

# High-selectivity partial oxidation of methane into synthesis gas: the role of the red-ox transformations of rare earth – alkali earth cobaltate-based catalyst components

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Catalyst selectivity and stability

## ABSTRACT

La<sub>1 + x</sub>Sr<sub>1 - x</sub>CoO<sub>4</sub> (x = 0; 0.25) and NdCaCoO<sub>3.96</sub> compounds with a layered perovskite-like structure synthesized by the solid state method and characterized by XRD, XPS, EDAX and H<sub>2</sub>-TPR were used as catalyst precursors for the partial oxidation of methane to synthesis gas. Catalytic tests were carried out in a quartz flow reactor using a CH<sub>4</sub>/O<sub>2</sub> mixture without dilution with inert gases. The higher activity of the NdCaCoO<sub>4 ± δ</sub>-based catalyst in comparison with La<sub>1 + x</sub>Sr<sub>1 - x</sub>CoO<sub>4</sub> is associated with the easier formation of Nd and Ca oxides and metallic cobalt in the course of NdCaCoO<sub>4 ± δ</sub> reduction in the POM environment. Preliminary reduction of the catalysts with hydrogen leads to a significant increase in synthesis gas production at 800–850 °C. Different activity and selectivity of NdCaCoO<sub>4 ± δ</sub> and La<sub>1 + x</sub>Sr<sub>1 - x</sub>CoO<sub>4</sub>-based catalysts can also be related to the different morphologies of metal-oxide nanocomposites that appear in the course of the reductive decomposition of cobaltates.

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## 1. Introduction

Synthesis gas is widely used in the production of alcohols, synthetic fuels, hydrogen and other chemical products [1–4]. Currently, the most common industrial method to produce synthesis gas is a process of methane steam reforming (SRM) [5–7]. Partial oxidation of methane (POM) and dry reforming of methane (DRM) are generally used in combination with the steam reforming of methane only. In comparison with SRM and DRM, the advantage of partial oxidation of methane comes from the lower energy consumption due to the exothermic character of the POM reaction. Moreover, an H<sub>2</sub>/CO = 2 ratio of POM products is favorable for the synthesis of methanol or hydrocarbons via the Fischer–Tropsch process.

The most active catalysts of POM are based on Ni, Pt, Ru and Rh supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub> and other substrates [8–11]. The disadvantage of nickel catalysts, despite their high activity, is their short lifetime due to deactivation caused by the coke formation and the sintering of the active particles. In the case of platinum metal catalysts, their high cost serves as a hindrance to broad application. Cobalt catalysts typically provide a lower methane conversion compared to nickel and noble metal-based catalysts. However, cobalt metal has higher melting and

vaporizing points that promote its lower sinterability and deactivation rate. Cobalt-based catalysts are also less active for the syngas methanation process [12]. Thus, the addition of CoO to the NiO/ZrO<sub>2</sub> precursor caused a significant reduction in carbon deposition [13], while no carbon deposition was observed in the case of the supported Co catalyst [8].

Moreover, mixed oxides with a perovskite structure can be used for POM catalysis [8,14–21]. Decomposition of the initial structure of these compounds in a POM environment results in the formation of composites containing finely dispersed particles of transition metals. Formed in this manner, metal particles have a high resistance to sintering and carbon deposition. Thus, Slagtern and Olsbye [18] studied LaMO<sub>3</sub> oxides (M – Rh, Ni, Co) with a perovskite structure as catalysts of POM. The initial structure was found to completely transform to a mixture of La<sub>2</sub>O<sub>3</sub> and transition metals during POM reaction. The most active and stable catalyst appeared to be the product of LaRhO<sub>3</sub> decomposition, which achieved methane conversion of 95% and selectivity toward CO formation of at least 98% for 120 h in the POM environment. At the same time, the reductive transformation products of LaNiO<sub>3</sub> were deactivated after just 17 h on stream, probably due to coke formation. In the case of LaCoO<sub>3</sub>, the products of methane total oxidation were primarily detected. However, after 30 h in the POM environment, it was found the formation Co metal particles dispersed over the La<sub>2</sub>O<sub>3</sub> matrix while the CO and H<sub>2</sub> concentration was increased in the outlet

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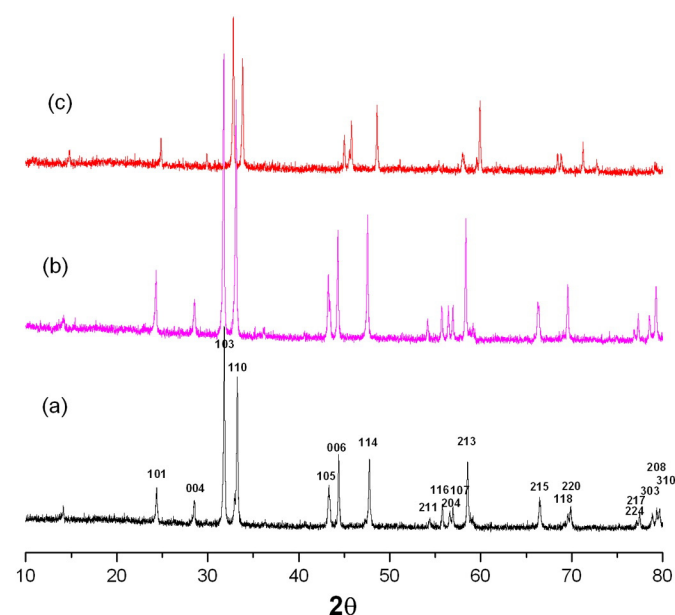
**Table 1**  
Functional properties of the Co-based catalysts of POM reaction.

Catalyst	T, °C	X <sub>CH<sub>4</sub></sub> , %	S <sub>CO</sub> , %	Working time, h	Gas mixture	Reference
Co/Al <sub>2</sub> O <sub>3</sub>	750	50	75	Deactivation during 2 h	CH <sub>4</sub> /O <sub>2</sub> /Ar – 2/1/4	[12]
Ca/Co/Al <sub>2</sub> O <sub>3</sub>	750	90	95	80	CH <sub>4</sub> /O <sub>2</sub> /Ar – 2/1/4	[12]
Co/CaO	850	60	70	Deactivation during 2 h	CH <sub>4</sub> /O <sub>2</sub> – 2/1	[8]
Co/La <sub>2</sub> O <sub>3</sub>	800	60	73	–	CH <sub>4</sub> /O <sub>2</sub> – 2/1	[8]
LaCoO <sub>3</sub>	800	25	0	–	CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> – 2/1/4	[16]
NdCoO <sub>3</sub>	820	40	50	–	CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> – 2/1/4	[16]
GdCoO <sub>3</sub>	730	70	75	–	CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> – 2/1/4	[16]
LaCoCuO <sub>3</sub>	900	68	46	–	CH <sub>4</sub> /O <sub>2</sub> /He – 2/1/37	[17]
LaCo <sub>0.5</sub> Ni <sub>0.5</sub> O <sub>3</sub>	800	50	65	–	CH <sub>4</sub> /O <sub>2</sub> /N <sub>2</sub> – 2/1/4	[19]
LaCo <sub>0.45</sub> Ni <sub>0.55</sub> O <sub>3</sub>	920	60	70	–	CH <sub>4</sub> /O <sub>2</sub> – 2/1	[21]
LaCo <sub>0.4</sub> Ni <sub>0.55</sub> Pt <sub>0.05</sub> O <sub>3</sub>	920	78	75	–	CH <sub>4</sub> /O <sub>2</sub> – 2/1	[21]

gases. In the following 50 h of reaction, the catalyst was gradually deactivated. According to others, no activity in CO and H<sub>2</sub> production was observed in the case of preliminary reduced LaCoO<sub>3</sub> due to the re-oxidation of Co/La<sub>2</sub>O<sub>3</sub> into the initial perovskite structure [16], while a GdCoO<sub>3</sub>-derived catalyst provided a CH<sub>4</sub> conversion of 73% and CO selectivity of 79 and 81% for CO and H<sub>2</sub>, respectively. It was found by XRD and XPS analysis that Co/Gd<sub>2</sub>O<sub>3</sub> formed during GdCoO<sub>3</sub> reduction remained stable to re-oxidation into the initial structure.

A feature of many mixed oxides with a perovskite structure is the high mobility of the oxygen sublattice. The presence of transition metals with variable oxidation states in these compounds promotes the appearance of defects in the anion sublattice. These defects could increase the mobility of lattice oxygen and affect the catalytic activity of perovskite and perovskite-like oxides. The high oxygen mobility in the compounds with a layered perovskite-like structure of K<sub>2</sub>NiF<sub>4</sub> type is often observed [22–24]. The oxygen mobility in the LaSrCoO<sub>4</sub> lattice was significantly higher than that in the LaCoO<sub>3</sub> perovskite [22]. The lattice oxygen of NdSrCu<sub>1-x</sub>Co<sub>x</sub>O<sub>4-δ</sub> and Sm<sub>1.8</sub>Ce<sub>0.2</sub>Cu<sub>1-x</sub>Co<sub>x</sub>O<sub>4+δ</sub> cobaltates is responsible for the high catalytic activity of these compounds in the total oxidation of methane to CO<sub>2</sub> and H<sub>2</sub>O [23].

Most known studies devoted to the catalytic properties of layered perovskite-like oxides have been generally focused on the total oxidation of methane at very high dilution of the reaction mixture with inert gases and relatively low temperatures. Briefly, the properties of several Co-based catalysts mentioned before are summarized in the Table 1.



**Fig. 1.** Diffraction patterns of as-prepared cobaltates: (a) – LaSrCoO<sub>4.00</sub>; (b) – La<sub>1.25</sub>Sr<sub>0.75</sub>CoO<sub>4.03</sub>; (c) – NdCaCoO<sub>3.96</sub>.

However, a NdCaCoO<sub>3.96</sub>-derived catalyst with a layered perovskite-like structure is proved to be active in POM catalysis with syngas formation selectivity close to 100% [25–28]. To reveal the reasons for this unusual feature, a comparative study of K<sub>2</sub>NiF<sub>4</sub>-like NdCaCoO<sub>4</sub> and LaSrCoO<sub>4</sub> behavior in the POM environment and the catalytic activity of both these compounds and possible products of their decomposition was performed.

## 2. Experimental

LaSrCoO<sub>4.00</sub>, La<sub>1.25</sub>Sr<sub>0.75</sub>CoO<sub>4.03</sub> and NdCaCoO<sub>3.96</sub> were prepared by a solid-state technique. Co<sub>3</sub>O<sub>4</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub> and CaCO<sub>3</sub> («Fluka», 99.9%) were used as raw materials. Stoichiometric amounts of preliminary calcined reagents were mixed in the planetary ball mill for 30 min at 600 rpm in heptane. After heptane evaporation, the powder mixtures were calcined in air at 1100 °C for 24 h. Then, powders were grinded again, pressed into pellets and calcined at 1200 °C for 10 h.

The phase composition of as-prepared and spent catalysts was determined by X-ray diffraction analysis (XRD) using both a Huber IMAGE FOIL G670 diffractometer (CuK<sub>α1</sub> radiation, Image Plate detector) and a Bruker AXS D8 Advanced Powder Diffraction System (CuK<sub>α1</sub> irradiation, VANTEC detector). Scanning was performed in a 2θ angle region from 10° to 80° with a 0.01° step. For the analysis of XRD patterns and refinement of unit cell parameters, the PDF-2 database of ICDD and “WinXpov” software (STOE) were used.

The ratio of cobalt ions in the different oxidation states in the synthesized compounds was determined by iodometric titration. The chemical composition of the surface of catalyst particles was analyzed by X-ray photoelectron spectroscopy (XPS) using a ThermoScientific Multilab 2000 employing Al K<sub>α1</sub> and Mg K<sub>α1</sub> radiation at a residual pressure of 10<sup>-9</sup> mbar. The binding energy spectra were calibrated using the C1s line (E = 284.6 eV) internal standard.

Reducibility of the as-prepared catalysts was studied by hydrogen thermo-programmed reduction (H<sub>2</sub>-TPR) using the Micromeritics Autochem II Chemisorption Analyzer RS232 Status and Autochem II 2920 V. 3.50 as a standard software instrument. The flow rate of the gas mixture (10% H<sub>2</sub>/90% Ar) was 50 ml min<sup>-1</sup>. The samples (0.1 g) were heated at 15 °C/min to 900 °C and held at this temperature for 30 min. The registration of the experimental data (sample temperature, duration of the experiment and the difference in hydrogen content of the initial and final gas mixtures) was carried out with a frequency of

**Table 2**  
Lattice parameters, oxygen non-stoichiometry and the fraction of Co<sup>3+</sup> in the synthesized cobaltates.

Composition	Lattice parameters		Co <sup>3+</sup> /(Co <sup>2+</sup> + Co <sup>3+</sup> )
	a, Å	c, Å	
La <sub>1.25</sub> Sr <sub>0.75</sub> CoO <sub>4.03</sub> ± 0.02	3.8174(6)	12.535(3)	0.81
LaSrCoO <sub>4.00</sub> ± 0.02	3.8041(7)	12.476(6)	1.00
NdCaCoO <sub>3.96</sub> ± 0.02	3.7358(3)	11.912(2)	0.92

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