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# UNIVERSITÀ DEGLI STUDI DI TORINO

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# Towards the understanding of the comonomer effect on Cr<sup>II</sup>/SiO<sub>2</sub> Phillips catalyst.

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**ABSTRACT:** The origin of the “comonomer effect” (i.e. the enhancement of ethylene polymerization rate in presence of  $\alpha$ -olefin comonomer) on Cr<sup>II</sup>/SiO<sub>2</sub> Phillips catalyst was investigated by means of *in-situ* FT-IR and Diffuse Reflectance UV-Vis spectroscopies. A non-polymerizing olefin, cyclohexene, was chosen as “comonomer” and introduced on the catalyst prior the monomer injection in order to produce only homo-polymers. Under our experimental conditions,  $\alpha$ -olefin (ethylene, propene and 1-hexene) homo-polymerization is enhanced up to a factor of 5. Our experimental data provide the first direct evidence that the comonomer strongly interacts with all the Cr<sup>II</sup> sites and that it is responsible for their structural and electronic rearrangement at a molecular scale, as proposed for the “trigger mechanism”. We also proved that the fraction of Cr active sites do not retain the comonomer during the olefin polymerization, meaning that the increased reactivity is due to a modification influencing the whole catalyst Cr sites.

**KEYWORDS:** Phillips catalyst, olefin polymerization, comonomer effect, trigger mechanism, spectroscopy

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In the field of ethylene polymerization catalysts, the term “comonomer effect” refers to an enhancement of ethylene polymerization rate occurring when a small amount of  $\alpha$ -olefin comonomer is introduced into the reactor along with ethylene. This phenomenon is known in the industrial practice since decades, but it is still mysterious especially because  $\alpha$ -olefins are incorporated into polyethylene chains with a rate 1-2 orders of magnitude slower than ethylene.<sup>1,2</sup> More important, a similar effect was reported also in presence of internal or cyclic olefins, which are not incorporated significantly into polyethylene,<sup>3</sup> and it is observed either when the olefin is introduced prior ethylene injection, along it or even when ethylene polymerization is already going.<sup>4</sup> So far this effect was studied on Ziegler catalysts and metallocenes,<sup>5-11</sup> while only a few literature is present on the chromium based Phillips catalyst.<sup>2,12-16</sup> Recently, McDaniel et al.<sup>2</sup> critically re-evaluated all the theories that have been advanced to explain the comonomer effect on the Phillips catalyst, which are: i) enhanced ethylene diffusion through a more branched polyethylene (i.e. less crystalline) due to the incorporation of comonomer itself;<sup>9,10,17-19</sup> ii) higher catalyst fragmentation due to  $\alpha$ -olefin incorporation;<sup>11,20</sup> iii) enhanced reduction of the chromium species in the oxidized catalyst and/or activation of dormant sites;<sup>13, 21-24</sup> iv) enhanced ethylene insertion due to the coordination of the comonomer to the chromium sites, which

goes under the name of “trigger mechanism” (i.e. a more electron-rich olefin coordinated to the chromium sites improves ethylene insertion during the whole polymerization process).<sup>2,25,26</sup> All these theories have several drawbacks and are not able to explain the experimental observations, except for the latter, which, is consistent with all the experimental data hence is considered as the most plausible one.<sup>2</sup> Accordingly, the comonomer effect would originate from a change in the chemistry of the active chromium sites upon coordination of the electron-rich  $\alpha$ -olefin comonomer. However, no direct experimental data indicating the presence of the  $\alpha$ -olefin in the coordination sphere of the active Cr sites are available so far.

In this letter we investigate the comonomer effect on a Cr<sup>II</sup>/SiO<sub>2</sub> Phillips catalyst by means of *in-situ* spectroscopic techniques. Although  $\alpha$ -olefins are commonly employed as comonomers, we used cyclohexene, which is not incorporated into the growing polyethylene and, as such, it should be considered as a “false comonomer”. This choice was dictated by the intention to maintain constant the properties of the homo-polymer, thus excluding hypothesis (i). Moreover, we employed as a support a non-porous and not fragmentizing silica (aerosil), hence discharging also hypothesis (ii). Finally, by working on the reduced Cr<sup>II</sup>/SiO<sub>2</sub> catalyst, we removed also the contribution of the comonomer in the faster reduction of

the oxidized  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  catalyst, thus excluding part of hypothesis (iii). We report the first spectroscopic (FT-IR and Diffuse Reflectance UV-Vis described in Section S1) evidences of a strong coordination of the comonomer to the  $\text{Cr}^{\text{II}}$  sites, and we correlate this experimental observation to the enhanced olefin polymerization rate, formulating a new hypothesis to explain the comonomer effect on the Phillips catalyst.

$\text{Cr}/\text{SiO}_2$  samples were prepared by impregnating  $\text{SiO}_2$  (aerosil, surface area ca.  $380 \text{ m}^2 \text{ g}^{-1}$  and almost absent porosity) with aqueous solutions of  $\text{CrO}_3$  leading to two separate batches of  $\text{Cr}/\text{SiO}_2$  having chromium loading of 0.5 wt% and 1 wt%, respectively.<sup>27</sup> Reduced  $\text{Cr}^{\text{II}}/\text{SiO}_2$  catalysts were prepared starting from these materials according to the steps described in Section S2.

Our first move was to test the influence of cyclohexene on the activity of  $\text{Cr}^{\text{II}}/\text{SiO}_2$  in the homo-polymerization of ethylene under our laboratory conditions. To this aim, ethylene polymerization at room temperature and low pressure ( $P_{\text{C}_2\text{H}_4} = 100 \text{ mbar}$ ) was followed within the first sixty minutes by means of FT-IR spectroscopy on  $\text{Cr}^{\text{II}}/\text{SiO}_2$  and on the same catalyst previously exposed to vapors of cyclohexene. In the adopted experimental conditions (which are representative of industrial pre-polymerization) the reaction proceeded about 1.5 times faster on the catalyst pre-contacted with cyclohexene. The effect of cyclohexene was much larger in the homo-polymerization of longer  $\alpha$ -olefins: for example, the homo-polymerization of propene was enhanced of five times, and that of 1-hexene more than three times. Figure 1 shows the *in-situ* FT-IR spectra collected within the first sixty minutes of propylene polymerization on  $\text{Cr}^{\text{II}}/\text{SiO}_2$  catalyst (parts a and b) and on the same catalyst pre-contacted with cyclohexene (parts c and d), in both  $\nu(\text{CH}_x)$  and  $\delta(\text{CH}_x)$  regions. All the spectra were subtracted from the spectrum of the catalyst before propylene addition (blue spectrum in Figure 2b) and normalized to the thickness of the pellet, to allow quantitative comparison.

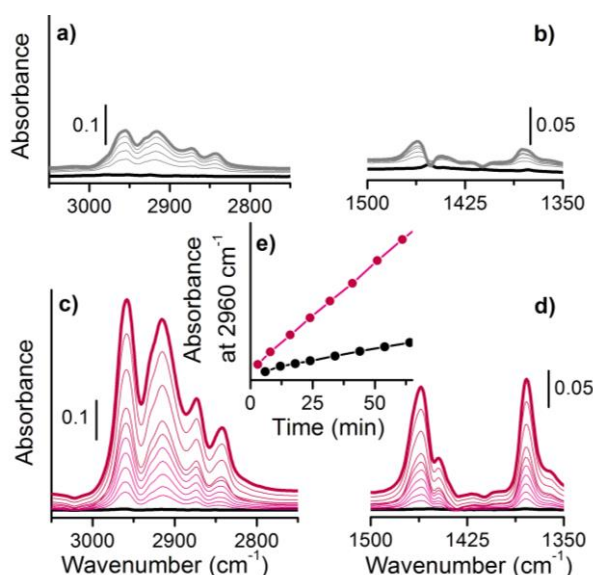


Figure 1: Time resolved FT-IR spectra collected during propene polymerization (at room temperature and  $P_{\text{C}_2\text{H}_4} = 100 \text{ mbar}$ ) on  $\text{Cr}^{\text{II}}/\text{SiO}_2$  (Parts a and b) and on the same catalyst pre-contacted with cyclohexene, (parts c and d). Parts a and c refer to the  $\nu(\text{CH}_x)$  region, whereas parts b and d) show the  $\delta(\text{CH}_x)$  region. The spectra are shown as a function of polymerization: 1 minute (black) and after 60 minutes of reaction (bold curves). All spectra have been subtracted to that of the catalysts prior propene addition and normalized to the thickness of the pellet in order to allow quantitative comparison. The vibrational contribution of gaseous propene was removed. Part e displays the intensity of the  $2960 \text{ cm}^{-1}$  IR absorption band versus time.

The absorption bands characteristic of polypropylene constantly grow as a function of time, evidently faster on the catalyst pre-contacted with cyclohexene. A plot of the intensity of the IR absorption band at  $2960 \text{ cm}^{-1}$  (chosen here as a reference band to monitor propylene formation) versus time (Figure 1e) reveals an almost linear dependence in both cases within the investigated one hour time interval. The slopes of these curves give an indication of the relative rate of polymerization, which differs of a factor of five. Figure S1 in the Supporting Information shows a similar result for 1-hexene homo-polymerization. These spectroscopic data confirm that also a cyclic olefin has a promoting effect on the homo-polymerization of ethylene and other  $\alpha$ -olefins over  $\text{Cr}^{\text{II}}/\text{SiO}_2$  catalyst, although it is not incorporated in the polymer.

In a second moment, we tried to understand the effects of cyclohexene on  $\text{Cr}^{\text{II}}/\text{SiO}_2$ , thus the reasons behind the enhanced polymerization activity. We observed that in presence of vapors of cyclohexene the  $\text{Cr}^{\text{II}}/\text{SiO}_2$  catalyst, originally pale blue in color, becomes dark blue; the color does not change also after prolonged degassing, as previously reported by McDaniel.<sup>2</sup> This observation is testified by the DR UV-Vis spectra (Figure 2a). The spectrum of  $\text{Cr}^{\text{II}}/\text{SiO}_2$  (black), characteristic of highly uncoordinated  $\text{Cr}^{\text{II}}$  sites,<sup>27-29</sup> is strongly perturbed after contact with cyclohexene (blue) in both spectral regions of d-d transitions (where the two bands originally at  $7500$  and  $12000 \text{ cm}^{-1}$  upward shift to  $13500$  and  $22000 \text{ cm}^{-1}$ ) and ligand-to-metal charge-transfer transitions (where the intense band at  $30000 \text{ cm}^{-1}$  drastically decreases in intensity). Although the presence of minor amount of  $\text{Cr}^{\text{III}}$  species cannot be completely discarded, the position and the relative intensity of the d-d bands point towards  $\text{Cr}^{\text{II}}$  species in a distorted 6-fold coordination. This indicates that cyclohexene does not react with the  $\text{Cr}^{\text{II}}$  sites but strongly interacts with them, determining an increase of their ligand sphere, as previously observed in presence of other simpler ligands (such as CO and NO).<sup>27</sup>

In order to clarify in which way cyclohexene interacts with the  $\text{Cr}^{\text{II}}/\text{SiO}_2$  catalyst, the same experiment was followed by means of transmission FT-IR spectroscopy. At high cyclohexene coverage the FT-IR spectrum (Figure 2b, light blue) is dominated by the absorption bands of liquid cyclohexene ( $\nu(\text{CH}_x)$  at  $3100\text{-}2750 \text{ cm}^{-1}$  and  $\delta(\text{CH}_x)$  at  $1500\text{-}$

1350  $\text{cm}^{-1}$ ), which is strongly physisorbed both at the silica surface and at the  $\text{Cr}^{\text{II}}$  sites. The interaction of cyclohexene with silica is testified by: i) the strong perturbation of the IR band at 3745  $\text{cm}^{-1}$ , due to  $\nu(\text{OH})$  of the surface silanols, which shifts to 3545  $\text{cm}^{-1}$ , and ii) the appearance of two characteristic IR absorption bands at 3023 and 1650  $\text{cm}^{-1}$ , which are ascribed to  $\nu(\text{C-H})$  and  $\nu(\text{C=C})$  of cyclohexene in interaction with isolated silanols ( $\text{CyHex}@/\text{SiO}_2$  in Figure 2b).<sup>30</sup> All these bands disappear upon degassing at room temperature, making possible to distinguish the vibrational manifestation of cyclohexene adsorbed on the much less abundant  $\text{Cr}^{\text{II}}$  sites. In

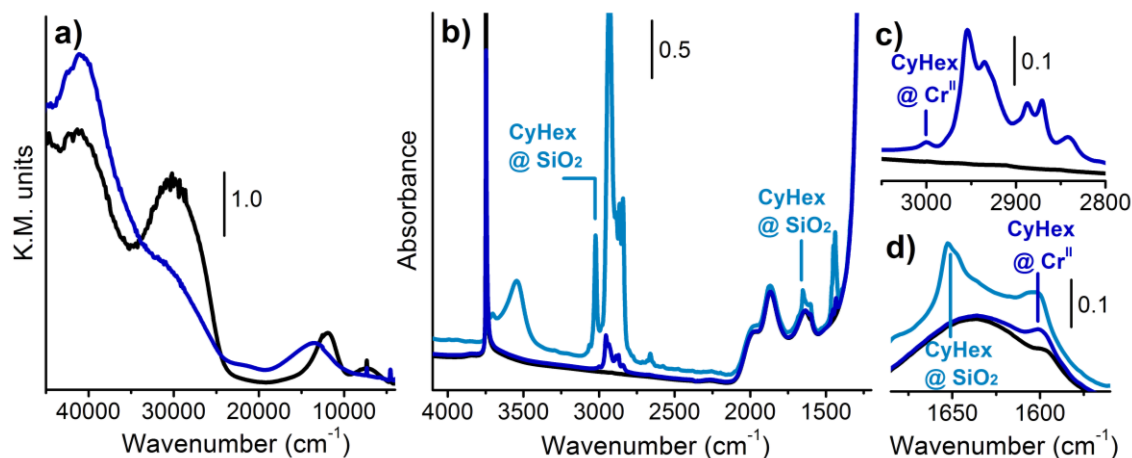


Figure 2: Part a): DR UV-Vis spectrum of  $\text{Cr}^{\text{II}}/\text{SiO}_2$  (black) and of the same catalyst pre-contacted with cyclohexene, after prolonged degassing at room temperature (blue). Parts b), c) and d): FT-IR spectra of  $\text{Cr}^{\text{II}}/\text{SiO}_2$  (black), of the same catalyst exposed to an excess of cyclohexene (light blue) and after prolonged degassing at room temperature (blue). Part b) shows the whole 4200-1200  $\text{cm}^{-1}$  range, whereas parts c) and d) are magnifications of the regions at 3050-2800  $\text{cm}^{-1}$  and 1680-1520  $\text{cm}^{-1}$ , respectively.

It was found that all the  $\text{Cr}^{\text{II}}$  sites are strongly interacting with cyclohexene. A fraction of them displays an additional coordination vacancy available to bind weak ligands such as CO, forming mixed cyclohexene-CO complexes characterized by peculiar vibrational features ( $\nu(\text{=C-H})$  at 2898  $\text{cm}^{-1}$  and  $\nu(\text{C=O})$  at 2171  $\text{cm}^{-1}$ , Figure 3a-c in light green). Only in presence of stronger ligands, such as NO, cyclohexene is completely displaced from the  $\text{Cr}^{\text{II}}$  sites and adsorbed back on the  $\text{SiO}_2$  surface (Figure 3g-i), with the concomitant formation of mainly di-nitrosyl complexes ( $\nu(\text{NO})$  at 1855 and 1741  $\text{cm}^{-1}$ , Figure 3i in dark green), as observed in absence of cyclohexene.<sup>27</sup> The displacement of cyclohexene from the  $\text{Cr}^{\text{II}}$  coordination sphere further testifies that no reaction occurred between cyclohexene and  $\text{Cr}^{\text{II}}$  sites, ~~which maintain their oxidation state~~. Further discussion is presented in Section S4.

As anticipated in the introduction, the higher polymerization rate shown by  $\text{Cr}^{\text{II}}/\text{SiO}_2$  pre-contacted with cyclohexene cannot be explained in terms of the formation of a different and less crystalline polymer, since cyclohexene is not incorporated into the homo-polymers. Moreover, the silica used as a support is non porous and does not fragment during polymerization. Finally, the chromium sites are already reduced and insertion of cyclohexene increases their ligand field. Hence, only two hypotheses remain to explain the experimentally observed enhancement of the olefin

particular, we focus the attention on the IR absorption bands at 3001  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$  ( $\text{CyHex}@/\text{Cr}^{\text{II}}$  in Figure 2c and d), which are assigned to  $\nu(\text{=C-H})$  and  $\nu(\text{C=C})$  of cyclohexene in interaction with the  $\text{Cr}^{\text{II}}$  sites through the double-bond, in similarity with other  $\alpha$ -olefins adsorbed on  $\text{Cr}^{\text{II}}/\text{SiO}_2$ .<sup>31</sup> The persistence of absorption bands due to vibrations involving the cyclohexene double bond confirms that it is mainly chemisorbed on the  $\text{Cr}^{\text{II}}$  sites and does not react with them.

This scenario was further confirmed by means of FT-IR spectroscopy of adsorbed probe molecules (CO and NO).

polymerization rate: 1) cyclohexene activates otherwise dormant sites (i.e. higher amount of active sites), or 2) cyclohexene promotes the trigger mechanism (i.e. the coordination of cyclohexene influences the monomer insertion on the chromium site during the whole polymerization process). In the following we demonstrate that FT-IR spectroscopy can help in the discrimination between the two hypothesis.

The key point was to understand the destiny of cyclohexene during olefin polymerization. To this aim, we chose to follow by FT-IR spectroscopy the homo-polymerization (at room temperature and low pressure) of deuterated ethylene (d-ethylene) on  $\text{Cr}^{\text{II}}/\text{SiO}_2$  pre-contacted with vapors of cyclohexene. Following this approach we were able to separate the vibrational manifestation of the growing d-homopolymer, whose  $\nu(\text{CD}_x)$  bands fall in the 2250-2000  $\text{cm}^{-1}$  region, from those of cyclohexene in interaction with  $\text{Cr}^{\text{II}}$  species,  $\nu(\text{CH}_2)$  in the 3050-2800  $\text{cm}^{-1}$  region. The FT-IR spectrum collected after one minute of reaction is shown in Figure 3d-f (green), compared to the spectrum of the catalyst prior insertion of d-ethylene (black). The occurrence of d-ethylene polymerization is testified by the growth of two IR absorption bands at 2196 and 2090  $\text{cm}^{-1}$  (Figure 3 f), typical of  $\nu(\text{CD}_2)$  of d-polyethylene.<sup>32,33</sup> Simultaneously, the IR absorption bands characteristic of cyclohexene strongly

adsorbed on Cr<sup>II</sup> sites change only slightly (Figure 3d). The major change involves the  $\nu(\text{C-H})$  band at 3001 cm<sup>-1</sup>, which decreases in intensity in favor of the band at 3023 cm<sup>-1</sup>, previously assigned to the  $\nu(\text{C-H})$  of cyclohexene in interaction with the silica surface. No other bands appear in this region, indicating that no mixed cyclohexene–d-ethylene or cyclohexene–polymer complexes are formed, as it was the case of CO (Figure 3a). Simply, d-ethylene displaces cyclohexene from a fraction of the Cr<sup>II</sup> sites, and forces it to adsorb back on silica, as it was the case of NO (Figure 3g).

In conclusion, the FT-IR data shown in Figure 3 demonstrate that we are in presence of two families of Cr<sup>II</sup>

sites: i) a small fraction of sites readily active in d-ethylene polymerization, which do not retain cyclohexene during the reaction; and ii) a larger amount of sites, which retain cyclohexene, at least during the first minutes of reaction, and hence behave as spectators. The removal of cyclohexene from the Cr<sup>II</sup> sites active in d-ethylene polymerization excludes the occurrence of a “trigger mechanism” during the whole polymerization process, thus the triggering effect can be taken into due for the first monomer insertion only. Moreover, being the number of Cr<sup>II</sup> sites active in ethylene polymerization small,

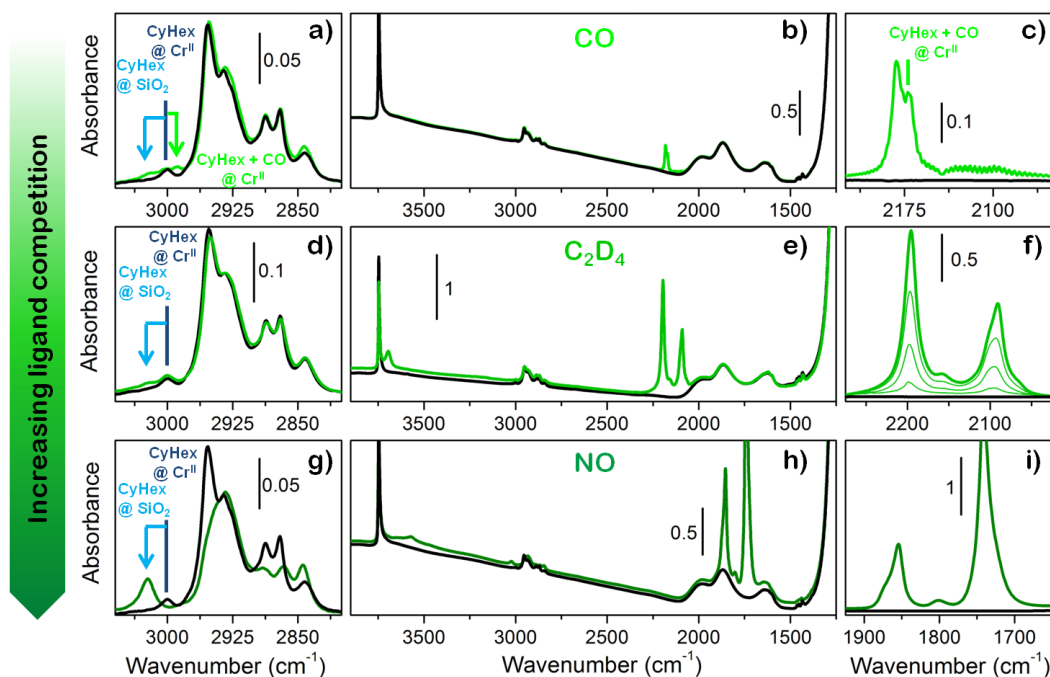


Figure 3: FT-IR spectra of Cr<sup>II</sup>/SiO<sub>2</sub> catalyst pre-contacted with cyclohexene (black) and upon dosing ligands having increasing interaction strength (shades of green): CO (top), C<sub>2</sub>D<sub>4</sub> (middle), NO (bottom). Parts a, d and g show the perturbation of the cyclohexene  $\nu(\text{CH}_x)$  modes in the 3050–2800 cm<sup>-1</sup>; Parts b, e and h show the whole spectra in the 3800–1250 cm<sup>-1</sup>; Parts c, f and i show the  $\nu(\text{CO})$ ,  $\nu(\text{CD}_x)$  and  $\nu(\text{NO})$  characteristic of each “ligand”.

activation of dormant sites cannot be considered. This observation is in agreement with the persistence of the dark blue color of the catalyst during the polymerization step.

The whole set of IR and UV-Vis spectroscopic results allowed to unravel the origin of the “comonomer effect” on the Cr<sup>II</sup>/SiO<sub>2</sub> Phillips catalyst. It was found that, albeit it is not incorporated into the polyolefin, cyclohexene increases the  $\alpha$ -olefin polymerization rate. The effect is greater for propene than for ethylene. We ruled out since the beginning possible contributions due to monomer diffusion in the polymer (because we produced homo-polymers), to the fragmentation of the support (we worked with a non-porous aerosil), and to the chromium reduction (the catalyst was already reduced, Cr<sup>II</sup>/SiO<sub>2</sub>).

The whole set of spectroscopic results reveal that most of the cyclohexene strongly interacts with all the Cr<sup>II</sup> sites, determining a general increase of their ligand sphere, while an

eventual oxidative reaction (i.e. from Cr<sup>II</sup> to Cr<sup>III</sup>) is negligible. We demonstrated that cyclohexene is displaced from a fraction of Cr<sup>II</sup> sites during olefin polymerization. This excludes also the occurrence of a “trigger” effect (cyclohexene is not retained on the chromium sites during the polymerization) and the activation of otherwise dormant sites (the fraction of active sites is very small). We believe that the origin of the comonomer effect has to be searched in a modification of the molecular and electronic structure of the Cr<sup>II</sup> sites by the comonomer. According to our new hypothesis, the more electron-rich comonomer (cyclohexene in our case) induces a molecular and electronic rearrangement of the Cr<sup>II</sup> sites, as already noticed for other ligands,<sup>34</sup> which favors the insertion of the first olefin during the initiation of the reaction. Most probably the rearrangement brought by the comonomer involves the lengthening of the distance of particular Cr sites from the extremely flexible silica support as previously

observed in presence of other ligands<sup>34</sup> and in particular of ethylene.<sup>35</sup> It is also worth noticing that all the Cr sites are in interaction with the comonomer, also the spectators. The presence of adsorbates on all the Cr sites likely influences the flexibility of the few active Cr sites. This explanation fulfills the data present in literature, and also those shown in this work, of lower induction times and higher reaction rate either if the comonomer is brought to contact with the catalyst prior, along ethylene injection and even when the polymerization reaction is already proceeding.<sup>4</sup> Finally, this work demonstrates the strength of spectroscopic techniques, often considered “ordinary” methods, in the investigation of molecular mechanism occurring at a few catalytically active sites.

## ASSOCIATED CONTENT

### Supporting Information.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Details on the catalyst's activation, spectroscopic techniques, IR band assignments.

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## ABBREVIATIONS

CyHex@Cr<sup>II</sup>, cyclohexene adsorbed on Cr<sup>II</sup> sites,  
CyHex@SiO<sub>2</sub>, cyclohexene adsorbed on SiO<sub>2</sub>.

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