Oxychlorination of Ethane over LaOCl/$LaCl_3$ Catalysts: Chlorination without a Reducible Metal Center

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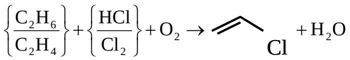
Introduction

Novel LaOCl/$LaCl_3$ catalysts have been discovered that enable the production of vinyl chloride monomer from ethane during oxychlorination[1]. This ethane-based process results 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/$LaCl_3$ occurs on a catalyst without a redox metal center, unlike the conventional $CuCl_2$ catalysts used for oxychlorination where the Cu-species are reducible. Lanthanum oxychloride catalysts have also been shown to be effective in chlorocarbon destruction[2] and more recently methane activation[3,4].

The overall ethane/ethylene chlorination chemistry capable over these novel LaOCl/$LaCl_3$ catalysts can be represented by reaction Scheme 1. A multi-functional approach was employed to characterize the surface reactivity and composition of these materials.



(1)

Materials and Methods

LaOCl catalysts were prepared either by the precipitation of an aqueous $LaCl_3$ solution with NH_4OH, followed by calcination at 550°C, or by the direct calcination of $LaCl_3 \cdot 7H_2O$ (Aldrich) at 600°C. Catalysts were characterized using a variety of spectroscopic and reactive techniques. Prior to analysis, LaOCl catalysts were typically activated for 3 hours in a 20% HCl/He stream at 400°C. The temperature-programmed and transient ethylene/O_2-pulse experiments were performed using an RXM-100 instrument (Advanced Scientific Design, Inc.) modified for chlorination chemistry. Products were resolved using a mass spectrometer combined with linear deconvolution of the reactor effluent mass fragments.

Results and Discussion

Catalyst characterization using unsteady-state reactivity studies, Raman, XPS, and EXAFS demonstrate that LaOCl/$LaCl_3$ catalysts have complex and rich surface compositions that are not represented by their bulk stoichiometry. Even after extensive activation in HCl or Cl_2 the catalyst surface contains a variety of chlorine, oxide, and hydroxide species. This surface composition changes with reaction conditions. Recent work on related materials, rare-earth oxysulfides, show similar phenomena: the surface composition of these rare-earth oxides is highly dependent on the reagent partial pressures[5]. The ethylene/O_2 pulses over our LaOCl/$LaCl_3$ catalysts show that hydrocarbon chlorination occurs through lattice chlorine, as only gas-phase oxygen, and therefore oxygen reduction on the time-scale of chlorination, is necessary for activity. The presence of gas-phase HCl or Cl_2 is not required but serves to rechlorinate the catalyst surface completing the catalytic cycle. Density functional theory calculations are consistent with this plausible mechanism directly related to reactivity of surface chlorine species and not gas-phase chlorine free-radicals. Selectivities and activities for various chlorinated hydrocarbons and COx change with surface chlorination levels, with the highest chlorination rates and selectivities observed on fully-chlorided catalysts. Figure 1 shows the deconvoluted mass spectral results for product selectivities during a series of ethylene/O_2 pulses. Changes in relative chlorocarbon selectivities are observed with partial surface dechlorination. The calculated change in overall chlorocarbon selectivity with surface composition is primarily driven by a decrease in chlorination rates relative to constant oxidation rates. Higher temperatures increase the amount of surface chlorine accessible for catalytic chlorination. The work to date shows that maintaining the catalyst surface in an optimal state of chlorination appears vital to achieve high rates and selectivities.

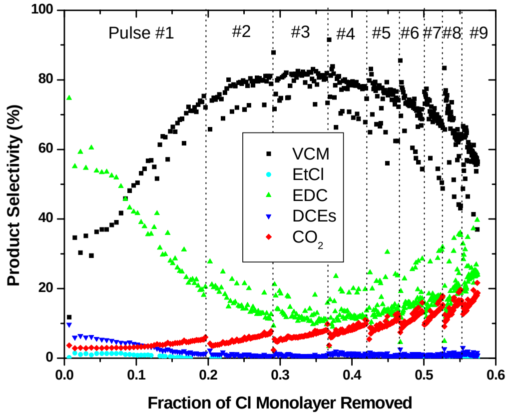


Figure 1. Catalytic selectivity for all C_2H_4/O_2 pulses at 400°C as a function of fractional chlorine removed from a theoretical monolayer of an activated LaOCl/$LaCl_3$ catalyst.

References

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