Brief Review of Catalytic Oxidative Coupling of Methane to Ethane and Ethene

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Abstract

Methane, the simplest hydrocarbon, is the major constituent of natural gas. Much of the methane produced worldwide is flared due to lack of pipelines. The prime use of methane is as a fuel for home heating and cooking, as well as electricity production. Because of its abundance, methane has the potential of becoming a major feedstock for petrochemical production. The problem is that methane is a stable molecule, and the direct conversion to useful chemicals is difficult.

In 1982 Keller and Bhasin[1] reported that many metal oxides can catalyze the oxidative coupling of methane to the more valuable chemicals ethane and ethene. In the presence of the catalyst, methane reacts with oxygen and forms the higher hydrocarbons ethane and ethene during oxidative coupling, shown in reactions (1) and (2) below:

$$2\ CH_{4\ (gas)} + \tfrac{1}{2}\ O_{2\ (gas)} \rightarrow C_2H_{6\ (gas)} + H_2O_{(gas)} \quad (1)$$

$$2\ CH_{4\ (gas)} + O_{2\ (gas)} \rightarrow C_2H_{4\ (gas)} + 2\ H_2O_{(gas)} \quad (2)$$

The catalytic deep oxidation of methane to carbon monoxide and carbon dioxide will also occur, shown as reactions (3) and (4) below:

$$CH_{4\ (gas)} + 3/2\ O_{2\ (gas)} \rightarrow CO_{(gas)} + 2\ H_2O_{(gas)} \quad (3)$$

$$CH_{4\ (gas)} + 2\ O_{2\ (gas)} \rightarrow CO_{2\ (gas)} + 2\ H_2O_{(gas)} \quad (4)$$

Unfortunately the yields of ethane and ethane obtained by Keller were small (5% maximum total C_2 yield) and the process temperature required was very high (800^{o}C). In the ensuing thirty two years, a vigorous search proceeded for an active coupling catalyst[2-23].

The first breakthrough occurred in 1985, when Lunsford[2] reported 19% C_2 yields when Li doped MgO was used as a catalyst. In 1986 Otsuka[3,4] reported rather spectacular C_2 yields of 30% with LiCl-MnO_2 and LiCl - NiO catalysts. In this case however, the catalyst was short lived, suggesting that chlorine in the catalyst is a reagent, and chlorine is known to inhibit the deep oxidation of methane.

Labinger[18] suggested in 1988 that there is a fundamental limit on the C_2 yield of 30%. The catalysts typically require high operating temperatures of 600 - 800^{o}C. Unfortunately these factors work against commercialization of the catalysts.

In order for an oxidative coupling catalyst to be commercially viable, three criteria must be met[18]. First a total C_2 yield (preferably as the more valuable ethene) of at least 30% is needed. Second the process should operate at lower temperatures to be less energy intensive. Finally the catalyst should have a long life. None of the metal oxide catalysts examined exhibits all of the necessary characteristics to be commercially viable. The discovery of such an oxidative coupling catalyst remains an elusive and sought after prize. The mechanisms by which the catalysts convert methane will be discussed and future research directions will be suggested.

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