OXIDATIVE COUPLING OF METHANE OVER SULFATED SrO/La$_2$O$_3$

CATALYSTS

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INTRODUCTION

Saturated linear hydrocarbons, particularly methane, are major components of natural gas and of the gas produced by certain coal gasifiers. While methane makes an excellent gaseous fuel, it is desirable to convert it via 1-step processes to higher molecular weight products for transportation, storage, and utilization as chemical feedstocks. The desired primary reactions are shown in Equations 1-4, while Equation 5 is also a reaction of interest:

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\begin{align*}
\text{(1)} & \quad \text{CH}_4 + 0.5 \text{O}_2 & \rightarrow & \text{CH}_3\text{OH} \\
\text{(2)} & \quad \text{CH}_4 + \text{O}_2 & \rightarrow & \text{CH}_2\text{O} + \text{H}_2\text{O} \\
\text{(3)} & \quad 2\text{CH}_4 + \text{O}_2 & \rightarrow & \text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \\
\text{(4)} & \quad 2\text{CH}_4 + 0.5 \text{O}_2 & \rightarrow & \text{C}_2\text{H}_6 + \text{H}_2\text{O} \\
\text{(5)} & \quad 2\text{CH}_4 + 2\text{CO}_2 & \rightarrow & \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O}.
\end{align*}
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After Keller and Bhasin published their research results for methane coupling over a decade ago, many laboratories have been striving to develop efficient methane conversion catalysts and technologies. Various aspects of the state of the art of methane oxidation, including early developments, have been reviewed by Foster in 1985, Gesser et al. in 1985, Pitchai and Klier in 1986, Scurrell in 1987, Lee and Oyama in 1988, Hutchings et al. in 1989, Amenomiya et al. in 1990, Lunsford in 1990 and 1991, Mackie in 1991, Hamid and Moyes in 1991, Krylov in 1993, and Zhang et al. in 1994. Therefore, the literature will not be extensively reviewed here.

While the catalytic oxidative coupling paths represented by Equations 3 and 4 show considerable promise, it is evident from patent examples that the process
conditions are still quite severe, i.e. the usual reaction temperature of 650-800°C is still too high. Reactions leading to oxygenates (Equations 1 and 2) are more difficult to conduct selectively, but they have been identified as being very desirable, particularly the oxidation to methanol. At the same time, the standard free energy of all the oxidations, Equations 1-4, is negative over a wide range of temperatures, establishing a thermodynamic driving force for these reactions even at room temperature should an effective catalyst be found. More practical considerations led us to seek a desirable temperature range of 350-650°C. The lower limit of 350°C is based on experience with the dehydration of most oxide catalysts, which lose water at temperatures ≤350°C. The upper limit of 650°C is in the range of temperatures at which uncontrolled free radical reactions will occur and often will lower the selectivity by driving the oxidation process to CO and CO₂.

Oxide catalysts were chosen here, in particular the very basic SrO/La₂O₃ catalyst that is active in the formation of methyl radicals, and therefore of C₂ hydrocarbons. However, the methyl radicals formed over SrO/La₂O₃ can be trapped by a subsequent catalyst bed, e.g. MoO₃/SiO₂, but not SiO₂, and at least partially converted to CH₂O. Since the formation of surface carbonates might be at least partially responsible for deactivation of basic catalysts under some methane conversion reaction conditions, the catalytic behavior and/or stability of the very basic SrO/La₂O₃ might be enhanced by acidic doping. With analogy to earlier findings that sulfate ion strongly enhanced the acidic properties of iron oxide, as well as alumina and titania, SO₄⁻ was used as an acidic surface dopant to improve the catalytic performance of the 1 wt% SrO/La₂O₃ catalyst.

EXPERIMENTAL

The 1 wt% SrO/La₂O₃ catalyst used in this study was prepared by AMOCO Oil Co. using the procedure described by DeBoy and Hicks. The sulfated SrO/La₂O₃ catalysts were produced by the incipient wetness impregnation technique. The appropriate amount of (NH₄)₂SO₄ was dissolved in deionized water, the measured quantity of SrO/La₂O₃ was added, and the slurry was continuously stirred with a magnetic stirrer until dryness was achieved. This was followed by drying the solid overnight at 120°C and calcination in air at 600°C for 6 hr. Prior to catalytic testing, the samples were activated in situ under air (or O₂) flow at 500°C for 1 hr unless stated otherwise. The gases used in this study were zero grade purity and were used without further purification.

Catalytic testing was carried out in a fixed-bed continuous-downflow 9 mm OD (7 mm ID) quartz reactor that narrowed just below the catalyst bed to 4 mm OD (2 mm ID). In nearly all tests, 0.1000 g of catalyst was used. The catalytic tests of the catalysts included the standard conditions of employing a CH₄/air = 1/1 reactant mixture at 1 atm (0.1 MPa) and with gas hourly space velocity (GHSV) = 70,000 ℓ/kg catal/hr over the range of temperatures of 500-700°C. Usually each test was carried out at steady state methane conversion at each designated set of reaction conditions for 1-3 hr. The principal products analyzed by on-line automated sampling of the exit gas using gas chromatography (Hewlett-Packard 5890 PC-controlled GC) were CO₂, C₂ hydrocarbons (C₂H₆ + C₂H₄), CO, and H₂O. Usually not included were C₃ compounds that were present in only small traces. Formaldehyde was collected in two water-filled scrubbers in series, the first was kept at room temperature and the second at 0°C, and then quantitatively determined by the modified Romijn's iodometric titration method. In this present research, the carbon mass balance was always better than 90% and usually better than 95%.