H_2}\right)^2\right]} \right\} \left(\frac{P_{H_2O} \theta_*}{K_{20}}\right)
$$

All $k_{f,i}$ and $k_{r,i}$ can be obtained from TST, as described in the manuscript. P_{H_2O}, P_{CH_3OH}, P_{H_2}, and P_{CO_2} are calculated assuming that the conversion is 0.052 (as obtained from the van't Hoff equation when P_{H_2}:P_{CO_2} = 1:1), and the total pressure, $P \in \{1, 10, 50, 100\}$ atm.

Similar expressions can thus be derived for the HCOO route.

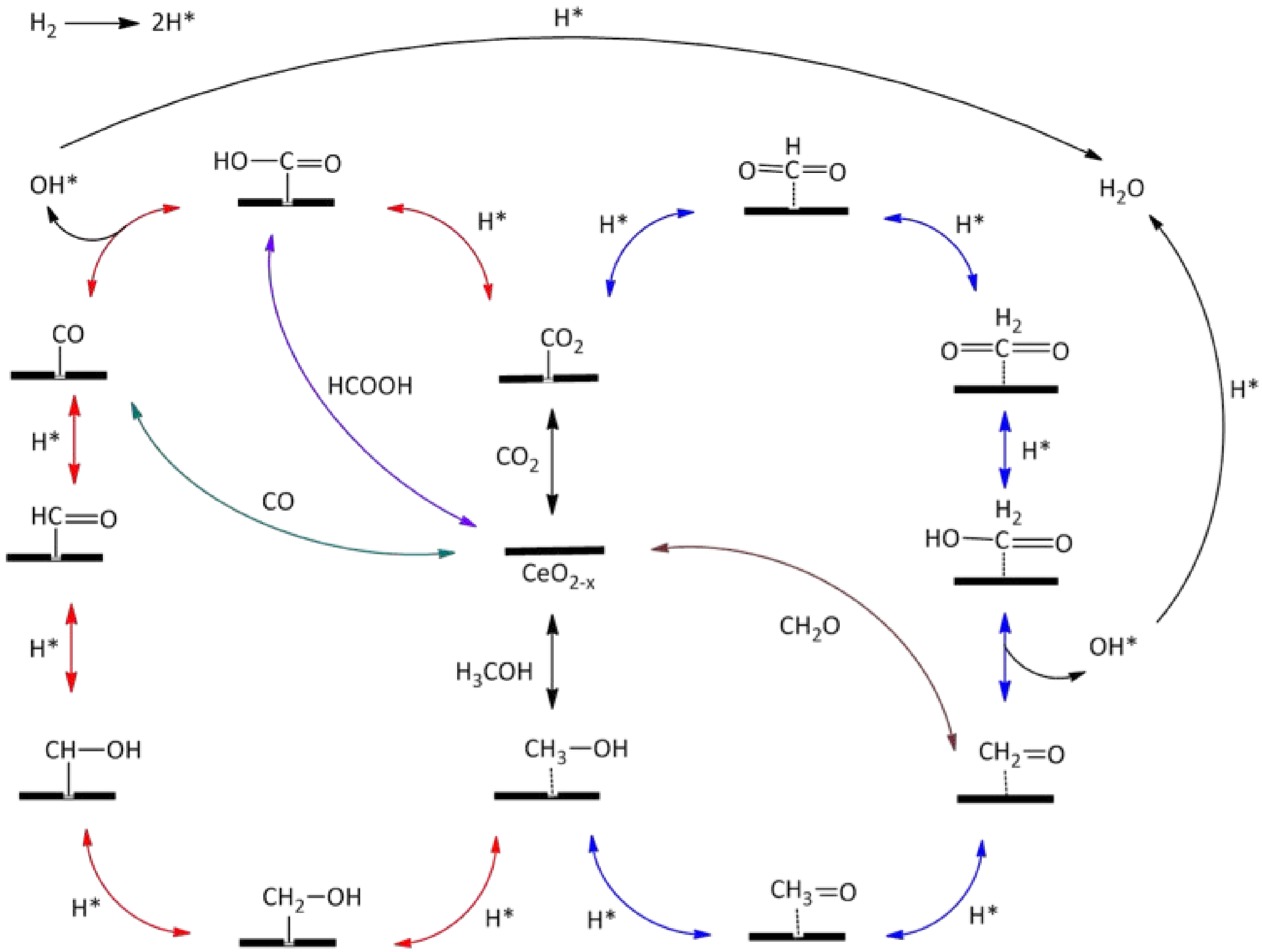

Figure 1 Reaction network for CO_2 hydrogenation on reduced ceria (110)