1. Experimental

1.1. CH_4 oligomerization

Catalytic reactions were carried out in a continuous flow tubular reactor made of Borosil glass (i.d.-10 mm, length-120 mm). In a typical experiment, 5 g of $AlBr_3$ (M/S. Aldrich, 99.99% metal basis) was taken into the 3-neck, 50 ml round bottom flask acts as an $AlBr_3$ reservoir. This flask is connected to glass reactor. Ar comes from a gas cylinder flows over the liquid $AlBr_3$, which is maintained at 100 °C. This Ar-saturates gas mixes with premixed methane and HBr (M/S. Aldrich, ≥99%) and passes into the reactor. The resulting feed stream to the reactor is in a molar ratio equal to CH_4:$AlBr_3$:HBr = 1:0.005:1.32. The nominal residence time is 60 sec. The reactor is heated to desired temperature using heat tape controlled by PID temperature controller. The temperatures of both $AlBr_3$ flask and reactor are measured by K-type thermocouple. All experiments are carried out inside the glove box under N_2 atmosphere. Prior to the experiments, reactor system was flushed with Ar gas for 1 h. The gases used were Ultra High Pure grade (99.99%) and were further purified by passing them through oxygen and moisture traps before entering the reactor. The gas flows were controlled by using rotameter (M/S. Matheson TriGas) and were calibrated prior to use.

1.2 Analysis of H_2 & Hydrocarbon Products

Downstream of the reactor, the product gas stream was neutralized by passing it through 0.2 N aq. KOH solution before the remaining product gas was analyzed by GC (M/S. Shimadzu, Model: GC-14A) equipped with FID and TCD. C_1-C_8 hydrocarbons were analyzed by using FID and H_2 concentration was monitored by using TCD. SH-1 capillary column (0.32 mmX0.5μmX50m) was used to separate hydrocarbons and RT Msieve-5A (30m x 0.53mm I.D.) was used to analyze hydrogen. The GC was calibrated using standard hydrocarbon mixtures supplied by M/S. Alltech.

The liquid products (oil) which are red in color (mixture of higher hydrocarbons and $AlBr_3$-HBr) at reaction temperature of 400 °C were collected at the knockout vessel located at the reactor outlet. Prior to analysis, the oil was hydrolyzed by adding water and the organic layer was analyzed using GC (Model: HP6890) with FID having SE-52 column.

The methane conversion and hydrocarbon selectivity were calculated as follows:

$$\% \text{ Conversion of methane} = \frac{n(CH_4)_{in} - n(CH_4)_{out}}{n(CH_4)_{in}} \text{ X } 100$$

% 'C' yield of product i = $[n_i C_i / X_{CH4}]$ X 100, where C_i = no. of C atoms present in the product i

n_i = no. of moles of product i

X_{CH4} = no. of moles of CH_4 converted

% Yield of H_2 = (H_2 mol produced / CH_4 mol converted) X 100