

Oxidative Coupling of Methane on a Mixed Oxide Catalyst.

Ananth Annapragada and Erdogan Gulari
Department of Chemical Engineering
University of Michigan, Ann Arbor, MI-48109.

We have developed a family of catalysts for the oxidative coupling of methane which achieve high activities and selectivities at temperatures lower than those currently in the literature. Typical figures are: At 575 °C, GHSV = 28800 Hr⁻¹, CH₄/O₂ = 2, total conversion = 11%, C₂ selectivity = 43%. In this paper, we plan to present the development of the catalyst, and our results on the identification of the active components. In addition we will also discuss our steady state, pulse and TPR experiments which have lent some insight into the mechanism of the reaction.

Our steady state activity measurement experiments identified that the catalyst was active both in unsupported and supported form. In general, the unsupported catalyst was more difficult to activate than the supported catalysts. Also, the unsupported catalyst had a much lower range of active compositions than the supported catalyst. We attribute this to the possible existence of a wider distribution of crystal phases in the supported catalyst. The fact that the most active compositions in both supported and unsupported catalysts occurred at the same composition of active components led us to believe that a characterization of the active species in the unsupported catalysts would give us some information about the active species in the supported catalysts. X-ray diffraction and ESCA studies identified a unique species in the active unsupported catalysts. However, this material in pure form was not active as a methane coupling catalyst. We concluded that some complex interaction between this species and the others in the active catalyst was the cause for the activity.

One of the problems we encountered during steady state studies on the catalyst was the fact that a catalyst composition which was active on one occasion was not necessarily active on another occasion under identical conditions. In general, active compositions would achieve a high level of activity approximately 45% of the time. This indicated the existence of multiple steady states either in the in-situ preparation of the catalyst or in the reaction itself. TPR studies indicated

that temperature hysteresis and multiple steady states did indeed exist for the coupling reaction in the vicinity of our operating conditions. Surface titration experiments on the catalysts operating in each of the two steady states indicated a difference in the way oxygen was incorporated into the catalyst during operation at the higher steady state.

Steady state activation energy measurements and suitably designed pulse experiments revealed that the reaction possibly occurred by the following steps:

- (1) Hydrogen abstraction from the methane to form CH_3 - species.
- (2) Coupling of the CH_3 - species to C_2H_6 .
- (3) Pyrolysis of the Ethane to Ethylene.
- (4) Oxidation of the Ethane and Ethylene to CO and CO_2 .

At this point we can only speculate, but we believe that the first two steps occur on the surface of the catalyst, while the last two occur in the gas phase. We attribute the success of this catalyst to its ability to abstract hydrogen from methane at a temperature low enough to support reversible oxygen incorporation into the catalyst.