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Tracking the reasons for the peculiarity of Cr/Al_2O_3 catalyst in ethylene polymerization

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Looking to the past, heading to the future. In this contribution we explain the reasons why the Cr/Al_2O_3 Phillips catalysts exhibit a faster kinetics profile in ethylene polymerization reaction with respect to Cr/SiO_2. Diffuse reflectance UV–Vis and FT-IR spectroscopies unequivocally demonstrate that, albeit several types of reduced Cr sites are stabilized by the Al_2O_3 support, only the 4-fold coordinated Cr^{2+} sites are active precursors in ethylene polymerization, as for Cr^{2+}/SiO_2. Nevertheless, kinetic experiments indicate that ethylene polymerization is 15 times faster on CO-reduced Cr/Al_2O_3 than on CO-reduced Cr/SiO_2. The difference is even more striking (two order of magnitude) when the reaction rates per active Cr sites are compared. Our experimental results suggest two reasons behind the faster polymerization kinetic of Cr/Al_2O_3: (1) the higher ionic character of the Cr—O—Al bond with respect to the Cr—O—Si one; (2) the nature of the ancillary ligands in the coordination sphere of the Cr active sites (which are mainly carbonates for CO-reduced Cr/Al_2O_3 and siloxane bridges for CO-reduced Cr/SiO_2).

1. Introduction

The Cr-based Phillips catalyst is among the most important heterogeneous catalysts for ethylene polymerization. It accounts for about 50% of the high density polyethylene (HDPE) world's demand, owning also a large share of linear low density polyethylene (LLDPE) market [1–3]. Generally speaking, the active phase is constituted by a highly dispersed chromium oxide supported on a high surface area material [4]. Porous silica has been traditionally employed, due to its tendency to fragment during the polymer growing. The smaller silica fragments generated in this process provide new chromium sites accessible for ethylene polymerization. Besides silica, almost all the high surface area oxides have been tested as supports, and some of them also found practical applications [5–9]. In this context, also alumina (Al_2O_3) was tested, but the resulting Cr/Al_2O_3 catalyst was left aside due to its tendency to fast deactivation, providing only 10–20% of the polymerization activity of Cr/SiO_2. Noticeably, alumina does not fulfil the fragility, porosity and high surface area standards required for boosting polymerization. Nevertheless, the Cr/Al_2O_3 catalysts do show some unique features compared to Cr/SiO_2, that could make them extremely appealing [5]: (1) a much faster kinetic profile (i.e. rapid development of polymerization upon ethylene addition); (2) a lower tendency to β-hydride elimination (the polyethylene produced in the absence of H_2 has an extremely high molecular weight, approaching the ultra-high classification); (3) an unusual tendency to distribute the branching evenly throughout the molecular weight distribution (nearly all the physical properties of the polymer are improved); (4) a much higher H_2 sensitivity as chain transfer agent (which implies the possibility of controlling the molecular weight distribution). The reasons behind these peculiar features must be searched in the molecular structure of the Cr sites.

The singular properties of Cr/Al_2O_3 stimulated us to carry out a complete spectroscopic investigation at a molecular level of the Cr sites, aimed at tracking the reasons behind the unusual features of Cr/Al_2O_3 in ethylene polymerization. The literature on the spectroscopic properties of Cr^{6+}/Al_2O_3 is wide, since this is one of the most used catalysts for propene dehydrogenation [10–25]. Opposite to the case of Cr^{6+}/SiO_2, for which the aggregation state and the structure of the grafted Cr^{6+} sites is still debated [5,7–9,20,22–24,26–35], there is a general consensus on that Cr^{6+} on Al_2O_3 exists primarily as (tetrahedrally coordinated) monochromate species [9,10,19–24]. Much less was done on reduced Cr/Al_2O_3, and the reference works remain those of Weckhuysen et al. dating back to the middle of 1990s [9,10,19–24]. More recently, Airaksinen et al. [25] studied the reduction of alumina-supported chromia containing 13 wt%

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chromium, by X-ray photoelectron and absorption spectroscopies, in situ temperature-programmed Raman and Diffuse Reflectance FT-IR spectroscopies, combined with mass spectrometry. According to these seminal works, after reduction by carbon monoxide or hydrogen mainly Cr^{3+} is formed, although the formation of Cr^{2+} in carbon monoxide reduction was also observed. In the last years spectroscopic methods have progressed enormously. For this reason, it is timely a systematic spectroscopic investigation on reduced Cr/Al_2O_3 catalysts, with the specific purpose to determine the structure of the reduced Cr sites and to correlate it with its unusual behaviour in ethylene polymerization with respect to Cr/SiO_2. Both H_2 and CO have been used as reducing agents as indicated by the literature [5]. Transmission FT-IR and Diffuse Reflectance UV–Vis-NIR spectroscopies coupled with molecular probes have been employed to confirm the presence of different Cr reduced species at the catalyst surface and to clarify which are those involved in the ethylene polymerization reaction.

2. Experimental section

2.1. Materials

The alumina-supported Phillips catalysts were prepared by wet-impregnation, using as a support a transition-Al_2O_3 (Aeroxide Alu C, Evonik-Degussa) characterized by a specific surface area of 100 m^2/g, and CrO_3 (Sigma-Aldrich) as Cr precursor, according to the procedure already adopted for the synthesis of Cr/SiO_2 [8]. Two Cr/Al_2O_3 samples differing in the Cr loading (1 wt% and 0.5 wt%, hereafter referred to as $0.5Cr/Al_2O_3$ and $1.0Cr/Al_2O_3$, respectively) were prepared: the former was used for the FT-IR measurement and the latter for DR-UV–Vis-NIR and kinetics experiments. The choice was done to optimize the spectral quality. Cross-checking experiments demonstrated that the spectroscopic properties are the same irrespective of the Cr loading, as already demonstrated in the past for the similar Cr/SiO_2 catalyst [8].

The catalysts were activated directly inside the measurement cells, that can be connected to a vacuum line allowing activations and gas dosages. The activation procedure was very similar to that well optimized for Cr/SiO_2 catalysts [8]. Briefly, the main steps are: (i) degassing in dynamic vacuum at increasing temperature up to 650 °C to dehydroxylate the alumina surface; (ii) oxidation at the same temperature in the presence of O_2, resulting in the grafting of the Cr species at the alumina surface; (iii) reduction in the presence of CO or H_2 at 350 °C, followed by removal of the gaseous phase at the same temperature; (iv) cooling down at room temperature. For probing the accessible Cr sites, CO was dosed at room temperature (equilibrium pressure $P_{CO} = 100$ mbar), followed by step-by-step expansions. The kinetics of ethylene polymerization was studied by sending 200 mbar of ethylene at room temperature over 0.5 g of catalyst inside a quartz reactor of known volume, and recording the ethylene pressure as a function of time. Similar experiments were repeated for the catalyst inside the FT-IR and DR UV–Vis cells, collecting the spectra as a function of time.

2.2. Methods

Transmission FT-IR spectra were collected at 2 cm^{-1} resolution with a Bruker Vertex70 instrument equipped with a MCT detector. The experiments were performed in situ and in controlled atmosphere within a quartz cell equipped with two KBr windows, allowing performing thermal treatments and measurements in the presence of gases. The FT-IR spectra were normalized to the optical thickness of the pellet.

Diffuse reflectance (DR) UV–Vis-NIR spectra were collected using a Varian Cary5000 spectrophotometer with a diffuse reflectance accessory. The samples were measured in the powder form, inside a cell made of optical quartz, allowing performing thermal treatments and measurements in the presence of gases. The reflectance (%R) signal was later converted into Kubelka-Munk values.

3. Results and discussion

3.1. The role of CO and H_2 as reducing agents for Cr^{6+}/Al_2O_3

The spectroscopic properties of Cr^{6+} on Al_2O_3 are well known in the specialized literature. While for Cr^{6+} on SiO_2 there is still a debate on the aggregation state of the Cr^{6+} species (both mono- and dichromates have been proposed [5,7–9,20,22–24,26,34,35], or even mono-oxo CrO_5 [27–33]), Cr^{6+} exist primarily as monochromate species on Al_2O_3 [9,10,19–24] (the corresponding DR UV–Vis-NIR spectrum is shown in Fig. S1a). Temperature-programmed reduction measurements have demonstrated that Cr^{6+} on Al_2O_3 are more reducible than Cr^{6+} on SiO_2 (i.e. their reduction is achieved at lower temperature), both in CO and in H_2 [5,36]. DR UV–Vis-NIR spectroscopy has been traditionally used to determine the final valence state of the reduced Cr sites in Cr/Al_2O_3, Cr/SiO_2 and variant thereof [8–10,19–24,36–40]. Although DR UV–Vis-NIR is often disused in favour of other methods (such as XANES or EPR), it remains one of the techniques most informative on the electronic properties of heterogeneous catalysts. In the specific case of Cr^{n+} sites on inorganic support, the literature on the topic is well assessed. DR UV–Vis-NIR spectroscopy has been used since the early 1990s not only to discriminate among various oxidation states and coordination geometries, but also to quantify the amount of each species as a function of the sample composition and treatment. For this reason, we started our investigation by collecting the DR UV–Vis-NIR spectra of Cr/Al_2O_3 reduced in CO and in H_2 at 350 °C (Fig. 1, spectra 1 and 1′, respectively).

The DR UV–Vis-NIR spectra demonstrate that in the adopted experimental conditions most of the Cr^{6+} species have been reduced in both cases. Indeed, the intense charge-transfer band at 27000 cm^{-1} characteristic of mono-chromates [9,10,19–24,41] is no longer observed. Both spectra are dominated by an intense band centred at 39000 cm^{-1}, which is straightforwardly assigned to an oxygen to chromium ($O \rightarrow Cr$) charge transfer transition [9,10,19–24,42,43]. In the low wavenumbers region, a multitude of bands are observed and assigned to d-d transitions of several types of reduced Cr sites, differing in the oxidation state and coordination geometry. In particular, a very broad envelop of d-d bands is observed in the spectrum of the CO-reduced catalyst, while that of the H_2-reduced catalyst displays more defined bands centred at 26,000, 16,000 and 10,500 cm^{-1}. The presence of a multitude of d-d bands suggests a larger heterogeneity of reduced Cr sites with respect of those obtained on Cr/SiO_2 systems [8], comprising both +3 and +2 oxidation states and different coordination geometries. It is worth noticing that the spectrum of the CO-reduced catalyst is comparable to those previously reported by Weckhuysen et al. for similar systems [9,10,19–24], which are unanimously considered as the reference spectra in this field.

The assignment of the d-d bands is straightforward on the basis of the specialized literature [9,10,19–24]. The UV–Vis spectra of 6-fold coordinated Cr^{3+} species (Cr^{3+}_{6c}) are expected to show two equally intense d-d bands centred at around 17,000 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{2g}$ transition) and 25,000 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{1g}$ transition) and a third one, rather weak, at 37,000 cm^{-1} (which is however always masked by the intense charge-transfer band at high energy) [20,23,44]. On the other hand, the spectra of undistorted 6-fold coordinated Cr^{2+} ions (Cr^{2+}_{6c}) in high-spin $3d^4$ complexes are known to show a single d-d band centred between ca. 10,000 and 20,000 cm^{-1}, which is ascribed to the $^5E_g \rightarrow {}^5T_{2g}$ transition [44]. For example, the hexa-