Polyethylene with Reverse Co-monomer Incorporation: From an Industrial Serendipitous Discovery to Fundamental Understanding

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1 Experimental details and supplementary experiments

1.1 Catalyst preparation

All catalyst samples under investigation were made and provided by Total Research and Technology Feluy, Belgium. A commercially available Phillips-type Cr/SiO$_2$ catalyst was used with the following properties: 1 wt% Cr, surface area of 500 m$^2$g$^{-1}$, pore volume of 1.5 cm$^3$g$^{-1}$ and D50 of 85 µm. The pale white pre-catalyst material was titanated and activated according to a procedure described by Debras et al.$^{[1]}$ The preparation procedure consists of the following steps. First, the Phillips-type Cr/SiO$_2$ pre-catalyst was dehydrated at 573 K in a fluidised bed in dry N$_2$ in order to remove physically adsorbed water, which prevents the formation of crystalline TiO$_2$. After drying, titanium isopropoxide (99.999 % trace metals basis, Sigma-Aldrich) was introduced into the N$_2$ stream at the same temperature by evaporation of the material, which was added as a suspension into the reactor. The total amount of titanium isopropoxide, flow rate and titanation time was adjusted in order to obtain an overall catalyst titanation amount of ～4 wt%. After titanation, the catalyst was flushed under N$_2$ for ～45 min at 573 K. In a next step, the temperature was gradually increased to 1048 K and the atmosphere changed from N$_2$ to dry air in which the catalyst material was activated for a period of 6 h. After this oxidation step, the prepared surface-titanated Phillips-type polymerisation catalyst had acquired an intense orange colour. X-ray fluorescence (XRF) analysis showed that the surface-titanated Phillips-type polymerisation catalyst had a titanium loading of ～4.7 wt%, slightly above the intended titanium loading. The activated surface-titanated Phillips-type polymerisation catalyst was kept under an inert atmosphere, and then transferred into a glove box under inert atmosphere for storage and further use. The physical properties of the catalyst material prepared are discussed in the next section.

Further modification of the Phillips-type Cr/Ti/SiO$_2$ catalyst included the reaction with triethylaluminium (TEAl) inside a DRIFTS cell prior to the feed of ethylene. The exact TEAl activation procedure has been described in the section 1.6 “DRIFT spectroscopy during ethylene polymerisation”. The Phillips-type Cr/Ti/SiO$_2$ catalyst treated with TEAl was prepared by wet impregnation of the activated catalyst for a nominal Al:Cr ratio of 2 with a 1.3 M heptane solution of TEAl (～94 wt% triethylaluminium, with ～6 wt% predominately tri-n-butylaluminium and less than 0.1 wt% triisobutylaluminium residue, Acros Organics) diluted with 2-methyl pentane (analytical standard, > 99.5 %, Sigma-Aldrich) dried over molecular sieves. The suspended catalyst was magnetically stirred for 3 h. All steps were performed under inert atmosphere in the glove box. Solvents were removed by heating at 323 K for 24 h in vacuum within a Schlenk line. This sample was used for STXM analysis to obtain an Al XAS-spectrum and the related spatial distribution (Figure 3d).
1.2 Nitrogen physisorption measurements

The nitrogen physisorption measurements were performed on a Micromeritics TriStar 3000 device at 77 K. This instrument determines the nitrogen adsorption and desorption isotherms by static volumetric measurements. The Phillips-type Cr/Ti/SiO$_2$ sample, stored in a solvent-free Ar glove box, was weighed and introduced into a N$_2$ physisorption flask. The sample is evacuated and cooled to the temperature of liquid nitrogen. The adsorption branch is determined by adding stepwise known amounts of nitrogen gas, until the saturation pressure of nitrogen is reached. The adsorption equilibrium pressure is determined at each addition of nitrogen. The desorption isotherm is determined in a similar way: nitrogen gas is removed stepwise, and the desorption equilibrium pressure is measured at each desorption step. The specific surface area is calculated from the adsorption isotherm using the Brunauer-Emmet-Teller (BET) model.$^2$ This value can be considered representative of the true specific surface if the sorption isotherm is of type IV. The pore size distribution is calculated from the desorption isotherm using the Barrett-Joyner-Halenda (BJH) model.$^3$ The total pore volume was defined as the single-point pore volume at p/p$_0$ = 0.95.

The titanation and activation at 1048 K in dry air of the commercial pre-catalyst lead to a material with the following properties: mean pore diameter of 12.4 nm, BET surface area of 367 m$^2$/g and pore volume of 1.13 cm$^3$/g$^{-1}$ of which only 0.0018 cm$^3$/g$^{-1}$ belongs to the micropore volume. The adsorption/desorption plot and pore size distribution are presented in Figure S1.

![Figure S1. Adsorption/desorption curves (a) and pore size distribution (b) of the activated Cr/Ti/SiO$_2$ Phillips-type catalyst obtained using N$_2$ physisorption.](S-2)
open, which is crucial for the diffusion of TEAl as well as ethylene to the oligomerisation and polymerisation sites inside the catalyst particle.

1.3 Ethylene polymerisation studies in a semi-batch reactor

Slurry polymerisation reactions with a Cr/Ti/SiO₂ Phillips-type catalyst in a semi-batch reactor were performed by Total Research and Technology (Feluy, Belgium) and the polyethylene product obtained was used for molecular weight distribution (MWD) and short-chain branching distribution (SCBD) analysis. The two catalyst materials with their properties are summarised in Table S1 and prepared following the same procedure as described in the catalyst preparation section was used for ethylene polymerisation. The reaction conditions, given in Table S1, were chosen in order to target the same molecular weight distribution and co-monomer content (Table S2) in the polymer.

Table S1. Catalyst properties and polymerisation conditions, used for the polymerisation reaction inside a semi-batch reactor, including the physical properties of the polyethylene product.

| Run | Cr (wt%) | Ti (wt%) | Externally added 1-hexene (wt%) | Al/Cr T (K) H₂ (NL) | Prod. (g/g) | HLMI (g/10min) | Density (g/mL) | Wax (wt%) | Mw/Mn | Mz/Mw |
|-----|----------|----------|---------------------------------|---------------------|-------------|----------------|---------------|-----------|-------|-------|
| 1   | 0.5      | 3.9      | 0                               | 2 373 5             | 1100        | 35.0          | 0.953         | 6.2       | 10.7  | 10.6  |
| 2   | 0.5      | 3.9      | 0.6                             | 0 370 0             | 1000        | 41.1          | 0.955         | 5.0       | 12.6  | 12.8  |

1.4 GPC-IR of polyethylene materials made

Molar weight distribution (MWD) of the polyethylenes produced inside the semi-batch reactor was measured externally by Polymer Char Company. The analysis was performed on a Polymer Char's GPC-IR instrument with an infrared IR5 detector with thermoelectrically cooled MCT sensor in order to obtain the MWD curve and short-chain branching distribution (SCBD) within the MWD. The sample preparation included only weighing of the samples (8 ml) into the vials, which were filled automatically with trichlorobenzene (TCB) solvent stabilised with 300 ppm of 2,6-di-tert-butyl-4-methylphenol (BHT). In order to prevent the polymer samples from being degraded, the vials were kept in a high temperature oven just until the polyethylene was dissolved. After dissolution, the polymer samples were automatically filtered using an in-line filter and 200 µl of the polymer solution was injected into the 13 µ GPC columns. The injection time was 55 min with a flow rate of 1 ml min⁻¹.

All calculations were performed using the GPC One software. MWD and molecular averages are based on a conventional calibration curve made with narrow polystyrene standards. To transform PS values into PE values, a factor Q using a PE as standard was applied. Ethylene-octene copolymer metallocene-based standards have been used to
calibrate the branching content in the IR detector. Short-chain branches per 1000 total carbon (SCB/1000TC) were calculated by subtracting the number of methyl end groups per 1000 TC assuming the absence of vinyl chain ends.

1.5 $^{13}$C NMR analysis of the polyethylene materials made

Preparation of the polyethylene samples produced inside the 4 L-sized semi-batch polymerisation reactor included dissolving 220 mg of polymer in 2 ml 1,2,4-trichlorobenzene (TCB, 99% spectroscopic grade, Sigma-Aldrich) at 408 K with occasional agitation to homogenise the sample, followed by the addition of 0.5 ml hexadeuterobenzene (HDB, spectroscopic grade, Sigma-Aldrich) and 1 or 2 drops of hexamethyldisiloxane (HMDS, 99.5+%).

Proton decoupled $^{13}$C NMR spectra were recorded on a Bruker Avance III 500 MHz (125.76 MHz, 90° pulse, 30 s delay between pulses, 240 scans, 1.29 s acquisition time) with a 10 mm cryoprobe at 403 K and an inverse-gated pulse sequence to avoid NOE effect. Gaussian multiplication ($lb = -0.2$ and $gb = 0.02$) was performed before Fourier Transform. The chemical shifts are referenced to the signal of the internal standard HMDS, which is assigned a value of 2.03 ppm.

The NMR analysis (Table S2) shows a similar amount of olefin incorporation, i.e. wt% of olefin incorporated as short branching of the polyethylene chain, for a catalyst when 1-hexene co-monomer was externally fed and for the catalyst that was modified by pre-contacting with TEAI and with the ethylene oligomers produced in-situ. Combined with the GPC-IR results presented in the main text (Figure 1), we have shown that we are able to produce two different types of polymer with similar overall amount of branching, but with different short-chain branching distributions. The increased amount of branching in the longer chains, achieved for the TEAI-modified catalyst, is a desired product feature from the industrial point of view as it leads to better mechanical properties.
Figure S2. a) $^{13}$C NMR spectra of the polyethylene samples produced inside a semi-batch reactor. (red) Spectrum of the polyethylene produced when \textit{in-situ} polymerisation was induced by the modification of the Cr/Ti/SiO$_2$ catalyst with TEAl. (blue) Spectrum of the polyethylene produced with externally added 1-hexene co-monomer with a regular Cr/Ti/SiO$_2$ catalyst. b) Enlarged region of the $^{13}$C NMR spectra showing the chemical shifts of ethyl (*) and (#) butyl branches,\textsuperscript{[6]} due to incorporation of 1-butene and 1-hexene, respectively. The chemical shifts are referenced to the signal of hexamethyldisiloxane (o), which is assigned to 2.03 ppm.

Table S2. $^{13}$C NMR analysis of the short-chain branching of the polyethylene samples produced inside a semi-batch reactor. Run 1 represents a polymerisation, which was performed without external addition of 1-hexene co-monomer, when \textit{in-situ} polymerisation was induced by the modification of the Cr/Ti/SiO$_2$ catalyst with TEAl. Run 2 represents a polymerisation, which was performed with externally added 1-hexene with a regular Cr/Ti/SiO$_2$ catalyst.

| Run | Cr (wt\%) | Ti (wt\%) | Externally added 1-hexene (wt\%) | Al/Cr | T (K) | H$_2$ (NL) | Olefin incorporation |
|-----|-----------|-----------|---------------------------------|-------|-------|-----------|---------------------|
|     |           |           |                                 |       |       |           | 1-butene (wt\%) 1-hexene (wt\%) 1-octene (wt\%) |
| 1   | 0.5       | 3.9       | 0                               | 2     | 373   | 5         | 0.1 0.7 -        |
| 2   | 0.5       | 3.9       | 0.6                             | 0     | 370   | 0         | - 0.9 -         |
1.6 DRIFT spectroscopy during ethylene polymerisation

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy experiments of the Phillips-type Cr/Ti/SiO$_2$ catalyst were performed in-situ under controlled atmosphere. The catalyst samples, prepared and stored in the glove box, were loaded under inert Ar atmosphere into a Praying Mantis High Temperature Reaction Chamber preventing any poisoning by atmospheric O$_2$ and H$_2$O. The FT-IR spectra were measured on a Bruker Tensor 37 spectrometer, with a liquid nitrogen-cooled MCT detector, in the spectral range of 4,000 – 600 cm$^{-1}$ with a 4 cm$^{-1}$ resolution and 32 s scan time. All ethylene polymerisation reactions were performed at 373 K and 1 bar. Lowering the partial pressure of ethylene, compared to the industrial conditions, helped to avoid saturation of the overall FT-IR signal as well as of the overlapping FT-IR bands of the gaseous reactant, i.e. ethylene, with the CH$x$ stretching bands of the polyethylene formed. As co-catalyst we have used 10 µL of 1.3 M solution of triethylaluminium (TEAl) in heptanes (~ 94 wt% triethylaluminium, with ~ 6 wt% predominately tri-n-butylaluminium and less than 0.1 wt% triisobutylaluminium residue, Acros Organics), which was injected through a silicon septum for an Al:Cr ratio of 2:1. The obtained co-catalyst – heptane mixture was evaporated into the nitrogen stream and let to pre-react with the catalyst by flowing through the catalyst bed, before the feed of the actual ethylene reaction mixture. This can be evidenced by the initial growth of the IR bands in the CH$x$ stretching region originating from the methyl and methylene groups of heptanes and TEAl (Figure 2a and Figure S3b). The excess heptane solvent was flushed off with nitrogen, causing the decrease of these bands, leaving only TEAl-modified cites (Figure S3c). Only after this step, the reactant mixture consisting of 45 vol.% N$_2$, 45 vol.% C$_2$H$_4$ and 10 vol.% H$_2$, was fed into the DRIFTS cell. All gases were provided by Linde with the following purities N$_2$ (99.999 %), H$_2$ (99.999 %) and C$_2$H$_4$ (99.95 %). The FT-IR data were analysed with the OPUS Spectroscopy Software. All spectra were normalised to the silica Si-O framework bands in the 2,100-1,750 cm$^{-1}$ spectral region. The spectral region below 1400 cm$^{-1}$ was not presented due to the high absorption of the Si-O bands of the silica support.
Figure S3. DRIFT spectra at several key moments during the modification of the Cr/Ti/SiO\textsubscript{2} catalyst with TEAl and subsequent reaction with ethylene: (a) shows the spectrum of the activated Cr/Ti/SiO\textsubscript{2} catalyst with sharp silanol stretching band and titanol shoulder at 3747 and 3722 cm\(^{-1}\), respectively. The addition of TEAl, dissolved in heptanes, can be noted by the CH\textsubscript{x} stretching groups in the spectrum (b). After the flushing of excess heptane solvent, TEAl-modified Cr/Ti/SiO\textsubscript{2} catalyst is obtained with the alkyl functionality (c). After this point, the ethylene reactant mixture was fed into the system and ethylene polymerisation was started, which can be observed from spectra (d) to (g). The OH stretching region is marked with (1), CH\textsubscript{x} stretching regions during the addition of TEAl (2), CH\textsubscript{x} stretching region of gas-phase ethylene (3) and growing polyethylene (4).

1.7 GC analysis of the gas phase collected during ethylene polymerisation

Polymerisation of ethylene was performed with Phillips-type Cr/SiO\textsubscript{2} and Cr/Ti/SiO\textsubscript{2} catalysts. Approximately 300 mg of the catalyst sample was loaded into a quartz cell under inert atmosphere. Before the feed of ethylene, the catalyst was pre-contacted with 0.1 mL of 1.3 M (for an Al:Cr ratio of 2:1) TEAl in heptanes, which was injected through a silicon septum into the N\textsubscript{2} stream of 10 mL min\(^{-1}\). After the stabilisation, the gas reaction mixture consisting of 45 vol.% N\textsubscript{2}, 45 vol.% C\textsubscript{2}H\textsubscript{4} and 10 vol.% H\textsubscript{2} or 50 vol.% N\textsubscript{2} and 50 vol.% C\textsubscript{2}H\textsubscript{4} was fed into the cell with a total flow of 10 mL min\(^{-1}\). Ethylene polymerisation was performed at 373 K and 1 bar of total pressure. The gas phase was continuously collected into 1 L Sigma-Aldrich Tedlar gas-sampling bags. After reaction, GC analysis of the gas phase was
performed on a Varian 430-GC Gas Chromatograph with a FID detector with a VF-5ms column by manual injection of 1 mL of the gas phase using a 1 mL gas-tight GC syringe. Column flow was set at 1 mL min\(^{-1}\) and column temperature kept at 305 K during the whole analysis. A calibration curve was made by the dilution of a reference light hydrocarbon gas mixture, provided by Linde Gas, with N\(_2\).

The GC results obtained are presented in Figure S4. The non-titanated Phillips-type Cr/SiO\(_2\) catalyst pre-contacted with TEAI is producing more ethylene co-monomers than the Cr/Ti/SiO\(_2\) catalyst; i.e., 0.3 vs. 1 %. Moreover, the olefin selectivity is clearly shifted towards the formation of 1-hexene when a non-titanated Phillips-type Cr/SiO\(_2\) catalyst pre-contacted with TEAI is used.

![Figure S4](image)

**Figure S4.** Gas phase concentrations of the olefinic products produced *in-situ* in the ethylene polymerisation reactions with (a1) a Cr/Ti/SiO\(_2\) and (b1) a Cr/SiO\(_2\) catalyst pre-contacted with TEAl. The relative ratio of olefinic species for both catalyst materials is given in the pie charts (a2 and a2).

### 1.8 SEM-EDX studies on fresh and polymerising catalyst particles

In order to investigate the morphology and chemical composition of the catalyst material and the polyethylene product formed on the single particle level before and after ethylene polymerisation in the DRIFT spectroscopy cell using the Phillips-type Cr/Ti/SiO\(_2\) catalyst, Scanning Electron Microscopy (SEM) analysis was performed on a FEI company XL30SFEG SEM microscope equipped with an EDAX Energy Dispersive X-ray (EDX)
analyser for elemental analysis. The catalyst samples and the obtained products after ethylene polymerisation within the DRIFTS cell were sprinkled on an aluminium plate covered with a carbon tape, sputter coated with a 10 nm layer of platinum in the Cressington sputter Coater 208HR with Cressington thickness controller MTM20, loaded into the sample holder and placed into the apparatus. The acceleration voltage of the electron beam was set to 10-15 keV. Several different particles of catalyst material and polyethylene product were analysed by EDX over 4-5 different points and concentrations of the elements were averaged.

Figs. S5a and S5b present a couple of Phillips-type Cr/Ti/SiO₂ catalyst particles of ~ 70 µm in diameter. The catalyst particles are mostly of an irregular shape with many cracks and crevices (Figs. S5a, S5b1 and S5b2), which might be crucial in delivering the ethylene monomer to the active sites inside the catalyst body and on the other hand fragmentation of the catalyst particle by the increasing amount of polyethylene formed. The manner of the fragmentation of the catalyst particle is very important from an industrial point of view since it affects the diffusion of ethylene, polyethylene production rate, yield as well as the optical properties. In the SEM images collected, after the polymerisation of ethylene in the DRIFTS cell at 373 K and 1 bar, polyethylene can be clearly observed (see Figs. S5c-S5f1). Moreover, due to the milder total pressure of 1 bar in comparison to several dozens of bar commonly used in industrial ethylene polymerisation, it is possible to visualise the initial stages of catalyst fragmentation. It is evident that not all catalyst particles were (already) active in the same way as can be concluded from the amount of the produced polyethylene on some of the catalyst particles.

The chemical composition of the Phillips-type catalyst particles and polyethylene formed, as measured by EDX, is presented in Table S3. For this purpose, two different catalyst particles and two different polyethylene particles have been examined. The oxygen-to-silicon ratio in the catalyst samples correspond to the ratio of these elements in the silica support. The Ti content is slightly higher than expected from the catalyst preparation. It has to be mentioned that the probed volume of the sample with the EDX analysis is ~ 1-2 µm in diameter from the surface of the material and therefore the Ti content increase could be explained by a higher amount of Ti in the Ti-rich shell of the catalyst particle. The amount of Ti in the areas probed by EDX can be estimated by excluding Pt from the mass balance, which gives the concentrations of 7 and 11 wt% of Ti in the catalyst samples Cat’ and Cat” respectively. The content of Cr has to be taken with caution due to the low concentration, detection limitation of the instrument and the overlapping of the Cr band with Ti and O bands in the X-ray spectra. After ethylene polymerisation, no Cr or Ti could be basically detected, and the main contribution in the X-ray spectra comes from the carbon of the polyethylene,
including the signal from the Pt coating (Figure S6). The Al K-edge originating from the addition of TEAl co-catalyst cannot be seen in the EDX spectra of the catalyst/polyethylene particle after ethylene polymerisation due to the fact of too low amount of added TEAl through the gas lines by evaporation (aimed for an Al:Cr ratio of 2:1). It is important to mention that the small amounts of carbon present in the fresh catalyst originate from the carbon tape used to increase the conductivity of the catalyst samples.

**Cr/Ti/SiO₂ Phillips catalyst before ethylene polymerisation**

![Scanning Electron Microscopy (SEM) images of the Phillips Cr/Ti/SiO₂ catalyst before polymerisation of ethylene (a and b) with magnified images of the highlighted areas (a1, b1 and b2); Bottom: SEM images of the polyethylene/catalyst mixtures after the in-situ polymerisation of ethylene inside the in-situ](image)

**Figure S5.** Top: Scanning Electron Microscopy (SEM) images of the Phillips Cr/Ti/SiO₂ catalyst before polymerisation of ethylene (a and b) with magnified images of the highlighted areas (a1, b1 and b2); Bottom: SEM images of the polyethylene/catalyst mixtures after the in-situ polymerisation of ethylene inside the in-situ
DRIFTS cell at 373 K and 1 bar, with TEAl co-catalyst and gas mixture of 45 vol.% N₂, 45 vol.% C₂H₄ and 10 vol.% H₂ (c, d, e and f) with magnified images of the highlighted areas (d₁ and f₁); EDX elemental analysis was performed over several points in the regions of a, b₁, d₁ and f.

Table S3. Elemental composition of two different Phillips-type Cr/Ti/SiO₂ catalyst particles and two different Cr/Ti/SiO₂ catalyst/polyethylene product particles obtained with the EDX analyser by averaging the composition at 4-5 different points. The labels in the parenthesis correspond to the SEM images of the samples where the EDX analysis was performed.

| Sample[a] | wt% Pt | wt% C | wt% Cr | wt% Ti | wt% O | wt% Si |
|-----------|--------|-------|--------|--------|-------|--------|
| Cat' (a)  |   21   |   6   |   1    |   5    |  36   |  31    |
| Cat'' (b₁)|   34   |   3   |   1    |   7    |  30   |  26    |
| PE' (d₁)  |    6   |   68  |   1    |   0    |  15   |  10    |
| PE'' (f)  |   43   |   52  |   0    |   1    |  1    |  3     |

[a] The labels in the parenthesis correspond to the SEM images (Figure S6) of the samples where the EDX analysis was performed.

Figure S6. Energy Dispersive X-ray (EDX) analysis in a Scanning Electron Microscopy (SEM) instrument of the Phillips-type Cr/Ti/SiO₂ catalyst under study and the polyethylene product formed after the polymerisation in the DRIFTS cell at 373 K and 1 bar. a) The elemental composition of the two different catalyst particles and the two polyethylene particles was averaged over 4-5 measurement points per sample. b) The EDX spectra belong to one of the measurement points of each particle.

The acquired data offered the possibility to study the catalyst and the catalyst/polymer particles at the micro- and nanoscale. In this respect, SEM-EDX was very useful for studying the morphology of the polyethylene, the fragmentation of the catalyst particle and the related elemental analysis. Unfortunately, the nature of the EDX analysis and the overlapping of the bands of probed elements could not give any further information on the coordination, phase and oxidation state of the constituting elements of the catalyst particle. Therefore, the STXM technique proved to be an indispensable micro-spectroscopy method for a detailed analysis of both the catalyst particle and the growing polyethylene material.
1.9 UV-Vis-NIR diffuse reflectance spectroscopy

UV-Vis-NIR Diffuse Reflectance Spectroscopy (UV-Vis-NIR DRS) measurements of the fresh Cr/Ti/SiO₂ catalyst, TEAl-modified Cr/Ti/SiO₂ catalyst prior to the ethylene feed and Cr/Ti/SiO₂ catalyst after polymerisation reaction (containing PE) were performed in a home-made sealable quartz cell with a Varian Cary 500 Scan spectrophotometer equipped with a diffuse reflectance spectroscopy accessory. For each measurement the cell was filled inside an Ar glove box, therefore keeping the samples from the contact with air. The spectra were measured against a halon white standard in 4,000-45,000 cm⁻¹ range, 33 ms data point scan time and spectral resolution of 17 cm⁻¹ and 7 cm⁻¹ in 12,500-45,000 cm⁻¹ and 4,000-12,500 cm⁻¹, respectively. Two artefacts in the measured spectra were corrected for the detector/grating and light source changeovers at 12,500 cm⁻¹ and 28,570 cm⁻¹, respectively, while the spectral feature at 11,250 cm⁻¹ is due to an instrumental artefact.

1.10 Electron paramagnetic resonance

The fresh Cr/Ti/SiO₂ catalyst, TEAl-modified Cr/Ti/SiO₂ catalyst prior to the feed of ethylene and the Cr/Ti/SiO₂ catalyst after polymerisation reaction (containing PE) were analysed in sealable J-Young quartz EPR tubes with a diameter 5 mm filled inside a glove box (Figure S7). The electron paramagnetic resonance (EPR) spectra were recorded at 100 K with an X-band Bruker EMXPlus spectrometer equipped with an EMX Standard Cavity. The microwave frequency was set to ~ 9.43 GHz at a microwave power of 2 mW. The spectrometer settings involved 70 mT sweep width with 350 mT centre field and a field modulation amplitude of 0.2 mT or 600 mT sweep width with 300 mT centre field and a field modulation amplitude of 0.5 mT. Furthermore, to rule out a possible reduction of Ti⁴⁺ species inside the Cr/Ti/SiO₂ catalyst by TEAl, EPR experiments of the TiO₂/SiO₂ material before and after modification with TEAl were performed under the same conditions (Figure S8).

Simulations of the measured EPR spectra were performed with the EasySpin software,[7] using the function ‘pepper’ for solid-state EPR and taking into account an anisotropic broadening (i.e., A and g strain). The Blueprint XAS toolbox (initially developed for other purposes) was used as graphical interface of EasySpin,[8] to optimise parameters for each species that compose the simulation, since it enables visualisation of each spectral component, the sum of the simulation and the experimental EPR spectra simultaneously. Simulated EPR active species and related simulation parameters are tabulated in Tables S4, S5 and S6.
Table S4. EPR Cr\textsuperscript{5+} γ-signals, and related properties, as observed in fresh, TEAl-modified and spent Cr/Ti/SiO\textsubscript{2} catalysts.

| Catalyst sample | γ-signal, its symmetry and relative contribution to the spectrum |
|-----------------|---------------------------------------------------------------|
| Fresh           | 100% A, axially symmetric                                      |
| TEAl-modified   | 57 % B, axially symmetric 43 % C, rhombic                     |
| Spent           | 46 % B', rhombic 54 % C, rhombic                              |

Table S5. Simulated EPR parameters for the different Cr\textsuperscript{5+} γ-signals observed in fresh, TEAl-modified and spent Cr/Ti/SiO\textsubscript{2} catalysts.

| Signal | Species            | Relative contribution (%) | g-factor | g\textsubscript{xx} | g\textsubscript{yy} | g\textsubscript{zz} | Sg\textsubscript{xx} | Sg\textsubscript{yy} | Sg\textsubscript{zz} |
|--------|--------------------|---------------------------|----------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| A      | Axially symmetric  | 100                       |          | 1.970                | 1.970                | 1.890                | 0.010                | 0.005                | 0.015                |
| B      | Axially symmetric  | 57                        |          | 1.980                | 1.980                | 1.915                | 0.008                | 0.008                | 0.012                |
| C      | Rhombic            | 43                        |          | 1.980                | 1.969                | 1.922                | 0.008                | 0.008                | 0.012                |
| B'     | Rhombic            | 46                        |          | 1.984                | 1.976                | 1.950                | 0.010                | 0.012                | 0.019                |
| C      | Rhombic            | 54                        |          | 1.980                | 1.969                | 1.922                | 0.010                | 0.012                | 0.019                |

Table S6. Simulated EPR parameters for the signal of isolated Ti\textsuperscript{3+} ions and (O\textsubscript{2}\textsuperscript{−}) superoxide radical anions detected in the TEAl-modified TiO\textsubscript{2}/SiO\textsubscript{2} material.

| Signal | Species          | Relative contribution (%) | g-factor | g\textsubscript{xx} | g\textsubscript{yy} | g\textsubscript{zz} | Sg\textsubscript{xx} | Sg\textsubscript{yy} | Sg\textsubscript{zz} |
|--------|------------------|---------------------------|----------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Ti\textsuperscript{3+} | Axially symmetric | 91                        |          | 1.964                | 1.964                | 1.917                | 0.043                | 0.043                | 0.050                |
| (O\textsubscript{2}\textsuperscript{−}) | Rhombic        | 3                         |          | 2.004                | 2.010                | 2.021                | 0.003                | 0.003                | 0.003                |
| (O\textsubscript{2}\textsuperscript{−}) | Rhombic        | 3                         |          | 2.004                | 2.010                | 2.025                | 0.003                | 0.003                | 0.003                |
| (O\textsubscript{2}\textsuperscript{−}) | Rhombic        | 3                         |          | 2.004                | 2.010                | 2.028                | 0.003                | 0.003                | 0.003                |
**Figure S7.** EPR spectra of the fresh (orange), TEAl-modified (green) and spent (grey) Cr/Ti/SiO₂ catalyst. a1, b1 and c1 show respectively Y-signal of [CrO₄]⁻³ species and δ-signal of mono-dispersed Cr³⁺ species dispersed on the Cr/Ti/SiO₂. Insets show magnified EPR spectra in the Cr³⁺ δ-signal range, while a2, b2, c2 show EPR spectra in the Cr⁵⁺ Y-signal range. It is important to note that the Fe³⁺ impurity is marked with *.

**Figure S8.** EPR spectra of the fresh (a) and TEAl-modified TiO₂/SiO₂ material (b) indicate a small reduction of Ti⁴⁺ species, testified by the appearance of signal of isolated Ti³⁺ ions (gₓₓ = 1.964, gᵧᵧ = 1.964 and gzz = 1.917) and formation of superoxide radical anions of type Ti⁵⁺(O₂⁻) (g>2). It is important to note that the intensities are not substantially higher than the signal of Fe³⁺ impurity marked with *. The overlay (c) of the magnified signal of TEAl-modified TiO₂/SiO₂ material (navy) and TEAl-modified Cr/Ti/SiO₂ Phillips-type catalyst (green) shows the absence of the reduction of Ti⁵⁺ by TEAl inside the Cr/Ti/SiO₂ catalyst, confirming that the observed EPR signal belongs solely to the axially symmetric and rhombic Cr⁵⁺ species.

### 1.11 XRD analysis of the activated catalyst

In order to rule out the formation of TiO₂ crystallites after the titanation and activation of the Cr/Ti/SiO₂ catalyst in dry air, an XRD analysis of the activated Cr/Ti/SiO₂ catalyst was performed by a Bruker-AXS D2 Phaser powder X-Ray diffractometer using a Co kα₁,₂ source with λ = 1.79026 Å. Measurements of the small-angle pattern were carried out between 1.5 and 5 ° 2θ using a step size of 0.022 ° 2θ and a step time of 33 s. A wide-angle XRD pattern
was acquired between 20 and 80° 2θ using a step size of 0.022° 2θ and a step time of 13.2 s. Furthermore, in order to resolve better the diffractions coming from 100% titania peaks, the analysis was performed in the 25 to 35° 2θ range with high step time of 1320 s.

The titanation procedure employed for the preparation of the catalyst materials included a reaction of titanium isopropoxide with a highly dehydrated pre-catalyst (i.e., a Phillips-type Cr/SiO₂) in a way which prevented the formation of bulk TiO₂. Ti becomes chemically bonded to the pre-catalyst instead of the forming of TiO₂ crystallites on the catalyst surface. Therefore, the diffractograms presented in Figure S9 show only an amorphous oxide support, although the size and amount of the TiO₂ crystallites could be too small to be detected with XRD. No ordering can be noted in the small-angle XRD diffractogram, while no TiO₂ crystallites were found in the wide-angle part of the diffractogram, even for the high step time in the 2θ range where 100% TiO₂ diffractions are expected. Due to the presented results, STXM, as an XAS technique, is critical for the characterisation of these types of materials since it is probing the local “short-range” structure and coordination of the examined elements, independent of the overall lack of crystallinity.

Figure S9. (a) The small-angle X-ray diffractogram of the fresh Cr/Ti/SiO₂ catalyst showing no ordering of the catalyst material. (b) Wide-angle X-ray diffractogram of the fresh Cr/Ti/SiO₂ catalyst showing only amorphous silica support (black) even for high accumulation times (red) for the angles were the 100%-peaks of TiO₂ are expected to appear.

1.12 STXM studies of fresh and polymerising catalyst particles

Sample preparation for the Scanning Transmission X-ray Microscopy (STXM) experiments included the embedding of (a) the Phillips-type Cr/Ti/SiO₂ catalyst and (b) the polyethylene product formed after the polymerisation in the DRIFTS cell with the Phillips-type Cr/Ti/SiO₂ catalyst treated with TEAl into an epoxy-based Struers Epofix Resin. The Phillips-type catalyst sample was ultra-microtomed into 300 nm slices, while the polyethylene sample was sectioned into 100 nm slices in order to avoid the saturation of the signal during the measurements at the C K-edge. The microtomed samples were placed
onto the Transmission Electron Microscopy (TEM) copper grids and as such used for the analysis. Due to the delicate sample preparation procedure, the three sets of samples had to be exposed to air prior to the STXM measurements.

The STXM experiments of the catalyst material and the polyethylene formed were performed at the Soft X-ray Spectromicroscopy (SM) 10ID-1 beamline of the Canadian Light Source (CLS) in Saskatoon, Canada, with a 40 nm zone plate. Several spectral ranges were examined depending on the element i.e. C K-edge (280-320 eV), Ti L$_{2,3}$-edges (452-477 eV), O K-edge (525-580 eV), Cr L$_{2,3}$-edges (572-592 eV), Al K-edge (1550-1595 eV) and Si K-edge (1835-1860 eV). X-ray absorption spectroscopy (XAS) spectral image sequences were obtained by collecting a series of images over small energy increments in the range of several tenths of eV bellow and above an X-ray absorption edge of the examined element. The probed area of single particles was ~100 µm$^2$ with spatial resolution of 50-100 nm, while the energy resolution varied from 0.1 eV around the absorption edge up to 1 eV at the pre-edge region where good energy resolution was not necessary in order to minimise the measuring time. The data was processed using the aXis2000 software package$^{[9]}$, which included the alignment of the spectral images and subtraction of the background spectrum after which the XAS spectra were obtained. The XAS spectra were integrated over the whole Phillips-type Cr/Ti/SiO$_2$ catalyst particle in the examined area in order to acquire a better quality the spectra of the element with the lowest loading i.e. Cr (0.98 wt%) or the element with a higher absorption energy i.e. Si and Al due to the small thickness of the sample. By subtracting the pre-edge from the edge spectral image, it was possible to obtain the elemental map of each probed element.

Figure S10a shows the overall XAS image of the polyethylene/catalyst particle after ethylene polymerisation in the \textit{in-situ} DRIFTS cell at 373 K and 1 bar. A clear start of the fragmentation of the catalyst particle, embedded in the epoxy resin, can be observed. In the STXM Ti map, presented on Figure S10b, we can still see the Ti-abundant shell of the Phillips catalyst particles with discontinuities in the cracks, which are filled with the produced polyethylene as already shown in Figure 4a of the main text.
Figure S10. a) The overall X-ray Absorption Spectroscopy (XAS) image and b) STXM Ti map of the polyethylene/ Cr/Ti/SiO$_2$ catalyst particle after the polymerisation of ethylene at 373 K and 1 bar in the DRIFTS cell shows the shell distribution of Ti and a clear start of the catalyst fragmentation process.

The XAS spectra of the Cr L$_{2,3}$- and Ti L$_{2,3}$-edges are shown in Figure S11. After ethylene polymerisation, the Ti$^{4+}$ species remain octahedrally coordinated. Even after reaction, Cr species could still be detected since the Cr/Ti/SiO$_2$ catalyst fragments were not yet dispersed in the polyethylene matrix due to the initial phase of the polymerisation and the related early stages of the fragmentation process. From the XAS spectrum of the Cr L$_{2,3}$-edge it can be concluded that Cr is pseudo-octahedrally coordinated, most probably in the form of dispersed Cr$_2$O$_3$.

Figure S11. X-ray Absorption Spectroscopy (XAS) data of the Ti L$_{2,3}$-edge (blue) and Cr L$_{2,3}$-edge (purple) with a smoothed spectrum (black) in the Cr/Ti/SiO$_2$ catalyst/polyethylene sample after the polymerisation of ethylene at 373 K and 1 bar in the DRIFTS cell.
2 References

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