Direct epoxidation of propene on silylated Au-Ti catalysts: A study on silylating procedures and effect on propane formation

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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 = $4.83 \cdot 10^{-7}$ 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,

$$C_{WP,PO} = \frac{(4.83 \cdot 10^{-7}).(3.5 \cdot 10^{2}).(25 \cdot 10^{-6})^2}{(9.33 \cdot 10^{-6}) \cdot (4.0 \cdot 10^{-2})} = 2.83 \cdot 10^{-7} \ll 1$$

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 = 4.83 · 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 · 10^{-5} m

n , reaction order = 1

C_{Ab}, 4 · 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]:

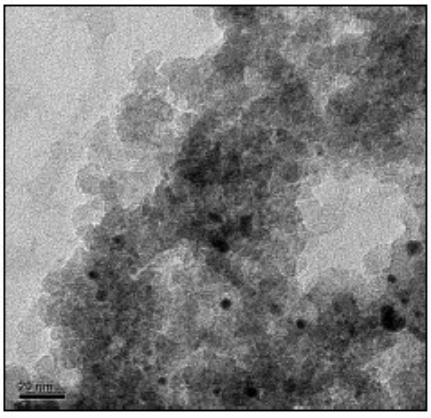
$$\frac{k_c d_p}{D_A} = 0.91 \cdot 91 \cdot Re^{0.49}.Sc^{1/3} \qquad \text{(S.4)}$$

Putting the values together we get:

$$C_M = \frac{(4.83 \cdot 10^{-7}).(3.5 \cdot 10^{2}).(25 \cdot 10^{-6}) \cdot 1}{(0.089) \cdot (4.0 \cdot 10^{-2})} = 1.18 \cdot 10^{-6} \ll 0.15$$

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

2. TEM of synthesized catalysts



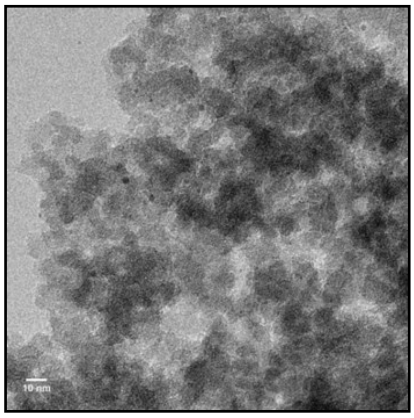
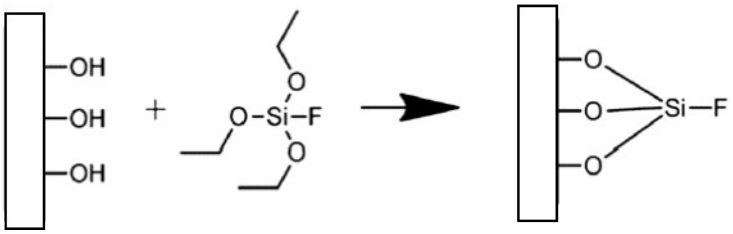


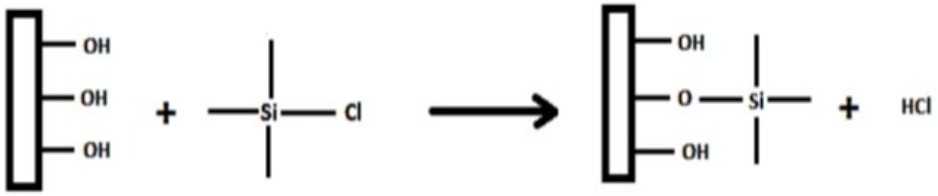
Figure S.1 TEM of Au(0.1)/Ti(1)SiO_2 (left) and Au(1)/Ti(5)SiO_2 (right)

3. Reactions using different silylating agents

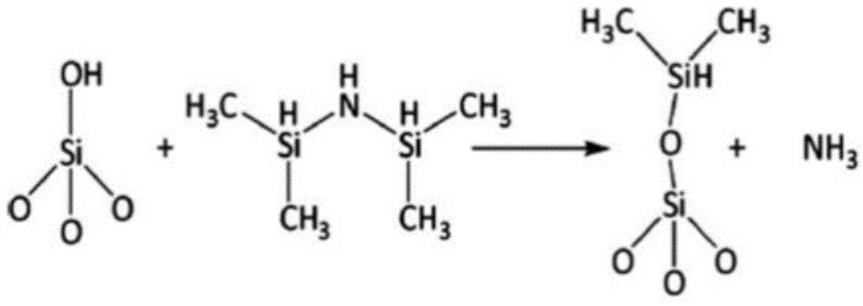
3.1 TEFS



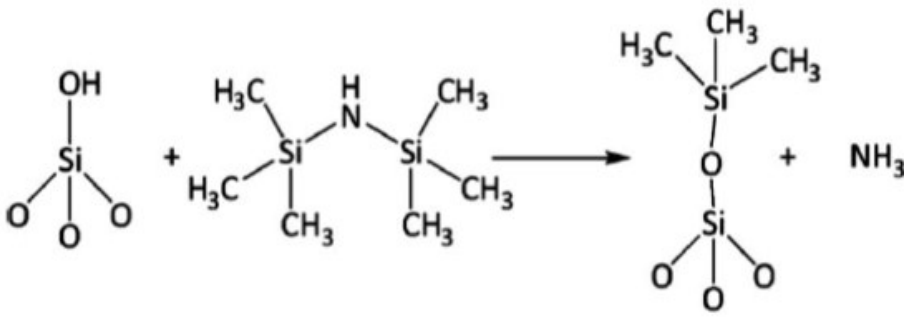
3.2 TMCS



3.3 TMDS



3.4 HMDS



4. Preliminary results

In the main text we note that liquid phase silylation procedures are not carried out on the Au loaded catalysts. This is because our initial results suggested that this led to in loss in catalytic activity as shown in Table S.1.

Table S.1: Performance of silylated and unsilylated catalysts[#]

Catalyst	**Unsilylated**	**Silylated (using TMCS in liquid phase)**
Conversion(%)	3.1	1.5
Selectivity to PO (%)	77	68
H_2 efficiency (%)	14	17
r_{PO} ($g_{PO}/kg_{cat}/h$)	71	29

[#] Reaction conditions: $H_2/O_2/C_3H_6/He$ = 1:1:1:7, Temp = 473 K, GHSV = 10000 $mL.g_{cat}^{-1}.h^{-1}$

References

[1] H.S. Fogler, Elements Of Chemical Reaction Engineering, Prentice Hall Professional Technical Reference, 2006.

[2] R. Perry, D. Green, Perry's Chemical Engineers' Handbook, Eighth Edition, McGraw-Hill Education, 2008.