

# Portfolio 07: Reaction mechanism and catalysis

CHEN3010/ CHEN5040: chemical reaction engineering

**Student ID:**

## General Instructions for take home Portfolios

1. The portfolio is an open-book task.
2. It is expected that you will complete the portfolio assessment on your own. You can use textbooks, the resources provided during class/ workshop etc. to answer the questions.
3. You are free to choose a solution technique. It is **not** required that you use the provided python code to answer the questions. You can use any tool (pen and paper, excel, ... ) and any technique (graphical, numerical, analytical) that you are comfortable with. However, some of the tasks will require use of coding/ computer.
4. The tasks will be a mix of theory questions, short calculation type and long numerical examples.
5. The portfolio tasks are not meant to take a lot of time. If you have understood and practiced the relevant content, it should take you around 2 to 3 hours at the most.
6. You are required to upload the portfolio answers on to blackboard:
  - Save your report as a **pdf** file (*Miri students should save it as a word file*).
  - Rename the file as STUDENTID\_Portfolio\_x.pdf (Where STUDENTID is your student ID, and x is the portfolio number) and
  - Upload it using assessment submission link on blackboard.

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# Introduction

Typically, an unpromoted, supported silver on  $\alpha$ -alumina catalyst reaches about 50% ethylene oxide (EO) selectivity. However, this selectivity can be significantly enhanced to around 90% with the addition of promoters like Cl, Cs, Re, Mo, Mn, and S (Pu et al. 2019).

Enhanced selectivity has a major implication in reducing CO<sub>2</sub> emissions as this process alone contribute about 9.3 million metric tons annually, making up 0.03% of global CO<sub>2</sub> emissions (Ghanta and Subramaniam 2017).

Understanding the different oxygen species that participate in both selective and unselective ethylene oxidation pathways is crucial for developing highly selective EO catalysts, which will improve economic efficiency and help reduce CO<sub>2</sub> emissions.

Recently, a team from Lehigh University has published study explaining the reaction mechanism for ethylene epoxidation by supported  $Ag/\alpha - Al_2O_3$  catalysts (Pu et al. 2024).

As a budding chemical engineer, you are tasked with understanding and summarizing the study for your manager. You are not expected to use AI tools for this assessment.

## Questions

1. Provide a summary of the study of Pu et al. (2024). Along with summary, your answer should address the following questions: (10 marks)
  - a. What were the different experimental techniques used in the study and how they were useful in understanding reaction mechanism, catalyst characterizing and/or testing?
  - b. How were the Density functional theory (DFT) calculations used in understanding kinetics?
  - c. What is the difference between Eley-Rideal and Langmuir-Hinshelwood kinetics?

2. Long term deactivation of the catalyst (10 marks)

Over period, catalyst deactivation occurs due to variety of reasons. Montrasi et al. (1983) studied activity of spent catalyst after 6 years of use in an industrial plant and compared it to that of a fresh catalyst. They reported a change in apparent activation energies.

For simplicity, we can divide the long term deactivation into three periods of catalyst activity (p1, p2, and p3). The relative activity of the catalyst in periods 2 and 3 to that in period 1 can be written as

$$r_{i,p2} = f_{i,p2}r_{i,p1} \quad r_{i,p3} = f_{i,p3}r_{i,p1} \quad (1)$$

$r_{i,p}$  is the rate of reaction  $i$  during period  $p$  (either reaction 1 or reaction 2).  $f_{i,p}$  is the deactivation factor for reaction  $i$  during period  $p$ . The values of  $f_i$  for reactions 1 and 2 (as described in portfolio 6) are as follows.

$$f_{1,p2} = 0.52; f_{1,p3} = 0.37; f_{2,p2} = 0.49; f_{2,p3} = 0.32 \quad (2)$$

Calculate the conversion, yield, and selectivity at the end of each period. You can adapt the code given in appendix for solving this question. Use all other data as provided in portfolio 6.

# Appendix

```
import numpy as np
from scipy.integrate import solve_ivp
import matplotlib.pyplot as plt

# constants

R = 8.314 # J/ (mol K)
RATM = 0.082 # atm dm3/ (mol K)
TRR = 523 # K

# Components
# 0: ethylene
# 1: oxygen
# 2: ethylene oxide
# 3: CO2
# 4: water
# 5: nitrogen

# Heats of formation at 298 K in J/mol
HF = np.array([-52470, 0, -52640, -393500, -285830, 0])

# Specific Heat Capacities J/mol K
CP = np.array([65, 30, 80, 45, 35, 30])

# reactions
# 0. C2H4 + 1/2 O2 -> C2H4O
# 1. C2H4 + 3O2 -> 2CO2 + 2H2O

# Stoichiometry
NU = np.array([
    [-1, -0.5, 1, 0, 0, 0], # Reaction 0: C2H4 + 0.5 O2 -> C2H4O
    [-1, -3, 0, 2, 2, 0] # Reaction 1: C2H4 + 3 O2 -> 2 CO2 + 2 H2O
])

# Adsorption constants (1/atm)
KEO, KE1 = 6.5, 4.33

# Heat of reaction at reference temperature J/mol
DELTA_HR_TR = np.dot(NU, HF)

# Functions

k0e = lambda t: 0.15 * np.exp((60700/R) * ((1/TRR) - (1/t)))
k1e = lambda t: 0.0888 * np.exp((73200/R) * ((1/TRR) - (1/t)))

# rates
r0e = lambda t, pe, po: k0e(t) * pe * po**0.58 / (1 + KEO*pe)**2
```

```

r1e = lambda t, pe, po: k1e(t) * pe * po**0.3 / (1 + KE1*pe)**2

def pbr(w,y,*args):

    # convert dependent variables
    f = y[:-1]
    t = y[-1]

    # convert args
    (pt, ua, ta) = args

    # total molar flow rate
    ft = np.sum(f)

    # mol fr.
    phi = f/ft

    # partial pressures
    p = pt * phi

    # extract partial pressure for ethylene and oxygen
    pe = p[0]
    po = p[1]

    # calculate reaction rates
    r0 = r0e(t,pe,po)
    r1 = r1e(t,pe,po)

    # Could also be written as an array
    # r = np.array([r1e(t,pe,po), r2e(t,pe,po)])

    # calculate rates of individual species
    r_e = -r0 -r1
    r_o = -0.5 * r0 - 3 * r1
    r_eo = r0
    r_co2 = 2 * r1
    r_h2o = 2 * r1
    r_n2 = 0

    # could also be written as
    # ri = np.dot(NU.T, r)

    # write mole balances
    # dfdw = ri

    df_e = r_e
    df_o = r_o
    df_eo = r_eo
    df_co2 = r_co2
    df_h2o = r_h2o

```

```

df_n2 = r_n2

# energy balance

delta_cp = np.dot(NU,CP)
delta_hr = DELTA_HR_TR + delta_cp * (t - 298)

# non-isothermal case
# replace dtdw with appropriate expression
qg = -r0 * delta_hr[0] - r1 * delta_hr[1]
qr = ua * (t - ta)

sum_fcp = np.sum(f * CP)

dtdw = (qg - qr)/sum_fcp

# dydw = np.append(dfdw,dtdw)
dydw = [df_e, df_o, df_eo, df_co2, df_h2o, df_n2, dtdw]

return dydw

# Problem data

# Heat transfer properties
ua = 300 # J/kg-cat s K

ta = 250 + 273.15 # k

# Inlet pressure and temperature
t0 = 250 + 273.15 # K
p0 = 2 # atm

# inlet flow rate mol/s
ft0 = 0.0093

# Inlet volume (mol) fraction
phi = np.array([0.06,0.12,0,0,0,0.82])

# Inlet molar flow rates for components mol/s
f0 = phi*ft0

# total catalyst weight kg
wcat = 0.1

# Differential equations
# 0: dF_e/dW
# 1: dF_o/dW
# 2: dF_eo/dW
# 3: dF_co2/dW

```

```

# 4: dF_h2o/dW
# 5: dF_n2/dW
# 6: dT/dW

initial_conditions = np.append(f0,t0)
args = (p0, ua, ta)

w_final = wcat

sol = solve_ivp(pbr,
                [0, w_final],
                initial_conditions,
                args=args,
                method='LSODA',
                dense_output=True)

# Extract solution

w = np.linspace(0,w_final, 1000)

# molar flow rate
f = sol.sol(w)[-1]

f_e = f[0]
f_o = f[1]
f_eo = f[2]
f_co2 = f[3]
f_h2o = f[4]
f_n2 = f[5]

# temperature
t = sol.sol(w)[-1]

# Calculate conversion, selectivity, max temperature etc. as required # after
# this point

x = 1 - f_e/f0[0]
sel = f_eo/f_co2

print (f'Final conversion: {x[-1]:.3f}; Final selectivity: {sel[-1]:.3f}\n')

plt.plot(w,x, label="Conversion")

plt.xlim(w[0],w[-1])
plt.ylim(0,1)
plt.grid()

plt.xlabel('Catalyst weight ($kg$)')
plt.ylabel('Conversion')

```

```
plt.show()
```

```
plt.plot(w,t, label="Temperature")
```

```
plt.xlim(w[0],w[-1])
```

```
plt.grid()
```

```
plt.xlabel('Catalyst weight ($kg$)')
```

```
plt.ylabel('Temperature')
```

```
plt.show()
```



## References

- Ghanta, Madhav, and Bala Subramaniam. 2017. "Development of a Sustainable and Economically Viable Process for Making Ethylene Oxide: A Case Study." In *Encyclopedia of Sustainable Technologies*, edited by Martin A. Abraham, 373–85. Oxford: Elsevier. <https://doi.org/10.1016/B978-0-12-409548-9.10085-5>.
- Montrasi, G. L., G. R. Tauszik, M. Solari, and G. Leofanti. 1983. "Oxidation of Ethylene to Ethylene Oxide: Catalyst Deactivation in an Industrial Run." *Applied Catalysis* 5 (3): 359–69. [https://doi.org/10.1016/0166-9834\(83\)80163-8](https://doi.org/10.1016/0166-9834(83)80163-8).
- Pu, Tiancheng, Adhika Setiawan, Alexandre C. Foucher, Mingyu Guo, Jih-Mirn Jehng, Minghui Zhu, Michael E. Ford, Eric A. Stach, Srinivas Rangarajan, and Israel E. Wachs. 2024. "Revealing the Nature of Active Oxygen Species and Reaction Mechanism of Ethylene Epoxidation by Supported Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Catalysts." *ACS Catalysis* 14 (1): 406–17. <https://doi.org/10.1021/acscatal.3c04361>.
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