Reaction Studies on Na_2WO_4-Mn/SiO_2 Catalyst for Oxidative Coupling of Methane

Aseem[a], Geofrey Goldwin[b], Marlon Conato[a], Jeffrey D. Rimer[a] , Michael P. Harold[a] and Ken Blackmon[b]

[a] University of Houston, Department of Chemical and Biomolecular Engineering, Houston, TX 77204
[b] Total Petrochemicals & Refining USA, Inc., LaPorte, TX 77571

The oxidative coupling of methane (OCM) to higher molecular weight hydrocarbons has great appeal as an alternative route to chemicals and polymers. The reaction system is challenging because of large differences in the reactivity of the reactant methane and desired products (e.g., ethylene, ethane, etc.) at the temperatures needed to activate methane. Moreover, the reaction system is highly exothermic and is noted for significant parametric sensitivity.

A large number of systems have been studied over the past few decades, but a catalyst and reactor concept has not been found that give sufficiently high C_{2+} yield. The most studied catalysts to date for the OCM reaction system have been alkali-promoted alkaline earth metal oxides, transition metal oxides and rare earth metal oxides. Na_2WO_4-Mn/SiO_2 catalyst has attracted a significant amount of attention because of its favorable catalytic performance. In this study we evaluate the activity of the catalyst in particulate and washcoat form using both fixed-bed and monolith reactor configurations. We also carry out a parametric study to quantify the effects of residence time, reaction temperature, oxygen concentration, and dilution.

The catalyst was prepared by the incipient wetness impregnation method and its structural properties were characterized by a variety of analytical techniques (e.g., XRD, BET, ICP and SEM). The prepared catalyst has a surface area of 2.6 m^2/g and was sieved to a size of 50-70 mesh. Residence time variations were accomplished by changing the weight of catalyst while keeping the flow rate constant, thereby avoiding changes in flow patterns inside the reactor. Figure 1 shows the dependencies of methane conversion, C_2 selectivity, and C_2 yield on residence time at 800^{o}C. The conversion of methane increased with increase in residence time but the C_2 selectivity decreased due to deep oxidation in the reactor with prolonged exposure to the catalyst.

We observed that, with higher CH_4/O_2 ratios and concentrated feed, the reactor system becomes quite sensitive to the operating conditions. In particular, the steep axial temperature limits the maximum oxygen concentration that can be used. By diluting the feed, the reaction can be conducted at higher CH_4/O_2 ratios. We will also show the effect of dilution of catalyst with inert and catalyst structure (i.e. particles vs. washcoat) on the product compositions. Washcoating is of particular interest since it reduces the contact time of C_2 hydrocarbons within the internal porous structure of the catalyst, thereby inhibiting deep oxidation.

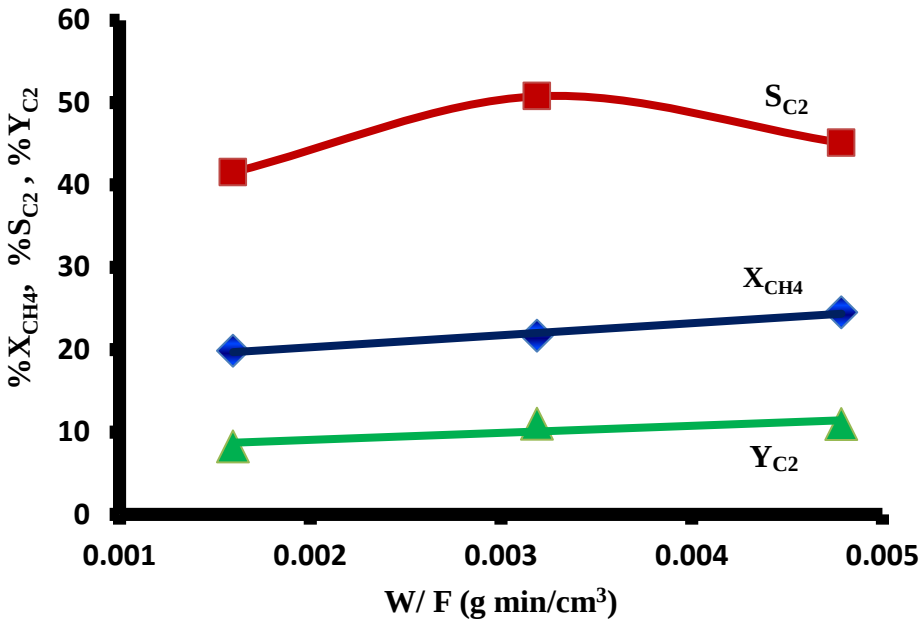


Figure 1. Dependence of CH_4 conversion, C_2 selectivity, and C_2 yield on space time at T = 800^0C and a CH_4:O_2 ratio of 3:1.