Chapter 14
Dual Role of Perovskite Hollow Fiber Membrane in the Methane Oxidation Reactions

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ABSTRACT

The Mixed Ionic and Electronic Conducting (MIEC) membrane reactors are of interest because they have the potential to produce high purity oxygen from air at lower costs and provide a continuous oxygen supply to reactions or/and industrial processes. The study of the dual role oxygen flux and catalytic performance of the unmodified and Ni-coated La0.6Sr0.4Co0.2Fe0.8O3-δ hollow fibre membranes (LSCF6428 HFM) in the methane oxidation reactions (i.e., partial oxidation of methane and methane combustion) by using air on lumen side and methane on shell side are shown in this chapter. The LSCF6428 HFM participates not only in the oxygen flux but also in the methane conversion to C2. A Ni-coated LSCF6428 HFM under lean O2/CH4 gradient (i.e., 0.5) showed the production of syngas, carbon dioxide and C2 products in agreement with the thermodynamic calculation. At rich O2/CH4 gradient (i.e., 1.0), the formation of carbon dioxide was facilitated. The main catalytic pathway at lean O2/CH4 gradient and H2 reduction treatment was partial oxidation of methane to C2 and syngas.

INTRODUCTION

The partial oxidation of methane (POM) to synthesis gas or syngas (CO/H_2) has attracted much attention in recent years. Syngas is a versatile feedstock for many industrial synthetic processes and can be easily transformed to methanol or hydrocarbons via the Fischer-Tröpsch reaction (Tang et al., 2007). These catalytic routes could transform natural gas reserves, whose principal component is methane, into more valuable chemicals and fuels. However, in order to apply the POM process at industrial level, cost effective methods for the supply of pure oxygen are required (Kondratenko et al. 2009; Ten Elshof, Bouwmeester & Verweij, 1995; Xu & Thomson, 1997). The current method for obtaining pure oxygen on a large scale is by cryogenic air separation (fractional distillation of liquefied air), PSA (pressure swing

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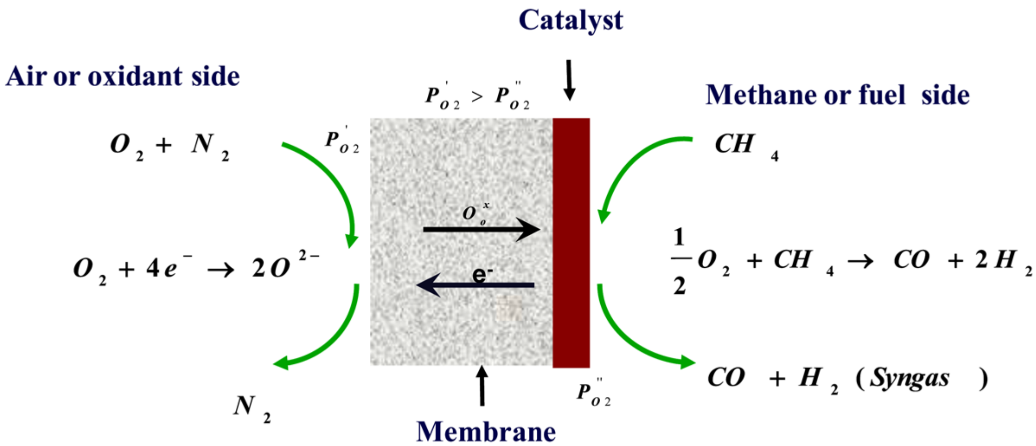
Figure 1. Reaction mechanisms for partial oxidation of methane through MIEC membrane. Adapted from (Bouwmeester, 2003; Hamakawa, et al., 2006; Thursfield & Metcalfe, 2006)



adsorption) and VSA (vacuum swing adsorption). The first process, cryogenic air separation, utilizes low temperatures and elevated pressures that make it very expensive (Baker, 2002), because it is energy intensive, although it produces 99.5% pure oxygen. The other processes, PSA and VSA, require less energy but produce lower purity oxygen (90-93%) (Bartholomew & Farrauto, 2006).

An alternative and more energy efficient method is the use of mixed ionic and electronic conducting (MIEC) metal oxide ceramic membranes (Tan & Li, 2006). The process is very promising because this enhances the performance of methane conversion processes due to simultaneous production of pure oxygen and syngas by combining oxygen separation and high temperature catalytic partial oxidation into a single unit, simplifying the process and reducing the capital costs (Bouwmeester, 2003; Caro et al., 2006; Hamakawa et al., 2006; Jin et al., 2000; Lui et al., 2008; Schiestel et al., 2005; Tan, Liu & Li, 2005; Thursfield & Metcalfe, 2007).

Figure 1 presents the simultaneous production of pure oxygen and syngas in MIEC membrane. At high temperature (800 to 1000) °C, in air or oxidant side, gaseous oxygen is adsorbed, dissociated and reduced to lattice oxygen .. on the membrane surface and diffuse through the combination of mobile oxygen vacancies and electronic defects (holes) since the oxygen partial pressure on the air side is lower than that on the methane side.

The driving for is the oxygen partial pressure difference across the membrane. On the fuel or methane side, the permeated oxygen is consumed by methane $\left(CH_4\right)$ for their partial oxidation to syngas $\left(CO \text{ and } H_2\right)$ or the complete oxidation to carbon dioxide and water. The MIEC membrane allow separation of oxygen from air supply at elevated temperature (>700 °C). By combining air separation and catalytic partial oxidation of methane to syngas into membrane reactor, it is expected that this technology will reduces the capital costs of natural gas to liquid (GTL) (Bouwmeester, 2003) and improves the selectivity and yields of the products (Au & Wang, 1997).

The overall aim of this chapter is to illustrate the potential application of LSCF6428 hollow fibre membranes in the methane oxidation reactions (i.e., partial oxidation and combustion), in which the LSCF6428 HFM can be used not only for oxygen flux but also catalyzing the methane oxidation reactions. This dual functionality can be tuned by the deposition of nickel through 5%Ni-LSCF6428 onto

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