



## Cobalt catalysts promoted with cerium and lanthanum applied to partial oxidation of methane reactions

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### ABSTRACT

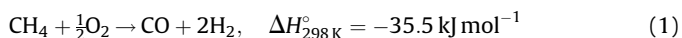
Catalysts of Co/Mg/Al promoted with Ce and La were tested in the catalytic partial oxidation of methane (POM) reaction. The addition of promoters was made by anion-exchange. X-ray diffraction (XRD) confirmed the formation of hydrotalcite phase for precursors. The mixed oxides were characterized as a mixture of Co<sub>3</sub>O<sub>4</sub>, periclase (Co, Al)MgO and/or spinel structure (Mg, Co)Al<sub>2</sub>O<sub>4</sub>. In the catalytic POM reaction over the promoted catalysts, a reduction in the carbon formation rate was found.

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### 1. Introduction

In the last years, the conversion of natural gas – whose main component is methane – into chemical products with higher aggregated value and applicability has been one of the most important catalysis fields. Besides natural gas, another growing source of methane is biogas, generated as a sub-product in the anaerobic treatment of waste water [1]. This treatment presents a great environmental impact due to the removal of the organic matter from waste water and to the fact that the biogas generated can be converted into energy. One of the principal applications of methane is synthesis gas (syngas) production. Syngas, a mixture of H<sub>2</sub> and CO, is widely used as intermediary in the chemical process industry, such as methanol and ammonium production and Fischer–Tropsch process.

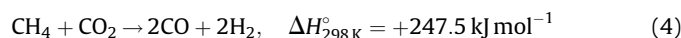
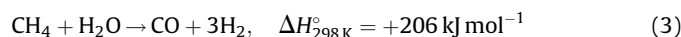
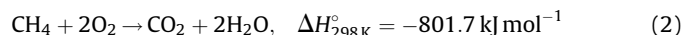
The partial oxidation of methane (POM), reaction (1), is a reaction that leads to a molar ratio of H<sub>2</sub>:CO = 2:1 suitable for syngas generation.



This reaction is mildly exothermic; however a small decrease for CO selectivity could lead to the formation of hot spots, with catalyst destruction [2]. It has been shown that catalysts obtained

from hydrotalcite-type precursors are coking resistant [3,4] and have potential to minimize the difficulties inherent to the POM process: high temperatures and catalyst deactivation.

The reaction pathway can also include parallel reactions such as total catalytic combustion of methane and reforming of the remaining methane with steam or carbon dioxide, reactions (2), (3) and (4), respectively [5].



Basile et al. [5] studied Ni/Mg/Al catalysts derived from hydrotalcites, prepared by thermal treatment at 900 °C, in POM, and observed that catalysts with low nickel content needed severe reduction treatment due to the formation of the solid solution of NiO–MgO, which presented high activity for the reaction. The catalysts with higher nickel content needed mild conditions for activation, but deactivated due to carbon formation. X-ray diffraction (XRD) and temperature-programmed reduction (TPR) analysis showed the presence of the NiO and (Ni, Mg)Al<sub>2</sub>O<sub>3</sub> phases for these catalysts.

Choudhary and Mamman [6] compared the behavior of the solid solutions CoO–MgO and NiO–MgO in POM at 700 °C and showed an inferior performance of Co catalysts to Ni catalysts when compared at molar ratio of CH<sub>4</sub>:O<sub>2</sub> = 2:1, however when

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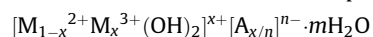
compared at molar ratio of  $\text{CH}_4:\text{O}_2 = 4:1$  the catalysts presented similar results.

Lucrédio and Assaf [4] studied the application of cobalt catalysts prepared by hydrotalcite-type precursors of Mg, Al and Co in the methane steam reforming and showed that these catalysts presented activity and selectivity for  $\text{H}_2$  and CO with low carbon formation in 30 h of reaction.

According to the literature, the utilization of cerium and lanthanum as promoters of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts in dry reforming of methane increased the thermal stability, resistance to carbon formation and catalytic activity [7].

The addition of small quantities of rare earth oxides, which have basic properties, to the structure of hydrotalcite, can change the hydrotalcites characteristics after thermal treatment by the increasing of hydrotalcites basicity [8].

The structure of the anionic clays, as shown below, presents good anion-exchange capacity, and the interlamellar space can be used to introduce cations with high cationic radius values, which are not compatible with the octahedral sites of brucite sheets, such as Ce and La, in the anionic complexes form [9].



Considering those aspects, the goal of this paper is to study the effect of the addition of promoters Ce and La in Co/Mg/Al catalysts, prepared from hydrotalcite-type precursors, in POM reactions to evaluate the products distribution and velocity of carbon formation.

## 2. Experimental

### 2.1. Synthesis

The unpromoted catalyst's precursor CoMgAl hydrotalcite-type (Ht) was prepared by the traditional technique of precipitation with carbonate. The promoted catalysts' precursors were prepared from Mg/Al/Co hydrotalcite obtained by precipitation with NaOH, which owns higher anion-exchange capacity than carbonate. This hydrotalcite was submitted to anion-exchange process with chelate type complexes of La and Ce for introduction of these cations into the CoMgAl-Ht, using the fact that  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  can react with the anionic chelating agent EDTA<sup>4-</sup>, making the highly stable complex  $[\text{Me}(\text{EDTA})]^{-1}$ . The conditions used in the precipitations were 65 °C of temperature and pH 10 controlled by NaOH 1 M addition.

(A) *Traditional method of precipitation (Tr-Co)*: prepared by dropwise addition of an aqueous solution (100 mL) containing Co(II), Mg(II) and Al(III) nitrates (5, 25 and 10 mmol) to a continually stirred solution of sodium carbonate (30 mmol in 200 mL). The resulting suspension was stirred at 65 °C for 1 h. Next, the precipitate was aged at the same temperature for 18 h without stirring. The precipitate was separated by filtration, rinsed with deionized water, dried in air at 80 °C for 24 h and reserved.

The lanthanum and cerium introduction was made by anion-exchange method (Ae-La/Ce-Co) due to the high value of ionic radius of lanthanum and cerium when compared to magnesium, according to the method described by Fonseca and Assaf [3,4] and Tsyganok et al. [10]: a lanthanum/cerium chelate complex was utilized for the synthesis below. It was prepared by adding lanthanum/cerium(III) nitrate solution (50 mmol in 100 mL of water) to tetrasodium EDTA solution (50 mmol in 100 mL of water) at 65 °C. This solution was denominated (Ce/LaY)<sup>-1</sup>.

(B) *Anion-exchange method (Ae-MeCo)*: for this method, first the CoMgAl-Ht was obtained through the addition of Co(II), Mg(II) and Al(III) nitrates (5, 25 and 10 mmol dissolved in 100 mL of water) to 1 M aqueous NaOH solution, with stirring. The resulting suspension was stirred at 65 °C for 1 h. Next, the precipitate was aged at the same temperature for 18 h without stirring and then reserved.

Lanthanum/cerium chelate solution was added to this suspension. The suspension was stirred for 24 h at room temperature and the precipitate received the same treatment as described in (A).

The hydrotalcites were calcined at 500 °C in air for 15 h, and denominated Tr-Co-Calc., Ae-LaCo-Calc. and Ae-CeCo-Calc.

### 2.2. Characterization

The surface composition was determined by X-ray photoelectron spectroscopy (XPS) analysis. The XPS measurements were performed using a Thermo VG MICROLAB 310-F instrument. The data were collected with Mg K $\alpha$  X-ray source using analyzer pass energy of 50 eV of energy. The calcined samples, mixed oxides, were used in form of pellets and fixed on a copper holder by copper tape. The charger was corrected using the C 1s peak.

The bulk composition was determined by energy-dispersive X-ray spectroscopy (EDS) analysis, using a scanning electron microscopy LEO 440 linked to an Oxford 7060 microanalyzer.

X-ray diffraction patterns were collected at room temperature in a URD-6 Carl Zeiss diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The spectra were scanned in the range  $2\theta = 3\text{--}80^\circ$  at a step rate of  $2^\circ \text{ min}^{-1}$ .

Specific surface area, average pore radius and total pore volume of mixture oxides were measured by adsorption of N<sub>2</sub> according to the method elaborated by Brunauer, Emmett and Teller (B.E.T.) using NOVA Data Analysis equipment.

Temperature-programmed reduction with hydrogen (H<sub>2</sub>-TPR) of the catalysts was performed in Micromeritics Chemisorb 2705 equipment, using 50 mg of catalyst and a temperature ramp from 25 to 1000 °C at  $10^\circ \text{ C min}^{-1}$ . A flow rate of the 30 mL min<sup>-1</sup> of 5% H<sub>2</sub>/N<sub>2</sub> was used.

### 2.3. Catalytic tests

The catalytic tests were performed in atmospheric pressure in a fixed-bed tubular quartz micro-reactor, in order to analyze the activity, product distribution and velocity of carbon formation as a function of reaction time. A specific apparatus was used and the analyses of the reactants and all the reaction products were carried out in-line by gas chromatograph (Varian, Model 3800) with two thermal conductivity detectors. The experimental methodology and the equipment used for these analyzes were previously described by the authors [11].

Prior to the reaction, 100 mg of the catalyst, sieved in the range of 60–100 mesh, right after the calcination process, were introduced into the reactor and reduced in situ in flowing of H<sub>2</sub> (50 mL min<sup>-1</sup>) at 550 °C ( $10^\circ \text{ C min}^{-1}$ ) for 1 h, to activate the catalyst. Next, the sample was heated to 750 °C under a flow of pure N<sub>2</sub>. The catalytic bed temperature was measured by the use of a thermocouple close to the reactor. The reaction was started in a hydrogen-free feed. The CH<sub>4</sub> flow was 40 mL min<sup>-1</sup> and the feed molar ratio used was CH<sub>4</sub>:O<sub>2</sub> = 2:1 and 4:1. Synthetic air was used like O<sub>2</sub> source. At the end of 24 h of catalytic test, the flow of CH<sub>4</sub>:O<sub>2</sub> was stopped and the catalyst was cooled under a N<sub>2</sub> stream.

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