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:

$$C_{WP} = \frac{-r_A'}{\rho_c R^2 D_e} C_{AS} < 1$$

$-r_A'$: Observed reaction rate = $2.25 \times 10^{-7}$ kmol/kg$_{cat}$/sec (taking the maximum PO rate found)

$\rho_c$: Solid density of catalyst = 350 kg/m$^3$

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

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

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

$D_e$: Effective diffusity given by:

$$D_e = \frac{D_{AB} \varepsilon_p \sigma_c}{\tau}$$

$D_{AB}$: Gas-phase diffusivity. $D_{AB}$ for a mixture of C$_3$H$_6$-He was calculated [2] to be $8.75 \times 10^{-5}$ m$^2$/s

$\varepsilon_p$: Pellet porosity = 0.4,

$\sigma_c$: Constriction factor = 0.8,

$\tau$: Tortuosity = 3.

$D_e = 9.33 \times 10^{-6}$ m$^2$/s
Putting the above values in S.1,

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

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]:

\[ C_M = \frac{-r_A \rho_b R n}{k_c C_{Ab}} < 0.15 \quad (S.3) \]

\(-r_A, \) Observed reaction rate = \(2.25 \cdot 10^{-7}\) kmol/kg\(_{cat}\)/sec

\(\rho_b, \) 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]:

\[ \frac{k_c d_p}{D_A} = 0.91 \cdot 91 \cdot Re^{0.49} \cdot Sc^{1/3} \quad (S.4) \]

Putting the values together we get:

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

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\(_3\)H\(_6\) 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 CO2 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 CO2. 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](image)

**Figure S.1** Yield calculated by two different methods

3. **Catalytic activity of 2%Au/TiO2**

![Graph of catalytic activity](image)
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$_{cat}$ 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 O₂, (b) O₂/H₂ and (c) O₂/CO.