



## Partial oxidation of methane to produce syngas over a neodymium–calcium cobaltate-based catalyst



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### ARTICLE INFO

#### Article history:

Received 21 August 2014

Received in revised form 13 October 2014

Accepted 17 October 2014

Available online 27 October 2014

#### Keywords:

Syngas

Hydrogen

Partial oxidation of methane

Layered perovskite

$\text{Nd}_{2-x}\text{Ca}_x\text{CoO}_{4\pm\delta}$

### ABSTRACT

Synthesis gas production by partial oxidation of methane (POM) ( $\text{CH}_4/\text{O}_2 = 1.8\text{--}4.5/1$ ) at  $850\text{--}960^\circ\text{C}$  over  $\text{NdCaCoO}_{3.96}$  was investigated using a fixed bed flow-type reactor. The  $\text{NdCaCoO}_{3.96}$ -derived catalyst demonstrated conversion of  $\text{CH}_4$  and  $\text{O}_2$  up to 90% while CO and  $\text{H}_2$  selectivities were over 90% at a  $\text{H}_2/\text{CO}$  ratio  $\sim 2$ . The decomposition of  $\text{NdCaCoO}_{3.96}$  at POM conditions results in the formation of finely dispersed  $\text{Nd}_2\text{O}_3$ , CaO, cobalt oxides and cobalt metal. The as-prepared catalyst exhibited excellent stability of the catalytic properties, and no activity decrease was observed for 140 h of reaction. Synthesis gas formation was accompanied by carbon deposition on the catalyst. However, this process has little or no influence on the catalytic properties of the material.

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### 1. Introduction

The conversion processes that convert natural gas to hydrogen, synthesis gas, or ethylene have attracted significant attention in recent years [1–5]. The production of hydrogen and synthesis gas has been widely studied due to their potential application as strategic sources of clean energy [6–8]. Hydrogen can be used in fuel cells, which are currently considered to be the lowest pollutant emission energy source. Simultaneously, the most economically available route from natural gas to valuable chemicals is the conversion of methane to synthesis gas [9]. Production of synthesis gas is currently produced on an industrial scale by steam reforming of methane [10]. However, the partial oxidation of methane (POM) has some advantages compared to steam reforming. First, the POM process produces syngas with a molar ratio of  $\text{CO}:\text{H}_2 = 1:2$ , which is favorable for the Fisher–Tropsch and methanol synthesis. In addition, POM is a more energy efficient process, which reduces the environmental impact.

The most well-known catalysts for the POM are transition metals including nickel [11,12]. The partial oxidation of methane

at  $700\text{--}900^\circ\text{C}$  over nickel metal on a refractory support was first described in [13]. Aging of the catalyst in a mixture of methane and oxygen at these temperatures results in the fast deactivation of the catalytic layer due to carbon deposition and significant loss of metal during the catalytic process [2,12,14].

Cobalt catalysts typically produce lower methane conversion and synthesis gas selectivity compared to nickel catalysts [11,12]. However, cobalt has higher melting and vaporizing points, and cobalt-based catalysts are less active for syngas methanation process. The addition of CoO especially to  $\text{NiO}/\text{ZrO}_2$  caused a dramatic reduction in carbon deposition [15]. In addition, no carbon formation was detected on the supported CoO catalysts [12].

The alternative approach for catalyzing POM involves the application of mixed perovskite-like oxides. These materials are able to produce finely dispersed metallic particles during the reduction process and to prevent the deactivation of the catalyst by suppressing coke formation [12,16]. Lago et al. reported that the preliminary reduction of  $\text{GdCoO}_3$  in situ resulted in cobalt metal being finely dispersed over a rare earth sesquioxide support. The as-prepared composite exhibited a methane conversion of 73% and a selectivity of 79 and 81% for CO and  $\text{H}_2$ , respectively, at  $730^\circ\text{C}$ . The La–Co–O-based catalyst that was obtained using a similar pre-reduction was active for methane combustion, and only trace amounts of CO and  $\text{H}_2$  were observed under the reaction conditions. XRD and XPS

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analyses of the spent La–Co–O catalyst indicated that under the reaction conditions, the metallic cobalt was completely reoxidized regenerating the original  $\text{LnCoO}_3$  perovskite structure [17]. According to [18], a second metal should be included in the perovskite structure to stabilize the small metal clusters formed on the catalyst surface.

Apart from the perovskite-type  $\text{ABO}_3$  complex oxides, the application of oxides with  $\text{K}_2\text{NiF}_4$ -like structures in POM catalysis has been very limited.  $\text{NdSrCu}_{1-x}\text{Co}_x\text{O}_{4-\delta}$ ,  $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{Cu}_{1-x}\text{Co}_x\text{O}_{4+\delta}$  [19] and  $\text{La}_{2-x}\text{K}_x\text{CuO}_4$  [20] are more useful as total combustion catalysts of methane and diesel soot, respectively, due to their chemical stability under the reaction conditions and the high mobility of the lattice oxygen. For  $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_{4+\delta}$  with a  $\text{K}_2\text{NiF}_4$ -like structure, efficient POM catalysis can be attributed to the cooperative effect of the lattice oxygen in the complex oxide and nanodomains of nickel obtained by the decomposition of precursor double-perovskite type  $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{FeNiO}_{6+\delta}$  in the POM environment [21].

The possibility of complex and individual oxides being reduced to metals under POM conditions makes it difficult to identify the contributions of various components to the catalytic effect of the whole system. Even for a single catalyst, the reaction between  $\text{CH}_4$  and  $\text{O}_2$  may follow different pathways depending on the state of the catalyst and the conditions applied [12]. In addition, identification of the various contributions is necessary to further optimize the catalytic system. In our preliminary communication [22], we reported the design of highly active and rather stable POM catalysts with 100% selectivity to synthesis gas based on the  $\text{K}_2\text{NiF}_4$ -like cobaltates  $\text{Ln}_{2-x}\text{M}_x\text{CoO}_{4\pm\delta}$  ( $\text{Ln} = \text{La}, \text{Nd}; \text{M} = \text{Sr}, \text{Ca}$ ) complex. Comparative analysis of the catalytic properties of  $\text{Nd}_{2-x}\text{Ca}_x\text{CoO}_{4\pm\delta}$  ( $x = 1; 0.75$ ) demonstrated the superior CO selectivity and better ( $\text{H}_2 + \text{CO}$ ) yield during POM reaction over the  $\text{NdCaCoO}_{3.96}$ -based catalyst. The current paper examines the details of the catalytic performance and chemical transformations of  $\text{NdCaCoO}_{3.96}$  in the POM reaction.

## 2. Experimental

### 2.1. Catalyst preparation

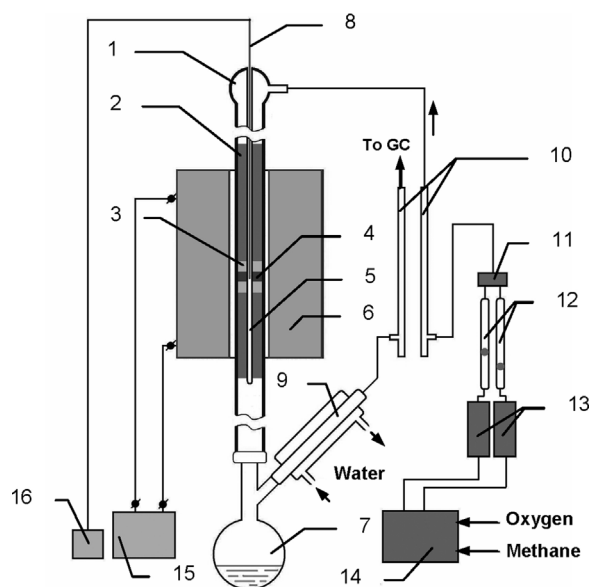
The preparation of  $\text{NdCaCoO}_{3.96}$  was performed using a solid-state synthesis method, as described in [23]. Corresponding amounts of preliminarily calcined  $\text{Nd}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{CaCO}_3$ , were mixed in a stoichiometric ratio in the planetary ball mill at 600 rpm in heptane for 30 min and then annealed at 1000–1200 °C for 24 h in air with intermediate grinding. After pressing the powders into pellets ( $\varnothing = 8$  mm), the samples were annealed at 1000–1200 °C in air followed by slow cooling to room temperature. After crushing the pellets in an agate mortar, a fraction of 100–250 mesh was selected by sieving.

### 2.2. Catalyst characterization

The as-prepared catalyst was characterized by XRD using a Huber IMAGE FOIL G670 diffractometer ( $\text{CuK}\alpha_1$  radiation). Phase analysis and crystal structure refinement were performed using the WinXPow software (STOE) and PDF-2 ICDD database.

Oxygen stoichiometry of the initial single-phase sample was determined by iodometric titration. The powder of the complex oxide was dissolved in diluted HCl with an excess amount of KI, and then, the solutions were titrated using standard thiosulfate solutions.

SEM analysis with secondary and backscattered electrons was performed with LEO-SUPRA 50 VP scanning electron microscope with a field emission cathode at  $U = 10$ –20 kV. The powder of the sample was fixed at the copper substrate using a carbon-based



**Fig. 1.** Single-pass plug-flow setup. (1) Quartz reactor, (2) quartz-glass insert, (3) quartz wool, (4) catalyst, (5) internal pocket for thermocouple, (6) electric furnace, (7) condensate receiver (round-bottom flask), (8) thermocouple, (9) water cooler, (10) flow meters, (11) gas mixer, (12) ball-in-tube flow meters, (13) adsorbent, (14) gas flows from META-CHROM, (15) furnace controller, and (16) temperature indicator.

conducting adhesive. EDX analysis at  $U = 15$  kV was performed by means of an energy dispersive INCA x-SIGHT spectrometer attached to a scanning electron microscope.

The specific surface area of the samples was measured by the single-point BET method at liquid nitrogen temperature with argon as adsorbate (volumetric system “Sorbto-meter”, Catacon, Russia).

The chemical composition of the particle surface and oxidation state of elements were analyzed by X-ray photoelectron spectroscopy (XPS) using a ThermoScientific Multilab 2000 employing  $\text{Al K}\alpha$  and  $\text{Mg K}\alpha$  radiations at a residual pressure of  $10^{-9}$  mbar. The binding energy spectra were calibrated using the  $\text{C}_{1s}$  line ( $E = 284.6$  eV) internal standard.

Temperature programmed reduction (TPR) was studied using a Micromeritics AutoChem 2 Chemisorption Analyzer in an  $\text{Ar}/\text{H}_2$  (10/1) gas mixture at a flow rate of  $50 \text{ cm}^3 \text{ min}^{-1}$ . The temperature of the samples ( $\sim 0.05$  g) was increased to 1000 °C at a heating rate of  $10^\circ\text{C min}^{-1}$ .

The carbon content in the spent catalyst was determined using an Elementar Vario Micro Cube CHN analyzer. Thermal analysis of this sample was performed in air with a heating rate of  $5^\circ\text{C min}^{-1}$  with a Netzsch STA 409 PC Luxx thermal analyzer equipped with a QMS 403 Aeolos quadrupole mass spectrometer.

### 2.3. Catalytic activity

The partial oxidation of methane was performed using a single-pass plug flow setup (Fig. 1) including a flow-fixed bed reactor (8 mm internal diameter, 650 mm length). The reactor was equipped with an internal pocket for a thermocouple ( $\varnothing = 4$  mm).

The catalyst was placed in a hot zone of the reactor at a distance of 500 mm from the inlet. The reactor was filled with quartz glass inserts to reduce the free volume upstream and downstream from the catalyst. These quartz inserts were tightly held in the thermocouple pocket.

5 mm quartz wool layers (mixer-filter) were placed at the inlet of the reactor and upstream and downstream from the layer of the catalyst. All of the tests were carried out with 0.1 g of catalyst. The catalyst bed height was only 1 mm to prevent temperature changes

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