



# Pre-reduction of the Phillips Cr<sup>VI</sup>/SiO<sub>2</sub> catalyst by cyclohexene: A model for the induction period of ethylene polymerization



Caterina Barzan<sup>a,\*</sup>, Alessandro A. Damini<sup>a</sup>, Andriy Budnyk<sup>b</sup>, Adriano Zecchina<sup>a</sup>, Silvia Bordiga<sup>a</sup>, Elena Groppo<sup>a</sup>

<sup>a</sup> University of Turin, Department of Chemistry, NIS Centre and INSTM, Via G. Quarello, 15A, 110135 Turin, Italy

<sup>b</sup> Southern Federal University, Zorge Street 5, 344090 Rostov-on-Don, Russia

## ARTICLE INFO

### Article history:

Received 16 July 2015

Revised 8 January 2016

Accepted 19 January 2016

### Keywords:

Phillips catalyst

Chromium

Induction period

Ethylene polymerization

Heterogeneous catalysis

## ABSTRACT

The pre-reduction of the industrially relevant Cr<sup>VI</sup>/SiO<sub>2</sub> Phillips catalyst by cyclohexene at room temperature was investigated by means of operando XANES, Diffuse Reflectance UV–Vis and transmission FT-IR spectroscopies. It was found that cyclohexene efficiently reduces the surface chromate sites (Cr<sup>VI</sup>) at room temperature to give mainly divalent chromium sites and aldehyde by-products, which are rapidly converted in ester species. These by-products remain in strong interaction with the reduced chromium sites, defining a complex and tunable ligand sphere, which controls the entrance of incoming molecules, including ethylene. Unlike the Cr<sup>VI</sup>/SiO<sub>2</sub> catalyst, the cyclohexene-reduced Cr/SiO<sub>2</sub> catalyst polymerizes ethylene already at room temperature with no induction time. The reactivity of cyclohexene with the Cr<sup>VI</sup> species mimics that of ethylene during the induction period on Cr<sup>VI</sup>/SiO<sub>2</sub> catalyst, simplified by the absence of the further polymerization step. Hence, the results discussed in this work are potentially useful to understand what happens during the induction period in the presence of ethylene.

© 2016 Elsevier Inc. All rights reserved.

## 1. Introduction

It has been more than sixty years since the first catalytic synthesis of polyethylene, and the importance of polyolefins in every-day life has been growing since then. Common belief relegates polyolefins to low cost applications, but recently these materials have demonstrated to be direct competitors to much more expensive high performance polymers for highly advanced applications. Polyolefins are mainly produced through catalytic polymerization, and in most of the cases by heterogeneous catalysis. The Phillips Cr/silica catalyst, patented in 1951 [1], is the oldest catalyst still employed for the industrial production of a significant fraction of polyethylene. It is obtained by impregnating a polymer-grade porous silica with a chromium precursor (at loadings lower than 1 wt%), followed by calcination at temperatures higher than 500 °C. During this step the chromium ions are anchored to the silica surface as isolated hexavalent chromates (Cr<sup>VI</sup> in the following), and simultaneously the silica support is dehydroxylated [2–7]. The Cr<sup>VI</sup> species are only the precursors of the active sites, which are obtained in the presence of ethylene at temperatures from 80 to 110 °C, during a variable induction period (also called “dormant

period”) without measurable activity, which depends on the reaction conditions. Thus, ethylene operates first as reducing agent, leading to the formation of lower-valent Cr<sup>VI-n</sup> species and oxidized by-products of ethylene, and secondly as monomer in the polymerization reaction [3,8–10].

Although sixty years passed from the first Phillips patent [1], the structure of the active sites at the molecular level and their oxidation state are still unresolved despite the numerous investigations also on well-defined Cr/SiO<sub>2</sub> systems prepared with a surface organometallic approach [2–4,11–17]. This is mainly due to the fact that reduction of the chromate species in the presence of ethylene and ethylene polymerization are extremely difficult to differentiate. Several strategies have been attempted in order to separate the reduction step from the polymerization one by using an external reducing agent prior to ethylene injection. The most used method involves carbon monoxide, which stoichiometrically reduces Cr<sup>VI</sup> sites to Cr<sup>III</sup> at 350 °C, resulting into a Cr<sup>III</sup>/SiO<sub>2</sub> catalyst extremely well characterized in the past [4–7,18–27]; this procedure removes the induction time and decreases the ethylene reaction temperature down to room temperature. Other pre-reducing procedures adopted in the industrial practice involve H<sub>2</sub>, methanol, alkanes, alkenes and metal alkyls (such as AlR<sub>3</sub>, BR<sub>3</sub>, MgR<sub>2</sub>, ZnR<sub>2</sub>) [3,28–30]. A pre-reduction step (i.e. treatment with reducing agents) allows not only to shorten the induction

\* Corresponding author.

E-mail address: [caterina.barzan@unito.it](mailto:caterina.barzan@unito.it) (C. Barzan).

time and to decrease the polymerization temperature (with important consequences in terms of sustainability, operating efficiency and overall economics of the process), but has also great influence on the properties of the produced polyethylene (characterized by high densities, good stiffness, high melting points, and low melt flow indices) [3,30–35]. This in turn suggests that the chromium species active in ethylene polymerization are structurally different depending on the pre-reducing process.

In this work we investigate the reduction of the  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  catalyst by cyclohexene. In the patent literature [36], cyclohexene is claimed to reduce  $\text{Cr}^{\text{VI}}$  sites, leading to a modified-catalyst displaying: (i) short induction times for ethylene polymerization and (ii) ability in polymerizing  $\alpha$ -olefins to obtain poly-1-alkenes. However, the mechanism of  $\text{Cr}^{\text{VI}}$  reduction by cyclohexene is unknown, as well as the reaction by-products; consequently, also the properties of the reduced chromium sites at a molecular level are not clear. Herein we applied XANES spectroscopy in operando and in situ DR UV–Vis spectroscopy to monitor the reduction of  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  by cyclohexene at room temperature; in addition, in situ FT-IR spectroscopy was used to get information on the nature of the cyclohexene oxidation by-products. The data discussed in this work represent a first attempt to define the properties of the chromium sites formed during reduction of a  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  catalyst in the presence of a non polymerizing olefin and are potentially useful to understand what happens during the induction period in the presence of ethylene.

## 2. Experimental

### 2.1. Materials

Two  $\text{Cr}/\text{SiO}_2$  samples were prepared by impregnating  $\text{SiO}_2$  (aerosil, surface area ca.  $360 \text{ m}^2 \text{ g}^{-1}$ ) with aqueous solutions of  $\text{CrO}_3$  having chromium loadings of 0.5 wt% (for DR UV–Vis and EPR measurements) and 1.0 wt% (for IR and XAS measurements), respectively. The chromium loading was low enough to avoid segregation of  $\text{CrO}_x$  during the activation treatments, but sufficiently high to guarantee a good sensitivity with all the techniques [4]. The  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  catalyst was obtained by activating the impregnated sample in the presence of oxygen at  $650 \text{ }^\circ\text{C}$ . This procedure was carried out in static conditions (two cycles of 30 min in pure oxygen, equilibrium pressure 100 mbar) for DR UV–Vis and FT-IR measurements, or in dynamic conditions (10%  $\text{O}_2$  in He, total flow 10 ml/min) for XAS measurements. Reduction of  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  by means of cyclohexene was achieved by dosing the vapor pressure of cyclohexene in the reaction cell, either in vacuum or by stripping the liquid with helium (depending on the operating conditions). Finally, ethylene polymerization experiments were performed with pure ethylene at room temperature, either in static (equilibrium pressure of 100 mbar) or in dynamic conditions (total flow 10 ml/min).

### 2.2. Methods

Cr K-edge XAS spectra were collected at the BM23 beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, F). The white beam was monochromatized using a  $\text{Si}(111)$  double crystal; harmonic rejection was performed by using silicon mirrors (4 mrad). The intensity of the incident beam was monitored by an ionization chamber. Due to chromium dilution, EXAFS spectra were collected in fluorescence mode, by means of a 12 elements germanium detector. The beam was vertically focused to a few micron. The samples were measured in the form of powder inside a quartz capillary 1.5 mm in diameter, placed in between two small regions of quartz wool. The capillary was connected to a line

which allowed fluxing different gas mixtures, and inserted inside an oven, allowing treating the sample (up to  $650 \text{ }^\circ\text{C}$ ), in the presence of different reagents.

XANES spectra were acquired with an energy step of 0.4 eV and an integration time of 2 s/point, up to  $k = 5 \text{ \AA}^{-1}$  in order to allow an easy normalization. Each XANES spectrum required an acquisition time of about 12 min as compromise between fast acquisition and quality of the spectra. The XANES spectra were normalized using the Athena program [37]. The adopted experimental set-up (beam vertically focused in order to fit the 1.5 mm capillary, only 4 mm of sample accessible to the X-ray beam) did not allow to collect EXAFS spectra with a satisfactory signal-to-noise ratio. For this reason the EXAFS spectra of  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  and of the same sample after reaction with cyclohexene were collected on samples prepared ad hoc inside the same 1.5 mm capillaries, but mounted in a different configuration. In particular, a longer part of the capillary was filled with the powder and was accessible to the beam (up to 10–14 mm). This allowed the collection of EXAFS spectra with a good signal-to-noise ratio. The EXAFS spectra were collected up to  $13 \text{ \AA}^{-1}$  with a variable sampling step in energy, resulting in  $\Delta k = 0.05 \text{ \AA}^{-1}$ , and an integration time that linearly increases as a function of  $k$  from 5 to 20 s/point to account for the low signal-to-noise ratio at high  $k$  values. Three equivalent EXAFS spectra were acquired and averaged before the data analysis. The extraction of the  $\chi(k)$  functions was performed using Athena program [37]. Once extracted, the  $k^3$ -weighted  $\chi(k)$  functions were Fourier transformed in the  $\Delta k = 1.0\text{--}3.0 \text{ \AA}$  range. The fits were performed in  $R$ -space in a variable  $\Delta R$  range, using the Artemis program [37]. Phase and amplitudes were calculated by FEFF6.0 code [38], using as input the small clusters indicated in Section S4.

Diffuse reflectance (DR) UV–Vis spectra were recorded on a Varian Cary5000 instrument on samples in the form of thick self-supported pellets (surface density ca.  $60 \text{ mg cm}^{-2}$ ), placed inside a cell equipped with a quartz suprasil window. Sample treatments were performed directly in the UV–Vis cell, in static conditions. The spectra were collected in reflectance mode, and successively converted in Kubelka–Munk units.

The EPR measurements were performed at liquid nitrogen temperature (77 K) and run on a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation.

Transmission FT-IR spectra were collected at  $2 \text{ cm}^{-1}$  resolution on a Bruker Vertex70 instrument, on samples in the form of thin self-supported pellets (surface density ca.  $10 \text{ mg cm}^{-2}$ ), placed inside a quartz cell equipped with two KBr windows. Sample treatments were performed directly in the IR measurement cell in static conditions.

## 3. Results and discussion

### 3.1. The potential of cyclohexene as reducing agent

At first, the effect of cyclohexene on the  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  catalyst was investigated by means of XANES and DR UV–Vis spectroscopies, which are extremely effective techniques to get information on the electronic properties of supported metal species, also when they are highly diluted as in the present case [4,39]. Fig. 1 shows the Cr K-edge XANES spectrum of  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  (black) and its time evolution in the presence of cyclohexene at room temperature (light gray); the last spectrum was collected after about 1 h of interaction (dark gray). The spectrum of  $\text{Cr}^{\text{VI}}/\text{SiO}_2$  is characterized by an intense pre-edge peak centered at 5993.5 eV, having a shoulder around 5991.3 eV (Fig. 1b), and an edge at 6006.7 eV (evaluated at the maximum of the derivative curve, shown in Fig. 1c) with a shoulder at 6001.0 eV. All these features are characteristic

Download English Version:

<https://daneshyari.com/en/article/6526966>

Download Persian Version:

<https://daneshyari.com/article/6526966>

[Daneshyari.com](https://daneshyari.com)