Methane Oxychlorination: Catalyst Development and Some Aspects of Reaction Chemistry

Michelle D. Casper,[*] Armando Araujo, Shahid Shaikh, and Edouard Mamedov
SABIC Technology Center, 1600 Industrial Boulevard, Sugar Land, Texas 77478, USA
**mcasper@sabic.com*

Introduction

Methane oxychlorination is considered a first step of methane two-step conversion to olefins via methyl chloride. Despite a long history of research on methane oxychlorination dating back to the 1920s, there are still several key technological challenges associated with this process. Among these are the development of a stable selective catalyst and the mitigation of methyl chloride consecutive reactions that reduce selectivity to this target product. This paper describes the approaches we have used to tackle these issues.

Materials and Methods

Catalysts were prepared from separate aqueous solutions of cerium chloride and lanthanum chloride by dissolving the appropriate amounts of $CeCl_3 \cdot 7H_2O$ and $LaCl_3 \cdot 7H_2O$ in de-ionized water at room temperature while stirring. The lanthanum chloride solution was added drop-wise to the cerium chloride solution. Then aqueous ammonium hydroxide solution (28.0-38.0% NH_3 basis) was added drop-wise to the mixed solution to precipitate lanthanum and cerium hydroxides. The suspension was stirred for 1 hour to ensure complete precipitation, followed by centrifugal separation of gel from supernatant. The gel was washed with water and centrifuged two times to remove residual base. After that, it was dried in air overnight at 75 ºC, and step-wise calcined in air at 120 ºC for 3 hours and at 550 ºC for 8 hours. The resulting powder was sized to 18-35 meshes and tested.

Catalysts were tested for methane oxychlorination to methyl chloride in a ½ inch O.D. fixed bed tubular reactor. The tube was made of Hastelloy and coated inside with Dursan® compatible with hydrogen chloride. Catalytic experiments were conducted at atmospheric pressure, temperatures from 400 to 450 °C, and feed flow rates 25-100 ml/min. The feed consisted of 20% CH_4, 20% HCl, 8.4% O_2 and 51.6% N_2. The reactor was loaded with catalyst (0.5-2 g) mixed with inert material. Contact time of the feed with catalyst varied from 0.5 to 6.5 seconds depending on catalyst amount and feed flow rate.

Results and Discussion

In an effort to find a new, more effective catalytic system, we prepared and tested different types catalysts, the results of which led us to focus on the Ce-La oxide system. Detailed study of the effect of their composition and preparation method on catalytic behavior resulted in the development of a catalyst with the Ce-to-La atomic ratio of 1. The catalyst of this composition prepared from metal chlorides was comprised of the phases of CeO_2, LaOCl and most likely a La solid solution in CeO_2. Under the standard reaction conditions, it provided 75-80% selectivity to methyl chloride at a methane conversion of 15%.

Methane conversion over this Ce-La oxide catalyst reasonably increased with increasing reaction temperature, pressure, and contact time. Variation of the feed flow rate at fixed contact time revealed the presence of diffusion limitation at flow rates lower than 50 cc/min. At higher flow rates, methane conversion was independent of flow rate and obeyed pseudo first order kinetics and Arrhenius law implying the absence of diffusion limitations. The selectivity to methyl chloride decreased with increasing pressure and did not depend on temperature. As a function of methane conversion, it declined linearly with an increase in this parameter.

Reaction network studies showed that methyl chloride (CH_3Cl) was the major primary product of methane oxychlorination. Small amounts of CO and CO_2 also formed directly from methane by parallel routes. Oxychlorination of CH_3Cl produced CH_2Cl_2, which consecutively converted to $CHCl_3$ and CCl_4 and then to CO.

To improve the selectivity to methyl chloride, we employed different approaches. In particular, doping the Ce-La oxide catalyst with tellurium increased selectivity by 5% at a fixed conversion of methane by reducing CH_3Cl oxychlorination to CH_2Cl_2. Additional improvement by 2-3% was achieved by decreasing the oxygen concentration in the feed. Herewith the selectivities to CH_2Cl_2 and CCl_4 did not change significantly, while the combined selectivity to CO and CO_2 decreased by 3%. It appears that the reduction of oxygen concentration in the feed mostly slowed down methane direct oxidation to carbon oxides, allowing more methane undergo oxychlorination to methyl chloride.

Significance

This work has proposed and studied a family of novel Ce-La oxide catalysts for oxidative chlorination of methane that is a first step of commercially attractive two-step process of methane conversion to olefins via methyl chloride.
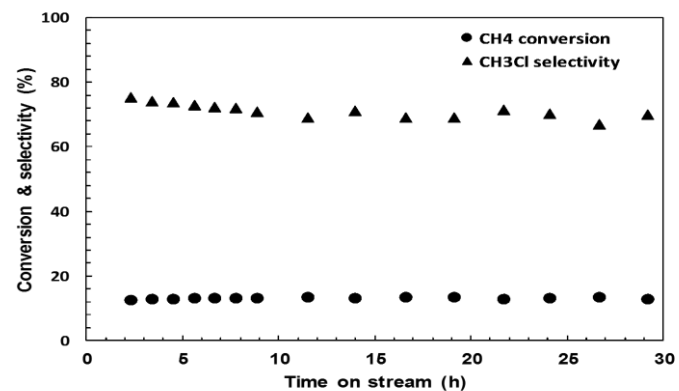

Figure 1. Time-on-stream behavior of Ce-La oxide catalyst at temperature 420 °C and contact time 2.4 seconds