

Reaction Analysis for Fun and Profit: Case Studies in Industrial Reaction Engineering

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Highlights

- Model-based scale-up for a catalyst manufacturing process
- Inherent tube to tube variability in multi-tubular reactors with diluted catalysts
- A model for chloride response of ethylene oxide catalysts
- Reactor modeling with reaction and deactivation kinetics for evaluating process options

1. Introduction

Interesting Reaction Engineering problems abound in the industrial production of chemicals. Useful engineering analysis in this setting must generally answer the question “what short, medium and long term actions will enable more efficient production”, so analysis must produce actionable knowledge. Four industrial case studies will be presented including process scale-up, reactor trouble-shooting, management of catalyst deactivation and kinetic investigations for mechanistic inquiry.

3. Results and discussion

Process scale-up activities are sometimes driven by the available processing equipment or by a recipe approach rather than by engineering analysis. Scale-up of a hydrogenation catalyst made with H_2PtCl_6 precursor using a “recipe” approach was failing. Modeling the vendor’s activation process allowed us to establish that high concentrations of HCl during the reduction were causing Pt sintering. Subsequent model-based activation protocols allowed us to go from 0% to 100% success at each scale of catalyst production. In this case, understanding the impact of kinetics and contacting pattern on the process was critical to success.

Many catalytic partial oxidations are done in multi-tubular reactors where part of the catalyst bed is diluted with inert particles. Temperature profiles in these reactors often show tube-to-tube variability, which hurts production rates and selectivity. We wished to determine whether purely statistical phenomena associated with use of mixtures of active and inert pills could partly explain the tube to tube variability. We showed that for reactor designs and catalyst dilution schemes of commercial interest, these pure statistical effects can cause significant operational challenges, including partial runaways within a multi-tubular reactor (Figure 1). Using phthalic anhydride production from ortho-xylene as a case study, we have shown how to create a map of (reactor/catalyst) designs that are inherently stable to this purely statistical effect [1]. Here, creating a statistical framework for reactor analysis was the key to generating practical design guidelines.

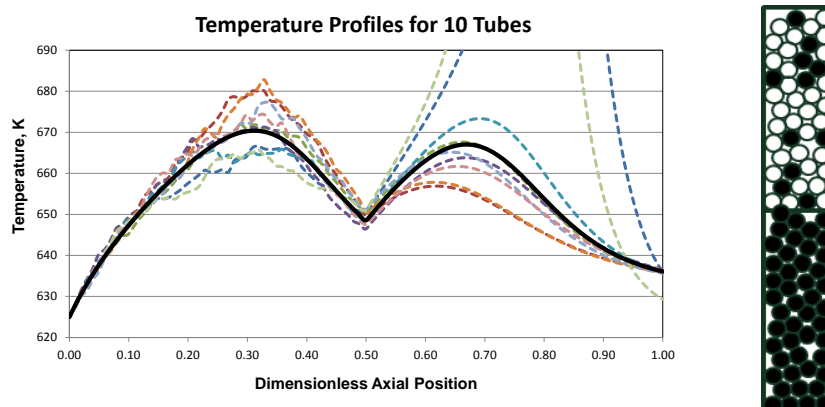


Figure 1. Simulated temperature profile for 10 tubes with random variability in the diluted zone

The kinetics and mechanism of Ethylene Oxide synthesis have proven to be remarkably complex. A critical part of commercial operation that is only partly addressed in the academic literature is the management of gas phase chloride promoter concentration to optimize the selectivity to ethylene oxide [2, 3]. Modern rhenium-promoted silver catalysts have very different chloride response than their Re-free predecessors. We find that recent, theoretically-based hypotheses suggesting that ethylene conversion to ethylene oxide (EO) and CO₂ proceeds through a common intermediate [4], along with evidence that chloride promotion decreases the activation energy for both reactions, but to differing degrees [5], can explain the observed chloride effects on both catalyst activity and selectivity, using LHHW-type kinetic models (Figure 2). In this unusual example, we have freedom to explore the kinetics to see if process or catalyst insights emerge.

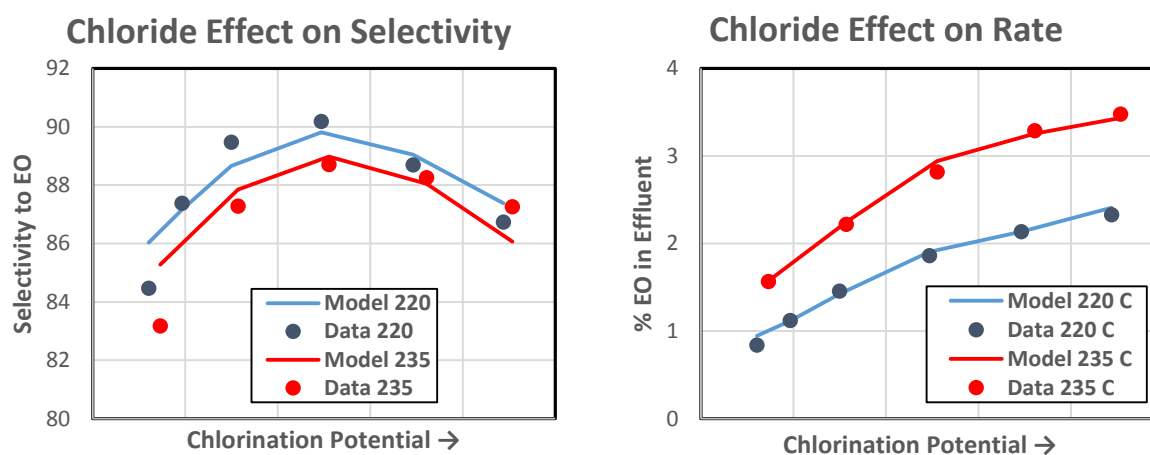


Figure 2. Model of chloride response of Re-promoted ethylene oxide catalyst

Catalyst deactivation is perhaps the most ubiquitous and poorly quantified pathology of industrial reactor operation. During scale up of a process to convert chlorinated alkanes to olefins, catalyst coking was much faster than anticipated. While hypotheses about the effects of hydrogen, HCl and a trace impurity existed, the development team could not agree on process design changes to mitigate the coking. By studying the kinetics of both the main reactions and the coking reactions and modeling dynamic deactivation of the pilot and commercial reactors we were able to determine the relative importance of the main reactant and trace impurity on coking and the kinetic effects of hydrogen and HCl on both the coking and hydrodechlorination reactions. The analysis allowed us to set clear priorities for both plant design and further catalyst development. Including detailed deactivation kinetics in the reactor analysis was the key to this project.

4. Conclusions

The need to understand the interactions between transport phenomena, thermodynamics, contacting patterns and reaction kinetics is essential to drive profitability and minimize the environmental footprint of industrial chemical production. Opportunities for analysis and optimization of new and existing processes are plentiful for those with solid engineering fundamentals and a desire to find practical solutions to industrial challenges.

References

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Keywords

“Industrial”, “Ethylene Oxide”, “Deactivation”, “Reactor Stability”