Real-time Analysis of a Working Triethylaluminium-Modified Cr/Ti/SiO$_2$ Ethylene Polymerization Catalyst with In Situ Infrared Spectroscopy

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A diffuse reflectance infrared Fourier-transform (DRIFT) study has been conducted at 373 K and 1 bar on an industrial Cr/Ti/SiO$_2$ Phillips-type catalyst modified with, and without, triethylaluminium (TEAl) as co-catalyst. The reaction rate of the polymerization of ethylene, as monitored by the increase in the methylene stretching band of the growing polyethylene (PE), has been investigated as a function of the titanium content. After an initial period of mixed kinetics, with the reaction rate significantly higher for the TEAl-modified catalysts compared with the non-modified catalysts, the polymerization proceeded as a pseudo-zero-order reaction with a reaction rate that increased as a function of titanium loading. Furthermore, it was found that the higher Ti loading caused the appearance of more acidic hydroxyl groups and modified the Cr sites by making them more Lewis acidic, ultimately shortening the induction time and increasing the initial polymerization rate.

Introduction

The ability of the Phillips Cr/SiO$_2$ catalyst[1–5] to polymerize ethylene without the intervention of any activator that introduces an initial alkyl ligand, from which the polyethylene (PE) chain could grow, makes the system rather different from Ziegler–Natta[6–9] and metallocene polymerization catalysts.[10–13] For ethylene polymerization to start, the Cr^{6+} species of the activated catalyst need to be reduced to Cr species in lower oxidation states, while the redox products (i.e., aldehydes and ketones)[14] should desorb from the coordination sphere of Cr. Subsequently, a hydride or an alkyl ligand has to be formed where a monomer can be inserted. Without the presence of any alkylating agents, these roles have to be performed by the ethylene monomer and are the cause of the reported induction period before the start of the ethylene polymerization.

These silica-supported chromium catalysts for the polymerization of ethylene have been extensively studied with infrared (IR) spectroscopy[15–17] to elucidate the nature of the chromium polymerization sites.[4,18,19] Most of the research included studies of model catalysts, where the main Cr species of the activated catalyst, that is, Cr^{6+}, are reduced with CO to Cr^{2+} species.[20] The catalyst in this form is afterwards examined with different probe molecules including CO, NO, and ethylene itself, in time-, temperature-, and pressure-resolved experiments.[21] To study this highly active system, temperatures and pressures are often set to very low values, that is, 77 K and under vacuum, which are needed to freeze possible reaction intermediates or examine the adsorption and desorption of probe molecules.[13,22–24] The experiments showed a high heterogeneity of Cr^{2+} sites, classified into three families, that is, Cr^2_A, Cr$^{2+}_B$, and Cr$^{2+}_C$, with respect to their ability to coordinate probe molecules (A > B > C). The exact initiation mechanism has not yet been agreed on, except that the initiation step follows ethylene coordination on Cr^{2+} via formation of d–π complexes.[4,25] In the case of the Cr/SiO$_2$ catalyst, which is not pre-reduced, the situation is even more complicated owing to the heterogeneity of the oxidation states of Cr and possible molecular structures.[1,3,4] The most recent hypothesis is that ethylene is able to reduce the surface Cr^{6+} sites to Cr^{3+} sites to form Cr–alkyl intermediates, which could represent the catalytically active sites.[26] It is for these reasons that kinetic studies of ethylene polymerization using the Phillips-type catalysts are rather difficult to perform.

Previous work from our group focused on the elucidation of the TEAl-induced selective oligomerization properties of Cr/SiO$_2$ and Cr/Ti/SiO$_2$ ethylene polymerization catalysts through both in situ and ex situ analyses of the catalyst materials involved as well as the produced PE and gas-phase molecules released during ethylene polymerization. A variety of methods have been used to make this possible, namely UV/Vis/NIR diffuse reflectance spectroscopy (DRS), GC, GC-MS, gel permeation chromatography (GPC)-IR, ^{13}C NMR, scanning transmission X-ray microscopy (STXM), EPR, XRD, and SEM-energy-dispersive X-ray (EDX). It was revealed that by varying the Ti loading it was possible to control the molecular weight and short chain

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branching distributions as titanium promotes β-hydrogen elimination (leading to shorter polyethylene chains) and inhibits the in situ generation of co-monomers.[27] Therefore, the Cr sites in the Ti-rich shell are producing shorter, more linear PE in comparison to Ti-scarce TEAl-modified Cr sites. The "reverse" co-monomer incorporation was established, as a higher concentration of co-monomer was produced in situ by Ti-scarce TEAl-modified Cr sites, and subsequently incorporated on the polymerization sites produced longer chains.[28]

Building further on the earlier EPR and UV/Vis/NIR DRS analysis of the oxidation states of Cr and Ti in $Cr/Ti/SiO_2$ catalysts,[27, 28] this paper concentrates on the in situ DRIFTS characterization and kinetic studies of Cr/SiO_2 and $Cr/Ti/SiO_2$ catalysts in their activated form, without the pre-reduction of Cr^{6+} species, with the goal to elucidate the influence of the titanium modification and use of TEAl as co-catalyst on the ethylene polymerization kinetics.

Results and Discussion

DRIFTS experiments with the Phillips-type catalysts without TEAl modification

In a first set of experiments, $Cr/Ti/SiO_2$ (CTS1 and CTS2) and Cr/SiO_2 (CS) Phillips-type catalysts, with the properties given in Table 1, were tested for the ethylene polymerization reaction without prior modification with TEAl. Polymerization was performed at 1 bar and 373 K by using the gas reactant mixture consisting of 45 vol.% N_2, 45 vol.% C_2H_4, and 10 vol.% H_2. The reactions were monitored in situ with DRIFT spectroscopy on a specially designed setup, which is outlined in Figure 1. As a showcase, the time evolution of the DRIFT spectra in the 600–4000 cm^{-1} region during the polymerization of ethylene over the CTS2 $Cr/Ti/SiO_2$ catalyst are presented in Figure 2a.

Table 1. Overview of the prepared Phillips-type ethylene polymerization catalysts and support materials with their textual properties.

Sample name	Calcination temperature [K]	Cr loading [wt%]	Ti loading [wt%]	Surface area [$m^2 g^{-1}$]	Pore volume [$cm^{-3} g^{-1}$]
S	1048	0	0	246	1.39
TS	1048	0	4.7	254	1.51
CS	1048	0.52	0	296	1.30
CTS1	1048	0.62	2.2	293	1.44
CTS2	1048	0.56	3.9	277	1.39

The spectra of several key points, that is, before the reaction, on the addition of ethylene, and after the reaction, are presented in Figure 2b. The fresh catalyst shows a highly dehydroxylated catalyst support, as testified by the sharp silanol stretching vibration at 3746 cm^{-1}. Another band observed at 3719 cm^{-1}, which appears only in the titanated catalyst samples, is assigned to the stretching vibration of an isolated titanol group and is an indication of the increased surface acidity. Thirdly, the low intensity band appearing at 3610 cm^{-1} is more difficult to assign. Recently, a band at similar wavenumber has been proposed as the stretching vibration of bridging Si-(μ-OH)-Cr^{3+} hydroxyl groups formed upon contact of ethylene with Cr^{3+} catalyst material, used to explain the initiation mechanism that involves the heterolytic activation of the Cr^{3+}—O bonds.[29a, 30] However, it was shown later that the combination of bands from the C—H vibrations of polyethylene could appear at the same wavenumbers, making it impossible to assign this vibration unequivocally to the Si-(μ-OH)-Cr^{3+}.[29b, 31] In the DRIFTS measurements performed in this study, such a band was observed in the activated Phillips-type catalyst before any contact with ethylene, co-catalyst, or other organic compound possessing CH_2 or CH_3 groups. Furthermore, during
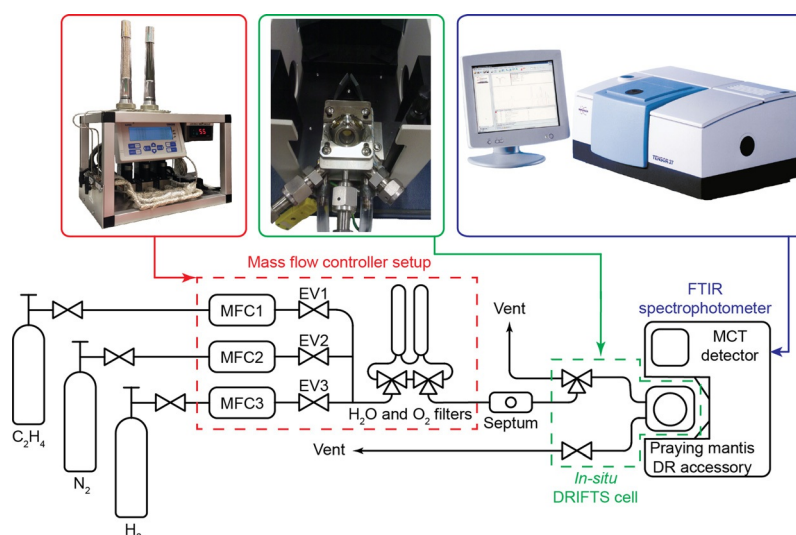

Figure 1. DRIFT spectroscopy setup developed for the testing of solid catalysts at 1 bar and temperatures in the range of RT to 1100 K. The operando setup includes changeable gas reactant sources, a mass flow controller setup (green), a septum for the injection of co-catalyst, a Praying Mantis High-Temperature Reaction Chamber (red), and a Bruker Tensor 37 spectrophotometer (blue). All lines and the reactor are traced and heated to the desired reaction temperature as monitored by a number of thermocouples.
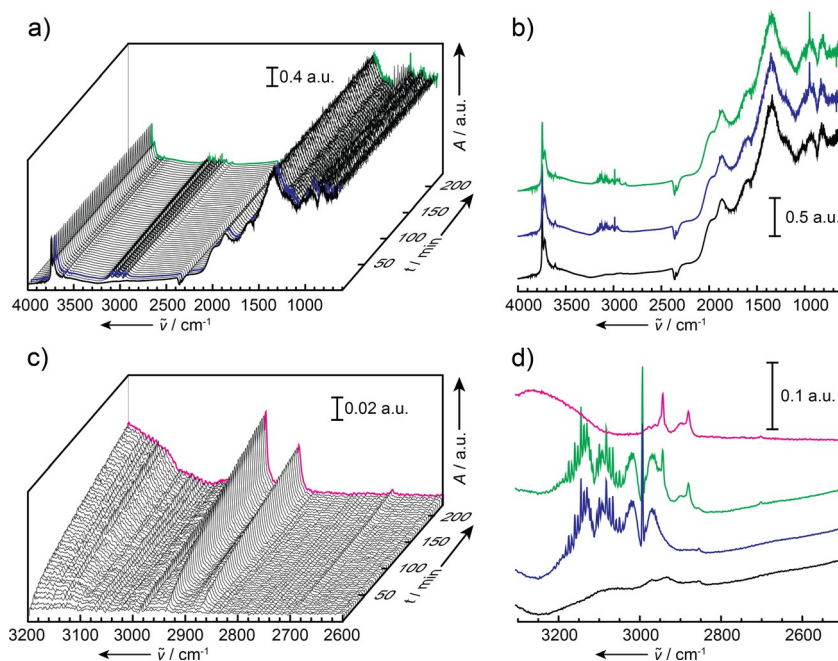
Figure 2. (a) In situ DRIFT spectra of the CTS2 Cr/Ti/SiO$_2$ catalyst during the reaction with ethylene inside the DRIFTS cell when no co-catalyst is used show minor polymerization activity. (b) Individual spectra of several key points, that is, before the reaction (black), start of the ethylene feed (blue), and after the reaction (green). The CH$_x$ stretching region after the subtraction of the spectrum of gaseous ethylene (c) show an increase in the bands of asymmetric and symmetric stretching vibrations of the methyl and methylene groups of the growing ethylene oligomer. Part (d) shows individual spectra in the CH$_x$ stretching region of the fresh catalyst (black), start of the ethylene feed (blue), and after reaction (green) before ethylene subtraction, and the ethylene-subtracted spectrum after the reaction (magenta). The bands appearing at 2300 cm^{-1} belong to the difference of the CO$_2$ concentration of the laboratory atmosphere between the measurement of the background spectrum and measurements during the in situ reaction.

the activation of the catalyst at 1048 K, all of the organic groups originating from Ti and Cr precursors were burnt off, therefore leading to the conclusion that the band at ~3610 cm^{-1} could be assigned to the bridging hydroxyl groups interacting with chromium or even titanium species, which could both exist at the silica surface. Besides the absorption bands in the OH stretching region, the high-intensity bands appearing below 2100 cm^{-1} belong to the vibrational modes of the silica support, limiting the information that can be obtained from this region, including the observation of potential oxidation byproducts. Furthermore, owing to the titanation of the catalyst, the so-called "silica window" in the 850–1000 cm^{-1} region is obscured by the absorption of Ti-O-Si vibrational modes.

The introduction of the ethylene/nitrogen mixture into the DRIFTS cell can be seen by the distinct gas-phase ethylene spectra in the 2900–3200 cm^{-1} region possessing characteristic rotational structure, which includes R-, P- and Q-branches depending on the rotational selection rules.[32] Ethylene polymerization starts slowly with the characteristic asymmetric and symmetric stretching vibrations of the CH$_2$ groups of the polymer, steadily increasing at 2938 cm^{-1} and 2875 cm^{-1}, respectively, and of the CH$_3$ groups at 2962 cm^{-1} and 2892 cm^{-1}. Figure 2c shows the different spectra in the CH$_x$ stretching region after subtracting the first spectrum after the ethylene is added, as gas-phase ethylene partially obscures the asymmetric CH$_x$ bands of the polymer. The polymerization of ethylene proceeds slowly, even after long contact time with ethylene,

which can be related to the low number of active sites as no scavenging agent was introduced that is able to completely purify the DRIFTS cell. The low amount of produced ethylene oligomers is reflected in the low intensity of the CH$_x$ stretching bands and could be the cause for their slight shift towards higher wavenumbers owing to diminished intermolecular interactions, which are otherwise present between the PE chains produced by using a highly active catalyst.

Furthermore, the CS Cr/SiO$_2$ catalyst containing no titanium, the CTS1 Cr/Ti/SiO$_2$ catalyst with the titanium loading of 2.2 wt% and the materials containing no chromium (TS and S), summarized in Table 1, were analyzed in the same manner. The latter showed no activity in the ethylene polymerization reaction, whereas the activity of the supported Cr catalyst was notably influenced by the Ti content. The increase in Ti loading shortens the induction period and increases the overall ethylene polymerization rate. Figure 3 shows the development of the symmetric stretching vibrations of the methylene groups of the growing polymer. The curves can be divided into two parts, that is, an initial nonlinear and a subsequent linear region. These differences in the operation of the catalyst can be explained by the assumption of a reaction rate given by the following equation:

$$r = k[\text{C*}]^m[\text{M}]^n \qquad (1)$$

where k is the reaction rate constant, [C*] is the concentration of the polymerization-active sites, [M] is the concentration of
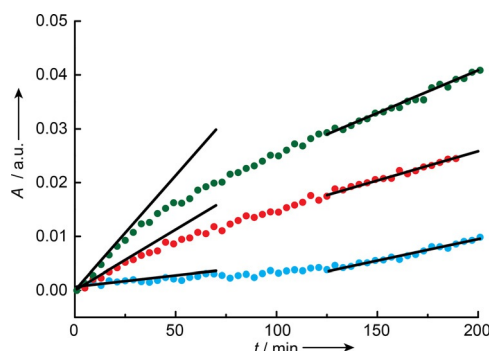
Figure 3. Comparison of the intensity change of the symmetric $\nu_s(CH_2)$ stretching vibration at 2874 cm^{-1} with CS (blue), CTS1 (red), and CTS2 (green) catalysts differing in their Ti loading with 0, 2.2, and 3.9 wt%, respectively.

the ethylene monomer, and m and n are the reaction orders in respect to the active sites and monomer. Because of the constant flow and excess of ethylene monomer, the reaction rate can be assumed to be independent of the concentration of monomer and have a reaction order $n = 0$, meaning that the catalyst surface is saturated with the monomer, which simplifies the equation to:

$$r = k[C^*]^m \tag{2}$$

During the initial period of development of the methylene stretching bands, the reaction rate is determined by the formation and activity of the active sites. At the start of the polymerization, the initial reaction rate (Table 2) increases with an in-

Table 2. Overview of the initial rate of ethylene polymerization (r_i), determined as the slope at the start of the polymerization, and the rate after the steady state is reached (r_s), determined as the slope of the linear fit, for the TEAl-unmodified CS, CTS1, and CTS2, and TEAl-modified CTS2 Phillips-type catalysts.

Sample name	Ti loading [wt%]	Al/Cr	r_i [10^{-4} min^{-1}]	$r_s = k_s$ [10^{-4} min^{-1}]	$R^2(r_s)$
CS	0	0	0.4	0.8	0.9973
CTS1	2.2	0	2.3	1.1	0.9917
CTS2	3.9	0	4.3	1.6	0.9786
CTS2	3.9	2	200	2500	0.9915

creasing amount of titanation (CS < CTS1 < CTS2). A higher titanium loading promotes the faster creation of active sites by making Cr^{6+} species more reducible.[1] During this period, the reaction rate order cannot be explained by either first or second order reactions, leading to mixed reaction order kinetics.

Over the course of time, the reaction rate decreases suggesting the possible poisoning of the active sites by the oxidation products of ethylene and it reaches a steady state exhibiting zero-order kinetics. At this stage of the reaction, the reaction rate is independent of the concentration of the Cr active sites and monomer, and equals the reaction rate constant (Table 2), implying that mass transfer limitations are of no issue under

the applied conditions. At this point, all ethylene polymerization active sites have been created. The differences in the rate constants between the polymerization reactions with the catalysts with varying titanium loading most probably originate from slightly different molecular structures of the active sites. The titanation of the catalyst increases the Brønsted acidity of the catalyst by the introduction of surface titanols. Furthermore, the titanation of the support causes Cr to become more electron deficient, hence making them more Lewis acidic, which can facilitate easier π-coordination of the ethylene monomer to the Cr site.[1]

DRIFTS experiment with the Cr/Ti/SiO$_2$ Phillips-type catalyst with TEAl modification

In the second part of the study, in situ DRIFTS measurements were performed during the modification of the Cr/Ti/SiO$_2$ catalyst with TEAl and subsequent polymerization of ethylene, which will be showcased for the CTS2 catalyst. Figure 4 shows the time evolution of the baseline-corrected DRIFTS spectra in the 600–4000 cm^{-1} spectral region. To facilitate comparisons, spectra of several key moments are presented in Figure 4b, including the spectrum of the fresh CTS2 catalyst, spectra during and after modification with TEAl, and spectra after the polymerization of ethylene and flushing of ethylene reactant. Figure 4c–d and Figure 4e–f show the characteristic OH stretching and CH stretching regions, respectively. The spectrum of the freshly activated Cr/Ti/SiO$_2$ catalyst and the absorption bands appearing at 3746, 3716, and 3610 cm^{-1}, is already described in the previous set of experiments. However, in this case, the catalyst was treated with the TEAl solution in heptanes, which was introduced into the DRIFTS cell by evaporation. The arrival of the co-catalyst is immediately observed by the rising CH$_2$ and CH$_3$ stretching vibration absorption bands in the 2800–3000 cm^{-1} region. After injection, excess solvent is flushed off by the constant nitrogen flow, leaving only the TEAl-modified catalyst.

TEAl can perform several plausible roles, few of which can be deduced from the DRIFTS data at this stage. TEAl indeed reacts with the free hydroxyl groups of the support, albeit to a small degree, as testified by the small intensity decrease in the OH stretching vibration bands. Possible reduction of chromium species cannot be followed by DRIFTS as the vibrations of the oxo-Cr species, expected at around 905 cm^{-1} and 1980 cm^{-1},[33,34] are obscured by the high absorption of the support. On the other hand, TEAl alkylates the catalyst surface, as shown by the remaining CH$_2$ and CH$_3$ bands of the ethyl groups after modification with the co-catalyst. However, it is difficult to determine the extent of the possible alkylation of the Cr sites and differentiate it from the alkylation of other sites on the catalyst surface, which can also become alkylated. The initial alkylation of Cr sites is considered to induce the formation of the first polyethylene chain, significantly decreasing the induction time, although the exact mechanism is not known yet. From the analogy with the work of Barzan et al., who studied the effect of hydrosilanes on the active site of the catalyst, it might be possible that TEAl could break a Cr−O
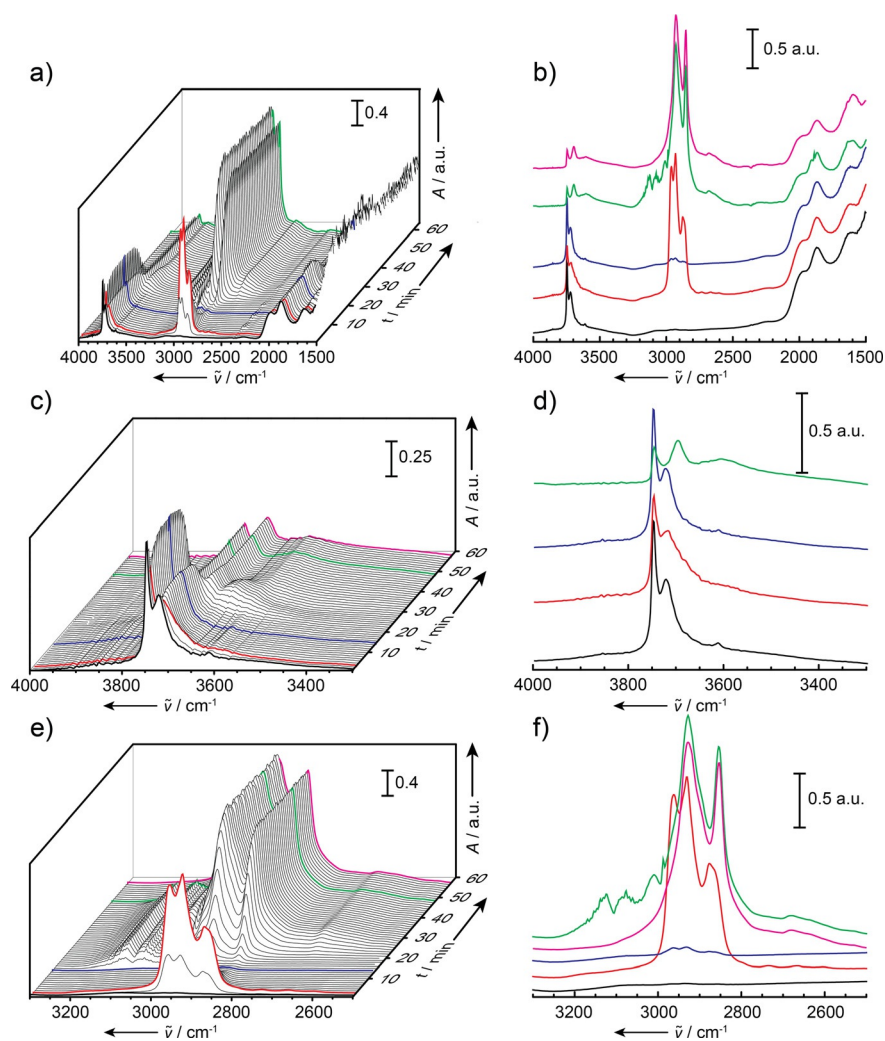
Figure 4. (a) In situ DRIFT spectra of the CTS2 Cr/Ti/SiO$_2$ catalyst during the pre-reaction with TEAl co-catalyst and subsequent ethylene polymerization inside the DRIFTS cell show a significant change in the polymerization activity. (b) Individual spectra of several key points, that is, before the reaction (black), after injection of TEAl dissolved in heptanes (red), after flushing of excess solvent (blue), at the end of the reaction (green), and after flushing of ethylene reactant (magenta). Spectra (c) and (d) show the OH and the CH$_x$ stretching regions, respectively, whereas the individual spectra of the same regions are shown in (d) and (f), with the color code described earlier.

bond with the silica support so that a -OAlEt$_2$ ligand is introduced instead of one rigid surface siloxy bond.[35]

Upon the start of ethylene flow and observing the gas-phase ethylene ro-vibrational spectrum, ethylene polymerization starts rapidly. The absorption signal of methyl and methylene stretching vibrations quickly reaches saturation, whereas the signal of the methyl groups can be hardly distinguished owing to the high activity of the catalyst and production of longer chains with small amounts of methyl end groups. Possible formation of shorter unsaturated oligomers cannot be deduced from the experiment performed under these applied conditions. The OH stretching region shows very interesting changes in the absorption profile. During the course of ethylene polymerization, the intensity of the isolated OH group band at 3746 cm^{-1} and lower acidity OH group at 3719 cm^{-1} decreases with the simultaneous development of the bands at 3696 and ~3650 cm^{-1}. The isosbestic point appearing at ~3700 cm^{-1} suggests the conversion of "free" hy-

droxyls groups to hydroxyl species hydrogen-bonded to the CH$_x$ groups of the growing PE chains. Furthermore, the broadening of the new bands is in line with the nature of the intermolecular interactions through hydrogen bonding. At slightly lower energies at ~3600 cm^{-1}, a new band evolves, which can be assigned to the combination of the CH$_x$ vibrations bands of the PE, obscuring the low intensity band at 3610 cm^{-1} assigned to the bridged silanols. The treatment of the Cr/Ti/SiO$_2$ Phillips-type catalyst with TEAl significantly changes the polymerization activity of the catalyst as can been seen by the comparison of the development of the CH$_x$ stretching bands of the growing PE in Figure 5. The activity of the catalyst is increased, showing basically no induction time, owing to the alkylation of the polymerization sites. In the case of the original catalyst, the CH$_2$ and CH$_3$ stretching vibrations appear at slightly higher energies, which can be explained by the lower amount of intermolecular interactions between the chains owing to considerably lower quantity of the produced PE.
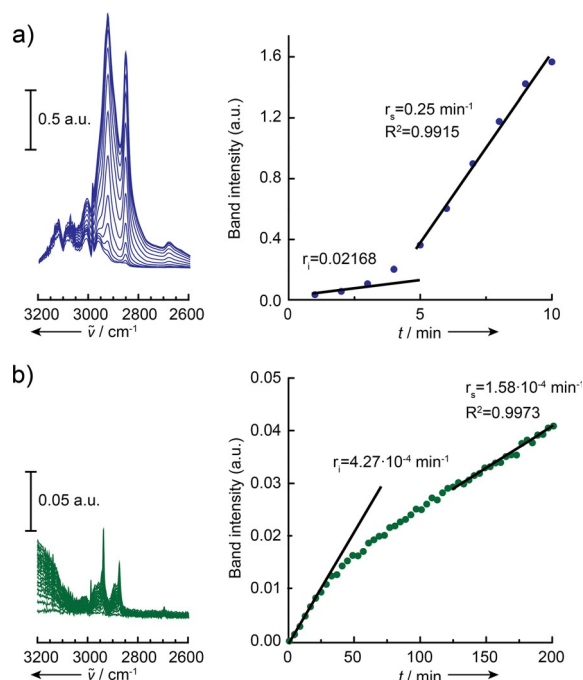
Figure 5. The TEAl-modified CTS2 Cr/Ti/SiO$_2$ catalyst (a) exhibits significantly higher polymerization activity than the original catalyst, which was not pre-treated with TEAl (b). For the sake of clarity, the gas-phase ethylene spectrum was subtracted from the DRIFT spectra of the latter. Right hand side plots show the development of the band intensity of the symmetric ν_s(CH$_2$) stretching vibration after the start of the polymerization.

Figure 6. The hydroxyl group stretching region of the DRIFT spectra of (a) the fresh catalysts, that is, silica gel S (black), TS (red), CS (blue), CTS1 (magenta), and CTS2 (green) and (b) after reaction with TEAl in heptane and subsequent flushing with N$_2$. The methyl and methylene group stretching region (c) shows the alkylation of the materials after reaction with TEAl. The DRIFT spectra are characterized by intensive absorption by the silica support in the region below 2100 cm^{-1}, which was excluded from the figure.

The analysis of the kinetic data shows a considerably higher initial rate of the reaction and the rate of propagation in the case of a TEAl-modified catalyst (Table 2). The quicker formation of the active sites can be attributed to the scavenging properties of TEAl to remove adsorbed ethylene oxidation products.[14] In this manner, TEAl can also facilitate the easier formation and the increase of the number of ethylene polymerization active sites. Unfortunately, these redox products could not be detected under the applied experimental conditions by means of DRIFTS, even in the case of the more active catalyst after the modification with TEAl. Furthermore, owing to the possible alkylation of a part of the chromium sites, as hypothesized earlier, their local structure can be changed, thus creating a different type of active sites that are allowing more favorable coordination of the monomers and their insertion into the PE chain during the chain propagation step, which could be reflected in an increase of the reaction rate constant.[36]

Comparison of the TEAl-modified Phillips-type catalysts and support materials

To investigate the influence of the titanation of the catalyst, besides the CS and CTS1 catalysts containing no and an intermediate amount of Ti, respectively, pure silica support (S) and titanated silica (TS) were also examined to rule out possible polymerization activity of these two materials modified with TEAl. The c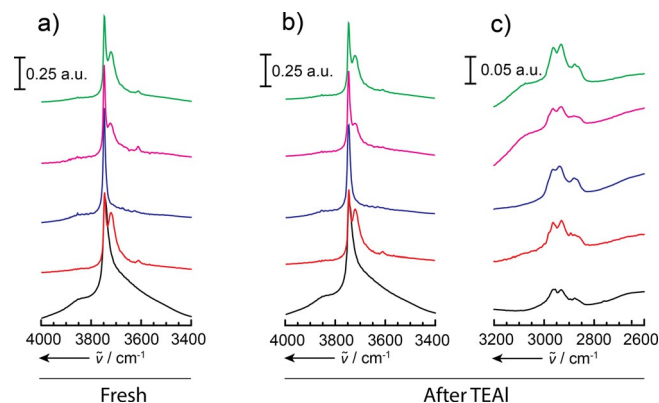omparison of the DRIFT spectra in the hydroxyl stretching group region of the fresh catalysts and support materials before the modification with TEAl is presented in Figure 6a. The absence of any methyl and methylene groups confirms the successful calcination of these materials and removal of the organic groups, which could have remained after the titanation with titanium isopropoxide. The hydroxyl group stretching region reveals the highly dehydroxylated nature of the materials. Besides the isolated silanol vibration at 3746 cm^{-1}, in the case of the titanated catalyst including the titanated silica sample, an additional band appears at 3719 cm^{-1} with an intensity proportional to the Ti loading. The low intensity band at 3610 cm^{-1}, previously assigned to the bridging silanol groups interacting with Cr or Ti centers, can be seen in the titanated samples regardless of the presence of Cr, leading to the conclusion that the origin of this band is the bridging silanols interacting with Ti species rather than with Cr species. Furthermore, its presence in the spectrum before the ethylene has been introduced to the system and reaction started, shows that the band cannot be attributed to the vibrational modes of methylene groups of polyethylene for the presented catalytic system.

Modification of the catalyst and support materials with TEAl, as already described in the case of the CTS2 catalyst, causes a small decrease in the intensities of the silanol and titanol stretching bands (Figure 6b). Furthermore, the reaction of TEAl with Ti centers diminishes their interaction with the hydroxyl groups, leading to the decrease in the band at 3610 cm^{-1}. The CH$_x$ stretching region (Figure 6c) reveals methyl and methylene groups present on the examined materials after their modification with TEAl.

Figure 7 shows the DRIFTS spectra after the polymerization of ethylene. The CS Cr/SiO$_2$ and CTS1 and CTS2 Cr/Ti/SiO$_2$ samples exhibit high activity upon the modification with TEAl, producing PE with the characteristic absorption profile in the CH$_x$ stretching region. As with the CTS2 catalyst, the decrease in the silanol and titanol stretching vibrations and their broaden-
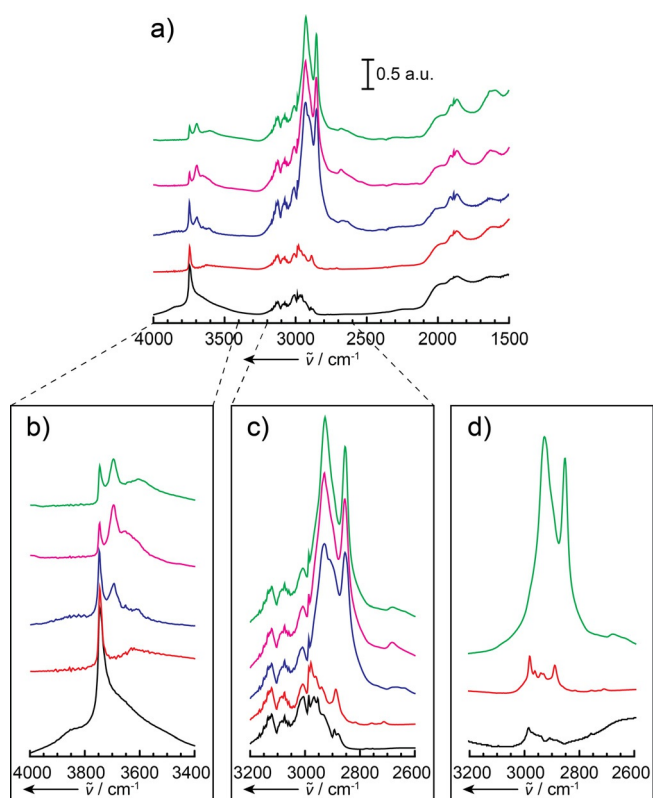
Figure 7. (a) DRIFT spectra of the TEAl-modified catalyst materials: silica gel S (black), TS (red), CS (blue), CTS1 (magenta), and CTS2 (green) after polymerization of ethylene inside the DRIFTS cell at 373 K and 1 bar. The hydroxyl and CH_2/CH_3 groups stretching regions are presented in (b) and (c), respectively. (d) Shows the CH_2/CH_3 stretching region of the silica gel, TS, and CTS2 catalyst after purging the DRIFTS cell with N_2.

ing and shift to lower energy can be observed as the consequence of the intermolecular interactions with the PE chains. The CS sample, however, owing to the absence of titanium and titanol groups, shows a simpler absorption profile containing only infrared absorptions resulting from the silanol groups. Interestingly, silica (S) and especially titanated silica (TS) modified with TEAl still show a certain reactivity towards ethylene, which can be seen in the CH_x stretching region after the reaction and flushing of the ethylene reactant. The observed absorption bands between 2850 cm^{-1} and 3000 cm^{-1} originate from the CH_2 and CH_3 groups of the CH_x stretching region after the reaction and flushing of ethylene hydrocarbon products formed. In the literature, $Ti(OR_4)/AlEt_3$ catalyst systems are already known and industrially exploited for the selective dimerization of ethylene.[37] In the case of the titanated silica, such ethylene oligomerization sites could have been created upon reaction of the material with TEAl. However, the absence of the absorption bands above 3000 cm^{-1} suggests the production of mainly saturated ethylene oligomers.

Conclusions

The performed in situ DRIFTS studies allowed the investigation of a working Cr/SiO_2 and $Cr/Ti/SiO_2$ Phillips-type catalysts at 1 bar and 373 K with minimal sample preparation, without the

previous reduction step with CO or modification of its form by pressing the catalyst powder into pellets. This setup offered the possibility of an investigation of the vibrational properties of a genuine catalyst material. In that respect, several catalyst formulations with an increasing degree of titanation have been characterized. The increase in the titanium loading exhibited a promotional effect on the shortening of the induction time and the increase of both the initial polymerization rate and the rate after the steady state has been reached. At this point, the reaction follows pseudo-zero-order kinetics and the reaction rate becomes independent of the concentration of the monomer and active sites. The reaction rate constant is influenced by the degree of titanation. This can be explained by an increased acidity of the support, which is the highest for the $Cr/Ti/SiO_2$ catalyst with the highest Ti loading (i.e., 3.9 wt %).

Furthermore, the catalysts of this study and reference support materials were also studied in the ethylene polymerization reaction after modification with TEAl as co-catalyst. The possible polymerization properties of TEAl-modified Ti/SiO_2 was excluded, while the observed alkylation of the Cr/SiO_2 and $Cr/Ti/SiO_2$ catalysts showed a promotional effect on the polymerization activity, which is deduced from the fast development of the methylene absorption bands of the produced PE in the operando DRIFT spectra and quantified by the comparison of the reaction rates of the TEAl-modified and unmodified $Cr/Ti/SiO_2$ catalyst with 3.9 wt % Ti.

Experimental Section

Sample preparation

The catalyst samples were provided by Total Research and Technology Feluy, Belgium. A silica pre-catalyst with ~0.5 wt % Cr loading, surface area of 318 $m^2 g^{-1}$, pore volume of 1.55 $cm^3 g^{-1}$, and D50 particle size diameter of 47 μm was heated to 543 K for dehydration under a nitrogen flow. Surface titanation of the samples with a target Ti loading of 2 wt % and 4 wt % was performed by using titanium isopropoxide (99.999 % trace metals basis, Sigma–Aldrich) added dropwise to the fluidized bed, following the method described by Debras et al.[38] The catalyst was subsequently activated at 1048 K in dry air to anchor and stabilize Cr^{6+} on the support and burn off organic groups. After the activation step, the catalyst was transferred to an Ar glovebox under inert atmosphere. The sample containing Ti was prepared by using a wide-pore silica support treated under the same procedure as the Cr pre-catalyst. The pure silica sample used as a reference included only calcination of Aerosil 300 at 1048 K in dry air. The prepared catalysts and their properties are summarized in Table 1.

DRIFT spectroscopy

Ethylene polymerization reactions were performed with a specially designed in situ setup (Figure 1), under a controlled atmosphere inside a Praying Mantis High-Temperature Reaction Chamber with ZnSe windows, whereas the catalyst and the PE product were studied with in situ diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy. The catalyst samples were loaded inside an Ar glovebox into the DRIFTS cell, preventing any contamination with moisture and oxygen; the cell was placed in the Praying

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