Partial oxidation of methane to syngas using Co/Mg and Co/Mg-Al catalysts

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Abstract

Partial oxidation of methane (POM) was studied over a series of Co/Mg-Al catalysts. Various commercial hydroxides with different Mg/Al ratios were used as precursors of the oxides employed as catalytic supports, as well as MgO prepared in the laboratory. The effects of Co loading, Mg content, and calcination temperature (400-750 °C) were studied in the POM reaction. The catalytic performance was evaluated at 800 °C in a fixed-bed tubular quartz reactor under a high space velocity of 300 L N CH₄/(g_{cat}·h) and a O₂/CH₄ molar ratio of 0.5. A very high activity was obtained during 3.5 h on-stream with a 20 % (m/m) Co catalyst prepared with a Mg-Al mixed oxide support having a MgO content of 63 % (m/m). This catalyst gave CH₄ conversions (91.3 %) very close to the maximum corresponding to the thermodynamic equilibrium. Such notable performance could be attained with the catalyst precursor subjected to calcination at 500 °C for 6 h and subsequent *in situ* reduction under H₂ flow at 800 °C for 2 h. Two main types of deactivation were generally observed in most of the samples that suffered either a very rapid cobalt re-oxidation upon their exposure to the POM reaction atmosphere or significant deposition of carbonaceous deposits of different kinds. The characterization of the spent samples by transmission electron microscopy (TEM) revealed the presence of carbon

deposits of different nature in the Mg/Al samples having a high MgO content, including filamentous carbon (whiskers), onion-shell like sheets and/or amorphous encapsulating layers. Conversely, no carbon deposits were observed in the spent Co/MgO catalyst, which underwent oxidation of the relatively less dispersed surface Co sites to form clearly defined crystals of Co oxides with particle diameters typically ranging between 25 and 100 nm.

Keywords: Cobalt catalysts; Coke formation; Methane; Mg-Al supports; Partial oxidation; Syngas.

1. Introduction

The valorization of unconventional natural gas sources can contribute to tackling some of the most important challenges that our energy system faces nowadays. Amidst the different valorization possibilities, the development of gas-to-liquid (GTL) technologies for converting natural gas into synthetic fuels and chemicals poses an attractive alternative [1]. The first and most important step in GTL technologies from the economic point of view is the production of synthesis gas (or ‘syngas’, a gas mainly composed of H₂ and CO), which is usually obtained by means of natural gas conversion, though other methane-rich resources such as biogas can be efficiently converted into syngas [2].

One of the most interesting routes for converting methane-rich gas streams into syngas is the catalytic partial oxidation of methane (CPOM) [3]. Among the most studied catalysts for the CPOM, those based on transition metals, mainly supported Ni and Co, appear as interesting alternatives to those catalysts based on noble metals due to their good performance, abundance and relatively low cost [4]. Conversely to Ni, Co-based catalysts have the advantage of having more resistance to deactivation by coke, though Co re-oxidation is easier than in the case of Ni [5].

Different strategies have been proposed to improve the catalyst stability of Co catalysts for CPOM, such as optimizing the preparation method, introducing some modifiers such as noble metals [3,6] or selecting alkaline earth compounds as supports or support modifiers [7–9]. In the same way, some

authors studied the effect of the material used as support on the catalytic performance in the CPOM reaction [10,11]. In this sense, MgO and Al₂O₃ are interesting catalyst supports, having influence on the metal reducibility as well as on the active phase stability [12,13]. Interestingly, despite a number of studies presenting promising results of Ni-based CPOM catalysts using mixed oxides derived from the thermal decomposition of hydrotalcite-like solids [14–17], the literature concerning the use of Mg and Al mixed oxides as supports in Co-based CPOM catalysts is scarce to date. Makoa *et al.* [7] used Co/Mg/Al spinel-like mixed oxides obtained by coprecipitation of the nitrate precursor salts in the CPOM reaction at high pressure (20 bar). As for the Co/Mg-Al CPOM catalysts prepared from hydrotalcite-like precursors, only Assaf's group has reported a study so far [18], though focus was placed on evaluating the effect of Ce and La as promoters on the catalyst performance.

However, there are some important issues related to the catalyst stability in unpromoted Co-based systems which still need to be studied in more depth, such as catalyst deactivation by formation of carbonaceous deposits on the catalyst surface or the diminution of surface active phase on the catalyst, which can be attributed to metal re-oxidation under the atmosphere of the POM reaction or to the solid-state reaction of the transition metal with the support. In fact, a remarkable lack of systematic CPOM studies using Co-based unpromoted catalysts can be highlighted, other than those pioneered by Ruckenstein's group using MgO as support [9,13,19,20]. Indeed, the study by Wang and Ruckenstein [9] represents a milestone in the CPOM using Co unpromoted catalysts. In that work, a 24 % Co/MgO catalyst yielded an outstanding performance, showing a very high stability through 120 h time-on-stream at 850 °C and high spatial velocity. The authors reflected the great influence of the calcination temperature on the formation of different species, relating the reducibility of the Co surface species with the catalytic activity. Therefore, the metal-support interaction plays a crucial role in attaining highly active but also very stable catalysts, especially in those reactions such as the CPOM, in which drastic reaction conditions can compromise the catalytic performance very easily.

In this work special focus has been put on the Co/Mg-Al system, by preparing a series of Co/Mg-Al catalysts by different methods to study the effects of the different interactions established by the

oxides species on the catalytic performance in the CPOM reaction. Two different Co contents, 10 and 20 % (m/m) and different calcination temperatures (400-750 °C) have been studied, and diverse Mg and Mg-Al oxides have been selected as catalyst supports. The effects of these variables on the dispersion and reducibility of surface Co species have been analyzed in relation to the catalytic performance in the CPOM reaction and, especially, focusing on the catalysts' stability.

2. Experimental

2.1. Catalysts preparation and characterization

A series of supported Co catalysts were prepared by incipient wetness impregnation using commercial Mg-Al double-layered hydroxides (Sasol Pural) as precursor supports having different MgO contents (MGx, where x is the nominal MgO content, that was between 5 and 70 mass %). The catalysts were prepared from cobalt nitrate hexahydrate as Co precursor and pure ethanol as solvent in the impregnations, being both high-purity reagents supplied by Panreac. Two Co metal loadings, 10 and 20 mass %, expressed as Co final content in the solids were obtained. The commercial Mg-Al hydroxides were calcined before impregnation (500 °C for 6 h in a muffle furnace) to give the oxide materials used as catalytic supports. After the impregnation step, the catalysts were dried for 12 h at 100 °C and calcined again generally at the same conditions as those used for the supports, although other temperatures were also tested (400-750 °C) in the case of the catalysts prepared with the Mg-Al support having a MgO content of 63 % and loaded with a 20 % of Co in the final solid (20Co/MG63). Lastly, two different calcination temperatures (500 and 750 °C) were also evaluated for those solids loaded with 10 % of Co, 10Co/MG5 and 10Co/MG63.

In addition, a MgO support was also prepared following a citrate sol-gel method similar to that described in the literature [21], which was subsequently impregnated to obtain 20 % of cobalt mass final content and calcined at two different temperatures, 500 and 750 °C for 6 h in a muffle furnace.

This catalyst was selected as reference to investigate the effect of the presence of Al₂O₃ in the support composition.

Table 1 summarizes the composition of the supports used as well as the prepared catalysts and the calcination temperatures (T_{cal}) employed in all cases.

Table 1. Summary of the different catalysts prepared and tested in this study.

Support	% Al₂O₃^a (m/m)	% MgO^a (m/m)	T_{cal} (°C)	% Co^a (m/m)	Catalyst
MG5	95.2	4.8	500	10	10Co/MG5(500)
			750	10	10Co/MG5(750)
			500	20	20Co/MG5
MG20	79.0	21.0	500	20	20Co/MG20
MG30	69.1	30.9	500	20	20Co/MG30
MG63	35.4	64.6	500	10	10Co/MG63(500)
			750	10	10Co/MG63(750)
			400	20	20Co/MG63(400)
			500	20	20Co/MG63(500)
			750	20	20Co/MG63(750)
MG70	28.3	71.7	500	20	20Co/MG70
MgO	0	100	500	20	20Co/MgO(500)
			750	20	20Co/MgO(750)

^a Composition of the supports before impregnation. Here, the cobalt content is the nominal one.

The calcined precursors of these catalysts were characterized under different techniques, including elemental analysis, N₂ adsorption-desorption at 77 K, temperature-programmed reduction (TPR), CO pulse chemisorption and X-ray diffraction (XRD). In addition, some of the spent catalyst samples were additionally characterized by means of transmission electron microscopy combined with energy-dispersive X-ray spectroscopy (TEM-EDS).

The actual composition of the calcined precursors prepared was determined by ICP-AES using a VISTA-MPX (VARIAN) spectrophotometer by the Servicio de Apoyo a la Investigación (SAI) of the Universidad Pública de Navarra (Pamplona, Spain).

N₂ adsorption-desorption isotherms were determined in a Micromeritics Gemini V 2380 equipment, using static volumetric measurements at 77 K, with previous preconditioning of the samples at 200 °C for 2 h under N₂ gas flow. The surface area of the different samples was determined using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution could be calculated using the Barrett-Joyner-Halenda (BJH) method.

TPR analyses were carried out using a Micromeritics AUTOCHEM II 2920 equipped with a TCD detector. About 50 mg of sample was reduced using 75 N mL/min of H₂ diluted in Ar (5 vol. % H₂) from room temperature through 950 °C under a 5 °C/min temperature ramp. CO pulse chemisorption measurements were conducted in the same apparatus. Firstly, the samples were pre-reduced in the same conditions as in the catalytic tests (750 °C, 2 h) and then cooled down until the chemisorption temperature (35 °C) was reached and kept stable. Pulse chemisorption was readily carried out using 10 vol. % CO in He. Metallic dispersion (% D_{Co}) was calculated from the ratio between the surface Co atoms determined by chemisorption assuming a 1:1 CO:Co stoichiometry and the actual total Co atoms in the sample derived from the elemental analyses. The cobalt degree of reduction (% R_{Co}) was estimated from the integration of the H₂ consumption provided by the TCD signals of the TPR analyses, whereas the average metallic cobalt particle diameter was calculated as follows:

$$D(\text{Co}^0) = (0.96 \times \% R_{\text{Co}}) / (\% D_{\text{Co}}) \quad (1)$$

The presence of spherical Co particles with a density of 8.9 g/cm³ and average cross-sectional area of 0.0662 nm²/Co atom was assumed.

XRD analyses were done with a Rigaku D/Max 2500 System diffractometer by the Servicio de Apoyo a la Investigación (SAI) of the Universidad de Zaragoza (Zaragoza, Spain). A copper anode was employed, selecting the wavelength ($\lambda = 1.5418 \text{ \AA}$) by means of a graphite monochromator. The measurements were completed in the 2 θ angle range from 3 ° to 85 ° with a scanning rate of 0.030 °/s. The TEM-EDS analyses were carried out at the Servicio de Microscopia Electrónica de Materiales of the Universidad de Zaragoza (Zaragoza, Spain). TEM images were obtained with a JEOL-2000 FXII

high-resolution transmission electron microscope equipped with an INCA 200 X-Sight (Oxford Instruments) computerized EDS analysis system and a CCD GATAN 694 camera.

2.2. CPOM tests

The different catalysts were tested in a Microactivity Reference V laboratory scale setup commercialized by PID Eng & Tech (Spain). The unit had a fixed-bed tubular quartz reactor (9 mm i.d.) configuration and the dry gas outlet of the setup was coupled to an online gas analysis system consisting of an Agilent 490 Micro Gas Chromatograph equipped with two analytical modules, a molecular sieve MolSieve5A, and a Poraplot Q column (PPQ), each of them connected to thermal conductivity detectors. The Molsieve 5A column allowed the detection of H₂, N₂, CO and CH₄, while the PPQ column was used for analyzing CO₂. N₂ was used as internal standard in the quantification of the different gases. A certified gas mixture having a composition of 25 vol. % of each H₂, CH₄, CO and CO₂ was used either in standalone mode or diluted in varying proportions with high-purity N₂ (99.995 % min.) to perform the calibration of the instrument before the tests. All the gases were supplied by Praxair S.A. (Spain) and fed in separately by means of four mass flow controllers (Bronkhorst HI-TEC EL-FLOW F201C).

All the solids were activated by *in situ* reduction before the POM reaction tests for 2 h at 800 °C, under a gas flow of H₂ diluted in N₂, (25 vol. % H₂). After the reduction step, and before initiating the reaction, a N₂ flow was fed into the reactor for 1 h until reaction temperature was reached. Finally, a CH₄/synthetic air mixture having a molar ratio according to the stoichiometry of the POM reaction, O₂/CH₄ = 0.5, was pre-mixed and fed into the reactor. The total volumetric flow of the reactant gas mixture was set at 169 N cm³/min.

The catalysts were tested in powder form under an absolute system pressure of 1.3 ± 0.1 atm and at reaction temperatures in the range of 750-850 °C. The catalysts had a particle size distribution (d_p) ranging between 100 and 200 μ m, and the catalytic bed was constituted by catalyst particles intimately

mixed with 1 g of commercial high-purity α -Al₂O₃ (99.5 % min., Strem Chemicals) used as inert filler. Gas hourly space velocities (GHSV) of 150 and 300 N L CH₄/(g_{cat}·h) were used.

3. Results

3.1. Catalytic tests

Firstly, the effect of the active phase content (10 and 20 % Co) was studied on the catalysts supported on the MG5 and MG63 mixed oxides. The conditions of the tests were the following: 4 h of POM reaction at 800 °C and a GHSV = 150 N L CH₄/(g_{cat}·h). The results of the catalytic tests using the lowest Co loading revealed a poor catalytic performance in all cases. The four catalysts prepared having a 10 % of Co loading, 10MG5(500 and 750) and 10MG63(500 and 750) presented a very high initial POM activity, yielding methane conversions between 83 % and 91 %, that were close to the one corresponding to the thermodynamic equilibrium at the reaction conditions (93.6 %). However, all of them suffered of a very poor stability and an evident deactivation, undergoing a very rapid decay in their catalytic performances after just a few minutes, followed by a stint in which the decay in activity was more gradual in the case of the 10CoMG63 samples. Both samples presented an evolution in methane conversions over time from *ca.* 60 % to final values around 20 % at the end of the runs, while the yield to hydrogen evolved from initial values of *ca.* 0.5 mol/mol to a negligible H₂ production after 130-160 min on-stream. The sample calcined at 500 °C outperformed that calcined at 750 °C throughout, showing a higher stability, though the evolution over time of their catalytic performances followed similar trends. In the case of the 10CoMG5 catalysts, the initial hydrogen yield was already low (0.2 mol/mol) and their decay in activity was much faster than that of their MG63 supported counterparts. In fact, after *ca.* 50 min on-stream, the 10CoMG5 catalysts did not show any activity towards syngas production and only maintained a residual activity toward methane combustion, yielding steady values below 20 % throughout. In view of these results, it was decided not to continue working with 10 % Co loading in further catalytic tests.

Next, the performance of the catalysts with a 20 % of Co loading is presented. The evolution over time of the different catalytic runs carried out at 800 °C and GHSV of 300 N L CH₄/(g_{cat}·h) is presented in Fig. 1, by depicting CH₄ conversions (Fig. 1a), H₂ yields (Fig. 1b) and H₂/CO molar ratios (Fig. 1c). For the sake of clarity, the results corresponding to the catalytic runs carried out with the 20Co/MgO(750) catalyst have not been included in Fig. 1, due to the utter lack of activity toward syngas production displayed by this catalyst from the very beginning of the CPOM tests. Initially, all the other catalysts showed a high activity, yielding CH₄ conversions close to thermodynamic equilibrium values in all cases. However, all of them suffered more or less severe deactivation except in the case of 20Co/MG63(500). The latter yielded an outstanding performance in terms of activity and stability. This catalyst secured the development of the CPOM reaction at levels of CH₄ conversion, and syngas yield very close to the thermodynamic equilibrium values during 4 h on-stream under the drastic reaction conditions studied. The H₂/CO molar ratio obtained using the 20Co/MG63(500) sample was equal to 2 throughout, which reveals the remarkable selectivity of this catalyst towards syngas production.

The strong effect of calcination temperature on the catalytic performance of the Co/Mg-Al catalysts tested was also verified with the 20CoMg63 solids calcined under different temperatures. As can be seen in Fig. 1, calcination above 500 °C resulted in a much worse catalytic performance. In fact, the 20Co/MG63(750) catalyst presented the worst performance in all the catalysts compared in Fig. 1, as reflected by a marked drop in activity since the initial moments of reaction. This could be attributed to the formation of highly crystalline spinel phases of Co, very difficult to reduce, the formation of which is favored by the use of high calcination temperatures. This is in agreement with the characterization results that will be presented and discussed later, specifically with the TPR and XRD analyses. As for the catalyst calcined at 400 °C it also yielded a worse performance than the one calcined at 500 °C. The results presented in Fig. 1 show that, in spite of having an initial activity close to the thermodynamic equilibrium, it began to deactivate gradually until *ca.* 90 min of reaction, when a sudden drop in activity was observed.

Furthermore, it can be seen the beneficial effect on the CPOM performance of having increasing Mg contents in the support of the Co/Mg-Al catalysts. In general, the catalytic stability increased with the Mg/Al ratio in the support. Interestingly, the H₂/CO ratios remained at values slightly above 2 throughout in those catalysts in which the MgO content in the support was higher than 30 % (with the exception of the 20CoMG63(750) sample). Initially all the catalysts achieved high levels of CH₄ conversion as well as yields to syngas. However, all of them suffered a progressive decay in activity, except the already mentioned 20Co/MG63(500) sample. The decay in activity could be attributed to deactivation caused by, on the one hand, re-oxidation of Co active sites in the Co/Mg-Al catalysts with MgO contents below 30 %, and, on the other hand, by deposition of carbonaceous deposits on the catalyst surface in the rest of the Co/Mg-Al samples, in agreement with the characterization of spent samples by TEM that will be presented and discussed later.

It is also worth comparing the catalytic performance of the sample with the highest Mg content (20Co/MG70(500)) and that of the Co/MgO sample calcined at 500 °C. The former catalyst performed worse than the 20Co/MG63(500) sample, but its deactivation was less marked than that of the other Co/Mg-Al samples having lower MgO contents. The evolution with reaction time of the CH₄ conversion and H₂ yield achieved with the 20Co/MG70(500) sample revealed a mild decay in activity that could be connected to the presence of segregated surface MgO species revealed by the characterization. As for the latter, the 20Co/MgO(500) catalyst showed a poor performance, undergoing a rapid decay in CPOM activity. After 60 min of reaction, this catalyst maintained a residual activity for converting CH₄, but no longer showing any selectivity toward syngas production. Such behavior differs from the previous results reported in the literature by Wang and Ruckenstein [9]. The discrepancy is even more accused if the results presented in that work using a 24 wt. % Co/MgO catalyst calcined at 800 °C are compared against those obtained with the catalyst that showed the worst performance in this study, 20Co/MgO(750).

Fig. 1. Catalytic performance of the 20 % Co/Mg-Al catalysts. Evolution over time of a) CH₄ conversion, b) H₂ yield and c) H₂/CO molar ratio.

3.2. Characterization of the fresh catalysts

Table 2 shows the results obtained from the N₂ adsorption/desorption data and the elemental composition of the different calcined precursors analyzed by ICP-AES.

Table 2. Results from the N₂ adsorption/desorption measurements and ICP-AES.

Catalyst	Textural properties			Elemental analyses		
	BET	Pore	Average	% Al	% Mg	% Co
	Surface Area (m ² /g)	volume (cm ³ /g)	pore size (nm)			
20Co/MG5	229	0.52	6.2	24.8	1.4	18.8
20Co/MG20	182	0.36	5.8	25.2	7.6	20.9
20Co/MG30	154	0.33	6.2	18.0	9.2	17.7
20Co/MG63(400)	122	0.29	8.8	10.6	22.5	17.6
20Co/MG63(500)	119	0.24	7.4	9.5	19.2	15.7
20Co/MG63(750)	83	0.24	6.6	10.2	21.5	16.8

20Co/MG70	83	0.22	7.9	9.1	26.3	19.9
20Co/MgO(500)	64	0.36	16.8	-	39.3	20.2

In general it was observed that all the catalysts supported on mixed oxides presented relatively high surface areas and pore volumes, with values ranging between 80 and 230 m²/g and 0.2 through 0.5 cm³/g, respectively. All the samples had a prevailing mesoporous structure, with the Co/Mg-Al catalysts having relatively small average pore diameters (4-9 nm), much smaller than those of the Co catalysts supported on MgO. Nevertheless, the specific surface area was very similar to that reported by Wang and Ruckenstein for a similar catalyst [9]. Regarding the influence of the Mg content and the calcination temperature on the textural properties, the results reveal certain trends. On the one hand, the higher the Mg content in the support was in the Co/Mg-Al samples, the greater the surface area was. On the other hand, the increase of the calcination temperature affected negatively the textural properties.

The results of the ICP analyses overall show a good concordance between the nominal contents of the formulated catalysts and the actual values obtained, though the actual Co contents of the samples prepared using the MG63 supports were generally lower compared to the other catalysts.

The XRD patterns of the calcined Co/Mg-Al catalysts (Fig. 2) exhibited a great similarity among them. However, some differences were observed in the formation of certain crystalline phases, as well as in the relative intensities of the characteristic peaks. On the one hand, in the case of catalysts with low Mg content (20Co/MG5, 20Co/MG20 and 20Co/MG30), the crystalline phases detected were those that could correspond to a mixture of crystalline phases composed of Co₃O₄, CoAl₂O₄ and/or MgAl₂O₄. On the other hand, in the supports that were composed of pure MgO (20Co/MgO) or contained a high Mg/Al ratio (20Co/MG63c400, 20Co/MG63c500, 20Co/MG63c750 and 20Co/MG70), the presence of MgO as segregated phase was detected. This would be in agreement with He *et al.* [22], who indicated that in mixed oxides derived from hydrotalcite structures, when the Mg content was relatively high, phase segregation and the generation of free crystalline MgO were possible. In addition, it was observed that the greater the amount of Mg in the Mg-Al supports was

and the higher the calcination temperature in the 20Co/MG63 catalyst was, the higher the segregation of MgO was.

Fig. 2. XRD patterns of the calcined catalysts precursors.

Fig. 3 shows the TPR profiles of the catalysts. In general, a distinctive peak is observed at relatively low temperatures in all cases, the maximum of which is located between 250 and 400 °C. This peak was attributed to the reduction of crystalline Co_3O_4 species with a low degree of interaction with the support. The maximum temperature increased with decreasing Mg contents in the supports or with higher calcination temperatures. This would indicate that a greater amount of Mg in the support leads to a weaker interaction with Co_3O_4 . Besides, it was observed that the reduction peak was more intense when the Mg content in the supports was higher. This could indicate that Mg favored the formation of Co_3O_4 species less embedded into the support until an excess of MgO is reached that could favor the integration of part of the Co oxides into its structure forming a (CoO-MgO) solid solution, which would be very difficult to reduce [23–25]. Furthermore, a second region characterized by the presence of another much wider reduction peak with less intensity was observed at higher temperatures in all cases, which was attributed to the reduction of more dispersed Co species, as previously reported

[6,26]. In the case of the 20MG63(750) catalyst, a peak with maximum temperature at around 900 °C was observed, which could be attributed to the partial reduction of Co-Mg-Al spinels.

Fig 3. TPR profiles of the calcined catalysts precursors.

Metallic cobalt dispersion results after reduction at 800 °C for 2 h derived from the CO pulse chemisorption data are presented in Table 3. Co dispersion was low and similar (1.0–1.5 %) in all the catalysts supported on the Mg-Al oxides obtained from the commercial precursors, which also presented similar mean Co particle diameters, in the range between 46 and 61 nm. These results are not surprising in view of the high metal load of the catalysts. In the case of the catalyst supported on MgO, the Co dispersion was even lower (0.4 %) presumably as a result of the strong interaction with the support as suggested by the very low degree of reduction achieved (37 %). The degree of reduction of Co was considerably higher when supported on the Mg-Al oxides, especially for the 20Co/MG70 catalysts that presented a high value of 95 % as well as a comparatively high Co dispersion after calcination at 500 °C. Conversely, the catalysts supported on MgO presented a poor degree of reduction, which highlights the interesting characteristics of hydrotalcite-derived mixed oxides supports. The low metallic dispersion and degree of reduction shown by the Co/MgO sample

could explain the poor performance displayed. Furthermore, the low degree of reduction is in agreement with the formation of the CoO-MgO solid solution, concordant with the characterization results obtained by TPR and the abovementioned discussions reported in the literature.

Table 3. CO chemisorption results.

Catalyst	% D_{Co}	% R_{Co}	D(Co⁰) (nm)
20Co/MG5	1.2	73	55
20Co/MG20	1.0	62	58
20Co/MG30	1.4	72	48
20Co/MG63(400)	1.4	82	56
20Co/MG63(500)	1.5	70	46
20Co/MG63(750)	1.1	69	58
20Co/MG70	1.5	95	61
20Co/MgO	0.4	37	106

3.3. Characterization of spent catalyst samples

In order to gain further insight concerning the differences observed in the catalysts' performances, TEM-EDS analyses of some fresh and spent samples were carried out. Figs. 4 and 5 show a selection of the images taken for 20Co/MG5 (A), 20Co/MG63(500) (B), 20Co/MG70 (C) and 20Co/MgO(500) (D), fresh and spent samples respectively. TEM images of the fresh samples (Fig. 4) revealed the presence of darker regions that could be attributed to cobalt oxide particles, in agreement with the EDS analyses carried out. The EDS analyses done in the darker regions of the Co/Mg-Al catalysts revealed a higher content of Co in those areas, whereas the Co/MgO sample had dark areas which were very rich in Mg and clearer areas that according to the EDS analyses had Co and Mg in similar atomic proportions, that could corroborate the formation of the CoO-MgO solid solution. In general, relatively small particle aggregates with a high degree of dispersion and homogeneous size (10-20 nm) of cobalt oxide species were observed in the catalysts supported on mixed oxides (20Co/MG5 (A), 20Co/MG63(500) (B), 20Co/MG70 (C)). In the case of the Co/MgO catalyst, these oxidized

cobalt particles were generally larger in size and having more clearly defined crystals embedded on the support's structure, though presenting a broader particle size distribution. This is in qualitative agreement with the TPR and CO chemisorption analyses previously discussed.

Interestingly, the presence of greater amounts of Mg in the Mg-Al solids derived from hydrotalcites seems to be linked to a higher degree of crystallinity (20Co/MG63(500) and 20Co/MG70) and a more homogeneous dispersion of the Co species on the support was detected. Overall, no significant differences were observed between the 20Co/MG63(500) and 20Co/MG70 fresh samples, while 20Co/MG5 presented a more uneven distribution of Co oxide species of darker color, and clearer regions that corresponding to Mg-poor crystalline alumina from the support.

Regarding the images of spent samples used in the POM reaction (Fig. 5), significant differences were observed compared to the homologous fresh samples. Firstly, different types of carbon deposits can be seen in the 20Co/MG63(500) and 20Co/MG70 catalyst samples, in the form of filaments and “onion-shell” structures of highly crystalline and graphitized carbon. The images also reveal the existence of greyish layers of material that could be attributed to the presence of amorphous carbon deposits on the surface of these spent samples. Furthermore, in spite of the C deposition detected, the high activity of these catalysts could be explained by taking into account the predominantly filamentous nature of the deposits of C, which raised the Co crystallites onto the top of the whiskers. These Co particles seemingly remained unaltered in size, as corroborated by darker areas on the tips of the filaments of around 10 nm of diameter.

Interestingly, no C deposition was detected in the catalysts supported neither in MG5 nor in MgO. In the case of the 20Co/MG5 catalyst, the presence of sintered areas of material could be clearly observed after its use in the CPOM reaction, with particle sizes ranging between 25 and 60 nm approximately. This evidenced that the main reasons for the fast deactivation of this catalyst were the joint oxidation and sintering phenomena of the Co active species. Similarly, massive sintering of the Co-containing particles was detected in the spent sample of the 20Co/MgO catalyst, observing big particles having sizes up to 270 nm. This could explain the changes in color observed for this catalyst

before and after the CPOM reaction (the fresh sample being black whereas the spent samples had a light grey appearance).

All these evidences could explain the results obtained and allowed to conclude that the main reason for the loss of stability in the Co/MG5 and 20Co/MgO was the joint combination of oxidation and sintering phenomena, while the main reason of the higher stability of 20Co/MG63(500) and 20Co/MG70 was that part of the Co remained in its metallic form at the tip of C filaments after reaction, whereas the more gradual deactivation in these catalysts would be caused mainly by the encapsulating nature of amorphous and/or graphitized surface C deposits that could be detected.

Fig 4. TEM images of the fresh catalysts: A) 20Co/MG5, B) 20Co/MG63(500), C) 20Co/MG70 and D) 20Co/MgO(500).

Fig 5. TEM images of the spent catalysts: A) 20Co/MG5, B) 20Co/MG63(500), C) 20Co/MG70 and D) 20Co/MgO(500).

4. Discussion

All these results can be explained by taking into account certain characteristics of the POM reaction. On the one hand, the role of the metallic Co as active phase of syngas production; on the other hand, the role exerted by oxygen as a reactant, which is involved in the desired methane partial oxidation reaction but it is also capable of oxidizing the metallic Co on the catalyst surface, hence resulting in oxidized cobalt species that are inactive in POM reaction, but being moderately active for methane combustion. Finally, the other components of the catalyst (Mg and Al in the case of the Mg-Al mixed oxides supports), can also be directly or indirectly involved in the process by interacting with the molecules of reagents, products or intermediate surface species. This backdrop shows a competitive process for oxygen in at least two reactions: the oxidation of the surface metallic Co, and the reactions involved in the formation of synthesis gas main products.

From the point of view of preserving the metallic function, a rapid consumption of the O_2 at the entrance of the catalytic bed through methane conversion reactions would be a favorable situation. What the results suggest is that if the CPOM rate is high enough, the oxygen allows to form CO and H_2 (and eventually CO_2 and H_2O) instead of oxidized cobalt. To achieve such scenario, the first instants of the feeding of the reactants are crucial regarding catalyst stability. In this way, as discussed by Bharadwaj and Schmidt [27], short contact times (< 0.1 s) and reaction temperatures above $750^\circ C$ favor the direct route of formation of the syngas products. However, this fact implies that the consumption of oxygen takes place via activated O species adsorbed on the catalyst surface, which in turn can set favorable conditions for the re-oxidation of surface metallic Co if the temperature, and hence the POM reaction rate, decrease.

The metal-support interactions seem to be also of great importance as concerns preserving the cobalt crystallites in their reduced state while still maintaining a significant dispersion, in which the Mg-Al oxides derived from hydrotalcite solids have excelled in various cases reported in the literature before [14,17,18,22,28]. As already mentioned, the TPR results indicated the presence of oxidized cobalt species that were easily reduced at relatively low temperatures ($250-400^\circ C$) suggesting that presented a low degree of interaction with the support. Increasing magnesium contents in the Mg-Al mixed oxides supports allowed that the metallic dispersion improved provided that the calcination temperature was adequate and that segregated MgO phases were not originated as consequence of an excessively high Mg/Al ratio as in the case of the MG70 support. All this goes to show that the interaction of the metallic particle with the support must be high enough to ensure an adequate dispersion of the active metal while preventing sintering upon exposure at high temperatures, though not excessively strong to result in the excessive formation of poorly reducible Co compounds such as spinels and/or CoO-MgO solid solutions. Therefore, a careful choice of the catalyst preparation conditions and Mg/Al ratio in the support are key to obtain highly active and stable catalysts under the demanding conditions of the CPOM reaction. On top of this, tuning the acid-basic properties of the support can help preventing the deactivation of the catalyst by the formation of encapsulating carbon

deposits. In this sense, polymeric CH_x carbon precursor species that lead to the encapsulation of the catalyst particles [2,29] are more prone to be formed in supports with strong basic properties, as a result of the formation of carbon species of aliphatic nature [30], though the resistance to coking becomes enhanced by the incorporation of Mg as support modifier as a result of the enhanced gasification of surface carbon species displayed by Mg-containing alumina supports. In fact, the alleviation of the deactivation by coking in Mg-Al oxides is derived from the formation of more easily oxidized and with higher hydrogen content carbonaceous species [31], which can also restrain the polymerization reactions leading to the formation of encapsulating coke [22]. However, as pointed by other authors, a good metallic dispersion resulting in small crystal sizes of the metal active sites can result in the preferential formation of filamentous carbon over encapsulating coke [28], in agreement with the findings from the present work.

Special mention deserves the distinct results encountered in this work using a 20 % Co/MgO catalyst compared to those previously reported by Wang and Ruckenstein [9]. It was somewhat surprising not to have a good catalytic performance, especially with regards to stability, though testing two different samples calcined at relatively low and high temperatures, though falling within the same interval of calcination temperatures used in that work and at fairly similar calcination times. Indeed, the characterization results present a good level concordance between both works, and the experimental conditions in the testing of the catalyst in the CPOM reaction are also fairly similar. In that work, the authors explained the outstanding performance of the Co/MgO catalyst calcined at 800 °C during 6 h to the intimate formation of the CoO-MgO solution, which upon reduction could form Co crystals of very small size, which would result in an activated solid counting a high Co dispersion on the catalyst surface and insensitive to coke formation. Indeed, when studying the effect of the calcination temperature, Wang and Ruckenstein found that the catalysts calcined at temperatures below 800 °C also presented Co_3O_4 and MgCo_2O_4 species in addition to the CoO-MgO solid solution, in agreement with the results obtained in this work. The authors concluded that being these species more easily reducible than the solid solution, they resulted in the formation of larger Co clusters on the surface

that could result in enhanced carbon formation and sintering. The former was not observed in this work, but the latter was indeed corroborated by the TEM analyses. Perhaps the different contact times of the reactants in both works could result in favored re-oxidation and sintering reactions in this work against carbon deposition. In addition, the lack of activity displayed by the 20Co/MgO(750) catalyst could be derived from an insufficient activation of the sample. Being more difficult to reduce, perhaps the activation conditions selected in this work resulted in a low amount of metallic Co available on the catalyst surface before reaction. All these facts could explain the discrepancies found.

5. Conclusions

In this work a series of Co/Mg-Al solids were prepared using MgO and Mg-Al oxides as supports. The use of these materials as catalysts was studied in the catalytic partial oxidation of methane (CPOM) under drastic conditions. It could be observed that the Co loading has a relevant role on maintaining the catalytic stability. A Co loading of 10 % (m/m) resulted in a very poor stability in samples prepared both on supports with low and high Mg/Al molar ratios. Conversely, when the Co loading was augmented to 20 % (m/m) a significant enhancement in stability was observed in most cases. The use of MgO as supports did not provide satisfactory results, contrarily to what was previously reported in the literature. This triggers interesting unknowns about the type of metal-support interactions that can take place in the Co/MgO system, which shall be analyzed in-depth in further dedicated studies.

One of the main conclusions that can be highlighted from the results obtained in this study is that it is crucial to preserve the Co metallic function and maintain it at an elevated degree of surface dispersion through the unfavorable conditions existing in POM. To fulfil such goals it is necessary a careful choice of the Co loading, the support nature and calcination and activation conditions.

Overall, it can be concluded that Co-based catalysts prepared on Mg-Al mixed oxides supports derived from hydrotalcite-like solids constitute an interesting alternative for producing syngas by means of CPOM. Co loadings of 20 % (m/m) resulted in the development of a highly active and stable

catalyst using a support that had a Mg/Al molar ratio of 2.2. This catalyst yielded an outstanding performance over 4 h time-on-stream in the POM carried out at 800 °C and high space velocity (300 N L CH₄/(g_{cat}·h)), securing very high methane conversions and high-quality syngas (H₂/CO molar ratios equal to 2) throughout. These results are at the vanguard of the state-of-the-art in the development of Co catalysts for the POM reaction.

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References

- [1] E. McFarland, Unconventional chemistry for unconventional natural gas, *Science* 338 (2012) 340–342.
- [2] A. Moral, I. Reyero, C. Alfaro, F. Bimbela, L.M. Gandía, Syngas production by means of biogas catalytic partial oxidation and dry reforming using Rh-based catalysts, *Catal. Today*. 299 (2018) 280–288.
- [3] B.C. Enger, R. Lødeng, A. Holmen, Modified cobalt catalysts in the partial oxidation of methane at moderate temperatures, *J. Catal.* 262 (2009) 188–198.

- [4] Y.H. Hu, E. Ruckenstein, Catalytic conversion of methane to synthesis gas by partial oxidation and CO₂ reforming, *Adv. Catal.* 48 (2004) 297–345.
- [5] Å. Slagtern, H.M. Swaan, U. Olsbye, I.M. Dahl, C. Mirodatos, Catalytic partial oxidation of methane over Ni-, Co- and Fe-based catalysts, *Catal. Today*. 46 (1998) 107–115.
- [6] R. Lødeng, E. Bjørgum, B.C. Enger, J.L. Eilertsen, A. Holmen, B. Krogh, et al., Catalytic partial oxidation of CH₄ to H₂ over cobalt catalysts at moderate temperatures, *Appl. Catal. A Gen.* 333 (2007) 11–23.
- [7] M.P. Makoa, N.J. Coville, V. D. Sokolovskii, Characterisation of Co/Mg/Al₂O₃ high pressure partial oxidation catalysts, *Catal. Today*. 49 (1999) 11–16.
- [8] V. Sokolovskii, N. Coville, A. Parmaliana, I. Eskendirov, M. Makoa, Methane partial oxidation. Challenge and perspective, *Catal. Today*. 42 (1998) 191–195.
- [9] H.Y. Wang, E. Ruckenstein, Partial Oxidation of Methane to Synthesis Gas over Alkaline Earth Metal Oxide Supported Cobalt Catalysts, *J. Catal.* 199 (2001) 309–317.
- [10] V.R. Choudhary, A.M. Rajput, V.H. Rane, Low temperature oxidative conversion of methane to synthesis gas over Co/rare earth oxide catalysts, *Catal. Letters*. 16 (1992) 269–272.
- [11] V.R. Choudhary, S.D. Sansare, A.S. Mamman, Low-temperature selective oxidation of methane to carbon monoxide and hydrogen over cobalt-MgO catalysts, *Appl. Catal. A Gen.* 90 (1992) L1–L5.
- [12] Y.-F. Chang, H. Heinemann, Partial oxidation of methane to syngas over Co/MgO catalysts. Is it low temperature?, *Catal. Letters*. 21 (1993) 215–224.
- [13] E. Ruckenstein, H.Y. Wang, Effect of calcination conditions on the species formed and the reduction behavior of the Cobalt-Magnesia catalysts, *Catal. Letters*. 70 (2000) 15–21.
- [14] T. Shishido, M. Sukenobu, H. Morioka, M. Kondo, Y. Wang, K. Takaki, et al., Partial oxidation of methane over Ni/Mg-Al oxide catalysts prepared by solid phase crystallization method from Mg-Al hydrotalcite-like precursors, *Appl. Catal. A Gen.* 223 (2002) 35–42.

- [15] F. Basile, L. Basini, M.D. Amore, G. Fornasari, A. Guarinoni, D. Matteuzzi, et al., Ni/Mg/Al anionic clay derived catalysts for the catalytic partial oxidation of methane, *J. Catal.* 173 (1998) 247–256.
- [16] K.M. Lee, W.Y. Lee, Partial oxidation of methane to syngas over calcined Ni–Mg/Al layered double hydroxides, *Catal. Letters.* 83 (2002) 65–70.
- [17] J.A. Velasco, C. Fernandez, L. Lopez, S. Cabrera, M. Boutonnet, S. Järås, Catalytic partial oxidation of methane over nickel and ruthenium based catalysts under low O₂/CH₄ ratios and with addition of steam, *Fuel.* 153 (2015) 192–201.
- [18] A.F. Lucrédio, G. Jerkiewicz, E.M. Assaf, Cobalt catalysts promoted with cerium and lanthanum applied to partial oxidation of methane reactions, *Appl. Catal. B Environ.* 84 (2008) 106–111.
- [19] E. Ruckenstein, H.. Wang, Carbon dioxide reforming of methane to synthesis gas over supported cobalt catalysts, *Appl. Catal. A Gen.* 204 (2000) 257–263.
- [20] E. Ruckenstein, H.Y. Wang, Combined catalytic partial oxidation and CO₂ reforming of methane over supported cobalt catalysts, *Catal. Letters.* 73 (2001) 99–105.
- [21] P.H. Courty, H. Ajot, C.H. Marcilly, B. Delmon, Oxydes mixtes on en solution solide sous forme tres divisee obtenus par decomposition thermique de precurseurs amorphes, *Powder Technol.* 7 (1973) 21–38.
- [22] L. He, H. Berntsen, E. Ochoa-Fernández, J.C. Walmsley, E.A. Blekkan, D. Chen, Co–Ni Catalysts derived from hydrotalcite-like materials for hydrogen production by ethanol steam reforming, *Top. Catal.* 52 (2009) 206–217.
- [23] Y. Boucouvalas, Z. Zhang, X.E. Verykios, Heat transport limitations and reaction scheme of partial oxidation of methane to synthesis gas over supported rhodium catalysts, *Catal. Letters.* 27 (1994) 131–142.
- [24] S. Tang, J. Lin, K.L. Tan, Partial oxidation of methane to synthesis gas over α -Al₂O₃-supported bimetallic Pt – Co catalysts, *Catal. Letters.* 59 (1999) 129–135.

- [25] D. Li, M. Lu, S. Xu, C. Chen, Y. Zhan, L. Jiang, Preparation of supported Co catalysts from Co–Mg–Al layered double hydroxides for carbon dioxide reforming of methane, *Int. J. Hydrogen Energy*. 42 (2017) 5063–5071.
- [26] G. Jacobs, T.K. Das, Y. Zhang, J. Li, G. Racoillet, B.H. Davis, Fischer–Tropsch synthesis: support, loading, and promoter effects on the reducibility of cobalt catalysts, *Appl. Catal. A Gen.* 233 (2002) 263–281.
- [27] S.S. Bharadwaj, L.D. Schmidt, Catalytic partial oxidation of natural gas to syngas, *Fuel Process. Technol.* 42 (1995) 109–127.
- [28] K. Christensen, D. Chen, R. Lodeng, A. Holmen, Effect of supports and Ni crystal size on carbon formation and sintering during steam methane reforming, *Appl. Catal. A Gen.* 314 (2006) 9–22.
- [29] C.H. Bartholomew, Mechanisms of catalyst deactivation, *Appl. Catal. A Gen.* 212 (2001) 17–60.
- [30] A.J. O'Malley, S.F. Parker, C. Richard, A. Catlow, Neutron spectroscopy as a tool in catalytic science, *Chem. Com.* 53 (2017) 12164–12176.
- [31] J. da S. Lisboa, D.C.R.M. Santos, F.B. Passos, F.B. Noronha, Influence of the addition of promoters to steam reforming catalysts, *Catal. Today*. 101 (2005) 15–21.