Aluminium substituted lanthanum based perovskite type oxides, non-stoichiometry and performance in methane partial oxidation by framework oxygen

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ABSTRACT

A series of Rh-promoted $La_{0.75}Sr_{0.25}(Fe_{0.80}Co_{0.20})_{(1-x)}Al_xO_{3-\delta}$ ($x = 0$, 0.10, 0.25, 0.40, 0.60) samples were investigated as oxygen reservoirs for the conversion of CH_4 to syngas at 873 K and 1 atm. Neutron powder diffraction studies revealed a decreasing rhombohedral distortion on increasing Al-content. XPS and TEM were employed to investigate surface chemistry and morphology of the Al = 0.25 sample. The influence of Al-substitution on the redox properties was studied by flowing titration whereas catalytic properties were studied by means of transient pulses of CH_4 and O_2, as well as of $^{13}CH_4$ and CO. The products (CO, H_2, CO_2 and H_2O) of the reaction between CH_4 and the studied oxides were successfully tuned by tailoring the redox properties of the reducible oxides through the Al-substitution.

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1. Introduction

Methane, the main component of natural gas, is a valuable raw material for chemical industry. Even so, remote natural gas resources are often left unexploited due to the lack of favorable gas transport solutions. Offshore, remote natural gas represents a particular challenge, since floating units for conversion of natural gas to more easily transportable liquid products must be light-weight and should not represent explosion risks associated with e.g. air distillation.

Conventional technologies for methane conversion to liquid products (methanol or C_{5+} hydrocarbons) proceed via synthesis gas (CO and H_2; syngas) production over Ni-based catalysts[1]. The reaction uses either steam or molecular oxygen as oxygen source, and may be described by the following reactions:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad \text{Steam reforming} \tag{1}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \text{Water-gas shift} \tag{2}$$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \text{Partial oxidation} \tag{3}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{Full oxidation} \tag{4}$$
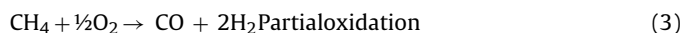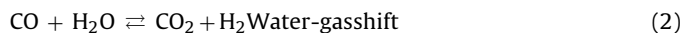
Both alternatives pose challenges for floating units. Steam reforming consists of Reactions (1) and (2). Methane conversion and syngas selectivity are both favored by high temperatures, and the reaction is typically carried out at 800 °C. Reaction (1) is strongly endothermic, and requires the use of narrow tubular reactors, typically 5–600 reactor tubes with diameter 70–130 mm in a single plant [1]. Therefore, the weight of the steam reforming process is prohibitive for floating offshore units. Partial oxidation (Reaction (3)) would ideally form syngas in a single step, but consists of full oxidation (Reaction (4)) followed by Reactions (1) and (2) [2]. Hence, it is carried out under similar conditions as the steam reforming process. The partial oxidation reaction is near isothermal and enables the use of a single reactor[1]. However, it requires an air separation unit, which may represent an explosion risk.

A chemical looping process potentially represents an attractive alternative for offshore conversion of natural gas to syngas, in particular if it would convert methane to syngas with high selectivity at moderate temperatures. In such a process, a reducible metal oxide

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(MO_x) first acts as oxygen source to methane (Reaction (5)), and is subsequently reoxidized in air (Reaction (6)):

$$CH_4 + MO_x \rightleftarrows CO + 2H_2 + MO_{x-1} \qquad (5)$$

$$MO_{x-1} + 0.5O_2 \rightleftarrows MO_x \qquad (6)$$
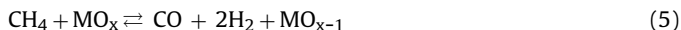
Perovskite type oxides are of great interest for applications such as oxygen separation membranes, electrodes for solid oxide fuel cells, oxygen carriers for chemical looping reactions, catalysts for methane partial oxidation or oxidative coupling and sensors [3–19]. In particular, their use as oxygen reservoirs in chemical looping reactions, especially in methane partial oxidation to syngas, has recently attracted attention. Several groups have reported the activity of various lanthanum ferrites and cobaltites (partly substituted with Sr) in the conversion of CH_4 to syngas by framework oxygen atoms, and their possible application in chemical looping processes [20–28].

Chemical looping materials should satisfy several requirements such as structural stability under reducing conditions, high oxygen capacity toward the desired oxygenated products and reversible behavior during several oxidation-reduction cycles. In addition, activity at low temperatures (800–950 K) in the conversion of CH_4 is highly desired.

It has previously been shown that $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-d}$ is stable during several cycles of oxidation and reduction under 20% O_2/Ar and 4% H_2/Ar atmosphere, respectively, at 1073 K [10]. The structural stability of perovskite oxides under reducing conditions can be further improved by introducing non-reducible cations into the structure (i.e. partial substitution of Fe and Co with Al, Cr or Ga) [29–34]. Such substitutions affect the physicochemical properties of the materials.

The oxygen capacity and the activity towards yielding desired oxygenated products are key issues in the conversion of CH_4 to syngas. Oxides characterized by high activity often convert most of the methane to undesired total oxidation products, CO_2 and H_2O [11,22].

In a previous contribution from our group, the chemical looping reaction of methane to syngas was studies at 873 K over $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-d}$ (LSFCO) and $La_{0.75}Sr_{0.25}Fe_{0.6}Co_{0.15}Al_{0.25}O_{3-d}$ with and without 0.5 wt% Rh promotion [35]. The oxide was first saturated in oxygen by pulsing 10% O_2/He over the material, followed by 10% CH_4/He pulses at 2 min interval to ensure bulk oxidation/reduction. Appreciable conversion of methane was observed for both materials even without Rh promotion. However, Rh clearly enhanced their catalytic activity. It was found that the oxygen capacity for selective CO (and H_2) production was higher for the material containing Al than for the LSFCO perovskite. Rh promotion did not affect the oxygen capacity or the product selectivity of the materials. Neutron diffraction measurements showed that Al entered the B site of the perovskite. In-situ XRD measurements revealed that the unit cell of the Al-containing perovskite was smaller, and furthermore that its contraction upon O_2 exposure was much less than for the LSFCO material. In both cases, the bulk structure was retained throughout 4 oxidation – reduction cycles at 800 and 1000 K. A correlation between syngas selectivity and the bulk oxidation potential was observed for both materials [35].

The same conclusion was reached for ceria-zirconia based materials at 873 K [36]. Both these studies strongly suggest that the syngas selectivity for these two major classes of chemical looping oxides is determined by the thermodynamic equilibrium of Reactions (7) and (8), where "O" is the oxygen partial pressure of the perovskite phase at any given degree of reduction:
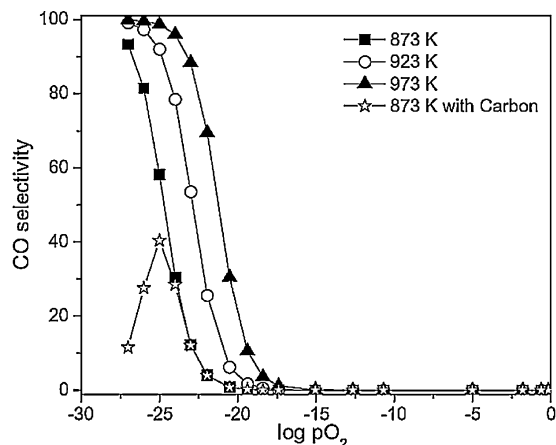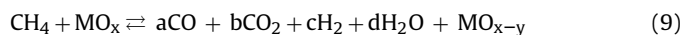
$$CO + "O" \rightleftarrows CO_2 \qquad (7)$$

$$H_2 + "O" \rightleftarrows H_2O \qquad (8)$$

Fig. 1. Calculated CO selectivity as function of oxygen partial pressure assuming equilibrium between CO, CO_2 and O_2 (and C in one case) based on standard ΔG of formation reported in NIST database. In the case of C, the standard ΔG reported for amorphous carbon was used. Reproduced from Ref. [35].

Fig. 1 shows the CO selectivity versus oxygen partial pressure when assuming gas phase equilibrium in Reaction (7). Similar curves are obtained for H_2 selectivity over H_2O (not shown). As may be seen, the "window" for selective partial oxidation of methane to syngas (>80% CO selectivity) at 873 K requires oxygen partial pressures below 10^{-25} atm. The window widens towards higher pO_2 with increasing temperature. If the hypothesis of thermodynamically driven syngas selectivity holds, the challenge in materials design for chemical looping reactions is to optimize oxygen release in the thermodynamic window between selective CO_2 and C formation in the temperature interval of interest. It would further imply that Reaction (5) above should be expanded to include both direct and indirect CO and H_2 formation, i.e.

$$CH_4 + MO_x \rightleftarrows aCO + bCO_2 + cH_2 + dH_2O + MO_{x-y} \qquad (9)$$

$$CO + MO_x \rightleftarrows CO_2 + MO_{x-1} \qquad (10)$$

$$H_2 + MO_x \rightleftarrows H_2O + MO_{x-1} \qquad (11)$$

In the present contribution, the effect of Al-substitution into $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ is investigated in detail. The aim is to explore possible correlations between partial oxidation of methane to syngas and oxide redox properties. $La_{0.75}Sr_{0.25}(Fe_{0.80}Co_{0.20})_{(1-x)}Al_xO_{3-\delta}$ (x = 0.10, 0.25, 0.40, 0.60) materials were prepared and characterized by X-ray and neutron powder diffraction and Rh-promoted samples were subjected to catalytic testing and thermodynamic measurements. Surface analysis of samples with x = 0.25 was performed by means of XPS and TEM.

2. Experimental

2.1. Material synthesis

Samples with nominal compositions $La_{0.80}Sr_{0.20}Fe_{0.80}Co_{0.20}O_{3-\delta}$ and $La_{0.75}Sr_{0.25}(Fe_{0.80}Co_{0.20})_{(1-x)}Al_xO_{3-\delta}$ (x = 0.10, 0.25, 0.40, 0.60) were prepared by the citric acid method. $Sr(NO_3)_2$ (Fluka, ≥99.0), Co(II)acetate tetrahydrate (Fluka, ≥99.0), La_2O_3 (Sigma-Aldrich, 99.99), $Al(NO_3)_3 \cdot 9H_2O$ (Merck, ≥99.0) and $Fe(NO_3)_3 \cdot 9H_2O$ (Merck, ≥99.0) were used as reagents. La_2O_3 was first dissolved in nitric acid while the other reactants were dissolved in water before mixing. A surplus of citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, 100%, VWR) was then added. The mixture was heated to 430 K and held at this temperature until dry. The dried gels were crushed and