Supplementary Materials

Liquid Phase Ethylene Epoxidation Over W-KIT-6 and Nb-KIT-6 Catalysts Using Hydrogen Peroxide as Oxidant

Wenjuan Yan[1, 2], Anand Ramanathan[1], Madhav Ghanta,[1,2,3] Bala Subramaniam[1, 2]*

[1]Center for Environmentally Beneficial Catalysis, Lawrence, Kansas 66047.

[2] Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045

[3]Currently with SABIC Innovative Plastics, Selkirk, NY 12158.

*To whom correspondence should be addressed. E-mail: bsubramaniam@ku.edu; Phone: 785-864-2903; Fax: 785-884-6051

Gas-liquid mass transfer limitations

At 50 bar and 35 °C, the volumetric mass transfer coefficient ($k_l a$) is estimated to be 0.0082 s^{-1} at a stirring rate of 1400 rpm.[1] The maximum concentration of H_2O_2 ($C_{H_2O_2}$) is taken as 3.56 mol/L. R_{EO} was estimated based on the EO formation rate as shown in Figure 1 (5.4×10^{-6} mol/L/s). The calculate value of α_1 is 1.83 (10^{-4}), which is significantly less than the empirical criterion for the elimination of mass transfer limitations shown in Eq. 1.

$$\alpha_1 = \frac{R_{EO}}{k_l a C_{H_2O_2}} < 0.1$$ Eq. 1

Liquid-solid mass transfer limitations

The Wilke-Change equation was used to estimate the diffusion coefficient of ethylene in MeOH, the dominant solvent in the reaction mixture.

$$D_{E-M} = \frac{7.4 \times 10^{-8} (\emptyset_M M_M)^{1/2} T}{\eta_M V_E^{0.6}}$$ Eq. 2

$\phi = 1.9$ for MeOH as solvent

The dimensionless groups (Schmidt number, Reynolds number, and Sherwood number) needed to calculate the mass transfer coefficient are estimated according to the following equations:

$$Sc = \frac{\nu_M}{D_{E-M}}$$ Eq. 3

$$Re = \frac{N d_{st}}{D_{E-M}}$$ Eq.4

$$Sh = 2 + 0.6Re^{1/2}Sc^{1/3}$$ Eq.5

$$Sh = \frac{k_s d_p}{D_{E-M}}$$ Eq.6

$$\alpha_2 = \frac{R_{EO}}{k_s a_p C_{H_2O_2}} = 3.0 \times 10^{-13}$$ Eq.7

The values of the various parameters are summarized in Table S1. Since $\alpha_2 << 0.1$, it is concluded that liquid-solid mass transfer limitations are insignificant.

Table S1. Summary of physical and transport properties for assessment of liquid-solid mass-transfer limitations

Parameter	**description**	**values**	**units**
$k_l a$	Volumetric mass transfer coefficient	0.0082	s^{-1}
$C_{H_2O_2}$	Initial liquid phase concentration of H_2O_2	3.56	mol L^{-1}
R_{EO}	Rate of reaction	5.4×10^{-6}	mol L^{-1} s^{-1}
α_1	Gas-liquid mass transfer resistance parameter	1.83×10^{-4}	--
D_{E-M}	Diffusion coefficient	1.8×10^{-5}	cm^2 s^{-1}
Sc	Schmidt number	352	--
Re	Reynolds number	56452	--
Sh	Sherwood number	1009	--
k_s	Mass-transfer coefficient	888	cm s^{-1}
α_2	Liquid-solid mass transfer resistance parameter	3.0×10^{-13}	--

Intraparticle mass transfer limitations

The extent of intraparticle mass transfer limitations is assessed by estimating the value of the Thiele Modulus. It is assumed that the epoxidation follows pseudo-first order kinetics (since initially, H_2O_2 is present in excess). Using the catalyst and transport properties listed in Table S2, the Thiele modulus is estimated according to Eq. 8.

$$\phi_{exp} = \frac{d_p}{6}\left[\frac{(n+1)\rho_p R_{EO}}{2D_e w C_{H_2O_2}}\right]^{1/2} = 0.001 < 0.2$$

Eq. 8

The estimated value of the Thiele modulus clearly suggests that intraparticle mass transfer limitations are insignificant at the investigated conditions.

Table S2. Summary of physical and transport properties required for assessment of intraparticle mass-transfer limitations

Parameter	**Description**	**Value**	**Units**
ε	Catalyst porosity	0.4	--
τ	Tortuosity	3	--
D_e	Effective diffusivity	$2.3*10^{-10}$	$m^2\ s^{-1}$
w	Catalyst loading density	0.015	$kg\ m^{-3}$
ϕ_{exp}	Thiele parameter	0.0011	--

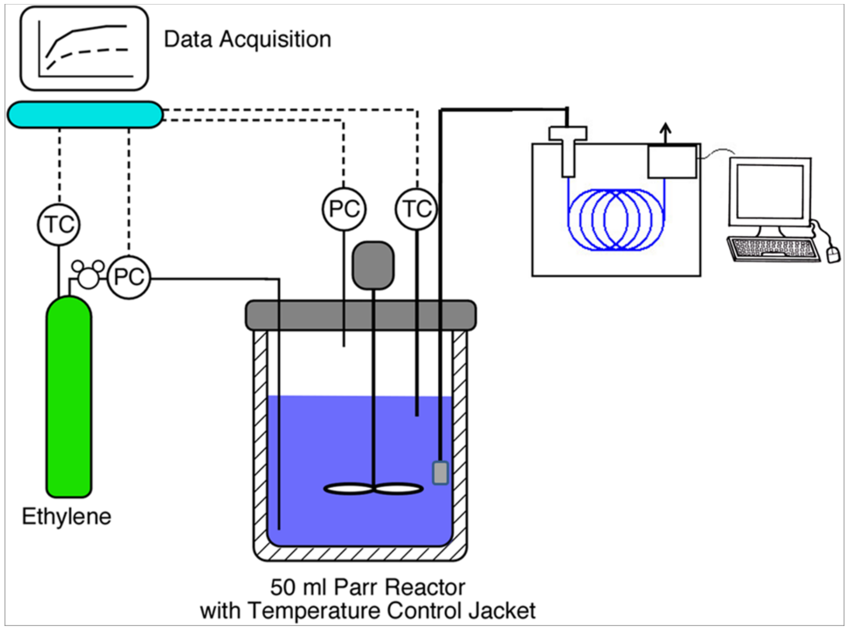

Figure S1. Schematic of experimental unit. [1]

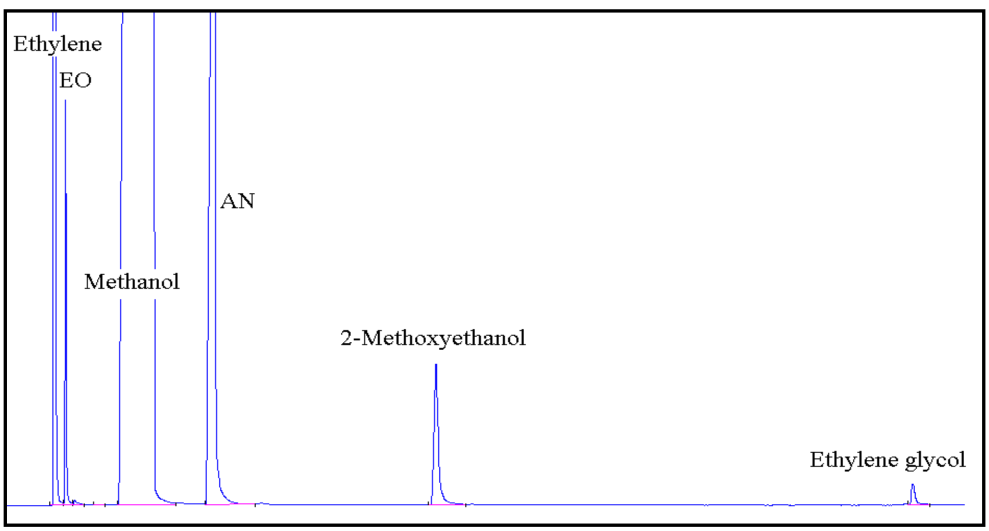

Figure S2. Sample GC/FID chromatogram of ethylene epoxidation reaction mixture showing various detected products.[1]

References

1. M. Ghanta, B. Subramaniam, H. J. Lee, and D. H. Busch, *AIChE J.*, 2013, **59**, 180–187.