Reduction and desorption with carbon monoxide in Cr/SiO$_2$ catalysts for ethylene polymerization

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Abstract

Cr/SiO$_2$ catalysts for ethylene polymerization, prepared with 1 wt.% Cr and different chromium precursors, were characterized by temperature-programmed reduction (TPR) and desorption of carbon monoxide. Complete reduction of Cr^{6+} to Cr^{2+} species was observed with CO at 623 K, but the reduction profile modified in the presence of Cr^{3+}, depending on the chromium precursor. The desorption of CO occurred in relatively low temperature for catalysts without Cr^{3+}, independent of the Cr_A^{2+}/Cr_B^{2+} active sites ratio. The desorption of CO was observed at higher temperature in the catalysts containing Cr^{3+}, suggesting modification of the Cr^{2+}–CO adsorption strength in the presence of Cr^{3+}. The desorption of CO$_2$ was detected in all catalysts, associated to the CO disproportionation reaction at lower temperatures or to the decomposition of carbonates and carboxilates species above 500 K. The desorption of CO agreed with polymerization activity results, showing the importance of this technique to characterize active chromium sites.
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1. Introduction

Cr/SiO$_2$ catalysts are used industrially in the ethylene polymerization [1]. The active chromium sites for polymerization are reported in the literature as Cr^{2+}, named Cr_A^{2+}, Cr_B^{2+} and Cr_C^{2+}, depending on the chromium coordination with the support, 2, 3 and 4, respectively [2–5]. These species can be obtained by reduction with carbon monoxide from hexavalent chromium species at 623 K [6,7]. However, trivalent chromium does not change in the same reduction conditions. The distribution of Cr^{3+}/Cr^{6+} species in calcined Cr/SiO$_2$ catalysts and, consequently, Cr^{3+}/Cr^{2+} species in the CO reduced ones depends on the precursor salt, support, calcination and reduction conditions [8,9].

Concerning the Cr^{2+} sites, Cr_B^{2+} and Cr_C^{2+} species interact with one or two superficial hydroxyls of the support, respectively [4]. These species can be identified by carbon monoxide chemisorption followed by infrared spectroscopy [2–4,10]. The Cr_A^{2+} and Cr_B^{2+} species are active in the poly-

merization and adsorb CO at 298 K, while the Cr_C^{2+} species is inactive and does not adsorb CO at 298 K [4]. This last species has been characterized by infrared spectroscopy of CO adsorbed at 77 K. Thus, CO is a contaminant in the ethylene polymerization reaction, even in low concentration, once it adsorbs in the active sites [11], competing with ethylene.

The desorption of CO in Cr/SiO$_2$ catalysts has been studied by spectroscopic techniques [12–15]. The experiments have focused adsorption at different CO partial pressures, at 298 K or at 77 K. At 298 K, Cr_A^{2+} and Cr_B^{2+} adsorb CO, yielding bands in the IR spectrum at 2179 and 2188 cm^{-1}, respectively. On the other hand, few results of temperature programmed desorption (TPD) have been published. Parker et al. [14] studied desorption of carbon monoxide adsorbed in a Cr/SiO$_2$ catalyst (0.95 wt.% Cr), previously reduced with CO. The infrared spectrum presented bands at 2183 and 2097 cm^{-1}, ascribed to CO bonded to chromium species, linear (Cr_A^{2+} and Cr_B^{2+}) and in bridge, respectively. The attribution of these bands was also made by Zecchina et al. [15]. Particularly, both references showed that the band at 2097 cm^{-1} represents CO weakly adsorbed in chromium site and it can be easily removed by vacuum. Zecchina et al.

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[15] ascribed the formation of isolated and paired chromium sites to the reduction of chromates and dichromates species, respectively. The isolated Cr and paired Cr–Cr sites give rise to linear and bridged-bonded CO adsorbed species, respectively. In fact, according to Parker et al. [14], the desorption of CO bonded in bridge is complete at 298 K, while the desorption of the linear-bonded form occurs at higher temperature (up to 473 K). This desorption behavior is different from the observed for CO on metals, for example, in metallic palladium [16]. In this case, the desorption of CO adsorbed linearly occurs at lower temperature, evidencing the largest stability of the CO–Pd adsorption in bridge.

Bensalem et al. [12] and Zecchina et al. [13] observed carbonate and carboxilate species on Cr_2O_3/SiO_2 and CrO_3/SiO_2 catalysts, respectively, after adsorption of CO and CO_2. The desorption of these species was studied by Bensalem et al. [12] in CrO_3/SiO_2 catalysts after reduction with CO, yielding CO_2. The authors suggest that at moderate temperatures (373–473 K) carbonate species prevails, but at larger temperatures it is converted to carboxilate, since at 673 K carbonate is not observed. Concerning the presented data, it is possible to suppose that carboxilate or monodentate carbonate species are still present on Cr/SiO_2 catalysts, reduced with CO, after the usual treatment of cleaning the surface with inert gas flow or vacuum in the reduction temperature (623 K).

Recently, we reported that the distribution of Cr^{6+} and Cr^{3+} species in calcined Cr/SiO_2 catalysts depends on the chromium precursor. It also influences the distribution of Cr^{2+} active sites, obtained after reduction with CO, and the activity in the ethylene polymerization [8,17].

The objectives of this study were to evaluate the reduction and desorption behavior of carbon monoxide adsorbed in Cr/SiO_2 catalysts, prepared with different precursors, using temperature programmed reduction (TPR) and temperature programmed desorption experiments. TPD of CO adsorbed was accomplished in the attempt of distinguishing the Cr_A^{2+} and Cr_B^{2+} sites by its adsorption strength for the comprehension of the catalyst structure. The goals were to determine whether different Cr^{2+} sites interact distinctively with CO and how this interaction is affected by the distribution of chromium species, which depends on the chromium precursor used in the preparation. There are not results in the open literature on the use of TPD analysis of CO adsorbed applied to Cr/SiO_2 catalysts. However, the adsorption and desorption of CO followed by infrared analyses are frequently reported [2–4,18]. In this case, desorption is promoted by vacuum or inert gas flow at different temperatures.

2. Experimental

2.1. Preparation of the catalysts

The catalysts were prepared by wet impregnation of aqueous solutions (15 cm^3/g support) of chromium(II)acetate, chromium(II)chloride or chromium(VI)oxide over commercial SiO_2 (299 m^2/g, 1.65 cm^3/g). Other chromium precursor, bis(triphenil)silylchromate (BTC), was prepared according to the methodology of Granchelli and Walker [19] and characterized by X-ray diffraction analysis [20]. The catalysts were dried at 393 K for 18 h and calcined at 773 K for 1 h under dry air flow, resulting chromium contents close to 1 wt.% Cr. Physical mixtures of CrO_3 and α-Cr_2O_3 (Aldrich) with the calcined silica were also prepared in an agate mortar. All the samples were characterized by atomic absorption spectroscopy.

2.2. TPR and TPD of carbon monoxide

The reduction and desorption of carbon monoxide analyses were accomplished in a Micromeritcs equipment (Model 2900) coupled with a mass spectrometer and a Balzers quadrupole. The samples were pre-treated with helium flow (AGA, 99.999 wt.%) at 773 K for 1 h. The reduction was accomplished using a 5 wt.% CO/He mixture flow (60 ml/min) and the temperature was raised up to 623 K (10 K/min). After this step the samples were cleaned with helium flow (60 ml/min) at 623 K for 1 h, followed by cooling to 298 K. Then, CO adsorption was carried out by passing a flow of 5 wt.% CO/He (60 ml/min) for 30 min. Finally, the desorption of CO was accomplished with helium flow (60 ml/min) and the temperature was raised up to 773 K (10 K/min), keeping at this temperature for 1 h. CO, CO_2, H_2O and H_2 masses were monitored at $(m/e) = 28$, 44, 18 and 2, respectively.

2.3. DRIFTS

Cr/SiO_2 catalysts were also submitted to diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) measurements on a NICOLET Magna IR 760 instrument equipped with a diffuse reflectance accessory and a vacuum cell from Spectratech. This analysis was carried out in the calcined samples to observe the bands in the 2500–4000 cm^{-1} region, ascribed to the interaction of chromium species with the surface hydroxyls of the support. The DRIFTS cell was filled with approximately 20 mg of the sample, and the treatment with helium flow (AGA, 99.999 wt.%) at 773 K for 1 h was carried out in situ. Spectra were recorded with a resolution of 4 cm^{-1} with a DTGS detector and quantified as the subtraction of the background spectrum from the calcined sample spectrum.

3. Results and discussion

3.1. TPR of CO

Table 1 presents the chromium contents of the catalysts and physical mixtures, obtained by atomic absorption spectroscopy, and the fraction of Cr^{3+} after calcination. In early

Table 1
Sample codes, atomic absorption and DRIFTS results for the Cr/SiO$_2$ catalysts and standards

Sample	Precursor	Cr (wt.%)	Cr^{3+} (%)[a]	I/I_{1CrA}	Cr$_A^{2+}$/(Cr$_A^{2+}$ + Cr$_B^{2+}$) (%)[a]
1CrA	Acetate	0.76	0	1.00	63
1CrB	BTC	0.75	76	1.56	91
1CrC	Chloride	0.64	25	1.08	78
1CrD	CrO$_3$	0.80	0	1.27	94
MFCrO$_3$	CrO$_3$	1.54	0	0.17	–
MFCr$_2$O$_3$	Cr$_2$O$_3$	2.00	100	–	–

[a] Ref. [17].

studies [8,17], we reported that the distribution of chromium species on calcined catalysts depends on the precursor, but not on its nature, organic or inorganic. The Cr^{6+} and Cr^{3+} distribution will affect the Cr^{2+}/Cr^{3+} ratio after reduction with carbon monoxide and, consequently, the activity of the catalyst in the ethylene polymerization. The amount of chromium in the hexavalent state was obtained by TPR, following the hypothesis of complete reduction of Cr^{6+} to Cr^{3+} with H$_2$. The Cr^{6+} species was characterized by diffuse reflectance spectroscopy (DRS) and TPR as chromate or CrO$_3$ species, independent of the precursor used [8].

Figs. 1–3 present the TPR results, in terms of CO and CO$_2$ profiles, for the 1CrA and 1CrB catalysts and the MFCrO$_3$ physical mixture, respectively. The 1CrC and 1CrD catalysts presented the same TPR profiles that the 1CrA. These samples presented a peak of CO consumption and a peak corresponding to the formation of CO$_2$, both with maximum around 600 K, ascribed to reduction of Cr^{6+} to Cr^{2+}, except for the 1CrB catalyst. This catalyst presented peak of consumption of CO shifted to 100 K in relation to the other samples.

The difference in the reduction profile of 1CrB catalyst (Fig. 2) was evaluated in terms of Cr-support interaction. Table 1 presents the DRIFTS results based on intensity of the infrared band of isolated hydroxyls on calcined samples,
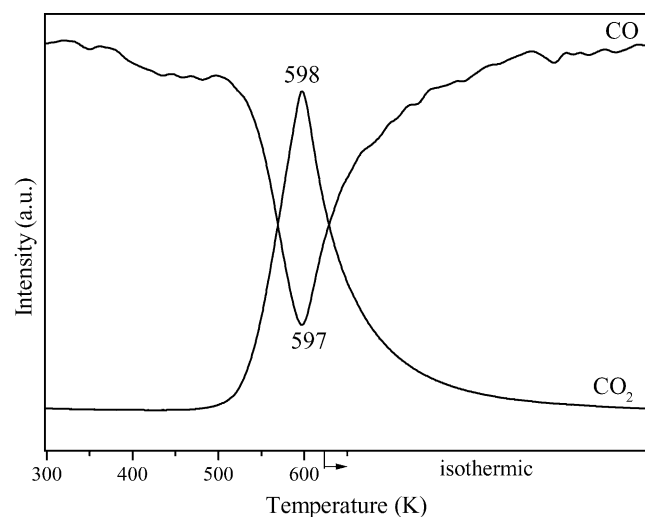

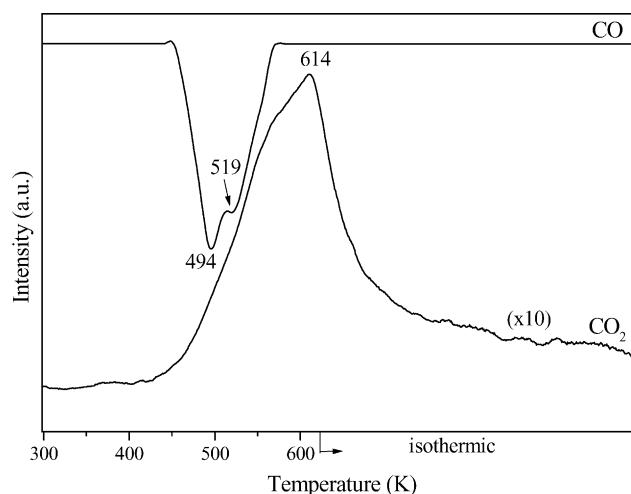Fig. 2. Profiles of mass 28 (CO) and 44 (CO$_2$) during TPR of CO for the 1CrB catalyst.

at 3745 cm^{-1}, normalized by the band of 1CrA catalyst and by chromium content (I/I_{1CrA}). As higher the intensities ratio, lower the interaction of chromium with the isolated hydroxyls of the support. The catalysts presented the following order of interaction: 1CrA ≈ 1CrC > 1CrD > 1CrB. Thus,

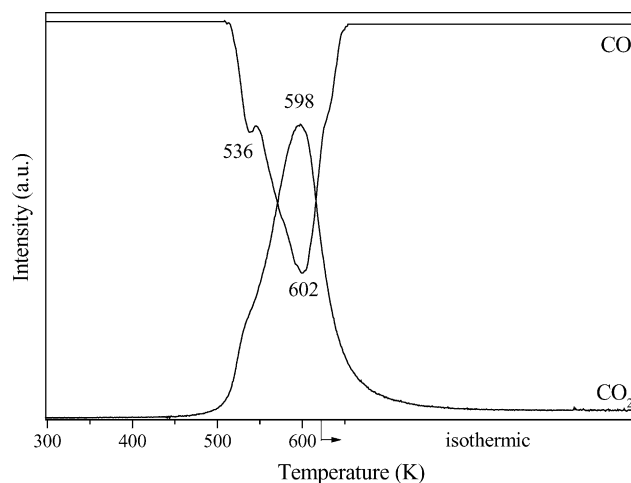Fig. 1. Profiles of mass 28 (CO) and 44 (CO$_2$) during TPR of CO for the 1CrA catalyst.

Fig. 3. Profiles of mass 28 (CO) and 44 (CO$_2$) during TPR of CO for the MFCrO$_3$ physical mixture.

the lower reduction temperature of 1CrB catalyst can be attributed to weak interaction between chromium and silica, regarding the lower interaction with the hydroxyls of the support than the other catalysts. Besides, it is possible to suppose that the higher amount of Cr^{3+} in the 1CrB catalyst (76 wt.%) influenced the reduction profile of Cr^{6+}. The shoulder observed at 519 K in Fig. 2 can also be ascribed to this low interaction. In previous studies [8], we have also observed distinct interactions in TPR profile of H_2 for this catalyst.

The 1CrC catalyst presented the same CO and CO_2 profiles that the 1CrA and 1CrD catalysts, in spite of presenting 25 wt.% of Cr^{3+} species (Table 1). This behavior can be due to the reducing strength of CO, making it difficult the observation of reducibility differences due to the lowest fraction of Cr^{3+} in this sample in comparison to the 1CrB.

$MFCrO_3$ physical mixture (Fig. 3) presented a peak of CO consumption at 602 K, as well as the 1CrA, 1CrC and 1CrD catalysts, and another one, of lower intensity, at 536 K. This peak was followed by a shoulder in the profile of CO_2. Probably, the physical mixture preparation favored the presence of particles of CrO_3 with bulk behavior and also heterogeneity, resulting in lower interaction with the support. These particles of CrO_3 would present reduction at lower temperature. CO consumption was not verified in the TPR of the $MFCr_2O_3$ physical mixture, since Cr^{3+} is not reduced to Cr^{2+}. However, little CO_2 desorption was observed in the $MFCr_2O_3$ physical mixture as in the calcined silica, at 497 and 350 K, respectively. It can be associated to the adsorption of CO_2 from the atmosphere in the exposed samples. Although part of this CO_2 has been removed during the initial treatment at 773 K, a residual fraction was just eliminated during the TPR analysis. However, CO_2 mass signal was not detected in the catalysts or in the $MFCrO_3$ physical mixture in the 350–497 K region, as verified in the support and in the $MFCr_2O_3$ physical mixture.

The consumption of carbon monoxide (in mmolsCO/mgCr), relative to the mass $m/e = 28$, was obtained discounting the fraction corresponding to the fragmentation of CO_2. The same reduction results were obtained using the data of CO_2 production or CO consumption. The consumption of CO in TPR (experimental CO) was compared with the theoretical consumption of CO, considering the Cr^{6+} present in the calcined catalyst (Table 1). All the catalysts presented complete reduction from Cr^{6+} to Cr^{2+}. The literature [6,7] reports that CO reduces Cr^{6+} to Cr^{2+} completely at 623 K, with formation of CO_2.

3.2. Thermal desorption of CO

Fig. 4A and B present the temperature programmed desorption profiles of CO and CO_2, respectively. CO desorption profiles showed a single peak in relatively low temperatures (<500 K) for all catalysts, except to the $MFCrO_3$ physical mixture, which presented two peaks. No desorption was observed at 298 K. Parker et al. [14] suggested two CO desorp-

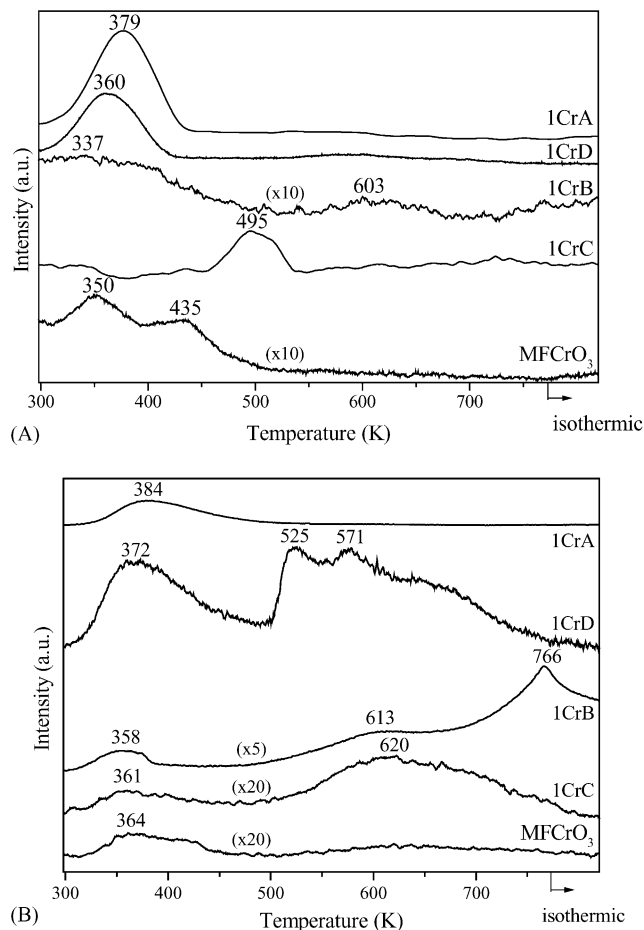Fig. 4. TPD profiles of CO (A) and CO_2 (B) for the catalysts and $MFCrO_3$ physical mixture.

tion temperatures: at 298 K, ascribed to bridged-bonded CO, and at higher temperature (up to 473 K), associated to linear configuration, corresponding to CO adsorbed in Cr_A^{2+} and Cr_B^{2+} sites. The absence of CO desorption at 298 K agrees well with the assignment of chromate or CrO_3 species in the calcined catalysts, reported in a previous paper [8], which after reduction are supposed to give isolated Cr sites and adsorption of linear-bonded CO [15]. The catalysts presented only one desorption peak at temperatures higher than 298 K, suggesting the predominance of linear-bonded CO.

Table 1 presents the $Cr_A^{2+}/(Cr_A^{2+} + Cr_B^{2+})$ ratios, obtained by infrared analysis [17]. Considering the 1CrA and 1CrD catalysts, without Cr^{3+} species, the use of different chromium precursors resulted in 63 and 94% of Cr_A^{2+} sites, respectively. Despite this difference, the CO desorption temperature did not change, 379 and 360 K, respectively, indicating similar $CO–Cr_A^{2+}$ and $CO–Cr_B^{2+}$ bond strength.
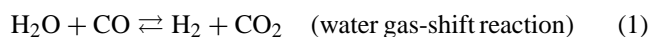
The desorption of CO also occurred at low temperature (350 K) for $MFCrO_3$ physical mixture (Fig. 4A), but other peak was observed at 435 K. The first peak was also verified at similar temperature for 1CrA and 1CrD catalysts, which just presented Cr^{6+} species after calcination and complete reduction to Cr^{2+}. The heterogeneity of the

chromium particles in this physical mixture in comparison to the catalysts probably changed the adsorption strength of the probe molecule. The MFCr$_2$O$_3$ physical mixture did not present CO desorption, in agreement with the absence of CO chemisorption due to no reduction of Cr^{3+} to Cr^{2+}, according to TPR result of this sample.

In the 1CrC catalyst, with 25 wt.% Cr^{3+} (Table 1), the desorption of CO occurred at higher temperature, 495 K. This fact can be attributed to the presence of Cr^{3+}, modifying the Cr^{2+}–CO adsorption strength. For the 1CrB catalyst, the small amount of Cr^{2+}, obtained from the complete reduction of Cr^{6+} (only 24 wt.%), resulted a low CO signal (Fig. 4A, magnification: 10-fold). Thus, the small amount of CO chemisorbed difficult the attribution of desorption peaks.

H$_2$ desorption was not observed in the experiments. The formation of H$_2$ in TPD of CO has been observed in metallic catalysts, attributed to the reaction of CO with water, called gas-shift reaction (Eq. (1)) [16,21]. In this case, the evolution of H$_2$ occurs simultaneously to the desorption of CO$_2$ in metallic catalysts.

The desorption of CO was followed by evolution of CO$_2$ (Fig. 4), except for the 1CrC catalyst. The occurrence of both CO and CO$_2$ desorption can be ascribed to the disproportionation of CO, according to Eq. (2). Note that simultaneous CO and CO$_2$ desorption occur in greater extent for the 1CrD catalyst. The 1CrA catalyst presented desorption peak of CO$_2$ at 384 K, close to the observed for the desorption of CO (379 K). The same behavior was verified in the analyses of the 1CrB, 1CrD and in the MFCrO$_3$ physical mixture. However, the 1CrB and 1CrD catalysts also presented desorption of CO$_2$ at higher temperatures, above 500 K, which can be ascribed to carbonates or carboxilates decomposition. Bensalem et al. [12] observed that the desorption of these species could occur up to 673 K.

$$H_2O + CO \rightleftarrows H_2 + CO_2 \quad \text{(water gas-shift reaction)} \quad (1)$$

$$2CO \rightarrow CO_2 + C \quad \text{(CO disproportionation reaction)} \quad (2)$$

In the analysis of the 1CrC catalyst (Fig. 4), the evolution of CO$_2$ does not coincide with the CO desorption peak. However, low CO$_2$ signal appears at higher temperature, close to the observed for the 1CrB and 1CrD catalysts, being attributed to the desorption of carbonate or carboxilate species.

Table 2 reports the amounts of CO desorption, normalized by the result of the 1CrA catalyst. For comparative analysis, the results of CO chemisorption and the ethylene polymerization activity from our previous work [8] are also reported. In this reference, we showed that the distribution of bivalent and trivalent chromium species in reduced Cr/SiO$_2$ catalysts depends on the chromium precursor. Samples of MFCr$_2$O$_3$ physical mixture and silica did not present CO chemisorption, as well as the MFCrO$_3$ physical mixture without previous reduction, evidencing the selectivity of this technique for the characterization of Cr^{2+} species (Cr$_A^{2+}$ and Cr$_B^{2+}$)

Table 2
Results of CO chemisorption, CO desorption and ethylene polymerization

Sample	Normalized CO chemisorption[a]	Normalized CO desorption	Normalized ethylene polymerization[a]
1CrA	1.00	1.00	1.00
1CrB	0.21	0.13	0.09
1CrC	0.29	0.77	0.30
1CrD	1.34	1.38	1.24
MFCrO$_3$	0.15	0.35	–

[a] Ref. [8].

[17]. The catalysts presented CO chemisorption in the following order: 1CrD > 1CrA ≫ 1CrC > 1CrB, being 1CrD also the most active in the ethylene polymerization [8]. This order was also observed for the CO desorption and for the activity in the ethylene polymerization.

The 1CrA and 1CrD catalysts, the highest active in ethylene polymerization, presented CO desorption at low temperature. This result is important by industrial point of view, because carbon monoxide is an important contaminant in the ethylene stream and inhibitor of the polymerization, competing with ethylene in the adsorption on the Cr$_A^{2+}$ and Cr$_B^{2+}$ active sites. The desorption temperature observed for CO was similar to the polymerization temperature with Phillips type catalyst, around 353 K. Besides, it seems to be a reliable technique to evaluate Cr^{2+} active sites for polymerization.

4. Conclusions

The presence of Cr^{3+} species modifies the reduction profiles of hexavalent chromium in Cr/SiO$_2$ catalysts, displacing the temperature to lower values. In the reduced catalysts without presence of Cr^{3+}, CO desorption occurs at relatively low temperatures, indicating weak interaction between CO and the chromium active sites. In the catalysts containing Cr^{3+}, desorption of CO occurs at higher temperature suggesting change of the Cr^{2+}–CO adsorption strength by the presence of Cr^{3+}. However, this interaction was not modified in function of distinct Cr$_A^{2+}$/Cr$_B^{2+}$ ratios, obtained with different chromium precursors. Desorption peaks of CO$_2$ above 500 K were ascribed to carbonates or carboxilates decomposition. Desorption of CO at low temperature is important by industrial point of view, once CO is one of the main contaminant of the ethylene stream and inhibitor of the polymerization, competing with the ethylene for the Cr^{2+} active sites. The catalysts presented CO desorption and activity in the ethylene polymerization in the following order: 1CrD > 1CrA ≫ 1CrC > 1CrB, showing the importance of this technique to evaluate Cr^{2+} active sites for polymerization.

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