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Unraveling the Catalytic Synergy Between Ti³⁺ and Al³⁺ Sites on a Chlorinated Al₂O₃: a Tandem Approach to Branched Polyethylene

Alessandro Piovano, K. S. Thushara, Elena Morra, Mario Chiesa and Elena Groppo*

Abstract: We have devised an original step-by-step approach to synthesize and characterize a bifunctional heterogeneous catalyst constituted by isolated Ti³⁺ centres and strong Lewis acid Al³⁺ sites at the surface of a chlorinated alumina. By employing a wide range of physicochemical and spectroscopic techniques, we demonstrate that the two sites, in close proximity, act in a concerted fashion for synergistically boosting ethylene conversion to branched polyethylene, using ethylene as the only feed and without any activator. The coordinatively unsaturated Al³⁺ ions promote ethylene oligomerization through a carbocationic mechanism and activate the Ti³⁺ sites for the traditional ethylene coordination polymerization.

In the last years, much research has been devoted to the development of new tandem catalytic approaches to olefin polymerization, which allow obtaining polyolefins with tunable properties in a one-pot reaction, using a single olefin feed.^[1-4] Tandem catalysis for branched polyethylene synthesis is one of such examples. To this aim, two cooperative components are engineered into a single catalyst. One component oligomerizes ethylene to short α -olefins, which are successively incorporated in the growing polyethylene chains through an “in situ branching” mechanism by a second, different, catalytic centre.^[5-7] This monomer-free process to branched polyethylene opens an attractive atom-efficient scenario, reducing costs of feedstock, loading, purification, storage, and downstream recycling.

Notable examples of tandem catalysts for olefin polymerization can be found in the field of homogeneous catalysis, where the catalysts’ design has reached unexpected levels of excellence, which competes even with some natural enzymes.^[8] Intermolecular tandem reactions are efficient only when the two catalytic sites are constrained in close spatial proximity, a condition that allows a rapid enchainment of the α -olefin co-monomers produced at the first site into the polyethylene chains growing at the second site.^[9, 10]

In this investigation, we have specifically devised an original step-by-step approach to synthesize and characterize a bifunctional heterogeneous catalyst for the production of branched polyethylene using ethylene as the only feed, without any activator. This approach differs from the typical methods in olefin polymerization field, in which heterogeneous dual-site catalysts are usually obtained by a partial modification of the original catalyst via the intervention of an external agent.^[7, 11-13] The catalyst is obtained by treating a transitional alumina with

TiCl₄ followed by H₂ reduction (similarly to what proposed in previous patents,^[14, 15] but never investigated in details), and benefits of the presence of Ti³⁺ sites in close proximity to exposed Al³⁺ Lewis acid sites on a highly chlorinated surface, each site explicating a specific catalytic function. We will demonstrate that the two sites cooperate to give a branched polyethylene. The novelty of our approach relies in the capability to follow, by means of a multi-technique characterization approach (Diffuse Reflectance (DR) UV-Vis, FT-IR and Continuous Wave (CW) and pulse Electron Paramagnetic Resonance (EPR) spectroscopies),^[16] each phase of the catalyst synthesis, including the in situ monitoring during ethylene polymerization, thereby enabling structure-property correlations to be established.

The δ -Al₂O₃₋₆₀₀/TiCl₄ pre-catalyst was obtained by exposing a δ -Al₂O₃ dehydroxylated at 600 °C (δ -Al₂O₃₋₆₀₀) to TiCl₄ vapors at 25 °C, followed by removal of excess TiCl₄. FT-IR spectra collected during the reaction demonstrate that TiCl₄ immediately reacts with surface hydroxyl groups (spectrum 1 in Figure 1b), grafting as –TiCl_x on the alumina surface and releasing HCl. This reaction is similar to the TiCl₄ grafting on dehydroxylated silica,^[17-21] but alumina has the unique capacity to stabilize the HCl on surface Al³⁺–O²⁻ acid-base pairs (spectrum 2 in Figure 1b).^[22] DR UV-Vis spectroscopy reveals the presence of a variety of grafted Ti⁴⁺ sites, having both oxygen and chlorine ligands, and displaying both 4-fold and 6-fold coordination geometries (spectrum 2 in Figure 1a, and Section SI-2.2).^[23-25]

The δ -Al₂O₃₋₆₀₀/TiCl₄/H₂₋₄₀₀ catalyst was obtained by reducing the pre-catalyst under H₂ at 400 °C. Under these conditions Ti³⁺ (3d¹) species are formed, as testified by X-band CW EPR (Figure S2) and DR UV-Vis (spectrum 3 in Figure 1a) spectroscopies. Reaction with O₂ and the subsequent formation of EPR active superoxide radicals demonstrates that at least a fraction of the Ti³⁺ sites present pre-existing coordinative vacancies (Figure S4).^[26] The simultaneous removal of chemisorbed HCl (spectrum 3 in Figure 1b) leaves an extensively chlorinated surface, as verified by complementary FT-IR experiments (Figure S1a). Although the formation of a crystalline AlCl₃ phase was excluded by XRPD measurements (Figure S1b), the chlorination may easily involve also sub-surface layers^[27-29] and has a key role in the catalysis, both enhancing the Al³⁺ Lewis acidity^[30] and positively affecting the Ti³⁺ centres activity.^[31] The final amount of Ti present in the catalyst (about 2 wt%, as determined by ICP analysis) is in good agreement with that expected by considering the involvement of all the surface OH groups (about 4 OH/nm²).

The local environment of the EPR active Ti³⁺ ions is revealed by Hyperfine Sublevel Correlation (HYSCORE) experiments at Q band frequency (34.3 GHz), which allow detecting the NMR transitions of magnetically active nuclei, in the surrounding of the paramagnetic center. A typical HYSCORE spectrum is shown in Figure 1c. The spectrum is

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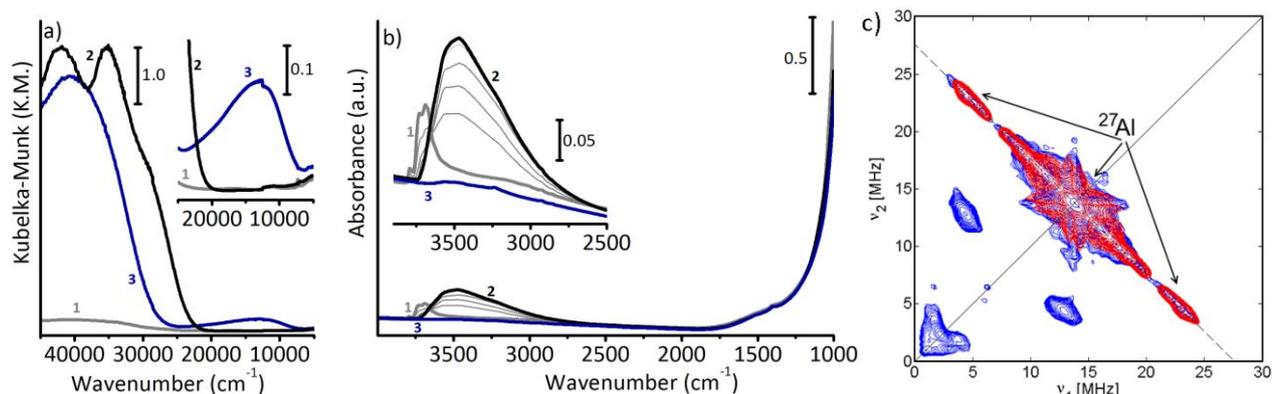


Figure 1. a): DR UV-Vis-NIR spectra of δ -Al₂O₃₋₆₀₀ support (1), of δ -Al₂O₃₋₆₀₀/TiCl₄ pre-catalyst (2), and of δ -Al₂O₃₋₆₀₀/TiCl₄/H₂₋₄₀₀ catalyst (3). The inset shows a magnification of the d-d region. b): FT-IR spectra as in a). The inset displays a magnification of the ν (OH) spectral region. Light grey spectra have been collected during pre-catalyst formation (from 1 to 2). c): experimental (blue) and simulated (red) Q-band HYSCORE spectrum, recorded at $T = 10$ K at observer position $B_0 = 1243.5$ mT corresponding to the maximum intensity of the ESE-detected EPR spectrum. HYSCORE spectra recorded at other field settings are reported in Figure S3 along with the Q-band ESE-EPR spectrum.

dominated by an extended ridge signal centered at 13.8 MHz (^{27}Al Larmor frequency at this field) with a maximum extension of about 21 MHz, arising from the hyperfine interaction of the unpaired electron localized on the Ti³⁺ with ^{27}Al nuclei of the alumina support. The ^{27}Al signal is consistent with a hyperfine interaction dominated by the isotropic Fermi contact contribution (a_{iso}),^[32] ranging between 5 and 20 MHz (Table S1). Such isotropic couplings provide a unique and direct proof for the presence of Ti³⁺-Cl-Al linkages, corresponding to a spin density transfer in the 3s Al orbital in the range [0.15-0.60]%, which is significantly larger than that observed for other systems involving M(3dⁿ)-L-Al linkages.^[33]

The activity of the δ -Al₂O₃₋₆₀₀/TiCl₄/H₂₋₄₀₀ catalyst was tested towards the gas-phase ethylene polymerization under very mild conditions (25 °C, $P_{\text{C}_2\text{H}_4} = 100$ mbar) and in the absence of any activator. In these conditions the activity was evaluated at approximately 50 wt% of polymer on the catalyst, a value that can increase reasonably of two orders of magnitude by adopting pressure and temperature industrial conditions, as reported in ref. 14. The formation of polymer fibrils is directly observed by SEM (Figure 2ab). SEC analysis (Figure 2c and Table S3) indicates that the obtained product is characterized by a bimodal molecular weight distribution. The lighter fraction ($M_p \sim 360$ gmol⁻¹), which melts in the range 115-125 °C and crystallizes at around 109 °C (Figure 2d), is consistent with polyethylene waxes synthesized via ethylene oligomerization. The heavier fraction has a molecular weight typical for a polyethylene produced with traditional Ziegler-Natta catalysts ($M_p \sim 195000$ gmol⁻¹), and exhibits a melting temperature ($T_m = 128$ °C, Figure 2d) characteristic of a branched polyethylene. The thermal and structural properties of the high molecular weight polymeric fraction are better appreciated in the analysis of the polymer extracted from the catalyst (Figure S6). The bimodal mass weight distribution of the resulting products is a clear demonstration of the co-existence of dual active sites in the δ -Al₂O₃₋₆₀₀/TiCl₄/H₂₋₄₀₀ catalyst, in good agreement with the spectroscopic data. In addition, the branched nature of the high

molecular weight polymeric fraction, obtained with ethylene as the only feed, indicates that the two sites do not work independently. Preliminary studies also revealed that temperature and pressure variations can change the relative abundance and the M_p of the two fractions, thus varying the length and the degree of the branches in the polymer.

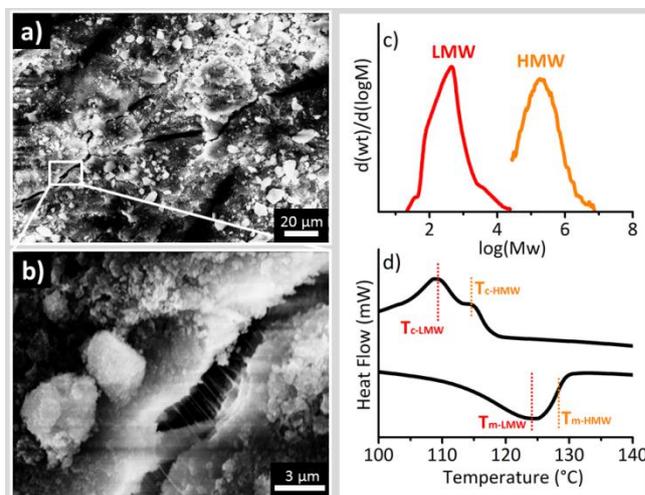


Figure 2. a) and b): Representative SEM images for the polymer/catalyst mixture after ethylene polymerization. c): Molecular weight distribution of the polymeric product produced with the δ -Al₂O₃₋₆₀₀/TiCl₄/H₂₋₄₀₀ catalyst. d): DSC curves of the polymer/catalyst mixture.

In order to isolate the contribution of the reduced Ti³⁺ sites from that of the Al³⁺ Lewis acid sites, ethylene polymerization on the δ -Al₂O₃₋₆₀₀/TiCl₄/H₂₋₄₀₀ catalyst was monitored in situ by means of FT-IR spectroscopy (Figure 3b, and Section SI-2.3) and compared with the FT-IR spectra of ethylene reaction on a chlorinated alumina, δ -Al₂O₃₋₆₀₀/CCl₄₋₄₀₀, used as a reference (Figure 3a). Upon dosage of ethylene at 25 °C on δ -Al₂O₃₋

$\delta\text{-Al}_2\text{O}_3/\text{CCl}_4\text{-400}$ a complex series of absorption bands gradually grow up in the $3000 - 2800 \text{ cm}^{-1}$ and $1600 - 1300 \text{ cm}^{-1}$ ranges (Figure 3a), indicating the formation and the limited growth of branched oligomers, along with allylic cationic species (band at 1535 cm^{-1}).^[34] The reaction stops after about 30 minutes. Similar results were achieved by using TiCl_4 as a simple chlorinating agent in non-reductant conditions. It is well known that chlorinated alumina displays activity in acid-catalyzed reactions, such as olefin oligomerization^[30, 35, 36] and double-bond shift isomerization,^[37, 38] involving a carbocationic mechanism. Moreover, AlX_3 Lewis acids are employed in industrial practise as initiators of carbocationic polymerization reactions,^[39] where propagation proceeds through repeated additions of ethylene to form the thermodynamically more stable carbocations (secondary and tertiary), which may migrate well away from the site of the initial attack.^[40] Strong Lewis acids (such as chlorinated alumina) can stabilize carbocations,^[41] promoting intramolecular hydrogen-transfer reactions, with the consequent formation of allyl cationic species.^[42]

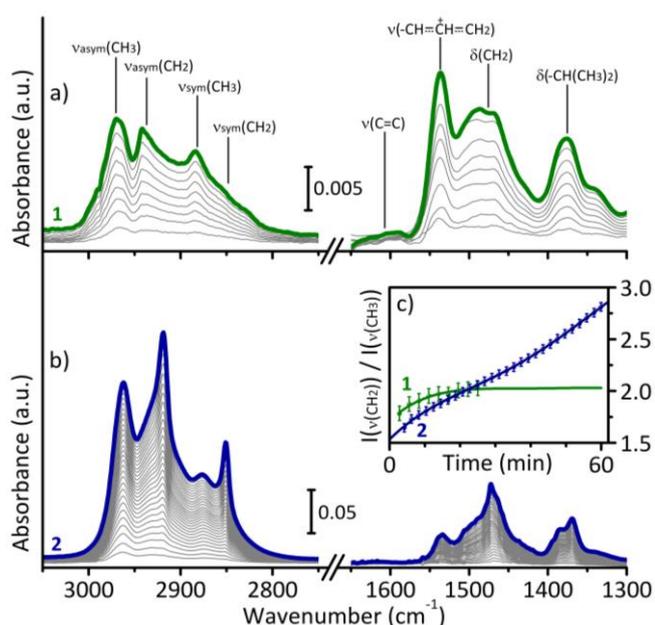


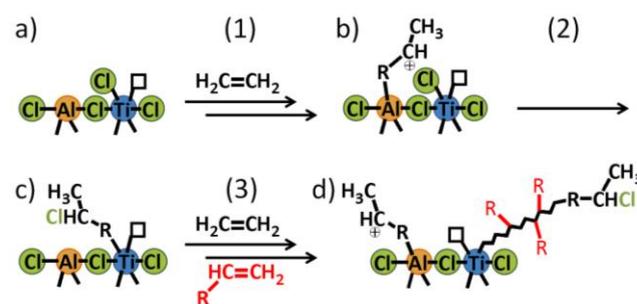
Figure 3. a): Background subtracted FT-IR spectra, in the $v(\text{CH}_2)$ and $\delta(\text{CH}_2)$ spectral regions, collected during ethylene oligo/polymerization (25°C , $P_{\text{C}_2\text{H}_4} = 100 \text{ mbar}$) on the $\delta\text{-Al}_2\text{O}_3\text{-600}/\text{CCl}_4\text{-400}$ catalyst. The whole sequence of spectra was collected in 25 minutes. b): the same as in a) for the $\delta\text{-Al}_2\text{O}_3\text{-600}/\text{TiCl}_4/\text{H}_2\text{-400}$ catalyst, collected in 1 hour. Note that in b) the absorbance scale is ten times the absorbance scale in a). c): Evolution of the CH_2/CH_3 intensity ratio as a function of time, as determined from the intensity of the absorption bands at 2918 and 2962 cm^{-1} in the FT-IR spectra of both $\delta\text{-Al}_2\text{O}_3\text{-600}/\text{CCl}_4\text{-400}$ (blue) and $\delta\text{-Al}_2\text{O}_3\text{-600}/\text{TiCl}_4/\text{H}_2\text{-400}$ catalysts (green). The ratio among the extinction coefficients, $\epsilon(\text{CH}_3)/\epsilon(\text{CH}_2)$ was fixed to 2.2.^[34]

A different spectral evolution is observed during ethylene reaction on the $\delta\text{-Al}_2\text{O}_3\text{-600}/\text{TiCl}_4/\text{H}_2\text{-400}$ catalyst (Figure 3b). At short contact time, the FT-IR spectra are very similar to those previously discussed, but after about 15 minutes the absorption bands associated to the vibrational modes involving CH_2 groups start to grow faster than those related to CH_3 groups. The $v(\text{CH}_2)$ absorption bands, which are sensitive indicators of the length of the alkyl chains,^[43] slightly red-shift over time, indicating the formation of long linear polyethylene chains. The CH_2/CH_3 intensity ratio as a function of time has been used to roughly

estimate the branching degree of the products during ethylene polymerization (Figure 3c). Both the catalysts show a similar behaviour in the first 15 minutes, where the acid-catalysed formation of branched oligomers prevails. However, for a longer reaction time the CH_2/CH_3 ratio becomes increasingly higher for the $\delta\text{-Al}_2\text{O}_3\text{-600}/\text{TiCl}_4/\text{H}_2\text{-400}$ catalyst, indicating that ethylene polymerization via coordination mechanism is now taking place.^[44]

The whole set of spectroscopic data shown above concur to the formation of bifunctional catalytic sites constituted by Ti^{3+} sites directly linked to strong Lewis acid Al^{3+} sites (Scheme 1a). The two sites exert specific functionalities, acting in a concerted fashion for synergistically boosting the olefin conversion. The acid-catalysed oligomerization of ethylene (Step 1 in Scheme 1) leads to the formation of branched cationic oligomers, stabilized by the presence of chloride ions on the catalyst surface (Scheme 1b). This step is necessary to activate the Ti^{3+} sites for ethylene coordination polymerization, since at the starting point they do not have any alkyl ligand, as requested by the widely accepted Cossee-Arlman mechanism.^[45] Hence, the oligomers produced via carbocationic mechanism on the Al^{3+} Lewis acid sites have the double function to dechlorinate and alkylate the Ti^{3+} sites (Step 2 in Scheme 1), as revealed by DR UV-Vis spectroscopy (Figure S5).^[46] Once the Ti sites are alkylated (Scheme 1c), ethylene polymerization takes place through the repeated insertion of the monomer and the simultaneous enchainment of the branched oligomers promoted by the Al^{3+} sites (Step 3 in Scheme 1), accounting for the production of a branched polyethylene (Scheme 1d).

In summary, the synergistic cooperation between Ti^{3+} and Al^{3+} sites on a chlorinated Al_2O_3 in tandem olefin conversion was proven for the first time, thanks to a multi-technique approach, which opens interesting perspectives not only in the field of olefin polymerization catalysis, but more in general in the investigation of tandem heterogeneous catalysts.



Scheme 1. Mechanism of ethylene conversion on the $\delta\text{-Al}_2\text{O}_3\text{-600}/\text{TiCl}_4/\text{H}_2\text{-400}$ catalyst (where R stands for a branched oligomeric alkyl group). $\text{R-CH}^+\text{=CH}_2$ represents the branched oligomers produced by Al^{3+} sites via carbocationic polymerization.

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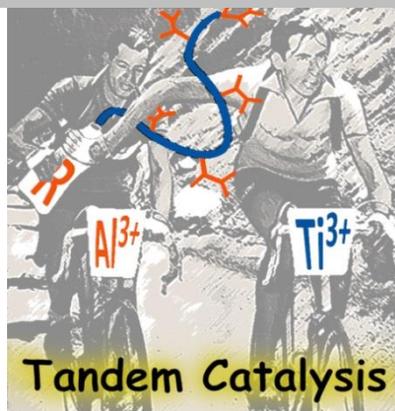
Keywords: tandem catalysis • operando FT-IR spectroscopy • EPR spectroscopy • Ti³⁺ sites • Ziegler-Natta catalysts

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