



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

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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.

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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 $>500^\circ\text{C}$. 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 $80\text{--}110^\circ\text{C}$) or in cyclohexane (solution at $125\text{--}150^\circ\text{C}$). Typically, the hexavalent catalyst is charged into a storage vessel, sometimes while still quite hot ($100\text{--}250^\circ\text{C}$) 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.

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