Hydrogen Effects in Catalysis

Fundamentals and Practical Applications

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28 Hydrogen Effects in Olefin Polymerization Catalysts

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I. INTRODUCTION

Catalysts for olefin polymerization by low-pressure processes had its origins in the discovery of a revolutionary new chemistry by Karl Ziegler at the Max-Planck Institute [1] and workers at Phillips Petroleum Company [2] in the early 1950s. It was soon realized that polyethylenes produced by these catalysts were structurally different from polyethylenes produced by high-pressure free-radical processes. Ziegler's discovery was subsequently extended to propylene polymerization by Natta [3], who made the seminal discovery that not only could propylene be polymerized to high-molecular-weight polymers, but the polymer so produced had an ordered structure, resulting in its unique physical properties. Commercial production of polyethylene and polypropylene based on the foregoing catalysts began in the mid-1950s and has grown substantially since then.

The olefin polymerization catalysts are a combination of a transition metal salt of groups IV to VIII metals (Ti, V, Cr, Co, and Ni) and a base metal alkyl of groups I to III (alkylaluminums). The Phillips catalysts, comprising chromium oxide on an inorganic support, are limited to the polymerization of ethylene. The chemistry of these catalyst systems for olefin polymerization has been reviewed extensively [4-6]. A wide variety of commercial processes, operating in solution, slurry, and gas phase, have been developed to exploit fully the potentials of these catalysts [7,8]. Simultaneously, our understanding of how these catalysts perform has advanced significantly in the past three decades [9-11].

Molecular hydrogen was used together with olefin polymerization catalysts in the late 1950s to regulate the molecular weight of polyolefins. The implications of this discovery to the commercial development of the polyolefin processes can hardly be underestimated. Molecular weight is one of the fundamental properties that determines the utility and end applications of a polymer; and without a simple and economical method of its control during the polymerization process, it is unlikely that polyolefins would have attained commercial success and the seminal discoveries of Ziegler and Natta would probably have remained mere laboratory curiosities.

Despite its almost universal application in polyolefin processes, relatively little attention has been bestowed on the role of hydrogen and the nature of its interaction with the olefin polymerization catalysts. The present chapter is an attempt to collect and collate all published information on the effects of hydrogen in olefin polymerization catalysts. In Section II we discuss briefly the chemistry of olefin polymerization catalysts. The hydrogen effects as applicable to specific classes of catalysts are described in Section III. In Section IV we review briefly the chemistry of transition metal-hydrogen interaction, knowledge of which substantially contributes to our understanding of the hydrogen effects in olefin polymerization catalysts.

II. CHEMISTRY OF OLEFIN POLYMERIZATION CATALYSTS

A. Classification

The olefin polymerization catalysts can be broadly classified as heterogeneous or homogeneous systems, the physical states referring only to the catalyst, not to the polymer. In the heterogeneous system, the catalyst is in a dispersed state coexisting with a liquid phase and the polymerization occurs mainly on the surface of the solid phase. Most practical catalysts for polyolefins are heterogeneous. Typical examples of heterogeneous and homogeneous catalysts are shown in Table 1.

B. Kinetic Features of Olefin Polymerization Catalysts

The elucidation of kinetic features of transition-metal-catalyzed polymerization of olefins provides important information, such as the rate law, activation energy, number of active centers, and average lifetime of the growing chain, which are of importance in the formulation of mechanisms. The principal kinetic features of both chromium- and titanium-based catalysts are well described in the literature [12-17]. The kinetic results are interpreted in terms of the familiar steps in a polymerization reaction: initiation, propagation, termination, and transfer.

Initiation:

$$C^{*}\text{-}R + H_2C{=}CH_2 \rightarrow C^{*}\text{-}CH_2\text{-}CH_2\text{-}R \qquad (1)$$

TABLE 1 Heterogeneous and Homogeneous Catalysts for Olefin Polymerization

Catalyst	State	Olefin	Structure
CrO_3/SiO_2	Heterogeneous	Ethylene	Linear polyethylene
$(\eta\text{-}C_5H_5)_2Cr/SiO_2$	Heterogeneous	Ethylene	Linear polyethylene
$TiCl_3/Et_3Al$	Heterogeneous	Ethylene	Linear polyethylene
$TiCl_3/Et_2AlCl$	Heterogeneous	Propylene	Isotactic polypropylene
$TiCl_4/Et_3Al$	Homogeneous	Ethylene	Linear polyethylene
VCl_4/Et_2AlCl	Homogeneous	Propylene	Syndiotactic polypropylene
$(\eta\text{-}C_5H_5)_2ZrCl_2/[Me_2AlO]_n$	Homogeneous	Ethylene	Linear polyethylene
$(\eta\text{-}C_5H_5)_2ZrMe_2/[Me_2AlO]_n$	Homogeneous	Propylene	Atactic polypropylene

$$C^*\text{-}H + H_2C{=}CH_2 \rightarrow C^*\text{-}CH_2\text{-}CH_3 \qquad (2)$$

Propagation:

$$C^*\text{-}(CH_2\text{-}CH_2)_n\text{-}R + H_2C{=}CH_2 \rightarrow C^*\text{-}(CH_2\text{-}CH_2)_{n+1}\text{-}R \qquad (3)$$

Transfer:

By β-hydride elimination:

$$C^*\text{-}(CH_2\text{-}CH_2)_n\text{-}R \rightarrow C^*\text{-}H + H_2C{=}CH\text{-}(CH_2\text{-}CH_2)_{n-1}\text{-}R \qquad (4)$$

With alkylaluminum:

$$C^*\text{-}(CH_2\text{-}CH_2)_n\text{-}R + R'_3Al \rightarrow C^*\text{-}R' + R'_2Al\text{-}(CH\text{-}CH_2)_n\text{-}R \qquad (5)$$

With hydrogen:

$$C^*\text{-}(CH_2\text{-}CH_2)_n\text{-}R + H_2 \rightarrow C^*\text{-}H + H_3C\text{-}CH_2\text{-}(CH_2\text{-}CH_2)_{n-1}\text{-}R \qquad (6)$$

With olefin:

$$C^*\text{-}(CH_2\text{-}CH_2)_n\text{-}R + H_2C{=}CH_2 \rightarrow C^*\text{-}CH_2\text{-}CH_3 + H_2C{=}CH\text{-}(CH_2\text{-}CH_2)_{n-1}\text{-}R \qquad (7)$$

Termination (spontaneous):

$$C^*\text{-}(CH_2\text{-}CH_2)_n\text{-}R \rightarrow C\text{-}(CH_2\text{-}CH_2)_n\text{-}R \qquad (8)$$

In Eqs. (1) to (8), C^* represents an active center on catalyst. The interpretation of kinetics according to Eqs. (1) to (8) is rendered more complex because of such factors as the creation and nature of active centers on the catalyst; the need for the reactant monomer to diffuse from the gas phase onto the solid catalyst surface, often through the intermediacy of a liquid

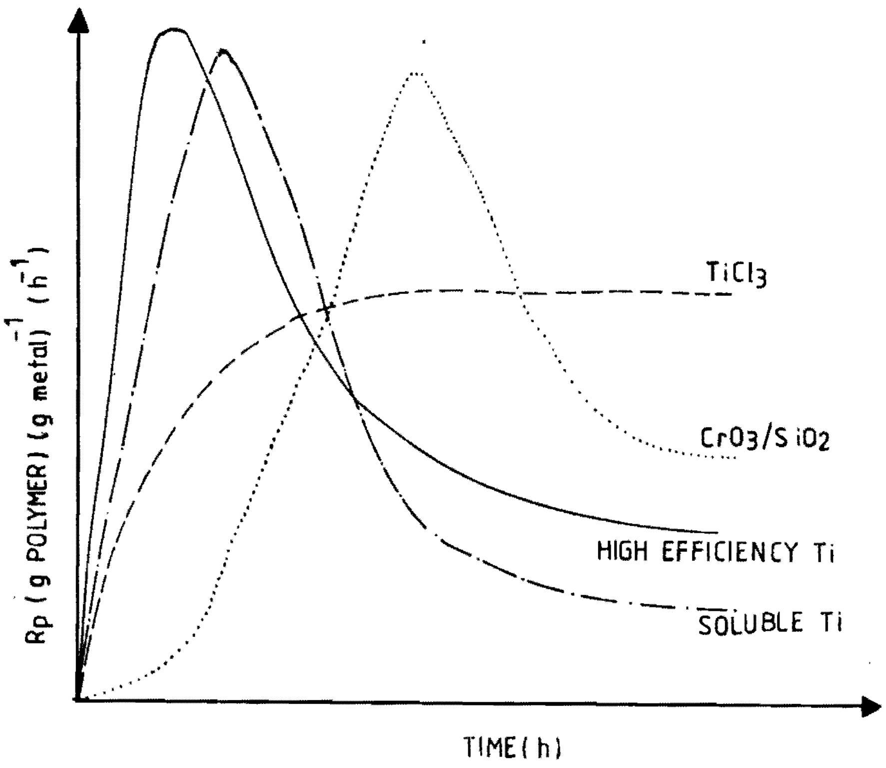


FIGURE 1 Typical kinetic profiles for olefin polymerization catalysts.

phase; followed by exothermic polymerization and the formation of a semicrystalline phase within the catalyst pores.

The kinetics of olefin polymerization are affected both by the nature of catalysts and the reaction conditions. Some typical kinetic profiles of olefin polymerization catalysts are shown in Fig. 1. The lifetimes of olefin polymerization catalysts are essentially determined by their kinetic profiles.

C. Nature of Active Centers and Their Determination

The kinetics and mechanism of olefin polymerization are better understood in relation to the nature and number of active centers on the catalyst. The growth of polymers occurs on this active center, which can be created either by a physical process of activation (CrO_3/SiO_2) or by a chemical process of reduction by alkylation of the transition metal with alkylaluminum. The active centers are best described as a coordinatively unsaturated electrophilic site on the catalyst which can chemisorb an olefin specifically and selectively through donation of the π electron into the vacant d orbitals of the transition metal.

Methods have been described in the literature for determination of the number of active centers, which essentially consist of determining the concentration of transition metal/carbon bonds [18-24]. However, no direct methods exist as yet to characterize the structure of an active center during polymerization in terms of its oxidation states, ligand environment, and support-metal interactions. This is presently largely in the realm of speculation.

D. Factors Determining Catalyst Activity

The activity of olefin polymerization catalysts is determined by (a) the nature, valency state, and type of ligands attached to the transition metal; (b) the

TABLE 2 Physical Characteristics and Activity of Olefin Polymerization Catalyst[a]

Catalyst	Surface area (BET) ($m^2\ g^{-1}$)	Bulk density ($g\ cm^{-3}$)	Pore volume ($mL\ g^{-1}$)	Activity (kg polymer/g transition metal)
CrO_3/SiO_2	300-600	n.a.	0.4-1.6	1000
$(\eta\text{-}C_5H_5)_2Cr/SiO_2$	300-600	n.a.	1-1.2	1000
$TiCl_3 \cdot 0.3AlCl_3$	40-50	0.1	0.2-0.3	1
$MgCl_2/EB/TiCl_4$	200	0.4-0.5	1-2	200

[a] EB, Ethyl benzoate; n.a., not available.

nature of alkylaluminum compound; (c) the physical state of the catalyst; and (d) the conditions of polymerization. Recent studies indicate that Cr^{2+} is active in ethylene polymerization [22], Ti^{3+} and Ti^{2+} are active for ethylene polymerization, and only Ti^{3+} is active for propylene polymerization [23,24]. The nature of alkylaluminum compounds by virtue of their ability to reduce higher-valent transition metal salts to lower-valence states profoundly affects the activity of the catalyst. It has been found that for certain zirconium-based ethylene polymerization catalysts a novel organoaluminum compound consisting of an Al-O bond (called aluminoxane) gives the highest catalyst activity [25].

The physical state of the metal catalyst has a considerable effect on the kinetics of polymerization and product properties. These include the crystalline form of the transition metal salt, the nature of the support and its interaction with the transition metal compounds, particle size, surface area, bulk density, crystallite size, and crystallite surface area of the catalyst. The latter two appear to be especially important for crystalline $TiCl_3$ catalyst, where active centers are believed to be located on well-defined lattice defects [26,27]. Recent developments in the area of high-efficiency olefin polymerization catalysts are entirely due to the ability of catalytic chemists to synthesize new catalyst composition with very desirable physical characteristics. The exhaustive literature in this area has been reviewed in a number of publications [28-32]. In Table 2 we summarize some of the physical characteristics of olefin polymerization catalysts and their relationship to polymerization activity.

E. Effect of Catalyst on Polymer Properties

The important properties of polyolefins which are at least in part determined by the nature of catalysts are (a) molecular weight, (b) molecular-weight distribution, and (c) degree of crystallinity or stereoregularity. Molecular weight is controlled by the addition of chain-transfer agents. The multiplicity of active centers which differ energetically and structurally, and their differential rate of decay with time, have been ascribed as major reasons for the breadth of molecular-weight distributions observed with heterogeneous catalysts [33]. On the other hand, homogeneous catalysts with a single active center lead to a narrower distribution of molecular weights. Under stationary-state conditions with high rates of initiation and low conversions, this value conforms to the most probable distribution as defined by Flory [34]. Many of the high-efficiency catalysts supported on magnesium chloride as support give a narrower distribution of molecular weights, indicating the greater degree of homogeneity of the active centers in the supported catalysts [35]. Catalyst also determines the degree of linearity of a polymer as well as stereoregularity. The latter is shown in Table 1.

F. Mechanism of Polymer Growth Reaction

The mechanism of polymer growth reaction and the origin of regiospecificity and stereospecificity in olefin polymerization have been the subject of a number of reviews [9-11,36-38]. The accumulated literature now favors a mechanism in which polymer growth occurs on the surface of the transition metal, which first gets alkylated by the alkylaluminum compound. The active site is envisaged as a metal center with both an alkyl substituent and a chlorine vacancy located on the edges of the titanium trichloride crystal. Growth occurs by complexation of the monomer onto the vacant site followed by insertion of the polymer chain at the transition metal/carbon bond.

It is believed that energetically and structurally distinct sites exist on the catalyst which favor either an isospecific insertion (leading to isotactic polymer) or random insertion (leading to atactic polymer). Different models have been proposed to describe these sites. According to one model, the active sites located on the edge favor isospecific propagation, while those at the corner of $TiCl_3$ crystallite favor random insertion of propylene [4]. Soga and co-workers proposed that a center having two vacant sites gives atactic polypropylene, while that having only one vacant site gave isotactic polymer [38]. Pino proposed that a metal atom bound to solid surfaces possesses centers of chirality by virtue of which the active center of catalyst favors complexation of one prochiral face of propylene over the other [10]. The precise features of the catalyst that exercise such sharp selection is not known.

Comparatively little is understood about the mechanism of polymer growth on chromium catalysts. The precise initiation mode is still a subject of debate. Propagation is believed to occur by an insertion of ethylene into a Cr-alkyl bond. In the case of a chromocene on silica catalyst, the *n*-cyclopentadienyl ligand is associated with the active center and does not take part in monomer insertion.

III. HYDROGEN EFFECTS IN OLEFIN POLYMERIZATION CATALYSTS

A. Titanium Catalysts for Ethylene and Propylene Polymerizations

Titanium Trichloride/Alkylaluminum Catalysts

Molecular hydrogen has come to stay as the molecular-weight-regulating agent of choice in the polymerization of ethylene and other α-olefins catalyzed by titanium-based Ziegler-Natta catalysts. Hydrogen is an effective chain regulator for a wide range of catalyst compositions and reaction conditions. In addition, it is easy to use, inexpensive, and does not leave a residue in the polymer.

The use of hydrogen as a molecular-weight regulator was first disclosed almost simultaneously by Natta's school [39,40], workers from Farbwerke Hoechst [41], and Hercules Powder Company [42]. According to Natta, the chain termination involves the hydrogenolysis of the metal-to-polymer bond which would result in the generation of transition metal hydride. The hydride is expected to add to an olefin, which would then complete the catalytic cycle (Fig. 2). Based on the study of chain-transfer kinetics of ethylene polymerization with α-$TiCl_3$ and Et_3Al, Natta established the relationship

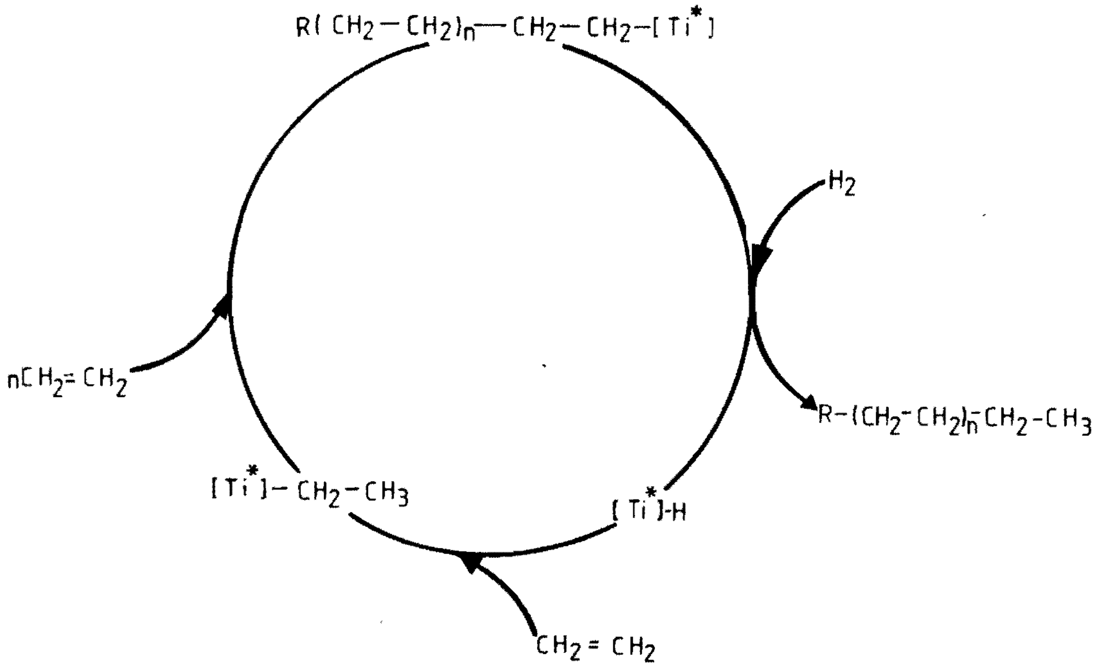


FIGURE 2 Catalytic cycle involving transfer of active catalyst center to hydrogen.

$$\frac{\overline{M}_n^0}{\overline{M}_n^H} = 1 + K(p_{H_2})^n \tag{9}$$

where $\overline{M}_n^0$ is the molecular weight of the polymer in the absence of hydrogen, $\overline{M}_n^H$ is the molecular weight of the polymer in the presence of hydrogen, p_{H_2} is the partial pressure of H_2 and k and n are constants. The value of n for this catalyst system was found to be 0.5. Using data published by Keii [15] for propylene polymerization for the $TiCl_3/Et_2AlCl$ system with an isotactic index of 94%, the value of n was found to be 0.9, whereas for the $TiCl_3/Et_3Al$ system having an isotactic index of 64%, the value of n was 0.5. Keii reported a value of n = 0.88 with $TiCl_3/Et_3Al$ and n = 1.0 for $TiCl_3/Et_2AlCl$ for ethylene polymerization in toluene as a diluent. For polymerization in the gas phase the values of n were reported to be 0.35 to 0.45 for $TiCl_3/Et_3Al$ and 1.0 for $TiCl_3/Et_2AlCl$ [43]. The value of n = 0.5 is consistent with a hypothesis wherein a dissociative chemisorption of hydrogen onto the titanium surface takes place followed by the rate-determining reaction of the hydrogen adatom with the metal-polymer bond. This is analogous to the Horiuti-Polanyi mechanism for hydrogenation of olefin over metal surfaces [44]. In contrast, if the attack of molecular hydrogen on the metal-polymer bond is the slow step, the transfer reaction is expected to be first order with respect to $[H_2]$ (n = 1), analogous to the Twigg (or Eley)-Rideal mechanism for hydrogenation [45]. The observed rapid exchange of H_2 and D_2 over a $TiCl_3/Et_3Al$ catalyst system supports the hypothesis of a dissociative chemisorption of hydrogen on these catalysts [46,47].

The relative rates of chain transfer to hydrogen, olefin, and alkylaluminum for ethylene and propylene polymerization have been reported by Zakharov and co-workers [48] and Grievson [49]. The results (Table 3) showed that the rate of chain transfer to hydrogen was substantially higher relative to chain transfer to olefin or alkylaluminum. Also, at a given $[H_2]$, the molecular weight of polypropylene was suppressed to a greater degree than that of

TABLE 3 Rate Constants for Chain-Transfer Reactions

Olefin	Catalyst	Temperature (°C)	K^M_{tr} (liter mol^{-1} s^{-1})	H_2 K_{tr} ($liter^{1/2}$ $mol^{1/2}$ s^{-1})	$AlEt_3$ K_{tr} ($liter^{1/2}$ $mol^{1/2}$ s^{-1})	Ref.
Ethylene	δ-$TiCl_3 \cdot 0.3AlCl_3/Et_3Al$	80	0.84	23	0.36	48
Propylene	δ-$TiCl_3 \cdot 0.3AlCl_3/Et_3Al$	70	0.04	5.9	0.054	48
Ethylene	γ-$TiCl_3/Et_2AlCl$	40	0.01	3	0.003	49

polyethylene. This could be a reflection of the relative strengths of the metal-polymer bond.

Conflicting reports on the effect of hydrogen concentration on the overall rates of olefin polymerization have appeared in the literature (Table 4). For polymerization of ethylene, both in diluent and gas phase, the overall rate decreased substantially with hydrogen present [39, 43, 50]. Natta and co-workers [39] found that if the hydrogen-ethylene mixture was replaced by ethylene at the same pressure, the rate returned to its original value. This indicated that hydrogen has no poisoning effect on the catalyst. Similar observations were made by Okura and co-workers [51]. Other workers have observed an increase in the rate of polymerization in the case of propylene when hydrogen was present [52-54]. More recent studies indicate a negligible effect of hydrogen on the rate of propylene polymerization [55]. With higher α-olefins, butene-1, and 4-methyl-pentene-1, hydrogen enhances the overall rate of polymerization [56, 57].

There appears to be no single explanation that accounts for all the observations. Assuming that both molecular hydrogen and olefin compete for the same active sites, hydrogen chemisorption should inhibit polymerization of olefin by causing a reduction in the number of active centers. This appears to be the case with ethylene, where Grievson [49] reported a reduction in the concentration of active centers with 50 mol % hydrogen ($[C^*] = 6 \times 10^{-3}$ mol per mole of $TiCl_3$) relative to a catalyst without hydrogen ($[C^*] = 1.5 \times 10^{-2}$ mol per mole of $TiCl_3$). Buls and Higgins [53] and Mortimer et al. [58] proposed that hydrogen must in some way help in the creation of new active sites on the catalyst to explain the rate increase observed by them for propylene polymerization in the presence of hydrogen. The possibility of additional new sites being created by reduction of Ti-Cl bond to Ti-H bond cannot be ruled out [43]. Pijpers and Roest [59] and Boucheron [60] proposed that in the absence of hydrogen, transfer occurs by β-hydrogen elimination, leading to unsaturation in the polymer. The chain-end double bond stays complexed to the active centers, thus inhibiting fresh complexation of olefin and causing a rate inhibition in the absence of hydrogen.

Sufficient data are not available in the literature to show which of the two factors, site activation in the presence of hydrogen or site deactivation by complexed unsaturated polymer, is responsible for the increase in the rate of propylene, butene-1, and 4-methyl-pentene-1 polymerizations. Precise determination of the number of active centers with and without hydrogen for α-olefin polymerization may help to resolve this question.

Other factors, such as the crystalline form of $TiCl_3$, the nature of alkylaluminum compound, the diluent, the ratio of Al/Ti, and the nature and concentration of reactive impurities also appear to have a significant role in determining the nature of response of the olefin polymerization rate to added

TABLE 4 Effect of Hydrogen on the Overall Rate of Polymerization

Olefin	Catalyst	Al/Ti	T (°C)	Pressure (kg cm^{-2})	Diluent	[H_2]	R_p [g polymer (g cat)$^{-1}$ h^{-1}]	Ref.
Ethylene	δ-$TiCl_3 \cdot 0.3\ AlCl_3/Et_3Al$	2	30	2	Toluene	0	23	49
						9×10^{-4} M	12	
	γ-$TiCl_3/Et_2AlCl$	1	50	3	Cyclohexane	0	10	50
						0.8 atm	6	
	δ-$TiCl_3 \cdot 0.3\ AlCl_3/Et_3Al$	3	35	0.4	Nil	0	19	43
						0.2 atm	9	
	δ-$TiCl_3 \cdot 0.3\ AlCl_3/Et_2AlCl$	3	35	0.4	Nil	0	8.9	43
						0.02	10.5	
						0.2	7.5	
	α-$TiCl_3/Et_3Al$	3	75	2	Heptane	0	15	39
						1 atm	6	
Propylene	δ-$TiCl_3 \cdot 0.3AlCl_3/Et_2AlCl$	1	55	0.4	Heptane	–	Dec. in rate with H_2	51
				0.4	Toluene	–	Inc. in rate with H_2	
	δ-$TiCl_3/Et_2AlCl$	–	60	1	Heptane	0	75	53
						1 atm	244	
	δ-$TiCl_3 \cdot 0.3AlCl_3\ Et_2AlCl$	-	70	4	Nil	0	1500	54
						0.6 atm	2000	
	δ-$TiCl_3 \cdot 0.3AlCl_3\ Et_2AlCl$	3	70	5	Heptane	0	95	55
						1.5×10^{-3} M	90	
Butene-1	δ-$TiCl_3 \cdot 0.3AlCl_3\ (iBu)_3Al$	2	70	3.5	Isooctane	0	111	56
						1 atm	226	
4-Methyl-pentene-1	γ-$TiCl_3/Et_2AlCl$	3	54	1	Heptane	0	75	57
						2 atm	118	

hydrogen. It has been reported that site activation by hydrogen is more pronounced in the presence of diethylaluminum chloride compared to triethylaluminum. This has been attributed to the poorer alkylating (reducing) ability of the former and the consequent inability to activate all available sites [43]. These sites are then activated by conversion to Ti-H sites.

The nature of the alkylaluminum compound and the Al/Ti ratio determines the relative population of oxidation states on Ti (4+, 3+, 2+). It has been reported [15] that transfer by hydrogenolysis of metal-polymer bond occurs only on the Ti^{3+} center, whereas Ti^{4+} promotes only an exchange between added hydrogen and the hydrogen on the β-carbon of the polymer chain.

For polymerization of α-olefins, it is understood that at least two distinct sites exist on the catalysts, one leading to isospecific propagation resulting in isotactic polymers and the other leading to atactic polymer. It is becoming increasingly evident that the effects of hydrogen on these centers are not similar. The atactic polymer is much lower in molecular weight, and although the weight fraction of this in the total polymer is small, the number of atactic polymer molecules produced frequently exceeds the number of isotactic molecules. Consequently, a large proportion of hydrogen is consumed to hydrogenate an atactic polymer. This factor could also lead to anomalous observations on the influence of hydrogen on the overall rate of polymerization, which is the sum of rates of isospecific and nonspecific polymerization. The two rates may need to be separated from the point of view of hydrogen effects.

Buls and Higgins [61] also made an interesting observation that in the absence of hydrogen, the isotactic polypropylene polymer chain is attached to the metal catalyst and that other forms of chain transfer (to propylene, alkylaluminum, and β-hydrogen transfer) are not predominant. This led them to the remarkable conclusion that propylene polymerization in the absence of hydrogen is not truly catalytic.

For propylene polymerization, the isotactic index, measured as heptane insolubles, experiences a small initial drop upon the introduction of hydrogen, which remains relatively constant with increasing hydrogen concentration until very high levels of hydrogen are reached. The isotactic index then begins to decrease steadily (Table 5). This observation was made with both Et_3Al and Et_2AlCl. The reduction in isotacticity with increasing hydrogen concentration favors a site activation mechanism wherein new active centers are being created on the surface of titanium catalysts. A majority of the new sites being created are nonstereospecific sites, where only random propylene insertion is possible, leading to atactic polymer formation.

The mechanism of chain transfer by hydrogen as proposed by Natta for propylene polymerization (Fig. 2) will require the presence of an isopropyl

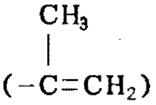
TABLE 5 Effect of Hydrogen on the Isotactic Index of Polypropylene

Catalyst	H_2 (bar)	R_p [g polymer $(g\ cat.)^{-1}\ h^{-1}$]	I.I (%)	Ref.
$\delta\text{-}TiCl_3 \cdot 0.3AlCl_3/Et_2AlCl$	0	332	96.7	8
	0.6	380	95.7	8
	1.5	341	90.6	8
	0	449	91.1	55
	0.3	479	89.2	55
$\alpha\text{-}TiCl_3/Et_3Al$	0	15	81.3	39
	1.0	6	76.5	39

TABLE 6 Reduction in Molecular Weight ($\overline{M}_w$) of Polypropylene and Polyethylene[a]

Polyethylene		Polypropylene	
$\overline{M}_w$	$[p_{H_2}]$ (psia)	$\overline{M}_w$	$[p_{H_2}]$ (psia)
700,000	0	480,000	0
270,000	0.5	110,000	0.2
210,000	1.0	72,000	0.5
170,000	2.0	60,000	1.0

[a] Conditions of polymerization: $TiCl_3$, Et_3Al, Al/Ti = 3, 75°C, heptane.
Source: Ref. 39.

end group, which indeed is found. Unsaturation at the chain end  $(-\overset{CH_3}{\overset{|}{C}}=CH_2)$ was found in the absence of hydrogen [61]. Using molecular tritium instead of hydrogen, Hoffman and co-workers [62] found that for 95% of the whole product, two tritium atoms per molecule of the polymer were incorporated. This was taken as evidence of a mechanism wherein each chain is initiated by a Ti-H bond and terminated by hydrogenolysis (Fig. 2). However, the authors did not rule out the possibility of H-T exchange at the β-carbon attached to the metal center. Such a process, which is known to occur, makes their experimental observation fortuitous.

π-Electron donors have been found to have desirable effects on the performance of titanium-based olefin polymerization catalysts [4]. Under optimum conditions, an electron donor causes an increase in polymerization rate, polymer molecular weight, and isotactic index. Consequently, to attain a desired molecular weight, a greater concentration of hydrogen is required for a donor-modified catalyst relative to an unmodified catalyst. No systematic study of hydrogen effects on the rates and stereospecificity with donor-modified titanium catalysts has appeared in the literature; thus no general conclusions can be drawn.

Some typical values of weight-average molecular weight obtained for polyethylene and polypropylene at different partial pressures of hydrogen are shown in Table 6. The fact that at very high hydrogen concentration the performance of titanium-based catalysts is adversely affected limits the use of this technique for the preparation of very low molecular weight resins, which have practical applications because of their high flow properties and ability to be shaped into intricate shapes and forms.

Diverse effects of hydrogen on the molecular-weight distribution of polyethylene and polypropylenes are reported in the literature [55,63-66] (Table 7). It is reported that hydrogen narrows [63] or broadens [65,66] the molecular-weight distribution of polyethylene or polypropylene or causes negligible changes [56,64] in it. The data available in the literature are inadequate to draw any general conclusions. Most authors have used a batch mode for hydrogen addition. This is expected to cause a broadening of the Q value due to the changing $[H_2]/[\text{olefin}]$ ratio over the course of the polymerization as hydrogen is consumed. In the case of propylene, the data reported in the literature are for the entire polymer (isotactic + atactic). However, as shown by Buls and Higgins [61], $\overline{M}_w$ of atactic polymer is drastically reduced by as much as 50% in the presence of hydrogen, and unless this effect is separated, any interpretation of hydrogen effect based on the Q value of the whole polymer could be highly misleading.

TABLE 7 Effect of Hydrogen on Molecular-Weight Distribution (Q)

Olefin		T (°C)	Pressure (bar)	$[H_2]$	Q	Ref.
Ethylene	$TiCl_4/(i\text{-}Bu)_3Al$	80	2	0	18	63
				6 vol %	9	
	$\gamma\text{-}TiCl_3/Et_2AlCl$	50	3	0	15	64
				20 vol %	13	
	$\gamma\text{-}TiCl_3/Et_3Al$	60	2	0	5	65
				1 atm	15	
Propylene	$\gamma\text{-}TiCl_3/Et_3Al$	75	n.a.	0	6	66
				1 atm	11	
	$\delta\text{-}TiCl_3 \cdot 0.3AlCl_3/Et_2AlCl$	70	5	0	5.8	55
				2 vol %	6.4	

High-Efficiency Titanium-Based Olefin Polymerization Catalyst

The efficiency of olefin polymerization catalysts based on titanium has dramatically improved within the past 10 years, bringing in its wake new industrial processes for polyolefins. The underlying chemistry of these processes has been well reviewed [16, 28-32, 67]. The key to the improved performance of these catalysts is the use of an activated magnesium chloride as a high-surface-area support for titanium chloride which probably bonds to the coordinatively unsaturated magnesium ions located at the side surfaces and crystal edges, the (110) and (101) faces, through chlorine bridges, forming stable surface complexes [67]. The patent literature is replete with examples of such catalysts and a substantial amount of industrial research is being invested in the preparation, characterization, and evaluation of high-efficiency catalysts. Consequently, much of the information regarding these catalysts is highly proprietary, emphasis being on the commercial exploitation of the catalyst.

Nevertheless, a number of recent publications have been addressed to a fundamental understanding of these catalysts [68-71]. Guastalla and Giannini [72] have reported on the influence of hydrogen on the polymerization of ethylene and propylene with a $MgCl_2$-supported catalyst. Using a $TiCl_4/MgCl_2/Et_3Al$ catalyst they found that the initial rates of polymerization of propylene increased by 150% when the partial pressure of hydrogen was changed from 0 to 0.6 bar. At $p_{H_2} > 0.6$ bar no further increase in rate could be observed. These authors also observed that the productivity of both atactic (ether-soluble) and isotactic (heptane-insoluble) fractions increases with increasing partial pressure of hydrogen. However, beyond a p_{H_2} of 0.6 bar, the productivity of the isotactic fraction dropped. The reduction in molecular weight of heptane-insoluble fractions was proportional to the square root of hydrogen concentration [$n = 0.5$ in Eq. (9)]. Interestingly, the activity of the same catalyst toward ethylene polymerization was substantially reduced in the presence of hydrogen. A similar observation was made by Böhm using a high-activity magnesium hydroxide-supported titanium catalyst [73]. Soga and Siono [74] studied the effect of hydrogen on the molecular weight of both atactic and isotactic polymer produced during polymerization of propylene using a $TiCl_4/MgCl_2$/ethylbenzoate/Et_3Al catalyst at 40°C and atmospheric pressures. They found that the catalyst activity, as well as the fraction of isotactic polymer, gradually decreased with an increase in hydrogen partial pressures. This was attributed to the decrease in molecular weight of the isotactic fraction, because of which it went into solution. No loss of isotacticity was observed with increasing hydrogen concentration. The value of exponent n in Eq. (9) was found to be 0.8 for isotactic fraction and 0.7 for atactic fraction. Although these values deviated from n = 1 or 0.5, Soga and Siono interpreted their result in terms of two distinct polymerization centers, one (C-1) having two vacant sites, giving atactic polypropylene, while the other center (C-2), having only one vacant site, giving isotactic polypropylene [38]. Dissociative chemisorption of hydrogen proceeds only on the C-1 center (n = 0.5), whereas molecular hydrogen is involved on the catalyst with the C-2 center (n = 1). In a related study Keii and co-workers [75] found the value of the exponent n to be 0.5 for polymerization of propylene using a supported catalyst (41°C, atmospheric pressure). Although the composition of the catalyst used in this study was similar to that used by Soga and Siono [74], different values of n were reported. In a more recent study, Chein and Ku [76] found that upon the addition of hydrogen, the number of active centers on titanium for ethylene polymerization increased by 50% and the number of isospecific active centers on titanium for propylene polymerization increased by 250%. The catalyst used was prepared by ball milling $MgCl_2$ with ethylbenzoate followed by reaction with p-cresol, triethylaluminum, and titanium chloride. Using a magnesium chloride-supported titanium catalyst of undisclosed composition, Jacobson [77] reported marginal increase in catalyst activity during propylene polymerization in liquid propylene. The reported effects of hydrogen on the rate, isotacticity, and molecular weight distribution of olefin polymerization using high-efficiency titanium catalysts are shown in Table 8.

In view of the complex structural features of $MgCl_2$-supported titanium catalysts, it is doubtful whether any general conclusions on the effect of hydrogen on the rates of polymerization of ethylene or propylene can be drawn. While interpreting results, it is necessary to recognize the following features of the supported catalysts: (a) surface characteristics such as surface area, crystallite size, porosity, titanium dispersion, and method of activation of support; (b) the presence or absence of an electron donor such as ethylbenzoate, which tends to weakly adsorb on the coordinatively unsaturated titanium sites; (c) the relative population of oxidation states on the catalyst surface and their stability, which is, in turn, controlled by the manner of reduction; and (d) the nature of the external electron donor generally used as a third component with propylene polymerization catalysts, which controls, by an as yet ill-understood manner, the relative rates of isospecific and nonspecific propagation.

Nevertheless, results available so far suggest that hydrogen suppresses the rate of ethylene polymerization, whereas the isospecific rate of propylene polymerization is enhanced by hydrogen. This observation is generally in agreement with results obtained using conventional titanium catalysts.

The isotactic index of polypropylene obtained with these high-efficiency catalysts is not generally affected by the addition of hydrogen [67, 72, 73]. The molecular-weight distribution of polypropylene and polyethylene obtained using a high-activity catalyst also did not change with increasing hydrogen concentration [78].

Supported catalysts also appear to show a more sensitive response to hydrogen. It has been reported that one-half as much hydrogen is needed to achieve the same polymer molecular weight as with a conventional catalyst system [76]. This could be a consequence of the higher concentration of active centers on supported catalysts (also capable of hydrogen adsorption) and the decrease in formation of the atactic fractions.

TABLE 8 Hydrogen Effect on High-Efficiency Catalyst

Olefin	Catalyst	Solvent	Pressure (bar)	Temp. (°C)	$[H_2]$ (bar)	Yield [kg polymer $(g\ Ti)^{-1}\ h^{-1}$]	I.I. (%)	Q	Ref.
Propylene	$TiCl_4/MgCl_2/Et_3Al$	Hexane	3	70	0	36.6	36	n.a.	72
					1.2	112.0	35.9	n.a.	
Ethylene	$TiCl_4/MgCl_2/Et_3Al$	Hexane	3	60	0	177	—	n.a.	72
					1.0	171	—	n.a.	
Propylene	$TiCl_4/MgCl_2/Et_3Al/EB$	Heptane	0.5	40	0	3.02	90.2	12.0	74
					0.2	2.5	85.9	10.8	
Propylene	Mg-Ti Catalyst/Et_3Al	Liquid pool	31	70	0	565	95.5	7.3	77
					1.0	647	92.2	7.4	
Ethylene	$Mg(OR)_2/TiCl_4/Et_3Al$	Diesel oil	6	85	0	611	—	9.1	73
					7 vol %	499	—	9.0	

Soluble Organometallics as Olefin Polymerization Catalysts

Despite the fact that soluble organometallics are more amenable to unequivocal mechanistic studies, very little is known about the hydrogen effects on homogeneous olefin polymerization catalysts. The reason could be the unfortunate lack of commercial interest in these catalyst types, which has also inhibited fundamental studies.

Doi and co-workers [79] studied propylene polymerization at -78 C with a vanadium triacetylacetonate/diethylaluminum chloride soluble catalyst system. In the absence of hydrogen, the polymerization showed all the features of a transfer-termination free-living polymerization with molecular-weight distribution approaching unity. Addition of hydrogen caused the molecular-weight distribution to increase to 2.0 [34]. The catalyst system thus showed predictable kinetics. The value of n in the exponent of Eq. (9) was reported to be 1.0 for a homogeneous catalyst. Kaminsky and co-workers studied the influence of hydrogen on the polymerization of ethylene using a homogeneous bis(cyclopentadienyl)zirconium dichloride/aluminoxane catalyst [80,81]. The addition of hydrogen suppressed catalyst activity. However, the loss of activity was reversible when hydrogen was removed from the system. The exponent of n in Eq. (9) was also found to be 1.0, in agreement with earlier studies [78,79]. Homogeneous catalysts required less hydrogen to effect a given reduction in molecular weight compared to that required by heterogeneous catalysts.

A value of 1 for the exponent n in Eq. (9) for homogeneous catalysts is indicative of a mechanism wherein the rate-determining step is the reaction of alkylated transition metal with molecular hydrogen. Studies of kinetics of homogeneous hydrogenation of olefins with similar catalysts appear to substantiate this view (see Section IV).

B. Chromium Catalysts for Ethylene Polymerization

Chromium on Silica

Chromium catalysts for ethylene polymerization are generally prepared from an amorphous silica gel and CrO_3 (Cr ca. 1%) followed by activation with dry fluidized air at 500 to 1000°C for a few hours. Surface properties of silica determine polymer properties such as bulk density, molecular weight, and its distribution [2.30].

One of the major limitations of the Phillips catalyst in industrial practice has been its inability to produce low-molecular-weight polyethylenes. It was recognized very early that CrO_3/SiO_2 showed a negligible effect of hydrogen as a chain transfer agent in comparison with the Ziegler-Natta type of catalyst. It has been reported that 20 mol % hydrogen, when used with CrO_3/SiO_2 catalyst, depressed polyethylene molecular weight by only 50% [82]. However, even when hydrogen was used, the polymer contained predominately vinyl unsaturation, indicating that hydrogen acts in some way other than hydrogenation to shorten the chain length [83]. The use of deuterium instead of hydrogen resulted in both -CHD and $-CH_2D$ groups. Exchange reactions led to the former, whereas the latter was believed to form as a result of the addition of Cr-D bond to an olefin [83].

The inability of hydrogen to control molecular weight with these catalysts has led to other methods of molecular-weight control, such as incorporation of titania in chromia [84,85], and by control of the hydroxyl population in the support [86]. With a given catalyst, the reaction temperature and ethylene pressure offer a further degree of molecular-weight control.

The lack of hydrogen effects on the chromium catalyst can be understood in terms of the active valence states of the chromium as well as strong metal-support interactions. Accumulated evidence now favors Cr^{2+} as active in polymerization. Catalyst activity and termination rate are inversely related to the hydroxyl population on the silica surface, as a surface hydroxyl group (silanol) can interfere with the reduction to Cr^{2+} [87]. It is conceivable that when hydrogen is added to the system, either fresh silanol groups are created or part of the existing silanol groups form water. Both of these can reoxidize Cr^{2+} to Cr^{3+}, the latter being less active for polymerization. On the contrary, for reactions such as hydrogenation of olefins, Cr^{3+} has been found to be the preferred valency [88]. An exhaustively reduced species where Cr^{2+} is the predominant valence state is inactive for hydrogenation. Cr^{3+} with a coordination number of 4 has two empty ligand sites, one on which the olefin is bound and the other which can accept a hydride ion by heterolytic dissociation of hydrogen. The following mechanism of hydrogenation over Cr^{3+} has been proposed by Burwell et al. [89, 90].

$$Cr^{3+}O^{2-} + H_2 \rightarrow [Cr^{3+}H^-]OH^- \qquad (10)$$

$$[Cr^{3+}H^-]OH^- + C_2H_4 \rightarrow [Cr^{3+}C_2H_5^-]OH^- \qquad (11)$$

$$C_2H_5^- + H^+ \rightarrow C_2H_6 \qquad (12)$$

The distinctness of the two sites, one active for polymerization and the other for hydrogenation, and their relative stability to surface hydroxyl groups could account for the poor hydrogen response of chromium/silica catalyst in ethylene polymerization.

More recently, aluminum phosphate has been used to replace silica in the Phillips catalyst [91, 92]. Interestingly, this support shows a greater sensitivity to hydrogen, and a wide range of molecular weights for polyethylene is accessible using hydrogen as a chain-transfer agent. In spite of this, polymers contained only vinyl unsaturation, indicating that β-hydrogen elimination is the preponderent chain transfer step [Eq. (4)]. In some unknown way, hydrogen must be assisting this process. The polymerization rate was not reduced by hydrogen. The reason for this major difference in hydrogen effect between the two supports, silica and aluminum phosphate, is not clear at present.

Another class of well-known chromium-based ethylene polymerization catalysts is that of the silica-surface-anchored chromium organometallics, discovered in the laboratories of Union Carbide Corporation in the late 1960s. A number of arene [93, 94], allyl [95, 96], and bis-cyclopentadienyl [97, 98] chromium compounds have been reported.

The organochromium compounds are usually more sensitive to hydrogen than are chromium oxide catalysts. In a study of the hydrogen effects of silica-supported chromocene catalysts, Karol and co-workers reported an order-of-magnitude higher hydrogen response than even $TiCl_3$-Et_2AlCl [99]. As expected, the polymer was fully saturated, indicating that hydrogenation of a Cr-polymer bond was the major transfer step. Polymers prepared from deuterium showed $-CH_2D$ groups, confirming this view [100]. Substitution of cyclopentadienyl with other π ligands such as indenyl or fluorenyl led to catalysts with poorer response to hydrogen [101]. It has been reported that unlike chromocene, diarene chromium and diallyl chromium produce vinyl unsaturation when hydrogen was used to control molecular weights [102]. Obviously, hydrogenation of the polymer-chromium bond is not the only prevalent mechanism; β-hydrogen elimination can also be important. Hydrogen caused a loss of catalyst activity. The molecular-weight distributions of polyethylene produced by chromocene on silica were relatively narrow compared to the oxide catalyst and did not change with hydrogen concentration.

On the contrary, chromium catalysts, which transfer by β-hydrogen elimination, produced broad-molecular-weight-distribution polyethylene.

Any explanation of the high hydrogen response of such catalysts should consider the role of both the η-cyclopentadienyl ligand and the support which is linked to the chromium atom through a Si-O-Cr bond. In the absence of silica, chromocene does not catalyze polymerization of ethylene. The presence of coordinatively unsaturated chromium is responsible for both efficient polymerization and hydrogenolysis. Propagation is believed to occur by repeated insertion of the olefin into a Cr-alkyl σ bond formed initially by an as-yet-unknown mechanism. In the mechanism originally proposed [99], the chromium-to-silica bonding was envisaged as chemisorption, and hence the active valence state of Cr was considered as 2+. Polarographic evidence was presented on recovered catalyst after polymerization to show that Cr^{2+} was the dominant valence state (85 to 95%), with 5 to 15% Cr^{3+}. The latter was attributed to inadvertent oxidation.

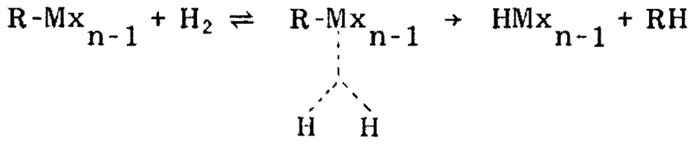
However, the proposal of an oxide-ligated chromium species [35] with a Si-O-Cr bond would require a formal oxidation state of Cr^{3+} for the active propagating center. Such a center can undergo hydrogenolysis by either (a) an oxidative addition/reductive elimination process involving $Cr^{3+} \rightleftharpoons Cr^{5+}$ states, (b) by a heterolytic dissociation process similar to that proposed for hydrogenation on Cr^{3+} [89,90], or (c) by direct interaction of molecular hydrogen with the metal center via a vacant orbital without net oxidation of the metal center. The relatively unstable Cr^{3+} could be stabilized by the presence of a hard Si-O ligand. The soft η-cyclopentadienyl ligand could offer a degree of stability to the Cr-carbon or Cr-hydrogen bond. Experimental data currently available cannot distinguish among mechanisms (a) to (c). Knowledge of the order of reaction with respect to hydrogen can distinguish between (a) and (b) or (c). The drop in catalyst activity with increasing hydrogen concentration can best be explained by the reaction of H_2 with surface hydroxyl or oxygen, generating water or hydroxyl groups, both of which can poison the active sites.

IV. CHEMISTRY OF TRANSITION METAL/HYDROGEN BOND

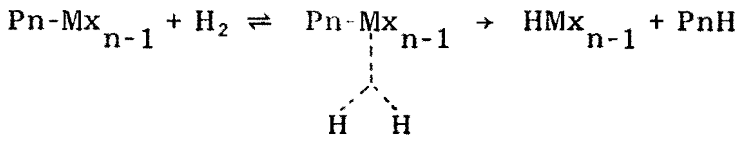
The chemistry of metal-hydrogen bond plays an important role in both heterogeneous [103] and homogeneous catalysts [104]. Examples of homogeneous catalytic processes involving transient transition metal/hydrogen bonds are hydrogenation [105], hydroformylation [106], olefin isomerization and H-D exchange [107], hydrocarbon activation [108], and dimerization-oligomerization of olefins [109,110]. Of these reactions, hydrogenation bears the closest resemblance to the mechanism of chain transfer in olefin polymerizations: In fact, transition metal acetylacetonates and alkoxides in conjunction with trialkylaluminum at high H_2/olefin ratios are effective olefin hydrogenation catalysts [111]. The rate of reaction was found to be first order with respect to hydrogen and zero order with respect to olefin. The activity of the metal decreased in the order Co > Ni > Fe > Cr > Ti > Mn > V, approximately the order of decreasing value of Pauling's d character. Bis(η-cyclopentadienyl)-titanium dichloride in conjunction with metal alkyls is a hydrogenation catalyst [112,113].

The activation of molecular hydrogen on transition metal complexes can occur by three elementary mechanisms: oxidative addition [114], heterolytic or homolytic dissociation [89,90], and direct interaction of dihydrogen with the metal [35,115]. Oxidative addition, which requires both a vacant site and a lone electron pair, involves an increase in the formal oxidation state of the metal by two units. The oxidative addition of hydrogen has been demonstrated in a number of low-valent d^8 transition metal complexes. Heterolytic dissociation is known for a variety of Lewis acid complexes and metal oxides and is facilitated by the presence of a base to stabilize the proton liberated [90]. Homolytic dissociation normally accompanies the chemisorption of hydrogen on metal surfaces. The direct interaction of H_2 with metal has been proposed more recently. It has been proposed that for d^0 metals with no acceptable higher oxidation states, oxidative addition is unlikely and dihydrogen can directly interact with the metal via a vacant orbital without net oxidation of that metal. Such reactions show a first-order dependence on $[H_2]$. Ligands that donate electrons (Cl, alkoxy) diminish the activity of metal toward hydrogenation. The recent isolation of a true complex between a Mo (O) and dihydrogen and its structural elucidation lends further credence to this process of hydrogen activation [116].

It is therefore reasonable to believe that such a process also operates during the hydrogenation of olefins with groups IVA and VA metal salts in conjunction with alkylaluminums as well as hydrogenation of the metal-polymer bond. The key steps in these reactions are



$$\mathrm{R\text{-}Mx_{n-1} + H_2 \rightleftharpoons \underset{H\quad H}{R\text{-}Mx_{n-1}} \rightarrow HMx_{n-1} + RH} \qquad (13)$$

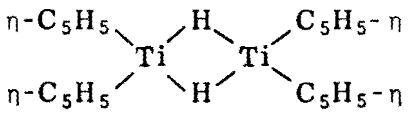


$$\mathrm{Pn\text{-}Mx_{n-1} + H_2 \rightleftharpoons \underset{H\quad H}{Pn\text{-}Mx_{n-1}} \rightarrow HMx_{n-1} + PnH} \qquad (14)$$

where R is an alkyl and Pn a polymer chain.

The hydrido-metal complexes can further react with an olefin by an insertion reaction. In a few cases the hydrido complexes can be isolated. Bercaw and Brintzinger showed that reaction of solid bis(η-cyclopentadienyl)titanium dimethyl with gaseous hydrogen gave two molecules of methane and an isolable μ-hydrido complex [117]:

$(\eta\text{-}C_5H_5)_2Ti(CH_3)_2 + 2H_2 \rightarrow$



$+ 2CH_4$ (15)

Similarly, reduction of bis(η-cyclopentadienyl)titanium dichloride with a variety of reducing agents gave an intermediate species with a μ-hydrido bridge. This intermediate has been implicated in the reduction of molecular N_2 by low-valent titanium species [118].

V. CONCLUSIONS

The literature information on hydrogen effects in olefin polymerization catalysts is scattered and at times contradictory. Nevertheless, some general conclusions can be drawn. In the case of ethylene polymerization with either a conventional or a high-efficiency titanium-based catalyst system, hydrogen causes a reduction in the polymerization rate. However, in the case of propylene and other higher α-olefins, the literature evidence suggests an increase in catalyst activity with added hydrogen. Our current understanding of the valence states responsible for ethylene and propylene polymerizations suggests

TABLE 9 Value of Exponent n in the Chain-Transfer Equation, Eq. (9)

Olefin	Catalyst	I.I. (%)	n	Refs.
Ethylene	α-$TiCl_3/Et_3Al$	–	0.5	39
	δ-$TiCl_3/Et_3Al$	–	0.35-0.45	43,15
	δ-$TiCl_3/Et_2AlCl$	–	1.0	43,15
	$(\eta$-$C_5H_5)_2ZrCl_2$/aluminoxane	–	1.0	81
	Silica/Mg/$TiCl_4/(i\text{-}Bu)_3Al$	–	1.0	119
Propylene	$TiCl_3/Et_2AlCl$	94	0.9	15
	$TiCl_3/Et_3Al$	64	0.5	15
	$MgCl_2/TiCl_4/Et_3Al$/EB	90.2	0.8/0.7	74
	$MgCl_2/TiCl_4/Et_3Al$	37	0.5	72
	$MgCl_2/TiCl_4$/EB/Et_3Al	70	0.5	75
	$V(acac)_3/Et_2AlCl$	Syndiotactic	1.0	79

that only Ti^{3+} is active for propylene polymerizations, whereas the lower-valence states Ti^{2+} and Ti^{1+} are also active for ethylene polymerizations [24]. It is apparent that the effects of hydrogen on these two centers are distinct. However, the detailed mechanism that leads to activation or deactivation of specific active centers needs to be elucidated further.

The order of reaction with respect to hydrogen, as indicated by the value of exponent n in Eq. (9) as a function of catalyst type, gives further insight into the nature of hydrogen interaction with olefin polymerization catalysts. Literature data are collected in Table 9. Although comparisons should be made with caution, the results indicate that the order of reaction with respect to hydrogen is invariably 0.5 for ethylene or atactic polypropylene; for isotactic polypropylene the value approaches 1.0. Fundamentally different molecular mechanisms seems to operate on different sites of the catalyst. Sites responsible for polymerization of ethylene and nonspecific polymerization of propylene appear to have a similar interaction with hydrogen, which is distinctly different from its interaction with stereospecific sites. The mechanism proposed by Keii and co-workers [75] appears conceptually plausible, wherein a catalyst with two vacant sites can dissociatively chemisorb hydrogen by a homolytic mechanism ($n = 0.5$), whereas a center possessing only one vacant site can interact with molecular hydrogen ($n = 1.0$). Ti^{3+} (d^2s^1), with one low-energy vacant orbital and responsible for isospecific propagation, appears to directly interact with molecular hydrogen [115], whereas lower-valent Ti^{2+} or Ti^{1+} (d^2 or d^1), with more than one easily accessible vacant orbital, interacts with hydrogen by a dissociative mechanism. Whether an oxidative addition or a simple homolytic dissociation process is involved cannot be answered at the moment.

With homogeneous catalysts, both for ethylene and propylene polymerizations, hydrogen reduces the polymerization rate and shows a reaction order of 1.0 with respect to H_2. Although the data are very limited, it appears that in these cases direct interaction of molecular hydrogen with the metal center (possibly in its highest valence state, d^0) is the predominant mechanism. The data available with organochromium catalysts are too few to draw any general conclusions at the present time.

It thus appears that all the mechanisms proposed for hydrogen interaction on transition metals, namely, oxidative addition, homolytic dissociation, and direct interaction of molecular hydrogen, have a role to play in determining the nature of hydrogen effects in olefin polymerization catalysts. The fact that hydrogen can respond selectively and specifically to different polymerization centers point out to its applicability as a probe for the nature of active centers. This feature of hydrogen effects in olefin polymerization catalysts, which has not been explicitly recognized in the literature, is both intriguing and alluring.

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