Methane Oxidative Chlorination catalysts evaluated using high throughput reactors.

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Introduction

A direct and selective route for the formation of Methyl-Chloride from methane and hydrochloric acid is highly desirable [1]. Rare earth oxide and oxychlorides have been reported as active and fairly stable catalysts for this reaction [2,3,4,].

Building on the previous work from at DOW and Munich University with LaOCl catalysts [2], a large number of Rare Earth oxide catalysts were prepared and evaluated. A multi-channel fixed bed reactor was used to test catalyst formulations simultaneously and was capable of measuring all of the products (except water) of the reaction $CH_4 + O_2 + HCl$. The reactor was used to evaluate the catalytic activity of several libraries of catalysts. A reference sample was used to benchmark test results and to ensure that the test system's performance matched a standard laboratory scale test reactor with known performance. 350 microliters of catalyst were used for each test allowing for post reaction characterization of the materials tested.

Materials and Methods

Bulk oxide catalysts were prepared by the co-precipitation of metal salt mixtures upon titration with a tetramethylammonium hydroxide. Supported catalysts were prepared using incipient wetness impregnation followed by calcination in air.

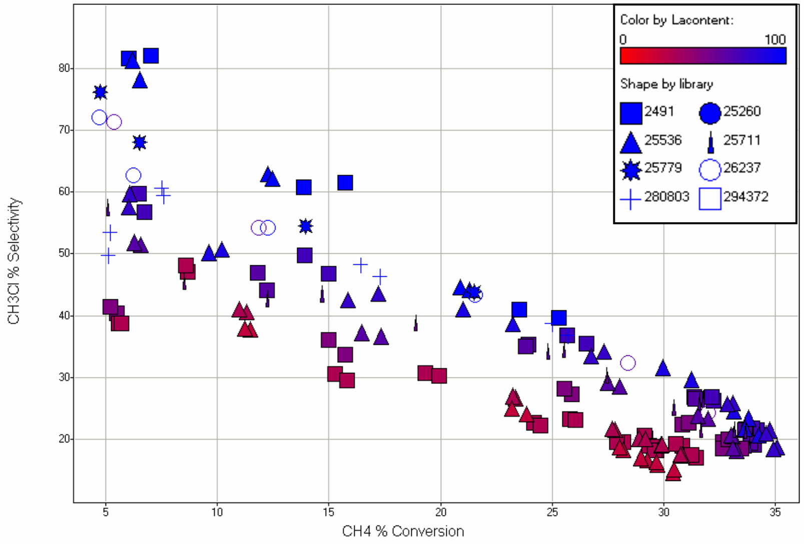
Testing was conducted in a reactor module consisting of 16 parallel Quartz tube channels utilizing a micromachined silicon-glass flow splitter to equally distribute reactant to the different channels. Preconditioning of the samples was conducted in pure HCl at 375ºC followed by activity measurements at 375ºC to 500ºC in 25ºC steps. A Maxum GC (Siemens) was used to measure the reaction product concentrations in the effluent stream from each channel.

Results and Discussion

Mixed La-Zr and La-Hf materials displayed a significant increase in methane conversion when compared to LaOCl. This can be attributed to the increase in surface area of the spent catalysts as Hf and Zr cannot be fully chlorinated. The selectivity toward CH_3Cl for these binary mixed oxides was dependant on composition and preconditioning of the catalysts. Selectivities similar to pure LaOCl were obtained for samples containing over 66% La (La/La+Zr molar ratio) calcined at 500ºC in air and for samples containing over 25% La calcined at 800ºC. The reduction of selectivity toward CH_3Cl is a due to the partial combustion activity of ZrO or HfO as measured for supported catalysts.

Supported catalysts on Silica also displayed activity comparable to or higher than the reference LaOCl catalyst with similar selectivity. Significant increases in activity were observed for supported binary catalysts containing Tb, Nd or Pr when compared to the sample containing La on Silica alone. In order to evaluate this result bulk PrO, NdO and TbO were tested. Both PrO and TbO showed good selectivity and activity compared to LaOCl. NdO, on the other hand, showed lower selectivity.

Figure 1. CH_3Cl selectivity versus Methane conversion for La-Zr and La-Hf bulk catalysts across multiple libraries.



Significance

Highly active catalysts for methane oxychlorination were identified. The high throughput workflows used also demonstrated the ability to quickly generate detailed activity data on a difficult-to-implement chemistry.

Figure 1. CH_3Cl selectivity versus CH_4 conversion for La-ZrO and La-HfO samples tested at different temperatures (375ºC to 500ºC) at a space velocity of about 500 h^{-1}.

References

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