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# Quality control for Ziegler-Natta catalysis via spectroscopic fingerprinting

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ABSTRACT

Commercial olefin polymerization catalysts are typically produced at a manufacturing site before transport to production facilities for storage and eventual use. During transport and storage, catalysts can deteriorate resulting in decreased catalytic performance due to contact with environmental factors. In this work, a spectroscopic toolbox was developed for quality assurance purposes of a third generation Ziegler-Natta catalyst for ethylene polymerization. A pre-activated, industrial Ziegler-Natta catalyst was exposed singly to heat, dry air, and moisture to study the specific environmental factors. Activity tests were performed with the polymer morphology inspected by SEM and image analysis. Catalyst characterization was conducted using Fourier Transform Infrared spectroscopy with CO and Diffuse Reflectance UV–Vis spectroscopy to relate unique spectroscopic fingerprints to different environmental effects. Reactivity towards gas-phase ethylene polymerization was tested using Diffuse Reflectance Infrared Fourier Transform spectroscopy. This work demonstrates the development of a new spectroscopic methodology useful for quality control in Ziegler-Natta catalysis.

## 1. Introduction

Although one of the industrial workhorses for the generation of isotactic polypropylene, the Ziegler-Natta (ZN) catalyst remains an important catalyst for the production of high density polyethylene (HDPE) [1,2]. The third generation ZN catalyst, consisting of atomically dispersed $TiCl_4$ on the (1 0 4) and (1 1 0) defect planes of a spherical $MgCl_2$ support, is activated by addition of an organoaluminum cocatalyst, typically triethylaluminum (TEA), and lacks the additional internal donors used for isotactic polypropylene production. Activation of the ZN catalyst with TEA generates a variety of atomically dispersed Ti(II) and Ti(III) species containing three to five ligands, these ligands comprised of a mixture of chloride and ethyl ligands, and one to three open vacancies [3–7]. Furthermore, small clusters of reduced $Ti(III)_XCl_Y$ have been known to form during the interaction with TEA [3–9]. Of these species, a 5-coordinated Ti(III) atom anchored to the (1 1 0) plane featuring an ethyl ligand and an open coordination site is widely considered to be the active site for olefin polymerization, although catalyst sites containing Ti(II) have also been proposed for ethylene polymerization [8,9]. The spherical-shaped morphology for the support is also crucial for reliable post-catalysis polymer processing as the final HDPE particle retains the original catalyst shape post polymerization [4,5,10–16].

Due to the reactivity of the material components, the fully activated ZN catalyst is sensitive to environmental factors, such as moisture, oxygen, heat, and light, that can lead to catalyst degradation i.e. oxidation of reduced Ti species to Ti(IV). While some of these factors may be mitigated by activating the catalyst immediately before polymerization, this remains a concern as some HDPE production lines rely on fully activated ZN catalysts generated at the catalyst production site. These fully activated catalyst are then shipped and stored at the chemical plant, allowing for the possibility of catalyst deterioration due to improper storage. While formation of HDPE with a consistent spherical shape is important for postproduction processing, non-ideal morphologies such as polyethylene "threads" produce inferior polymer products and can result in unwanted reactor fouling [4,5,10,11]. It is therefore imperative for industrial actors to have access to diagnostic tools to predict a catalyst's performance for quality control purposes before use on the industrial scale.

Our goal is to develop such a diagnostic toolkit to understand catalyst structure as related with catalytic performance and polymer morphology for a series of deteriorated ZN catalysts. To this end, a third generation ZN catalyst, not containing internal donors, was synthesized and activated using TEA. Portions of this activated

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catalysts were then singly exposed to dry air, moisture, or an extended heat treatment to simulate deterioration for different environmental conditions. Activity experiments were conducted using industrial conditions and the morphology of polymer products analyzed using Scanning Electron Microscopy (SEM) and image analysis. The catalysts were characterized using Fourier Transform Infrared (FT-IR) spectroscopy with CO as a probe molecule to study Lewis acidity. Diffuse Reflectance Ultraviolet–Visible (DR UV–Vis) spectroscopy was used to study the oxidation state of Ti species. Ethylene reactivity experiments were monitored using Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS).

## 2. Experimental

### 2.1. Materials and conditions

Anhydrous 99% $MgCl_2$, TEA, heptane, and 99% KBr were purchased from Sigma and was used as such. 15% CO balance Ar, 3.5 Ethylene, 4.0 Oxygen, and 6.0 Nitrogen gas cylinders were purchased from Linde Gas Group. Unless otherwise stated, all manipulations were conducted in $N_2$ inert atmospheres using gloveboxes or Schlenk techniques.

### 2.2. Catalyst preparation

All materials were produced using air and water free conditions. ZN catalyst $C_{AsSuch}$ was prepared according to literature procedure [17] with the chemical synthesis by the addition of increasing amounts of chlorinating agents (i.e. $ClTi(OR)_3$) to a magnesium alkoxide solution in heptane. Addition of $TiCl_4/TiOR_4$ mixtures and a final addition of $TiCl_4$ generated the solid, spherically titanated catalyst. The active catalyst, $C_{AsSuch}$, was then activated with TEA, filtered, dried, and stored under inert atmosphere away from light. No internal donors were used for the catalyst preparation. The dry air treated catalyst, $C_{DryAir,}$ was prepared by stirring a portion of the $C_{AsSuch}$ catalyst in dry, oxygenated heptane for 24 h at room temperature before solvent removal. The moisture treated sample, $C_{Moisture}$, was prepared by stirring a portion of the $C_{AsSuch}$ in water-saturated, deoxygenated heptane for 24 h before solvent removal. The heat-treated sample, $C_{Heat}$ ,was prepared by storing a portion of the dry, powdered $C_{AsSuch}$ catalyst under an inert atmosphere in an oven at 323 K for 5 days away from light.

### 2.3. Activity testing

#### 2.3.1. Ethylene polymerization via autoclave

Polymerization reactions were performed in a 4 L autoclave with an agitator, a temperature controller, and inlets for feeding of ethylene and hydrogen. The reactor was dried at 403 K with $N_2$ for one hour and then cooled to 313 K.

The reactor was loaded with 2 L of isobutane, 6 wt% of 1-hexene, 120 ppm of TEA as a scavenger, 0.2 mol of $H_2$, and pressurized with ethylene to 23.4 bar. Polymerization started upon catalyst injection (5 mg), was performed at 358 K and was stopped after 60 min by reactor depressurization. Reactor was flushed with nitrogen prior opening and the polymer was dried at 323 K overnight under reduced pressure.

### 2.4. Characterization methods

#### 2.4.1. Catalyst composition

Elemental composition of dried $C_{AsSuch}$ samples were determined by ICP-MS analysis to contain an 8.0% weight loading of Ti.

#### 2.4.2. Surface area determination

$N_2$ physisorption isotherms were measured to determine surface areas and pore volumes using a Micromeritics Tristar 3000 setup. The samples were outgassed at room temperature for 1 h prior to performing the measurements at liquid nitrogen temperature. Surface areas were determined using the Brunauer – Emmett–Teller (BET) theory.

#### 2.4.3. SEM

Polymer samples were deposited on a double face adhesive carbon tape, and then metalized with platinum.

#### 2.4.4. Polymer sphericity via image analysis

Polymer samples were analyzed using a Retsch Technology® Camsizer® to study the particle morphology. Free flowing polymer powder entered through a DR100-75 RT metering feeder and a high-speed camera photographed individual particles as they passed in front of the camera. Analysis of the digital images determined the two-dimensional area and an average circumference of the particles. The ratio of the two-dimensional area to the square of the average circumference value was multiplied by a constant, 4π, to determine a sphericity value. For a perfect sphere, the sphericity value equals 1. Deviations from the spherical shape produce smaller values that asymptotically approach zero.

#### 2.4.5. FT-IR spectroscopy with a CO probe

A pellet was prepared inside of an inert, $N_2$ atmosphere glovebox using a hand press. Pellets of 10.0 ± 0.2 mg were prepared from premade catalysts to allow for quantitative comparison between catalyst samples. The pellets were loaded into a specialty transmission IR cell fitted with $CaF_2$ windows in a glovebox. Spectra were taken using a Perkin-Elmer 2000 instrument using 32 scans at a resolution of 4 $cm^{-1}$. The sealed cell was connected to a gas delivery and vacuum system, evacuated carefully to prevent interaction with air/moisture, and cooled with liquid nitrogen to 87 K. The sample was then dosed with increasing amounts of CO at 87 K until the sample was saturated, 15 mbar.

#### 2.4.6. DR UV–Vis spectroscopy

Samples were loaded inside of an inert atmosphere glovebox into 0.20 ml quartz cuvettes with a sealable cap. Spectra were taken with an Avantes DR UV–Vis probe spectrometer held at an angle to the quartz cuvette to prevent direct reflection from the probe. Anhydrous $MgCl_2$ was used as a blank.

#### 2.4.7. Polymerization via DRIFTS

DRIFTS measurements were taken on a Perkin-Elmer instrument fit with a MCT detector. An air-free Harrick Praying Mantis high temperature reaction cell was used to conduct all ethylene polymerization measurements. A background was taken using finely ground KBr. The cell was then loaded inside an inert atmosphere glovebox with roughly 40.0 mg of catalysts powder and closed to prevent interaction with water or oxygen. The cell was connected to the spectrometer and the lines flushed with 6.0 Nitrogen for 20 min before switching to an ethylene flow of 5 ml/min. During this time, the sample was heated to the reaction temperature of 358 K. After reaching the required temperature, spectra were taken of 32 scans at a resolution of 4 $cm^{-1}$ were taken every minute and the ethylene gas flow was directed through the cell. Reactions were monitored until polymer signal saturation or for 2 h, depending which occurred first.