Selection of carbon catalysts for the industrial manufacture of phosgene

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Acknowledgements

• The teams in the Huntsman laboratories in the Netherlands and Belgium

  Willem van der Borden
  Klaas van der Velde
  Mark Smit
  Remy Scheringa

  Khalid Ahrika

• Don Jones for the preparation of the Aspen Custom Model
Introduction

• Phosgene used industrially in the manufacture of polyurethanes, polycarbonates, pharmaceuticals and agrochemicals.

• Gas phase reaction of chlorine with an excess of carbon monoxide over an activated carbon catalyst

• Highly exothermic process with peak temperatures reaching over 500°C

• Issue with catalyst lives in different plants

• Focus on the evaluation of commercially available catalysts
  - Chemviron
  - Donau Carbon
  - DuPont
  - Norit
  - Pica
Reaction Thermodynamics

\[ \text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2 \quad \Delta H = -109.55 \text{kJ mol}^{-1} \quad \Delta S = -136.94 \text{J mol}^{-1} \text{K}^{-1} \]

- Thermodynamics limits conversion at high temperatures
Lab Scale Catalyst Testing

NRV-x = Non Return Valve
MFC-x = Mass Flow Controller
V-x = (Three-way) valve
TR = Temperature recording
PR = Pressure recording
PI = Pressure indicator
= Nitrogen (N₂)
= Chlorine (Cl₂)
= Carbon monoxide (CO)
= Mixture Cl₂/CO
= Phosgene/CO
= Phosgene/CO/N₂
= NaOH/H₂O (10% w/w)
= Scrubber fume exhaust

To fume hood

Oxygen & moisture trap

Oven

Mixing chamber

FTIR Gas cell

Polyurethanes
• Reaction “lights off” as temperature increases

• Comparison of catalysts at low temperature/conversion
Lab Scale Catalyst Testing

Measurement of Catalyst Activity

- Wide spread of catalyst activity is observed
- Synthetic carbon DuPont IPC shows significantly lower activity
Measurement of Catalyst Effectiveness Factor

- Effectiveness factor ($\eta$) measured using string of full size catalyst particles
- Approximates to a series of CSTRs at low conversion
- Direct comparison of same mass of full size particles and crushed catalyst
- Effective diffusivities within catalyst pores calculated from measured effectiveness factors
Characterisation of plant catalyst

Mercury porosimetry

- Increase in pores between 10 and 100nm in diameter
- Burn out of pores by oxidation
  - CTC or CO₂ formation (trace O₂ levels typically 50-500ppm in Cl₂)
Catalyst Oxidative Stability

Temperature Programmed Oxidation with 2500ppm O₂

- Temperature ramped to 575°C and held for 3 hours
- Temperature stepped down at 3 hour intervals – 550, 500, 450, 400, 350°C

100ml/min He
0.25 ml/min O₂
0.1g catalyst (250-300μm)
Oxidative Stability - 2

Temperature Programmed Oxidation with 2500ppm O₂

• All samples show Arrhenius behaviour – $E_{act} \sim 120-170\text{kJmol}^{-1}$

• Norit RX3extra and Donau Supersorbon K40 show lowest oxidation rates
2-D Phosgene Reactor Model

Aspen Custom Modeler

- Re-parameterised literature kinetics - from Potter and Baron (1951)

- Incorporates catalyst effectiveness (pore diffusion)

- Two parameter heat transfer model

- Correct physical properties

- Model structure provides flexibility in terms of bed configuration
  - length, tube and particle diameters, different catalysts etc
  - counter and co-current coolant flow
  - flow mal-distribution through different tubes
Phosgene Reactor Modelling

Prediction of axial temperature profile in lab reactor

- Excellent agreement between model and lab reactor data
Phosgene Reactor Modelling

Prediction of axial and radial temperature profile in plant reactor

Industrial Phosgene Reactor (WO03/72237)

- Reactor tube diameter: 39.3mm
- Number of tubes: 1256
- Catalyst bed length: 2.7m
- Phosgene production rate: 10000 kg/hr
- CO excess (bed inlet): 4.2%
- Inlet pressure: 4 bar.a
- Coolant temperature: 60°C
- Inlet gas temperature: 50°C

- Predicted peak temperature of 547°C (545°C observed)
Conclusions

• Have developed an approach for the evaluation of catalysts for phosgene manufacture

• A 2-dimensional reactor model has been developed to predict catalyst performance in industrial scale reactors
  - improved catalysts lives

• There are several areas for improvement
  - Improved kinetic description of catalysts especially at high conversion
  - Better data for validation
    Temperature profiles and exit chlorine concentrations
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