Epoxidation of propene using Au/TiO_2: on the difference between H_2 and CO as co-reactant

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1 Mass transfer limitations

1.1 Internal diffusion: *Weisz-Prater Criterion*

The absence of internal mass transfer limitations was evaluated using the Weisz-Prater criterion [1], where if C_{WP} is lower than 1, the internal mass transfer effects can be neglected:

$$C_{WP} = \frac{-r'_{A,Obs}\rho_c R^2}{D_e C_{AS}} < 1 \qquad \text{(S.1)}$$

$-r'_{A,Obs}$, Observed reaction rate = $2.25 \cdot 10^{-7}$ kmol/kg_{cat}/sec (taking the maximum PO rate found)

ρ_c, Solid density of catalyst = 350 kg/m^3

R, Particle size = 25 µm = $2.5 \cdot 10^{-5}$ m

C_{AS}, Concentration of reactant A on surface. A = Propene. Considering 10 vol% propene,

C_{AS} = $4 \cdot 10^{-3}$ kmol/m^3

D_e, effective diffusity given by:

$$D_e = \frac{D_{AB}\varepsilon_p\sigma_c}{\tau} \qquad \text{(S.2)}$$

D_{AB}, Gas-phase diffusivity. D_{AB} for a mixture of C_3H_6-He was calculated [2] to be $8.75 \cdot 10^{-5}$ m^2/s

ε_p, Pellet porosity = 0.4,

σ_c, Constriction factor = 0.8,

τ, Tortuosity = 3.

D_e = $9.33 * 10^{-6}$ m^2/s

Putting the above values in S.1,

$$C_{WP,PO} = \frac{(2.25 \cdot 10^{-7}).(3.5 \cdot 10^{2}).(25 \cdot 10^{-6})^{2}}{(9.33 \cdot 10^{-6}) \cdot (1.6 \cdot 10^{-2})} = 3.29 \cdot 10^{-7} \ll 1$$

Therefore, this system does not suffer from internal mass transfer limitations.

1.2 External Diffusion: *Mears Criterion*

The absence of external mass transfer limitations can be evaluated using the Mears criterion [1]:

$$C_M = \frac{-r_{A,}^{'} \rho_b R n}{k_c C_{Ab}} < 0.15 \qquad \text{(S.3)}$$

$-r_{A,Obs}^{'}$, Observed reaction rate = $2.25 \cdot 10^{-7}$ kmol/kg_{cat}/sec

ρ_b, bulk density of the catalyst bed = 350 kg·m-3

R, Particle size = 25 µm = $2.5 \cdot 10^{-5}$ m

n , reaction order = 1

C_{Ab}, Bulk of propene. If C3H6 = 10 vol. %,

C_{AS} = $4 \cdot 10^{-3}$ kmol/m^3

k_c mass transfer coefficient = 0.089 $m.s^{-1}$

k_c was calculated from the Sherwood number using the correlation from Perry's Handbook [2]:

$$\frac{k_c d_p}{D_A} = 0.91 \cdot 91 \cdot Re^{0.49}.Sc^{1/3} \qquad \text{(S.4)}$$

Putting the values together we get:

$$C_M = \frac{(2.25 \cdot 10^{-7}).(3.5 \cdot 10^{2}).(25 \cdot 10^{-6}) \cdot 1}{(0.089) \cdot (1.6 \cdot 10^{-2})} = 1.38 \cdot 10^{-6} \ll 0.15$$

It can thus be concluded that the system does not suffer from external mass transfer limitations.

2. Yield calculation with and without CO_2 in $CO/O_2/C_3H_6$ case

The yield was calculated by two methods to justify the assumption that CO2 is mainly formed from CO oxidation. As observed in Fig S.1, they are quite close. When CO_2 is not considered, the values are slightly more (by ~3%), as expected; this could indicate that a small part of propene (via PO) is converted to CO_2. This is also evidenced in SSITKA. Due to the negligible difference, the assumption is well justified.

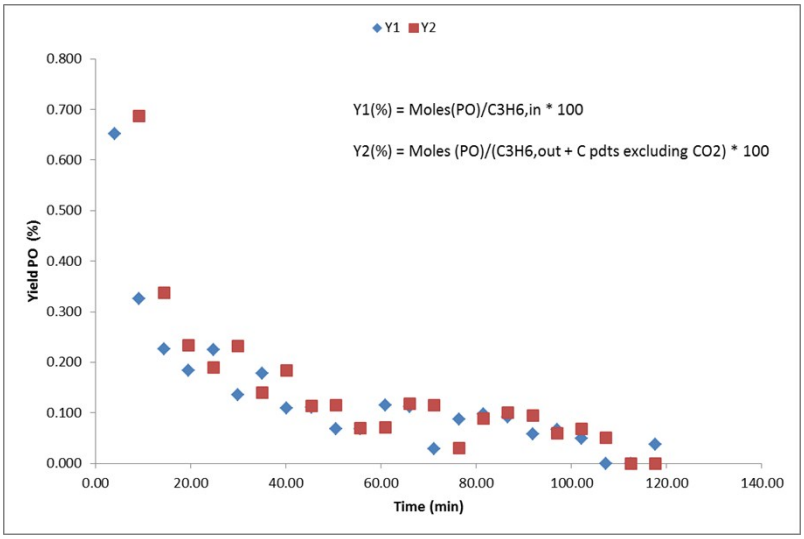

Figure S.1 Yield calculated by two different methods

3. Catalytic activity of 2%Au/TiO_2

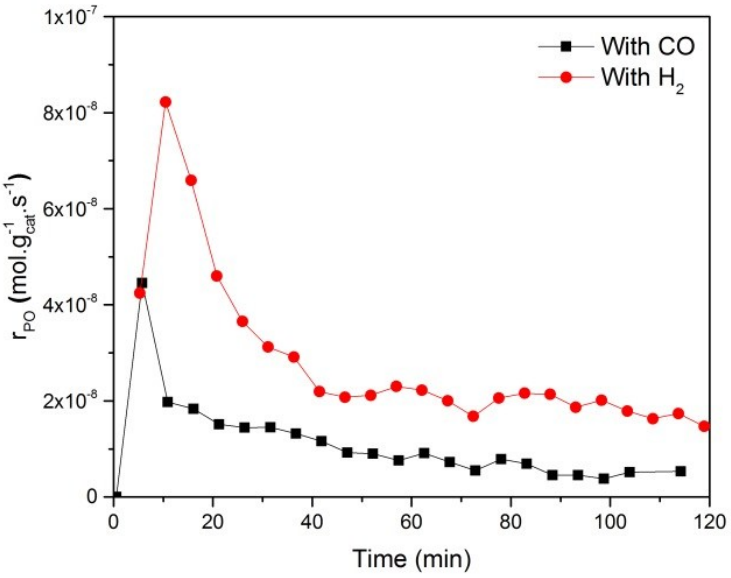

Figure S.2 Time-on-stream formation rate of PO during a 2 h catalytic test over 2%Au/TiO_2-NM at $X/O_2/C_3H_6/He$ = 1:1:1:7, where X = CO (black box) and X = H_2 (red circles) at 50 °C, GHSV = 10000 mL g_{cat}^{-1} h^{-1}

4. Oxygen vacancy formation using H2 and CO

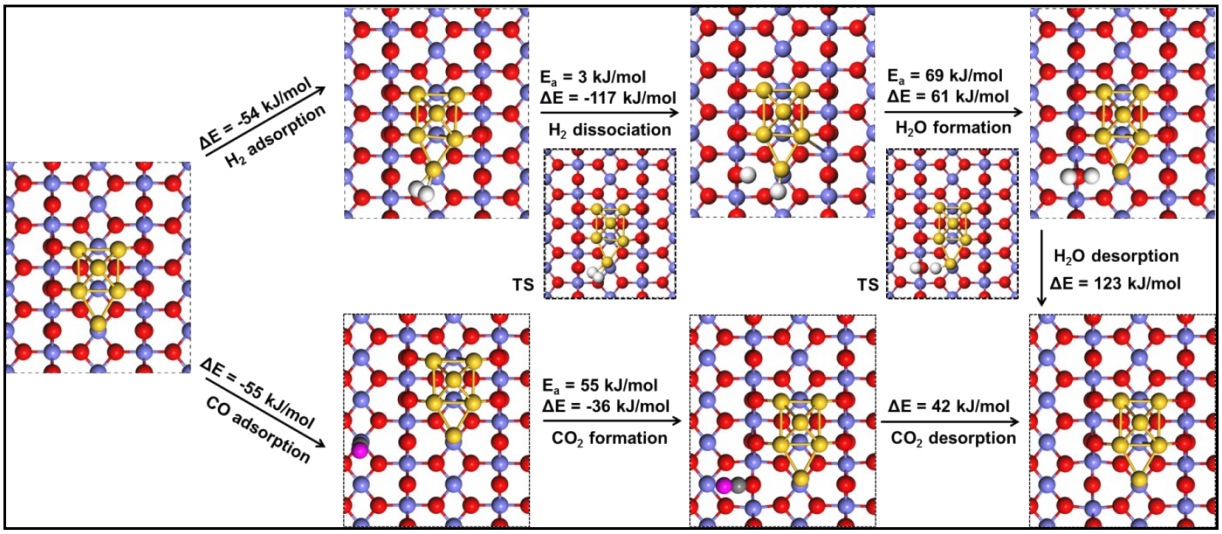

Figure S.3 Reaction energy diagram with elementary reaction steps for the oxygen vacancy creation using (a) H2 and (b) CO, via formation of water and CO_2 respectively

4. Transition states for PO formation

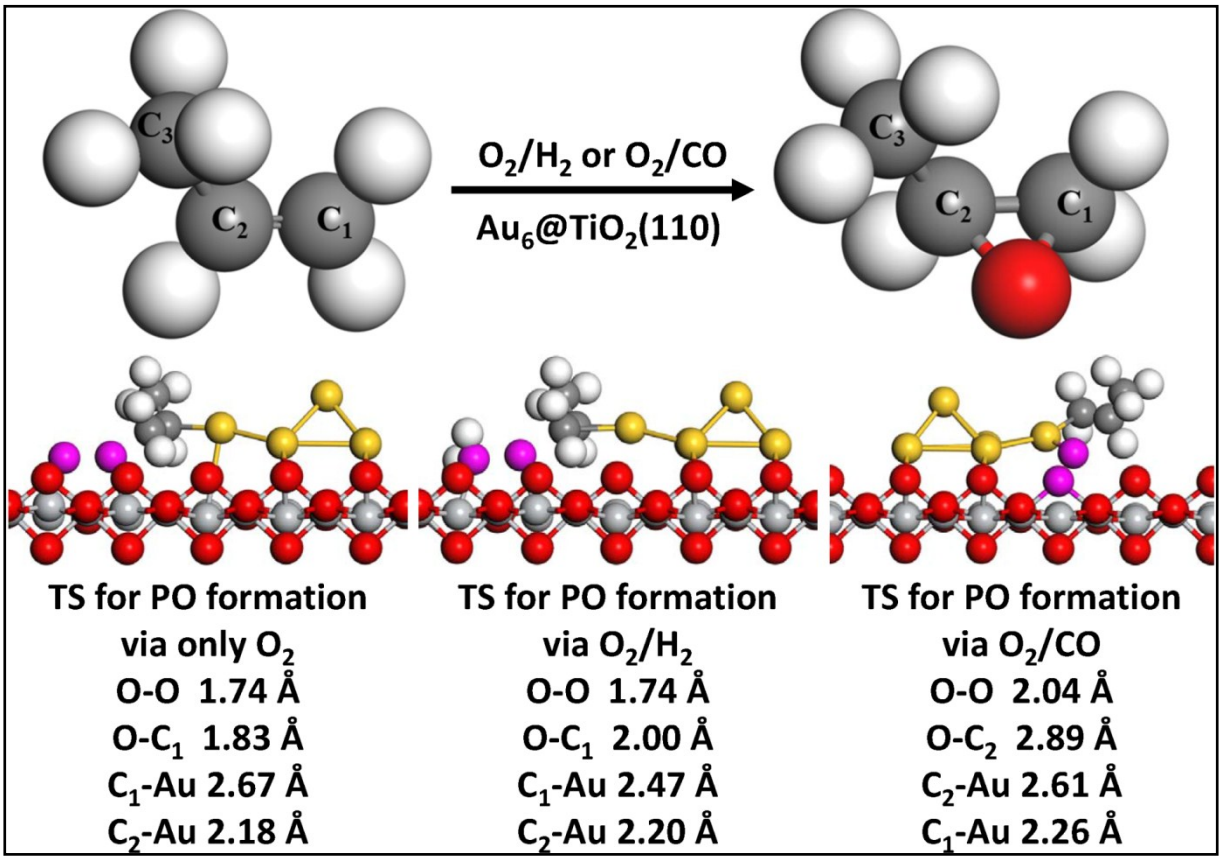

Figure S.4 Transition states for PO formation using (a) only O_2, (b) O_2/H_2 and (c) O_2/CO