

# REACTOR SCALE-UP FOR FLUIDIZED BED CONVERSION OF ETHANE TO VINYL CHLORIDE

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## *Summary*

Novel LaOCl/LaCl<sub>3</sub> catalysts have been discovered that enable the production of vinyl chloride monomer from ethane. An ethane-based process would result in both capital savings and raw materials savings when compared to the current most effective vinyl technology. These materials are unique in the world of chlorination/oxychlorination as the mechanism for chlorination over LaOCl/LaCl<sub>3</sub> occurs on a catalyst without a redox metal center, unlike the conventional CuCl<sub>2</sub> catalysts used for oxychlorination where the Cu species are reducible. This report will focus on the engineering approaches taken and the challenges encountered in the scale-up of a fluidized bed reactor based on this catalyst technology. The objective is to highlight the application of chemical reaction engineering principles to a real industrial reactor scale-up, with special attention to the unexpected and atypical challenges encountered in this development effort.

## *Keywords*

Computational catalysis, multiphase and particulate reactors

## **Introduction**

A new process for direct conversion of ethane to vinyl chloride monomer (VCM)<sup>1</sup> offers attractive process economics as well as increased flexibility with respect to site selection by elimination of the need for access to a source of ethylene. A team from The Dow Chemical Company invented a new catalyst material that provides economically viable selectivities, conversions, and rates for this reaction. This discovery led to formation of a larger, multifunctional team to develop and demonstrate the scale-up of this fluidized bed reactor technology.

## **Reaction Kinetics**

Experimental data were acquired at 400°C and ambient pressure in plug flow packed bed reactors for the development of a preliminary kinetic model for this complex network of reactions. These lab scale reactors were designed with adequately small diameters,

sufficiently long bed lengths, and efficient external heat transfer in order to ensure nearly isothermal and plug flow performance. Several candidate models were developed and preliminarily evaluated: these models utilized LHHW-type rate expressions based on various assumptions about the reaction network and rate limiting steps. All of these models were developed prior to more mechanistically targeted work described later. The performance of the catalyst in the lab reactors was found to change with time-on-stream, limiting the quality of the data used for this preliminary analysis. In particular, the development of quantitatively accurate models based on steady-state fixed bed reactor data may be inhibited or even prevented by long time constant variations in the catalyst composition or structure caused by changes in the gas phase composition.

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## Fluidization Engineering

As the scale-up effort proceeded ahead of the pace of kinetic model development, a few of the candidate kinetic models were implemented in an engineering model of a fluidized bed reactor based on the model described by Werther<sup>2</sup>. In addition, cold flow tests were conducted in a six-inch diameter vessel to evaluate the hydrodynamics of fluidization by measuring average bubble rise velocity and diameter using differential pressure measurements, video image analysis, and dual fiber optic probe measurements. The optic probe technology was also employed in the high temperature, corrosive environment of the six-inch diameter pilot plant reactor. This method determined the mean bubble velocity by cross-correlating waveforms from two optic probes spaced at a known vertical distance. Catalysts from two different vendors were evaluated. The material with better catalytic properties fluidized in a vigorous bubbling or slugging regime, providing relatively poor gas-solid contacting. Although formally a Geldart type A material, this catalyst exhibited characteristics of streaming flow, more characteristic of Geldart type B particles. In contrast, the material with inferior catalytic properties fluidized well, with bubble sizes in the range preferred for commercial operation.

## Catalysis

During and after later stages of the scale-up effort, LaOCl/LaCl<sub>3</sub> catalysts were characterized in their working state through the use of Raman and x-ray photoelectron spectroscopies, reactive probe techniques, and DFT (density functional theory). The bulk state of the working catalyst was found to be typically much different than the surface composition, which was much richer in chemistry. Reactive pulse techniques showed that hydrocarbon chlorination occurs through lattice chlorine, as the presence of gas-phase HCl or Cl<sub>2</sub> was not necessary. Gas-phase oxygen, and therefore oxygen reduction on the time-scale of chlorination, was necessary for activity. Density functional theory offered a plausible mechanism directly related to the reactivity of surface chlorine species and not gas phase chlorine free radicals. Selectivities and activities for various chlorinated hydrocarbons and CO<sub>x</sub> changed with surface chlorination levels, with the highest chlorination rates and selectivities observed on fully-chlorided catalysts. The calculated change in selectivity with surface composition was primarily driven by a decrease in chlorination rates relative to constant oxidation rates. Higher temperatures increased the amount of surface chlorine accessible for catalytic chlorination. The work suggested that maintaining the catalyst surface in a state of high chlorination was vital to achieve high rates and selectivities.

## Pilot Plant Results

The relatively poor hydrodynamic performance of the better catalytic material led to a compromise at the pilot plant scale in order to make progress toward project timelines while giving the catalyst vendor time to improve the hydrodynamic performance of the spray-dried catalyst. This compromise implemented internals as a means of controlling bubble size, thereby improving gas-solid contacting. While the ultimate project objective would be to utilize only heat exchanger internals in the full-scale reactors, this temporary solution enabled the project team to attain a marked increase in the productivity of the more selective catalyst, simultaneously demonstrating reactor performance targets for productivity, selectivity, and conversion in the pilot plant reactor. In experiments separated by more than a month, the same batch of catalyst gave a VCM yield of 79 to 81% and a VCM productivity of 0.050 to 0.055 g /g LaOCl-hr under reactor conditions that simulated complete recycle of the reaction byproducts ethylene, HCl, and 1,2-dichloroethane.

## References

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