Applied Catalysis A: General 423–424 (2012) 91–99

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Reduction of Cr(VI) polymerization catalysts by non-olefinic hydrocarbons

Eric Schwerdtfeger, Richard Buck, Max McDaniel*

Chevron-Phillips Chemical Co, Bartlesville, OK 74004, United States

ARTICLE INFO

Article history:
Received 17 December 2011
Received in revised form 14 February 2012
Accepted 16 February 2012
Available online 25 February 2012

Keywords:
Phillips catalyst
Ethylene polymerization
HDPE
Polyethylene
Reduction
Chromium
Alkane oxidation

ABSTRACT

The Phillips Cr(VI)/silica catalyst, which is widely used for commercial ethylene polymerization, is usually considered to be reduced to a lower-valent active Cr species in the reactor upon contact with ethylene or other α-olefin monomers. In this paper, however, the case is presented that Cr(VI) is actually quite reactive with other hydrocarbons to which it is also often exposed, including alkanes and aromatics. Redox products from these reactions are identified, and the effect on catalyst polymerization activity and polymer character is described.

1. Introduction

Polyethylene is the world's most commonly used polymer, and a significant portion of it (HDPE in particular) is made with the Phillips Cr/silica catalyst. Discovered in 1951 at Phillips Petroleum Company [1,2], this catalyst is made by impregnating a chromium compound onto a high-porosity silica carrier to a loading of about 1 wt% Cr, followed by calcination at >500 °C. During this high temperature "activation" step the chromium is oxidized and reacts with surface hydroxyl groups to become anchored to the support as hexavalent chromate or dichromate species such as illustrated in Scheme 1A.

This is the catalyst precursor. The active sites responsible for ethylene polymerization are formed when this surface-anchored Cr(VI) is then reduced to a lower-valent isolated species [2,3]. This is usually thought to occur in the polymerization reactor with ethylene as the reducing agent, such as shown in Scheme 1B. Surface Cr(II) and formaldehyde have most often been suggested as the by-products of this redox reaction [4–7], although other possible products have also been proposed [8,9], and some recent data from this laboratory (to be presented elsewhere) likewise argues for a more complicated reduction pathway. As the chromium is reduced, from tetrahedral Cr(VI) to a probably octahedral lower-valent species, the potential coordination sphere is expanded, and in the absence of other ligands, coordinative unsaturation is created that initiates polymerization.

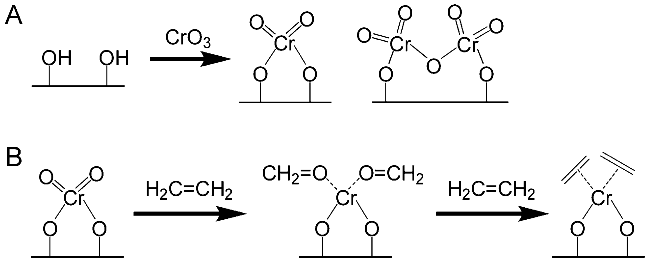
In commercial practice, the hexavalent catalyst precursor usually also comes into contact with other hydrocarbons, such as the reaction solvent or diluent. These commonly include paraffins, such as isobutane, n-butane, cyclohexane, hexanes, isopentane, and even mineral oil. Ethylene comprises only a small part of the typical reaction mixture, e.g. only 3–5 wt% in isobutane (slurry at 80–110 °C) or in cyclohexane (solution at 125–150 °C). Typically, the hexavalent catalyst is charged into a storage vessel, sometimes while still quite hot (100–250 °C) after calcination, into which one of these non-olefinic hydrocarbons is immediately introduced. Afterward the catalyst is then stored under one of these hydrocarbons at ambient temperature for hours, days, and sometimes weeks, prior to introduction into the reactor where it can contact ethylene.

Although the reactivity of the Phillips Cr/silica catalyst with alkanes has not been investigated to our knowledge, some hexavalent chromium compounds have been reported to oxidize many organics, including olefins, alcohols, carbonyls, and even alkanes [10]. Thus, there is reason to suspect that in some commercial usage the Cr(VI) could be reduced even before contact with ethylene. In this paper we explore this possibility. The reactivity of the hexavalent catalyst with various paraffins and aromatics has been investigated, and the resultant implications for the formation of the active species and the polymerization mechanism is discussed.

---

* Corresponding author. Tel.: +1 918 661 9974; fax: +1 918 661 1900.
E-mail address: Max.McDaniel@sbcglobal.net (M. McDaniel).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.02.023



Scheme 1. (A) Formation of Cr(VI)/silica catalyst precursor; (B) reduction of Cr(VI) by ethylene to lower valent active species, as suggested by Ref. [4] and others.

2. Experimental

2.1. Catalyst preparation

An attempt was made to select a range of catalysts (Cr/silica and Cr/silica-titania), activation temperatures (600 °C to 850 °C), Cr loadings (1% to 5%), and Ti loadings (0%, 2.5%, 4.5%) that are still representative of commercial operations. Detection of products was enhanced by higher Cr loadings and lower activation temperatures, which produce higher conversion to Cr(VI).

Cr/silica catalysts were prepared from grade 951 silica, obtained from W.R. Grace Co., which was impregnated to incipient wetness with an aqueous solution of chromic trioxide, followed by drying overnight in a vacuum oven at 110 °C. The final catalyst contained either 1 or 3 wt% chromium, and had a surface area of approximately 600 m^2/g and a pore volume of approximately 1.0 mL/g. Cr/silica-titania catalysts were made by ter-gelation of silica, titania, and chromium (III) hydroxide (from a solution of Cr nitrate) according to Dietz [11]. This yields a catalyst containing either 2.5 or 4.5 wt% Ti, 1.0 or 3.0 wt% Cr, a surface area of 480 m^2/g and a pore volume of 2.5 mL/g. Like the impregnation technique, this method leaves the Cr on the surface.

The next step, activation or calcination, anchors the chromium to the surface and converts trivalent chromium on the catalyst into the hexavalent form [3]. All of the catalysts used in this study, whether Cr/silica or Cr/silica-titania, were found to contain 90–100% of the chromium as Cr(VI). To activate these catalysts, about 10 g was placed in a 4.75 cm quartz tube fitted with a sintered quartz disk at the bottom. While the catalyst was supported on the disk, dry air was blown up through the disk at the linear rate of about 1.6–1.8 standard cubic feet per hour. An electric furnace around the quartz tube was then turned on and the temperature was raised at the rate of 400 °C/h to the indicated temperature, such as 600 °C or 800 °C. At that temperature the catalyst was allowed to fluidize for 3 h in the dry air. Afterward the catalyst was collected and stored under dry nitrogen, where it was protected from the atmosphere.

2.2. Reduction of the catalyst

Activated catalyst containing Cr(VI) was then exposed to various non-olefinic hydrocarbons in one of two ways. In the first method, the catalyst was contained in a glass vessel sealed with Teflon-seated valves. Enough of the hydrocarbon liquid was added to just submerge the catalyst. Then the sealed vessel was allowed to stand for hours or perhaps days as desired. Sometimes it was shielded from light in a foil wrap. Other times it was exposed to ambient fluorescent light. After the specified time had passed the liquid was sampled and injected into a GC–MS instrument for analysis of products.

As a second step the vessel was then drained of as much of the hydrocarbon as possible, and the remainder was removed by evaporation in a nitrogen flow at 25 °C. A solution of methanol or ethanol and 5–10% water, as indicated in each experiment, was then added to again just submerge the catalyst. The solution also often contained 0.3% HCl to encourage hydrolysis of ligands on the chromium. After the ethanol solution was allowed to contact the catalyst for the specified time, usually about 1 day, it was sampled and analyzed by GC–MS.

In the second method of reduction the catalyst was left in the fluidized bed where it was activated, as described. Dry nitrogen was used to fluidize the catalyst, and the temperature was set as described (usually at 100 °C). About 5 mL of non-olefinic hydrocarbon was then injected into the nitrogen stream, where it evaporated over a period of about half an hour. The vapor was carried up through the catalyst bed where it reduced Cr(VI). After passing through the catalyst bed, the nitrogen was directed through a cold trap where the oxidized hydrocarbon was collected and later analyzed by GC–MS.

As a second step in this second method of contact, the catalyst bed was then exposed to water vapor at 100 °C in order to hydrolyze any remaining ligands left on the chromium. About 5 mL of water was injected into the nitrogen stream where it evaporated over about half an hour and passed up through the catalyst bed. After exiting the catalyst bed, the nitrogen was then directed through another cold trap, where the water and hydrocarbon oxidation products were collected and later analyzed by GC–MS.

2.3. Analysis by GC–MS

Gas chromatography was performed using a Varian 3800 GC analyzer equipped with two separate all-purpose capillary columns (30 m × 0.25 mm × 0.25 μm) and flame ionization (FI) detector. In a typical injection, a 5 μL aliquot was removed by syringe from the sample vial and injected into a GC port held at 250 °C using a split ratio of 20:1. The carrier gas used was ultra-high purity helium and was electronically controlled throughout the run to a constant flow rate of 1.0 mL/min. In a typical run, the initial column temperature was held at 70 °C for 2 min, then ramped at 20 °C/min to 250 °C and then held at 250 °C for 9 min. In cases where FI detection was used, the FI detector on the GC was maintained at 300 °C.

Mass spectral analysis was performed in conjunction with a Varian 320 MS instrument connected to the GC unit using electron ionization at 70 eV. The nominal mass range scanned was 50–900 m/z using a scan time of 0.5 s. Nominal detector voltage used was 1200 V.

2.4. Polymerization

Polymerization runs were made in a 2.5 L steel reactor equipped with a marine stirrer rotating at 400–500 rpm. The reactor was surrounded by a steel jacket through which a coolant was circulated. The temperature of the coolant was precisely controlled through instrumentation so that the temperature in the reactor could be controlled to within 0.5 °C.

Unless otherwise stated, a small amount (0.01–0.10 g normally) of the solid catalyst was first charged under nitrogen to the dry reactor. Next 1.2 L of isobutane liquid was charged and the reactor heated up to 105 °C. Finally ethylene was added to the reactor to equal 3.8 MPa (550 psig), which was maintained during the experiment. The stirring was allowed to continue for the specified time, usually about 1 h, and the activity was noted by recording the flow of ethylene into the reactor to maintain the set pressure.

After the allotted time, the ethylene flow was stopped and the reactor depressurized and opened to recover a granular polymer powder. In all cases the reactor was clean with no indication of any wall scale, coating or other forms of fouling. The polymer powder