

Activity of Low-Co/Al-Ratio Mixed Oxides Derived from Co-LDH Precursors in the Flameless Combustion of Methane

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Abstract

Co-LDH or Co-LDH-Gibbsite precursors were prepared by wetness impregnation and co-precipitation of 9% CoII. Mixed oxides obtained from the calcination at 800°C were characterized by XRD, FTIR and SEM-EDS. XRD showed only spinel and periclase crystalline phases. The activity of total methane combustion for five mixed oxides was tested at atmospheric pressure between 350°C and 600°C. The material obtained from the Co-LDH-Gibbsite precursor ignites methane at $T < 350^\circ\text{C}$ and completes the combustion at 565°C. The FTIR and SEM-EDS of the most active materials indicate that low Co/Al ratios facilitate the formation of surface cobalt spinel, thus improving methane combustion over mixed oxides.

Keywords: Layered double hydroxides; Mixed oxides; Cobalt spinel; Methane total combustion.



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1. Introduction

The cobalt spinel, Co_3O_4 , is known to be active in hydrocarbon total oxidation [Tian, et al. \[1\]](#) but in the bulk, it suffers sintering at moderate to high temperatures, precluding its utilization under operational conditions, e.g., in thermoelectric power plants. According to [Ulla, et al. \[2\]](#), supporting cobalt in MgO could circumvent sintering, but a CoO–MgO solid solution is formed.

According to [Liotta, et al. \[3\]](#), the activity of cobalt spinel in hydrocarbon total oxidation should be primarily attributed to a redox mechanism involving the transfer of lattice oxide species from the cobalt spinel to the hydrocarbon, reducing the lattice cobalt species. In a second step, gaseous oxygen re-oxidizes the lattice cobalt species and regenerates the lattice oxide species. Thus, it is clear that an active material should present non-sinterizable, highly disperse and supported Co_3O_4 .

In a review on materials for methane combustion, [Chen, et al. \[4\]](#) noted that considerable efforts have been made in this research area, but it is hard to find a low-cost, easy-to-prepare material with the needed characteristics.

Layered double hydroxides have been used as precursors of oxide materials. [Jiang, et al. \[5\]](#), investigated the activity of mixed oxides obtained from the calcination of Co-LDH precursors in the methane combustion. The best material they prepared had an ignition temperature of 450°C and underwent complete combustion at 600°C. [Genty, et al. \[6\]](#) prepared a series of Co-Al mixed oxides from LDH and studied the toluene total oxidation. For their best material, they demonstrate a relationship between the ratio of surface Co^{II} and the reducibility of the Co-Al mixed oxide, which suggests a Mars Van Krevelen mechanism. [Zhao and Li \[7\]](#), have studied the deposition of Ag nanoparticles (Ag NPs) on Co-LDH through a self-redox process. The highest activity in methane combustion was observed for the material with the highest low-temperature reducibility and the most abundant surface Co^{III} and surface adsorbed oxygen species.

Concerning the mixed oxides derived from the calcination of LDH, there are several proposals for their structure and composition; see, for instance, [Leont'eva, et al. \[8\]](#).

Herein, we report the preparation and characterization of Co-LDH and Co-LDH-Gibbsite precursors and the activity on methane total combustion of their mixed oxides obtained by calcination. It was found that a Gibbsite-rich LDH afforded a suitable material for methane oxidation, with ignition at $T < 350^\circ\text{C}$.

2. Material and Method

The hydrated nitrates of Co^{II} , Mg^{II} and Al^{III} , as well as sodium carbonate and sodium hydroxide, were purchased from VETEC-Sigma-Aldrich, Brazil. All chemicals were of analytical grade and were used as received. In all preparations, deionized water was used.

1. Preparation of precursors: A hydrotalcite that was rich in Gibbsite and was donated from CENPES-Petrobras (Brazil), LDH (Mg-Al-CO_3^{2-} , 3:1:3 molar ratio), and two Co-LDH samples ($\text{Co-Mg-Al-CO}_3^{2-}$,

1.5:1.5:1:3 molar ratio) prepared by the co-precipitation method at variable pHs were used in this work. The precursors were prepared according to a modified procedure of Jiang, *et al.* [5]. The LDH was aged under agitation at room temperature for 20 h. One of the cobalt-containing LDH samples was also aged under agitation at room temperature for 20 h, and the other was aged under reflux for 12 h. All precursors prepared by co-precipitation were filtered under reduced pressure, washed several times with deionized water and dried in an oven at 110°C overnight.

- Preparation of mixed oxides: Five mixed oxides were prepared at a nominal cobalt loading of 9 wt %. This nominal percentage of Co^{II} was chosen to compare with previous work on Co-MgO, taken as a reference for the activity tests, after Ulla, *et al.* [2]. The wetness impregnation method was employed to prepare three mixed oxides, two of which were obtained from commercial HT and LDH without previous calcination and were named MO 004 and MO 010, respectively. A third material, named MO 011, was prepared from the calcined LDH at 800°C for 5 h; that is, cobalt was impregnated on mixed oxides. The other two materials, named MO 010 and MO 003, were prepared by calcination at 800°C for 5 h of Co-LDH precursors aged at room temperature and under reflux, respectively.
- Characterization: Precursors and mixed oxides were characterized by X-ray powder diffraction (Rigaku Ultima-IV, Cu-K α , λ = 1.5418 Å, 40 kV, 5°-80° 2 θ , 0.02° min⁻¹), FTIR (Bruker Vertex 70, ATR, 4000 – 400 cm⁻¹), and SEM-EDS (INSPECT, ETD detector, 20 kV).
- Combustion tests: Typically, 1.0 g of the mixed oxide and SiC (2:8 wt/wt) was introduced in a fixed bed quartz reactor. The tests were carried out at atmospheric pressure using a flow (100 mL.min⁻¹) of 2.5% mol of CH₄, 10% mol of O₂ and N₂ balance. Tests were carried out in quadruplicate in a kinetic regimen between 350°C and 600°C, with intervals of 50°C, and were monitored by GC-MS (HP 6890A, TCD detector, H-PLOT Q 5 Å molecular sieve).

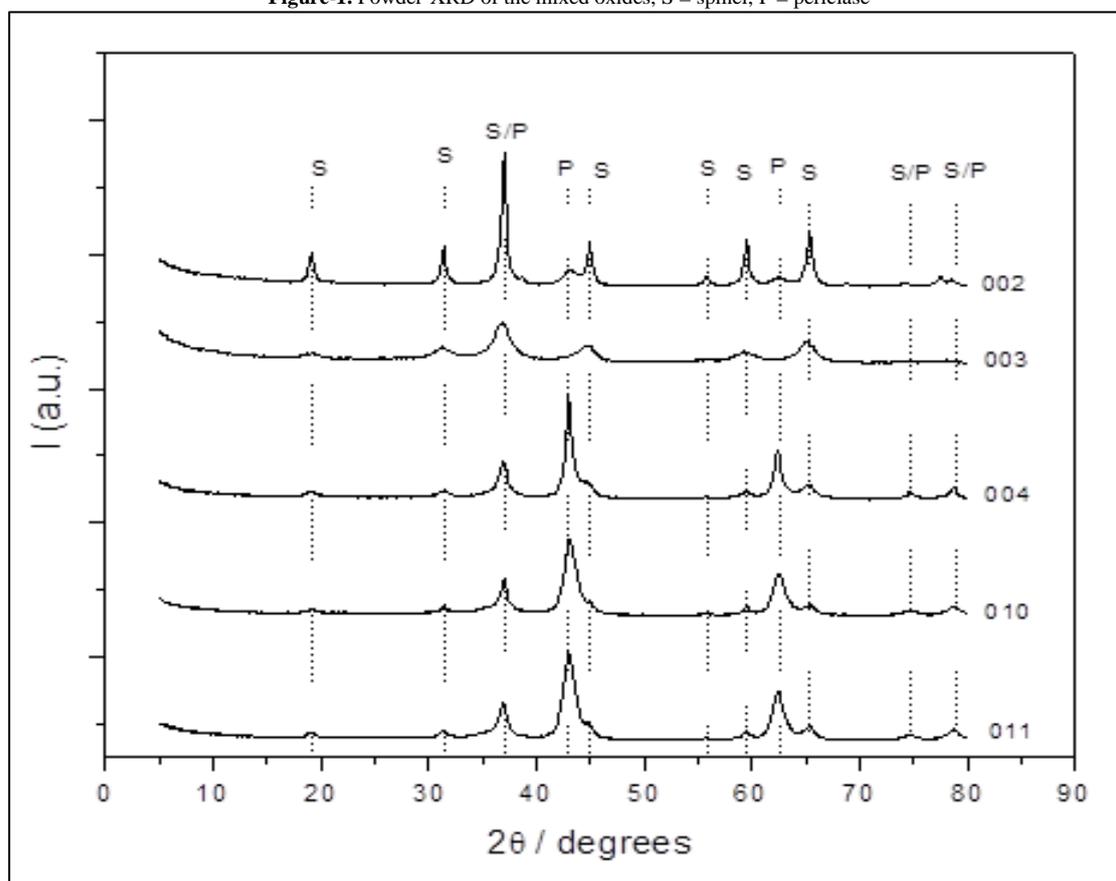
3. Results

Precursors and mixed oxides were characterized by XRD and FTIR. The mixed oxides were tested for methane total oxidation, and the most active mixed oxides were also analyzed by SEM-EDS.

3.1. XRD

The XRD of the LDH and Co-LDH prepared in the laboratory were indexed to synthetic hydrotalcite (JCPDS 01-089-0460). The XRD of the commercial HT support showed, as expected, peaks of both hydrotalcite (JCPDS 01-089-0460) and Gibbsite (JCPDS 00-033-0018). The XRD of the mixed oxides (Figure 1), except for MO 002, show peaks of periclase (JCPDS 01-071-1176) more intense than those of spinel (JCPDS 01-075-1797). Inversion of the relative intensities of the XRD peaks of this material when compared to the other mixed oxides indicates Jiang, *et al.* [5] a low content of periclase in MO 002.

Figure-1. Powder-XRD of the mixed oxides, S = spinel; P = periclase



The spinel peaks of MO 003 are less defined and less intense, and the periclase peaks are superposed on the spinel peaks due to the lower resolution of the diffractogram. From the XRD of all materials, it is not possible to determine which spinel is present ($\text{Co}^{\text{II}}\text{Co}^{\text{III}}\text{AlO}_4$, CoAl_2O_4 , Co_3O_4 or MgAl_2O_4) or if there is a predominant spinel or if there is a mixture of different spinels [5, 9]. However, the diffractograms show no other crystallographic phase, which indicates either a high dispersion of surface cobalt species or the cobalt partially substitutes for the magnesium and/or aluminum in the spinel crystalline structure. At the same time, the XRD results from formation of CoO could not be discarded, as it forms a cubic structure of the periclase type.

Surprisingly, the XRD of the calcined Gibbsite-rich hydrotalcite does not show peaks of any alumina (Al_2O_3) crystalline phase. This could be attributed to the incorporation of the Al^{III} species from the Gibbsite in the spinel species.

However, as this material is the most active one, there should be a synergism between the support, that is, mixed oxides and the cobalt species in the methane combustion, since the low ignition temperature measured for this material contrasts with literature reports for an alumina support. Xiao, *et al.* [10], found that complete methane conversion to CO_2 does not occur at significant rates at temperatures below 450°C for Al_2O_3 alone.

3.2. Combustion Tests

All materials were selective in the total oxidation of methane. Table 1 lists the temperatures of conversion of 10, 50 and 90% (T10, T50 and T90, respectively). Mixed oxide 004 showed the best results when compared to the other materials prepared in this work and when compared to the reference one, Co-MgO. At this point, it is important to note that the ignition begins at temperatures below 350°C for the MO 004, which was the initial temperature of the combustion test set-up.

Table-1. Temperatures ($^\circ\text{C}$) of conversion rates of 10, 50 and 90%

Material	T10	T50	T90
Co/MgO	375	478	575
002	420	506	570
003	420	*	*
004	<350	482	565
010	370	518	*
011	415	520	600

* does not reach the mentioned conversion in the temperature range

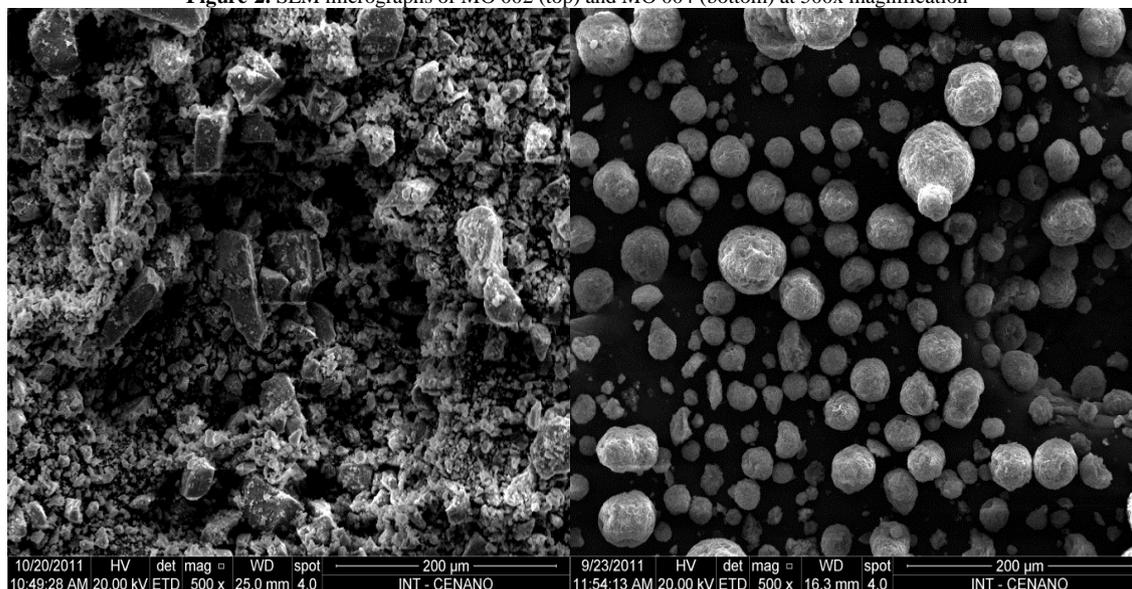
MO 002 and MO 011 also presented respectable performance, when considering the higher conversion rates (T90). MO 003 and MO 010 were not efficient for methane oxidation and do not reach T90 within the investigated temperature range.

From the data listed in Table 1, MO 004 and MO 002 deserve further investigation due to the lower ignition temperature and the second best T90, respectively. Moreover, as discussed in previous sections, MO 004 was prepared over a Gibbsite-rich LDH, and MO 002 showed an “inverse” intensity of spinel and periclase peaks in the XRD.

3.3. SEM-EDS

The morphology and surface elemental composition of MO 002 and MO 004 were investigated by SEM-EDS. In the micrographs, it is clear that the morphology is quite different for these materials; that is, the co-precipitated material is composed of non-uniform particles, whereas the impregnated one is composed of round-shaped particles.

Figure-2. SEM micrographs of MO 002 (top) and MO 004 (bottom) at 500x magnification



Mapping of the surface revealed homogeneous dispersion. EDS of the materials, measured at a magnification of 5000 times, afforded the atomic percent values (At. %) listed in Table 2.

Table-2. Surface composition (At. %) of the most active materials

Material	002	004
Element		
O	21.89	31.32
Mg	21.72	41.65
Al	16.06	20.93
Co	40.33	6.10
Co/Al ratio	2.51	0.28

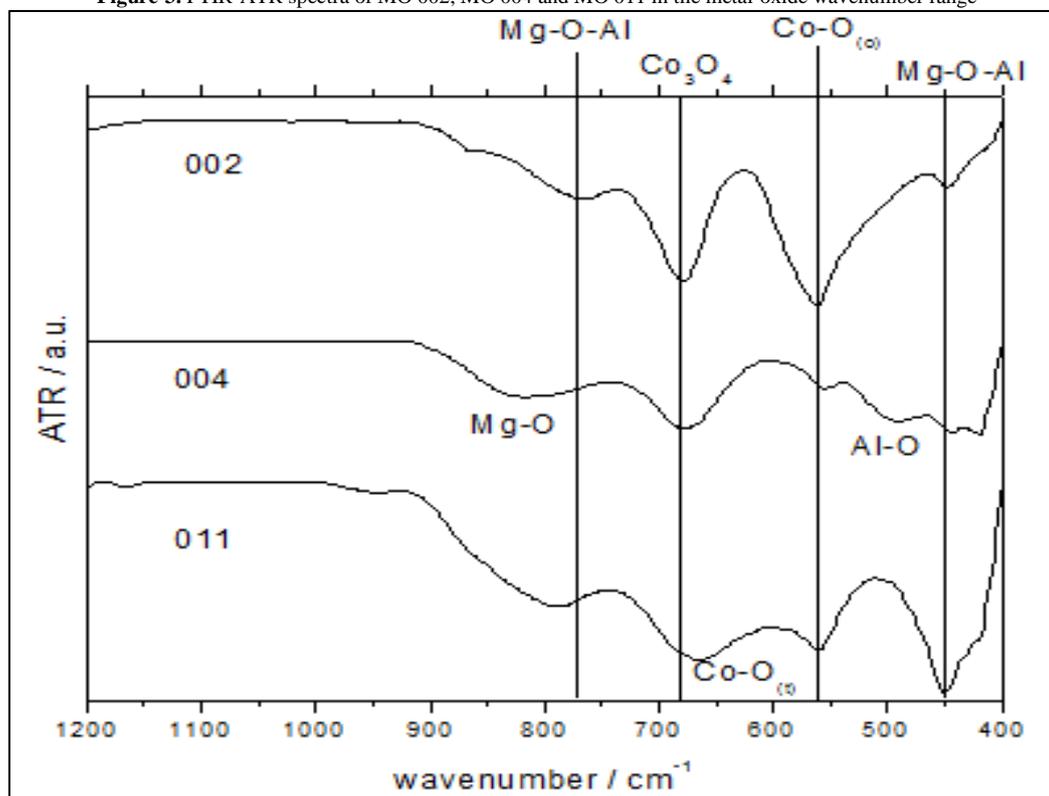
The Co/Al ratio, according to Herrero, *et al.* [11], is an important factor in the estimation of the availability of Co^{II} species; that is, the lower the Co/Al ratio is, the higher is the Co^{II} species availability. Herrero also reports that in order to oxidize Co^{II} to Co^{III} , the Co/Al ratio must be higher than 5. As shown in Table 2, the Co/Al ratio for MO 002 and MO 004 is lower than 5.

Liotta, *et al.* [3], also noted that a high concentration of surface Co^{II} species is associated with oxygen vacancies in the cobalt spinel, which are responsible for the hydrocarbon combustion activity. Thus, in order to distinguish the different oxide species present in the materials, they were analyzed using FTIR spectra.

3.4. FTIR

The FTIR spectra of the precursors presented bands typical of LDH materials [11, 12]. The FTIR spectra of all materials presented an intense and broad band at approximately 3400 cm^{-1} , assigned to the OH stretching of chemisorbed water molecules [11, 13, 14]. The absence of bands at 3630 cm^{-1} and $3550 - 3590\text{ cm}^{-1}$, assigned to hydrogen-bonded hydroxyl groups, confirms the collapse of the lamellar structure. Interestingly, a band at 1360 cm^{-1} , assigned to carbonate, was observed for all catalysts, indicating that oxycarbonate species were formed. Except for MO 003, a band at 850 cm^{-1} was observed which was assigned to the ν_2 mode of carbonate. Such observations are consistent with the calcination temperature of 800°C , which is lower than the reported temperature of 1000°C , for total collapse of the Co-LDH with loss of carbonate species. However, such a high temperature would also sinter the cobalt spinel eventually present on the supports.

Figure-3. FTIR-ATR spectra of MO 002, MO 004 and MO 011 in the metal-oxide wavenumber range



As shown in Figure 3, bands assigned to Mg-O-Al bending are observed at $783\text{--}770\text{ cm}^{-1}$ and $442\text{--}450\text{ cm}^{-1}$ for MO 002, MO 004 and MO 011. Characteristic bands of cobalt spinel, at 677 cm^{-1} , were observed only for MO 002 and MO 004, whereas for MO 003 and MO 011, bands assigned to Co-O stretching in octahedral sites were observed at approximately 660 cm^{-1} , and those for tetrahedral sites were observed at approximately $550\text{--}560\text{ cm}^{-1}$ [5, 13, 15].

4. Discussion

FTIR results, XRD patterns, EDS quantitative results and combustion tests indicate that the active phase is cobalt spinel. The most active materials (MO 004 and MO 002) present bands assigned to Mg-O-Al bending, indicating the formation of mixed oxides with a higher content of Mg and Al compared to the other materials. Common to the two most active materials is the absence of bands assigned to cobalt in tetrahedral sites and the observation of bands assigned to cobalt spinel. These three factors altogether corroborate with the hypothesis that in the most active samples there are more cobalt spinel species.

Finally, a hypothesis for the role of the low Co/Al ratio in the enhanced activity may be advanced. During calcination, at least two types of spinel are formed: one is composed of aluminum, magnesium and cobalt, and the other is the cobalt spinel. Presumably, the former should be a mixture of several sub-types. In the low-Co/Al-ratio LDH, as there is a relative excess of Al^{III}, this trivalent cation should prevail in the spinel structure, leaving non-oxidized Co^{II} species. In the other supports, with no relative excess of Al^{III}, calcination incorporates both Al^{III} and part of Co^{III}, formed during calcination. In other words, in samples containing Co^{III}, it is supposed that this ion preferentially occupies the trivalent sites in the mixed oxides. Thus, there is less available cobalt for cobalt spinel formation, and as mentioned before, excess aluminum hinders oxidation to Co^{III}. Therefore, the sites of trivalent cations in the mixed oxide structure are occupied by Al^{III}.

5. Conclusion

Mixed oxide materials derived from calcination at 800°C of Co-LDH and Co-LDH-Gibbsite precursors with nominal Co loading of 9% (wt.) were active in the total combustion of methane at atmospheric pressure in the 350°C-600°C range. The most active material was derived from the Co-LDH-Gibbsite precursor, igniting methane below 350°C and completing the combustion at 565°C. XRD of the mixed oxides were assigned exclusively to spinel and periclase crystalline phases. Mixed oxide FTIR spectra indicate the collapse of the LDH lamellar structure and formation of oxycarbonates. In the M-O wavenumber region, it was found that the most active materials present bands assigned to Co₃O₄. EDS shows that the most active materials present low Co/Al ratios, which corroborates the preferential formation of surface-active Co₃O₄ species.

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Conflicts of Interest

The authors declare no conflict of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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