Solution Combustion Synthesized Catalytic Materials for Oxidative Coupling of Methane

Ranjita Ghose, Hyeon Tae Hwang and Arvind Varma*
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
*avarma@purdue.edu

Introduction
The reserves of natural gas are abundant. In this context, the catalytic oxidative coupling of methane (OCM), given by (1), is an attractive alternative for ethylene production, as compared to current processes based on crude oil.

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{H}_2\text{O} \]  

OCM has been investigated in the past and catalytic materials studied include metal oxides/complex metal oxides of alkali earth, transition and rare earth elements [1]. Solution combustion synthesis (SCS) is a novel one-step method for the synthesis of nanostructured complex metal oxides with tailored composition, phase, oxidation state, and surface areas by variation of tunable synthesis parameters [2-4]. In this work, SCS was used successfully for synthesis of OCM several catalyst series.

Materials and Methods
(a) Catalyst Preparation
All catalysts in this work were made by the SCS technique, for which the details are available elsewhere [2-4]. In summary, metal nitrates (cation precursors) are mixed to achieve the required stoichiometric amounts then heated, causing evaporation of water. At a critical temperature, self ignition and combustion of the remaining viscous mixture results in formation of complex metal oxides with uniform phase composition. The SCS catalyst powders were calcined at 950 °C for 4 hours, and then sieved into agglomerates with diameter 125 – 250 µm.

(b) Catalyst Performance Measurements
The experiments were conducted in a fixed-bed reactor. To decrease the homogeneous reaction of hydrocarbons and oxygen to CO, CO\(_2\) and H\(_2\)O under the high temperatures required for OCM, the heated reactor volume was decreased by using a hollow quartz cylinder which also housed the thermocouple. The catalytic activity for the Sr-Al catalyst series was measured with Sr/Al = 0.5, 1, 1.25, 1.5 and 2 and \(\varphi = 1\). The \(C_2\) yield was maximum (11.5%) for Sr/Al = 1.25 at 800 °C. From the XRD plots for the Sr-Al oxides, it was found that the primary phase formed was double perovskite type with the formula Sr\(_2\)Al\(_2\)O\(_6\). As the Sr/Al ratio increased from 0.5 to 1.25, the relative intensity of the double perovskite peaks increased and was highest for Sr/Al = 1.25, which also corresponds to the catalyst with the highest \(C_2\) yield. The catalyst performance thus appears to correlate with the proportion of double perovskite phase in the Sr-Al oxides.

Results and Discussion
(a) Sr-Al Catalysts
The Sr-Al catalyst series was synthesized with varying Sr/Al ratios of 0.5, 1, 1.25, 1.5 and 2 and \(\varphi = 1\). The \(C_2\) yield was maximum (11.5%) for Sr/Al = 1.25 at 800 °C. From the XRD plots for the Sr-Al oxides, it was found that the primary phase formed was double perovskite type with the formula Sr\(_2\)Al\(_2\)O\(_6\). As the Sr/Al ratio increased from 0.5 to 1.25, the relative intensity of the double perovskite peaks increased and was highest for Sr/Al = 1.25, which also corresponds to the catalyst with the highest \(C_2\) yield. The catalyst performance thus appears to correlate with the proportion of double perovskite phase in the Sr-Al oxides.

(b) La-based Catalysts
La-Sr series showed higher maximum \(C_2\) yield at lower temperature (13% at 720 °C, with ethylene/ethane = 1.7) than the Sr-Al catalysts series, indicating that addition of La to Sr and Al is beneficial for OCM performance.

(c) Na\(_2\)WO\(_4\)-Mn/SiO\(_2\) Catalysts
The SCS synthesized 10%Na\(_2\)WO\(_4\)-5%Mn/SiO\(_2\) and 5%La-10%Na\(_2\)WO\(_4\)-5%Mn/SiO\(_2\) catalyst showed good performance at standard conditions. Under optimum CH\(_4\)/O\(_2\) ratio of 2, a high \(C_2\) yield of 27% at ethylene/ethane ratio ~3.6% was obtained for the 5%La-10%Na\(_2\)WO\(_4\)-5%Mn/SiO\(_2\), which is among the highest reported in literature. This catalyst was tested for about 48 hours, and showed no deactivation within the error of measurement. This is attributed to homogeneous composition, as compared to similar catalysts prepared by conventional method that result in enrichment of active components on the catalyst surface, which is associated with their loss with time on-stream.

Significance
A novel catalyst preparation method was used to synthesize three promising catalyst series for the OCM reaction. This technique allowed convenient variation of metal ratios in the catalyst and facilitated study of catalyst performance. The solution combustion synthesized catalysts exhibit among the highest \(C_2\) yields, and a higher ethylene/ethane ratio as compared with catalysts prepared by conventional techniques in the literature. Several results described above are forthcoming in a recent publication [5], while the NAM presentation will also include additional work currently in progress.

References