Review

Ziegler-type hydrogenation catalysts made from group 8–10 transition metal precatalysts and AlR₃ cocatalysts: A critical review of the literature

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ABSTRACT

Ziegler-type hydrogenation catalysts (group 8–10 transition metal precatalysts plus AlR₃ cocatalysts) are one of the most important families of industrial hydrogenation catalysts, especially for polymer hydrogenation. Despite their ∼40 year history of industrial use, there is a need for improved fundamental understanding in order to make further, rationally directed improvements in these catalysts. This review examines the existing literature on Ziegler-type hydrogenation catalysts, specifically: (i) the variables important to catalyst synthesis, (ii) the catalyst formation reaction mechanism, (iii) the compositional and structural nature of the active catalyst species, and (iv) the mechanism of catalytic hydrogenation. This review also (v) discusses the current approaches to the homogeneous versus heterogeneous catalysis question, with the goal of identifying if Ziegler-type hydrogenation catalysts are homogeneous (e.g., monometallic) versus heterogeneous (e.g., nanoclusters) as the true catalyst(s). A summary of the main insights from each section of the review is also given.

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1. Introduction

In 1953, while studying the polymerization of ethylene using trialkylaluminum (AlR$_3$), Ziegler and co-workers [1–5] discovered the "nickel effect". When one experiment gave a majority of butene instead of the expected higher molecular weight polyethylene, a search for the cause of this unanticipated result revealed that small amounts of residual nickel salts, mostly Ni(acac)$_2$, were present from having cleaned the metal autoclave with sulfuric acid. These nickel salts had reacted with AlEt$_3$ to cause the observed change in catalysis, and the phenomenon was therefore termed the "nickel effect" [4]. These and other investigations into catalysts and polymerization products led to the 1963 Nobel Prize shared by Karl Ziegler and Giulio Natta [5]. The industrial and technological potential of Ziegler–Natta[1] catalysts was subsequently realized with remarkable speed [5]. Interest in variations on these catalysts for their potential use in *hydrogenation, particularly for polymer hydrogenation*, was considerable (Appendix C, Table C.1), and began in the early 1960s [2,6].

1.1. Polymer hydrogenation

Diene polymers such as polyisoprene and polybutadiene, or styrenic block copolymers (SBCs, Scheme 1) that contain polyisoprene or polybutadiene blocks, have multiple commercial applications [6]. They possess the desired physical properties of high strength, wide range of hardness, and ease of processing. The olefins in these polymers allow them to undergo post-polymerization modification (including crosslinking, isomerization, cyclization, and hydrogenation) to create new polymers possessing desired physical and chemical properties [7]. Of the various desired types of modifications possible, hydrogenation is arguably the most important [6]. The primary purpose of polymer hydrogenation is to make the resultant polymer more resistant to the deleterious effects of thermal, oxidative, and ultraviolet radiation exposure. A main pathway for degradation of polymers containing olefinic groups occurs by autoxidation of allylic positions in the polymer to allylic –OOH groups and subsequent oxidation products [8]. Non-hydrogenated SBCs with their unsaturated olefinic midblock regions are prone to these effects.

SBCs were first produced in the early 1960s by Shell Chemical Co. with the trade name KRATON^{TM} polymers [9]. Roughly one decade later, hydrogenated SBCs with improved thermal and oxidative stability were also being produced (see Appendix C, Table C.1). Without selective hydrogenation of the olefinic blocks of SBCs, the polymers become yellow, brittle, and of little use in many applications where exposure to heat, air, and light are unavoidable. Hydrogenated SBCs would have found wider application shortly after their introduction were it not for their relatively high cost due to the extra expense of the hydrogenation step [6]. Development of more economically favorable catalytic hydrogenation processes has, and continues to, alleviate this added expense. The use of homogeneous (soluble)[2] [10–19] hydrogenation catalysts has helped by allowing for more complete polymer hydrogenation [6]. Ziegler-type hydrogenation catalysts, the focus of this review, are one of the most important families of soluble catalyst commonly used for the purpose of polymer hydrogenation. Consequently, the timeline for the industrial development of Ziegler-type hydrogenation catalysts mirrors that of hydrogenated styrenic block copolymers (SBCs) [9].

1.2. An important distinction: Ziegler-type hydrogenation catalysts versus Ziegler–Natta polymerization catalysts

A broad definition of Ziegler–Natta catalysts includes any catalyst formed by reaction between a transition metal compound precatalyst and a group 1, 2, 13 or 14 alkyl or aryl halide cocatalyst [6,20,21]. It is important to make a distinction between the late-metal *Ziegler-type hydrogenation catalysts* of interest herein versus the currently popular *Ziegler–Natta polymerization catalysts*. Classic Ziegler–Natta olefin polymerization catalysts are formed by the reaction between early metals such as TiCl$_3$ plus Et$_2$AlCl and are heterogeneous catalysts with active sites on TiCl$_3$ crystallites [20,22]. Homogeneous variants of Ziegler–Natta polymerization catalysts have been developed using metallocene compounds such as [Cp$_2$MX$_2$] (Cp = cyclopentadiene, M = Ti or Zr, and X = Cl or CH$_3$) [21–26]. At first these precursors were tested with AlR$_3$ cocatalysts, but the discovery that small amounts of water had an activating effect led to their use with methylalumoxane (MAO), a historically enigmatic cocatalyst formed by incomplete reaction between AlMe$_3$ and water [20,21,26–35]. Metallocene compounds of early transition metals dominate the field of homogeneous Ziegler–Natta polymerization catalysis, although rare-earth metals have been used as well [21,22,36]. The bulk of research on Ziegler–Natta catalysts has been focused on *polymerization*; the term "*Ziegler–Natta catalyst*" is, therefore, practically synonymous with "*polymerization catalyst*" [5,20].

However, herein we consider a different type of Ziegler-based catalyst made from non-zero-valent group 8–10 transition metal (M) precatalysts plus AlR$_3$ cocatalysts, and used for hydrogenations. Therefore, for the purposes of this review, the term "Ziegler-type *hydrogenation* catalysts" will be reserved for catalysts prepared from group 8–10 transition metals plus AlR$_3$. Such Ziegler-type catalysts have found wide use [37], including the hydrogenation [38] of a variety of compounds such as olefins, aromatics [2,39], and diene-based polymers as already mentioned [6,9]. The catalysts most commonly used for such industrial hydrogenation reactions

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[1] Early on, Karl Ziegler [5] referred to these catalysts generally as "organometallic mixed catalysts," and preferred the specific title "Mülheim catalysts" because of where the original work was done. Guilio Natta named them Ziegler catalysts [1,5]. They are usually now called Ziegler–Natta catalysts in the case of polymerization (as opposed to hydrogenation) catalysts.

[2] See the references listed [10–19] for a more in-depth discussion of the terminology of "heterogeneous versus homogeneous" catalysts, and the problem of distinguishing between the two. Briefly, the classic use of the terms heterogeneous and homogeneous is in reference to the phase of catalyst and substrate. If the substrate is in solution, as is typical for hydrogenation reactions such as polymer hydrogenation, a homogeneous catalyst would be soluble whereas a heterogeneous catalyst would not. However, the true catalytically active species in catalyst systems formed of a transition metal complex under reducing conditions may be soluble metal complexes, films, powders, or nanoscale colloids formed in situ [10]. The latter is soluble, but it shares characteristics with heterogeneous catalysts due to the heterogeneity in its active sites [11]. Such a catalyst is also sometimes called "micro-heterogeneous" [19]. For the sake of clarity in this review, the terms "soluble" and "insoluble" will hereafter refer to the phase of the catalyst. The terms "homogeneous" and "heterogeneous" will refer to whether the catalyst species has, respectively, only one or multiple types of active sites [16].
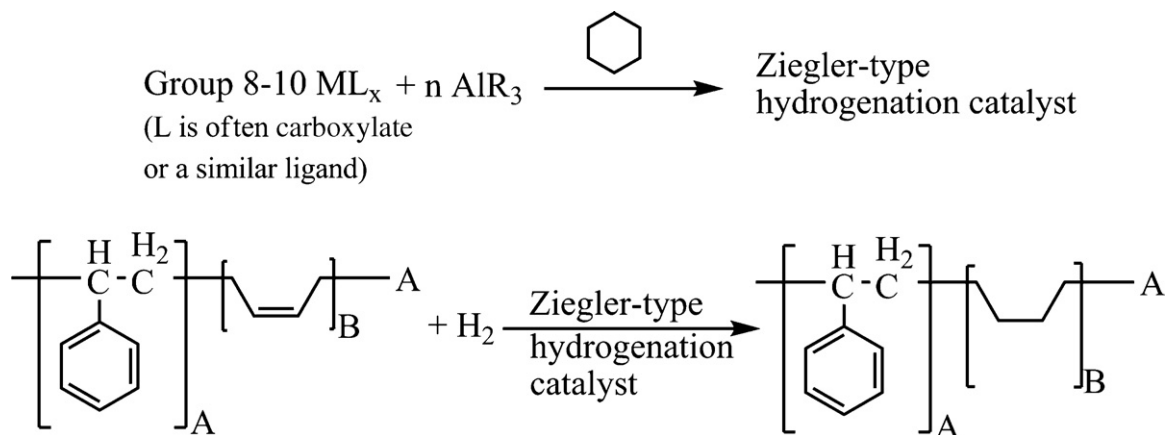
Scheme 1. A Ziegler-type hydrogenation catalyst is formed by combination of a group 8–10 transition metal precatalyst and a trialkylaluminum cocatalyst in a hydrocarbon solvent. Ziegler-type hydrogenation catalysts are employed for the hydrogenation of olefins, aromatics, and polymers, for example the industrially important process of selective styrenic block copolymer (SBC) hydrogenation shown here. Ziegler–Natta or other *polymerization* catalysts are *not* a subject of this review.

are derived from first row, group 8–10 transition metal compounds [6,9]. The most frequently encountered are Co or Ni chelate compounds such as the divalent acetylacetonate (acac) or carboxylate salts, combined with AlR_3 cocatalysts. It is reasonable to suspect differences between this family of late transition metal Ziegler-type hydrogenation catalysts and the broader family of Ziegler–Natta catalysts based on early, high-valent transition metals [23,34], others having previously noted that the nature of these catalysts "probably is different when nickel salts, for instance, are replaced by titanium complexes or when $AlEtCl_2$ is substituted for $AlEt_3$" [40]. Furthermore, we have largely excluded from discussion herein those systems which contain additives or ligands that coordinate through P or N atoms such as PPh_3 or $[(CH_3)_2N]_3PO$ [41–45]. Our focus herein is on what is understood, and especially on what remains unknown, about *Ziegler-type hydrogenation catalysts* based on a careful, critical examination of the existing literature.

1.3. Overview of the main sections of this review

Despite the history of the industrial application of Ziegler-type hydrogenation catalysts, opportunities remain for further improvements in hydrogenation rates, selectivity, stability, and applicability in hydrogenation of a wider range of materials [2,6,46]. Surprisingly little fundamental understanding of Ziegler-type hydrogenation catalysts exists [9,37]. Increased fundamental understanding of Ziegler-type hydrogenation catalysts would allow for *rationally-directed* improvements [9,37,47,48]. Consequently, increased knowledge of Ziegler-type hydrogenation catalysts is highly desirable [9,37].

Published research papers seeking greater knowledge of Ziegler-type hydrogenation catalysts have generally investigated one or more of four basic issues: (i) the variables important to catalyst synthesis and their effect on catalyst properties, particularly the catalyst's hydrogenation activity; (ii) the reaction between the transition metal precatalyst and cocatalyst components; (iii) the compositional and structural nature of the active catalyst species; and (iv) the postulated mechanism of catalytic hydrogenation. Our examination of the literature in this review is organized according to these four basic categories.

The first section of this review examines the *effects of variables* in the preparation of Ziegler-type hydrogenation catalysts, especially in terms of how they influence the resulting catalyst activity. The most important variables of catalyst preparation appear to be the: (i) identities of the transition metal precatalyst and the AlR_3 cocatalyst; (ii) ratio of these two components and the role of impurities, particularly H_2O; (iii) solvent; (iv) identity of the substrate;

(v) details of component addition (such as order and rate, presence of substrate, atmosphere, and temperature); and (vi) aging of the prepared catalyst before use in hydrogenation reactions.

The second section of this review evaluates what is known about the reaction between the catalyst precursors, and whether the resulting catalysts are homogeneous (e.g., single metal organometallics) or heterogeneous (e.g., nanoclusters). Specific questions in this regard include: (i) how are the catalysts formed?; (ii) how many transition metal atoms constitute the active catalyst species?; (iii) what are their oxidation states?; (iv) what is the form and role of the cocatalyst?; and (v) what is known about the mechanism of the catalytic hydrogenations? This second section which follows is divided into two parts; studies that support a homogeneous catalyst hypothesis are examined first, and those that support a heterogeneous catalyst hypothesis are examined second. Many authors supporting a heterogeneous catalyst hypothesis have claimed formation of nanoclusters, for which we herein coin the term "Ziegler nanoclusters" [13,49,50].[3]

The third section of this review is a discussion of the future outlook for additional fundamental studies of Ziegler-type hydrogenation catalysts. Possible reasons why the desired depth of understanding of Ziegler-type hydrogenation catalysts has remained elusive—despite several decades of research on the topic—are presented, along with thoughts about and what can potentially be done to improve this situation and provide the desired, additional knowledge.

2. Studies of Ziegler-type hydrogenation catalysts

2.1. Effect of preparation variables on Ziegler-type hydrogenation catalysts

Because of their rapid adoption by industry [5], research in Ziegler-type hydrogenation catalysts initially focused on optimization of the processes for which they were used [47,48]. This included the catalyst synthesis step, for which a wide variety of possible starting components, methods, and conditions exists. Many observations on how variables of catalyst synthesis affected the activity of the resulting hydrogenation catalysts were made early on. Table 1 contains a concise summary of the relevant literature, and gives an overview of the breadth of systems explored.

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[3] See the references listed for a definition of the distinction between modern nanoclusters and traditional colloids [3,49,50].

Table 1
Catalyst preparation variables.

Authors	Catalyst systems	Results	Ref.
Sloan, Matlack, and Breslow (1963)	Acac salts of Fe(III), Co(II and III), Ni(II), Ru(III), or Pd(II) (also Cr(III), Cu(II), Mn(II and III), Mo(VI), V(V), or Zr(IV)) + 1.2–2.6 Al(i-Bu)$_3$, AlH(i-Bu)$_2$, or AlEt$_3$	Most active: Co(III) > Fe(III) > Cr(III). Cu(II) salts fail to form effective hydrogenation catalysts. Use of AlClEt$_2$, BEt$_3$ SnEt$_4$, P(n-Bu)$_3$, ZnEt$_2$, or Mg(n-Bu)Br as cocatalysts results in either no reaction or an inactive ppt. at 30–50 °C and 3.7 atm H$_2$. Ketones, aldehydes, nitriles, nitro compounds, azo compounds, and esters are *not* hydrogenated.	[57]
Lapporte and Schuett (1963)	Ni(2-ethylhexanoate)$_2$ + AlEt$_3$, also Co, Fe, Cr, or Cu salts + AlEt$_3$ for arene hydrogenation	The highest catalytic activity and amount of gas evolution (> 95% ethane) is at Al/Ni = 3–4. The activity for benzene hydrogenation decreases according to Ni ≥ Co > Fe > Cr > Cu. Catalytic activity is highly dependent on the anion of the Ni(II) precursor; carboxylates, especially 2-ethylhexanoate is good, but halides are poor. Benzene hydrogenation is poisoned by PPh$_3$.	[39]
Kroll (1969)	Fe(acac)$_3$, Co(acac)$_2$, or Ni(acac)$_2$ + Al(i-Bu)$_3$ or a p-dioxane adduct of Al(i-Bu)$_3$	Relative catalytic activities are Co > Fe > Ni. The highest activities are achieved at Al/M = 6 for M(II), 8–10 for Fe(III). It is very difficult to properly adjust the Al/M ratio due to impurities such as oxygen and H$_2$O always present, even after careful purification. The poisoning action of excess Al cocatalyst can be overcome by making a p-dioxane adduct of Al(i-Bu)$_3$ before catalyst synthesis. Improved kinetics are observed when the catalyst is allowed to age overnight.	[75]
Lapporte (1969)	2-Ethylhexanoate salts of Ni, Co, Fe, Cr + AlEt$_3$	Activity order: Ni > Co > Fe > Cr. The anion of the Ni salt has a significant effect on the activity: 2-ethylhexanoate > benzoate > acac > acetate > chloride, mirroring solubility. Activities are equal for Ni(2-ethylhexanoate)$_2$ + AlEt$_3$, Al(i-Bu)$_3$, or Al(C$_6$H$_{13}$)$_3$ catalysts. The highest catalytic activity is observed when Al/M = 3–4 for M(II). The olefin affects the hydrogenation rate: monosubstituted > unsymmetrically disubstituted > cyclic > symmetrically disubstituted. Nitrobenzene and PPh$_3$ act as catalyst poisons.	[58]
Shmidt et al. (1970)	Co(C$_{17}$H$_{35}$CO$_2$)$_2$, Fe(C$_5$H$_7$O$_2$)$_2$, Ni(C$_5$H$_7$O$_2$)$_2$, Ni(C$_6$H$_6$NO)$_2$, Ni(C$_7$H$_6$NO$_2$)$_2$, Ni(C$_9$H$_6$NO)$_2$, Ni(C$_4$H$_7$N$_2$O$_2$)$_2$, or Ni(NO$_3$)$_2$[P(C$_6$H$_5$)$_3$]$_2$ (also Ti(C$_5$H$_5$)$_2$Cl$_2$ or Ti(OCH(CH$_3$)$_2$)$_4$) + AlEt$_3$	Activity as influenced by precatalyst anion: acac > o-aminophenoxide > salicylaldoximate > 8-quinolinoxide > dimethylglyoximate, the same as the decreasing order of the ligand dissociation equilibrium constant of the precatalyst. Catalytic activity is improved if the AlEt$_3$ is "added to the precatalyst in the absence of the acetylenic hydrocarbon, and if the catalyst solution absorbs hydrogen beforehand." Various ligands are added to the prepared catalyst solutions.	[42]
Falk (1971)	Co(2-ethylhexanoate)$_2$ or Ni(2-ethylhexanoate)$_2$ + AlEt$_3$ or (n-Bu)Li, cyclopentyllithium, phenyllithium, ethyllithium, or (sec-Bu)Li	Catalyst prepared by slowly adding (over 90 min) the Co or Ni solution to a solution of AlEt$_3$ in a N$_2$ atmosphere. Slight impurities affect activity and change the Al or Li(alkyl)/M ratios optimal for selectivity. Li alkyls are generally inferior to AlEt$_3$ as cocatalyst. Catalyst solutions do not deteriorate after being stored for several months.	[79]
Esselin et al. (1986)	Ni(acac)$_2$, Fe(acac)$_3$, Ni(octoate)$_2$, or Co(octoate)$_2$ + 1, 3, or 6 AlEt$_3$ or GaEt$_3$	Catalytic activity trends: Ni > Fe, and AlEt$_3$ > GaEt$_3$. Optimal activity occurs at Al/M = 3 for Ni catalysts and at Al/M = 6 for Fe catalysts. Catalyst preparation is done at room temperature. Ni(acac)$_2$·2H$_2$O dried to ≥80% to give, on average, (Ni(acac)$_2$)$_3$.	[40]
Reguli and Staško (1987)	Ni(3,5-diisopropylsalicylate)$_2$, Ni(acac)$_2$, Ni(stearate)$_2$, or Ni(benzohydroxamate)$_2$ + 1, 2, 3, 4, 5, or 6 AlEt$_3$, Al(i-Bu)$_3$ or LiBu.	Catalytic activity by precatalyst anion: diisopropylsalicylate > acac > stearate > benzohydroxamate, which correlates well with the solubility sequence of corresponding Ni salts (activity is also dependent on the solvent). The Al/M ratio strongly influences activity, the optimum is 1.5–4 depending on the catalyst precursors. Traces of O-containing compounds, especially those with acidic H, poison the catalysis, but could be partially offset by additional cocatalyst. Ni precipitates in the presence of aromatic solvents resulting in loss of catalytic activity. Order of addition: solvent, precatalyst, and then cocatalyst. Catalyst was prepared both in the presence and absence of cyclohexene substrate; the presence of cyclohexene increases the resulting catalytic activity when AlEt$_3$ or LiBu are the cocatalysts used, but the opposite effect is observed with Al(i-Bu)$_3$. Temperatures from 20 to 45 °C during the catalyst preparation reaction have no effect on optimal Al/M. The time of catalyst aging before use in hydrogenation, and Ar versus H$_2$ preparation atmosphere have no influence on activity.	[70]
Alvanipour and Kispert (1988)	Co(stearate)$_2$ + 2 AlEt$_3$	Naphthalene, quinoline, isoquinoline, 6-methylquinoline and 2-methylquinoline can be hydrogenated with the catalyst employed, but dibenzothiophene nitroquinolines and 4-chloro-2-methylquinoline cannot. Compounds containing sulfur, nitro, and chlorine groups act as poisons.	[67]

Table 1 (*Continued*)

Authors	Catalyst systems	Results	Ref.
Barrault et al. (1994)	$Co(acac)_2$ + 0.5, 1.0, or 1.5 $AlEt_3$	Higher Al/Co ratios give increased activity and lower selectivity. The catalyst is ∼3 times more active for the hydrogenation of cinnamaldehyde than for 2-pentyl-2-nonenal. For 2-pentyl-2-nonenal, the catalyst is more active, but less selective at a given conversion when pre-treated with CO_2/H_2 (syngas) than with just H_2. "The final catalytic properties. . . depend on the activation process."	[37]
James et al. (1998)	$Ni(OAc)_2$ + 0.5 $Zn(OAc)_2$ + 4.5 $AlEt_3$	Hydrogenation of 2-methoxy-4-propylphenol with the catalyst at 90 °C under 50 atm H_2 for 24 h gives a 65.2% conversion with 92.2% of the product being 2-methoxy-4-propylcyclohexanol. The catalyst is poisoned by Hg(0).	[84]
Šabata and Hetflejš (2002)	$Ni(2\text{-ethylhexanoate})_2$ or $Ni(acac)_2$ + "Li-diene," *n*-BuLi, or $AlEt_3$	Catalytic activity trends: $Ni(2\text{-ethylhexanoate})_2 > Ni(acac)_2$, and "Li-diene" > BuLi, or $AlEt_3$. Catalytic activity depends on Li or Al/M ratio, temperature, and particular method used in catalyst formation, the optimal being: Li/Ni is 8–10, cocatalyst added rapidly to the Ni compound at 50 °C, and kept at that temperature for 10 min before allowing to cool. Batches of catalyst prepared fresh daily to avoid changes in activity due to aging.	[69]
Nindakova et al. (2006)	$Co(acac)_2 \cdot nH_2O$, $n = 0$, 0.5, or 1.5; or $Co(acac)_3$ + 2, 4, 6, 8, 12, or 16 $AlEt_3$	$AlEt_3$ added to the Co salt dropwise under an atmosphere of H_2 before the introduction of substrate. Using $Co(acac)_2 \cdot nH_2O$, the optimum Al/Co ratio depends on n: $n = 0$, Al/Co = 3.5–4; $n = 0.5$, Al/Co = 8–10. The $n = 0.5$ catalyst has a higher hydrogenation activity than the $n = 0$ catalyst. As [Co] decreases the optimal Al/Co ratio increases. Higher activities are achieved in heptane solvent than in toluene.	[19]
Belykh et al. (2006)	$Pd(acac)_2$ + 2, 4, 6, 8, 10, 15, or 16 $AlEt_3$	$AlEt_3$ is added dropwise under flowing H_2 to $Pd(acac)_2$ in the absence of substrate; the optimal Al/Pd is 4. When H_2O or O_2 traces are present, no decrease in activity at high Al/Pd is observed up to Al/Pd = 80. Use of modifiers, such as PPh_3, $OPPh_3$, ethanol, the order of component addition, the substrate used, and catalyst loading affect the catalyst activity. The effect of modifiers is dependent on Al/Pd.	[81,114]
Finke and co-workers (2009)	$[(1,5\text{-COD})Ir(\mu\text{-}O_2C_8H_{15})]_2$, $Co(neodecanoate)_2$, or $Ni(2\text{-ethylhexanoate})_2$ + $AlEt_3$	At room temperature, and under an N_2 atmosphere, $AlEt_3$ in cyclohexane is added to a cyclohexane solution of the transition metal precatalyst with 1000 rpm stirring in the absence of olefinic substrate. However, *simultaneous* addition of $Co(neodecanoate)_2$ and $AlEt_3$, Al/Co = 2, results in higher hydrogenation activity. Alternatively, the hydrogenation activity of the catalyst is independent of the order of addition for Al/Co = 3. The optimal Al/Ir is 1, Al/Ni is 2, and Al/ Co is from 2 to 4. $AlEt_3$ was added rapidly to the Ir precatalyst and at rate of 1 drop every 5 s for the Ni precatalyst. Rigorous drying of glassware and solvents was performed throughout these studies; however, for the Co system intentionally added H_2O decreases hydrogenation activity. The following catalyst preparation variables have, at most, minor effects on hydrogenation activity of the Co system: (i) $AlEt_3$ versus $Al(t\text{-}Bu)_3$ cocatalyst; (ii) temperature during mixing of catalyst components (e.g., 30 °C vs. 60 °C); (iii) individual versus batch preparation; and (iv) use of neat $AlEt_3$ added at a slower rate.	[52–56]

Catalyst preparation variables have not been exhaustively investigated despite their importance. The paucity of "systematic order" in the literature [51][4] (i.e., which catalyst synthesis variables influence catalytic properties for which specific systems and why) is apparent in the many systems explored and the apparent contradictions among some of the findings (vide infra). This was noted recently by Shmidt and co-workers [19]: "contradictory published data on the interaction of catalytic system components do not allow us to interpret reliably the general concepts of the effect of the composition of the system on the properties of catalysts." Therefore, gaining a better understanding of how variables in catalyst preparation affect the resulting catalytic properties is the first major goal of the field of Ziegler-type hydrogenation catalysts.

2.1.1. Identities of the precursors

The first obvious variable in the synthesis of Ziegler-type hydrogenation catalysts is the identity of the specific transition metal precatalyst and AlR_3 cocatalyst employed. As expected, industry favors use of the inexpensive first row metals (Fe, Co, and Ni) rather than the more expensive second and third row metals in the same groups (i.e., Ru and Os, Rh and Ir, Pd and Pt) [2,6,22]. Early studies surveyed potential catalyst precursors to ascertain which were promising as useful catalysts resulting in similar sequences for the most active metals, Ni > Co > Fe > Cr > Cu [57,58]. Also, the catalytic activities of *soluble* Ni and Co Ziegler-type hydrogenation catalysts were found to be generally superior to pre-activated, *supported* Ni or Raney Co catalysts [58]. There is a lack of agreement about whether Ni or Co systems are the most active for polymer hydrogenation, a discrepancy caused at least in part by a lack of standardization in polymer feed quality [46], differences in properties of precursor solutions such as water content or level of acidity (which, of course, readily react with the AlR_3 component, thereby indirectly influencing catalytic activity) [40], or both. Whether the Ni and

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[4] We have found, paraphrasing what A.K. Galwey has written about a different area [51], that there is: little ability to carry out inductive prediction across ostensibly similar Ziegler-type hydrogenation catalyst systems, few established trends on which to expand, and therefore no coherent and generalized theory.

Co catalysts favored by industry have the absolute best activity, selectivity, and lifetime is arguable; however, the fact that they are industrially favored signifies that they likely have an advantageous balance of low cost, ease of synthesis, and desirable catalytic properties.

Another aspect of the precursor identity is the anion in the transition metal salt. The literature has included claims of the use of alkoxides [59–63] or halides [43–45,64]. However, a catalyst poisoning effect of halides has also been reported [65–67]. A few patents have claimed the usefulness of sulfur-containing anions such as sulfonate, salts of sulfur-containing acids [60,68], $M(SO_x)_n$ (and partial esters thereof), and metal salts of sulfonic acids $M(RSO_3)_n$ [62]; however, those patents do not report the control of comparing the activity of catalysts containing S-element anions to the activities of those made from the more common, generally favored anions acac and carboxylate. Precatalyst compounds with inexpensive 2-ethylhexanoate ligands, as well as the catalysts made from them, tend to be soluble in the hydrocarbon solvents typically used. In one study, the anion in Ni salt precatalysts had a significant effect on the resulting catalytic activity in a sequence that corresponded to the solubility of the precatalysts: 2-ethylhexanoate > benzoate > acac > acetate > chloride [58]. Similar findings correlating precursor solubility and catalytic activity have been made by others [69,70]. However, whether the increased catalytic activity is the influence of solubility, a result of the formation of different amounts of catalyst, or due to catalyst species with different activities, is not clear.

The choice of alkyls in the AlR_3 cocatalyst has also been of much interest. In a 1968 patent, Kroll [64] stated that it was generally agreed, even as of 1968, that the choice of cocatalyst does affect the catalyst activity. Many studies appear to favor AlR_3 with relatively short alkyl chains such as $AlMe_3$ [71], $AlEt_3$ [46,63,44,72–74], or $Al(i\text{-Bu})_3$ [57,70,75], but use of triarylaluminum [72,76,77] has also been reported. Lapporte [58] found with $Ni(2\text{-ethylhexanoate})_2$ that $AlEt_3$, $Al(i\text{-Bu})_3$, and $Al(C_6H_{13})_3$ were equivalent in the resulting catalytic activity of hydrogenation of a variety of substrates and at a variety of conditions. Some patents have described the preferred cocatalyst as $R_{3-n}AlH_n$ where $n = 0–2$ [59,45,65,66]. In general, the preferred cocatalyst appears to vary with the particular system; therefore, the need remains for studies elucidating the roles of the cocatalyst in both the catalyst formation and substrate hydrogenation processes.

2.1.2. Molar ratio of the precursor components (precatalyst and cocatalyst) and the role of impurities, particularly H_2O

Several reports claim that the Al/M ratio (M = the transition metal of the precatalyst) was a key factor affecting the resulting catalyst [70,69,63]. It has been noted that when too little cocatalyst was used, it failed to adequately "activate" the catalyst, resulting in decreased activity [40]. On the other hand, it was also reported that when *too much* AlR_3 cocatalyst was used, it acted as a catalyst poison [75]. Most reports agree that there is an optimum Al/M. In general, the optimum Al/M seems to be highly dependent on the specific system used [57,78], and ranges from 1.5 to 4 are typical, at least with a Ni precatalyst [39,70].

The most important difficulty regarding optimization of Al/M appears to have been the presence of contaminants, especially those containing oxygen atoms, acidic protons, or both [75,79]. The most ubiquitous of these is almost surely H_2O. Despite the occasional claim that oxygen-containing species such as water were *not* important considerations in catalyst preparation [59,77], for most systems, water and other such species are generally thought to have a significant influence. This is as expected for a system employing a water-sensitive, AlR_3 cocatalyst [80].

The activity of Ziegler-type hydrogenation catalyst systems are often reduced by oxygen-containing contaminants, with water being the prime example [40,63,70,72]. Reguli and Staško [70] found that this poisoning effect could be offset by the addition of more cocatalyst, the additional AlR_3 ostensibly acting to scavenge contaminants. Esselin and co-workers opted to use acac salts instead of $M(\text{"octoate"})_2$ (M is Ni or Co) because solubilization of the "octoate" compounds required a variable amount of free acid in the precatalyst solution (the term "octoate" is industry jargon for a C_8 carboxylate, frequently 2-ethylhexanoate) [40]. Additional potential contaminants are residual polymerization catalyst and excess alcohol from termination of the polymerization reaction [65,73]. Overall, these studies report the effects of O-containing contaminants as detrimental to the activity of the Ziegler-type hydrogenation catalyst systems used.

However, in other Ziegler-type systems the reaction of oxygen-containing species with the cocatalyst has been exploited to *improve* the catalytic system. This has been done in two ways: (i) by simply stopping the poisoning effect of excess cocatalyst [64,75,77,81], or (ii) by actually increasing the activity of the resulting catalyst [19,61,78]. In US Patent 3,937,759, Baumgartner and Balas claim that addition of one mole of $AlEt_3$ per mole of Ni to an *active* hydrogenation reaction will halt the reaction. This effect was found to be reversible by addition of a sufficient amount of alcohol to react away the $AlEt_3$ that had been added to stop the reaction [82]. In such cases where water is used, one might expect a reaction between H_2O and the AlR_3 compound to form Al–O–Al bonded compounds known as alumoxanes [20,34,80]. Hoxmeier et al. [62], claimed that a catalyst prepared with alumoxanes was useful for hydrogenation reactions. However, the complicated effects of the interaction of the catalyst components with H_2O on the resulting catalyst properties is an important, yet still incompletely understood, aspect of Ziegler-type hydrogenation catalysts, effects that depend on the AlR_3/M ratio of the catalyst, as well as the amount of H_2O (or ROH, etc.). The effects of H_2O, ROH, and other such compounds on Ziegler-type hydrogenation catalysts is another area that begs for a more detailed and fundamental understanding, one using carefully controlled conditions beginning from a definitively characterized precatalyst.

2.1.3. Solvent

Studies of Ziegler-type hydrogenation catalysts have tended to use inert hydrocarbons, mostly alkanes such as cyclohexane [70] or heptane [57], but also aromatic solvents like benzene, toluene, or xylenes [70]. Inert hydrocarbons are commonly used because they lack lone-pair electrons that would be reactive with the Lewis acidic AlR_3 cocatalyst [58,70,72]. The relative merits of such solvents have elicited only a little discussion in the literature. Catalytic activity is very dependent on solvent in the study by Reguli and Staško [70]; their NiL_2 plus AlR_3 or LiBu catalysts became less active in the order: cyclohexane > xylene > toluene > benzene > chlorobenzene. The aromatic solvents resulted in an inactive Ni precipitate being formed [70]. Shmidt and co-workers [19] reported that with their $Co(acac)_3$ plus 50 $AlEt_3$ catalyst, activity for the hydrogenation of 1-hexene was 17-fold higher in heptane instead of toluene. However, Sloan et al. [57] reported the hydrogenation of a wide variety of substrates with a wide range of catalysts in solutions of heptane or toluene, and made no mention of differences in hydrogenation rates or formation of precipitates based on which solvent was used. It is still unclear exactly how and why such prominent differences are seen with different solvents in some instances, but not others. In short, a further examination of solvents under carefully controlled conditions is another aspect of Ziegler-type hydrogenation catalysts that merits additional attention.

2.1.4. Identity of the hydrogenation substrate

Numerous substrates have been tested with Ziegler-type hydrogenation catalysts, from simple olefins to various polymers, even those with polar, acidic, or oxygen-containing functionalities [58,61,69,76]. However, not all hydrogenation attempts with a variety of substrates have been successful [57,67]. In a 1988 paper, Alvanipour and Kispert hydrogenated naphthalene and some quinolines using a Co(stearate)$_2$ plus AlEt$_3$ catalyst [67]. However, attempts to hydrogenate 4-chloro-2-methylquinoline, nitroquinolines, or dibenzothiophene failed [67]. They believed that substrates containing chloro, nitro, and sulfur groups acted as catalyst poisons by coordinating to the catalyst [67].

In general, and as one might expect, the rate of hydrogenation was found to have some dependence on the identity of the substrate [37]. Several reports revealed a decreasing hydrogenation rate with increasing substitution about the olefinic bond while using a variety of catalysts including Ni(2-ethylhexanoate)$_2$ plus AlEt$_3$ [58], Ni(3,5-diisopropylsalicylate)$_2$ plus Al(i-Bu)$_3$ [70], and a non-Ziegler-type, but related Cr(acac)$_3$ plus Al(i-Bu)$_3$ catalyst [57]. The known exception to this trend was reported by Sloan et al., namely that the diallyl olefin cyclohexene is among the most rapidly hydrogenated olefins [57]. Overall, the catalyst activity is dependent on the identity of the substrate as one might expect. However, the details of the effects seen require further scrutiny and explanation, for example, what rate laws are seen for the different classes of olefins?

2.1.5. Other aspects of catalyst synthesis

The catalyst component addition order, rate of component addition, and whether or not the substrate should be present during catalyst synthesis have been points of concern in the literature. There is wide disagreement on these issues between researchers, and among different systems, as to the effects, if any, of the above-noted variables on catalysis [45,64]. Various reports have stated preferences for: (i) slow addition of the precatalyst solution to the cocatalyst solution [79]; (ii) addition in the opposite order, but still slowly [77]; or (iii) keeping Al/M molar ratios essentially constant during the reaction, either by simultaneous addition or by rapid addition of a solution of the cocatalyst to a solution of the transition metal precatalyst [63]. Likewise, different reports have expressed, oppositely, the benefits of preparing the catalyst in the presence of substrate [68], or in the absence of substrate [62]. In 1987 Reguli and Staško [70] observed that the presence of cyclohexene during the catalyst synthesis reaction increased the hydrogenation activity of the resulting catalyst when AlEt$_3$ or LiBu were used as cocatalysts, but that the presence of cyclohexene inexplicably had the *opposite* effect when Al(i-Bu)$_3$ was employed as the cocatalyst.

Another detail occasionally discussed is the gas present (i.e., N$_2$, Ar, or H$_2$) during catalyst synthesis. Shmidt and co-workers [42] obtained a higher activity if "the catalyst solution absorbs hydrogen beforehand." However, Reguli and Staško [70] found that conducting their Ni(3,5-diisopropylsalicylate)$_2$ plus Al(i-Bu)$_3$ catalyst preparation in an atmosphere of either Ar or H$_2$ ultimately had no influence on the resulting catalyst activity. The question, then, is whether there is something special about using H$_2$ as opposed to the inert gasses N$_2$ or Ar (i.e., whether the key is just to provide an O$_2$ and H$_2$O-free atmosphere, or is H$_2$ acting as a reductant during the catalyst preparation). A subtlety here may be whether one is carrying out reactions in solution under H$_2$ gas with the first row group 8–10 metals versus those with second or third row transition metals, since only the latter are reduced to metal zero compounds under an atmosphere of hydrogen and standard conditions [83].[5] Overall,

it appears that the primary purpose of the atmosphere employed is to ensure conditions free of O$_2$ and oxygen-containing impurities such as H$_2$O. That said, reduction/activation of the catalyst when H$_2$ is used has not been adequately tested via careful control experiments with and without H$_2$ in Ziegler-type hydrogenation catalyst systems.

The temperature of catalyst preparation is another variable occasionally mentioned in the literature [41], with different temperatures often being employed for different systems. For example, temperatures reported for optimal catalyst preparation range from 50 °C (followed by holding the solution at that temperature for 10 min before being allowed to cool [69]), to heating the catalyst after the synthesis reaction at 90 °C under 1 atm of N$_2$ for 2 h [84]. In general, and despite various claims of reaction temperatures that lead to an optimal catalyst, activity as a function of reaction temperature has also not been systematically studied.

The effects that temperature and other variables in catalyst preparation (order and rate of precursor addition, presence of substrate, and atmosphere) have on the activity of the resulting catalysts appear to depend on the individual system used. It is clear that they have not been adequately studied, or even reported in some cases. Additionally, *how* these and other variables influence catalyst activity will not be fully understood without studying how these variables are affecting first (i) the products of the catalyst synthesis reaction (i.e., the composition and structure of the resulting catalyst), and second (ii) the kinetics and mechanism of the catalysis.

2.1.6. Aging of prepared catalyst

Another factor that has garnered mention in the literature as potentially significant for the activity of Ziegler-type catalysts is the aging of prepared catalyst solutions. The issues of whether or not prepared catalyst solutions have a significant "shelf-life" before deactivation or precipitation is related to this topic. It has been noted for some systems that in the catalyst solution, a precipitate often formed if it was stored at a high temperature for long periods of time [68]. Šabata and Hetflejš [69] took the precaution of making fresh batches of catalyst daily to avoid changes in activity due to aging. In contrast, others have allowed the prepared catalyst to age overnight [67,75], claiming that it improved reproducibility of the kinetic experiments [75]. Reguli and Staško reported that the time of catalyst aging before use in hydrogenation had no influence on activity [70]. However, the actual experimental results, including what aging times were examined, were not reported [70]. Conclusions regarding the effects of catalyst aging cannot be drawn from this assortment of results for Ziegler-type hydrogenation catalysts as a group; the outcome is dependent on the individual system, requiring independent optimization of each set of conditions. Without a more detailed understanding of the fundamental chemistry involved, the contradictory results prevent the ability to develop a consistent picture of the phenomenology of Ziegler-type hydrogenation catalyst aging.

2.1.7. Conclusions for the section on catalyst preparation variables

The above survey of variables makes apparent that there are many important details involved in preparation of Ziegler-type hydrogenation catalysts, specifically: the identities of the transition metal precatalyst and the AlR$_3$ cocatalyst; the ratio of these

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[5] Standard reduction potentials (E°, 25 °C, 1 atm) versus SHE in volts for M^{n+} + ne$^-$ ⇌ M, where M is: Fe^{3+}/Fe = −0.037, Fe^{2+}/Fe = −0.447, Co^{2+}/Co = −0.28, Ni^{2+}/Ni = −0.257, Ru^{2+}/Ru = 0.455, Rh^{2+}/Rh = 0.600, Pd^{2+}/Pd = 0.951, Ir^{3+}/Ir = 1.156,

Pt^{2+}/Pt = 1.18, and 2H$^+$/H$_2$ = 0.000. The most commonly used precatalysts of first row group 8–10 transition metals Fe, Co, and Ni therefore have unfavorable potentials for reduction by H$_2$ gas under standard conditions, unlike second and third row transition metals [83]. Hence, if a second or third row transition metal precatalyst was used, pretreatment by even 1 atm of H$_2$ at standard conditions could influence the catalyst formation reaction, at least from a thermodynamic perspective.

two components and the role of impurities, particularly H_2O; the solvent; the identity of the substrate; the details of component addition such as order and rate, presence of substrate, atmosphere, and temperature; and any aging of the prepared catalyst before use in hydrogenation reactions. Furthermore, the question of *how* these variables have the effects they do is an open one. The ability to explain the effects of these variables in catalyst preparation is hampered by the fact that the effects themselves are often dissimilar for ostensibly similar, but ultimately somehow different, systems. Therefore, it is desired to perform studies of the catalysts under conditions that are either optimized, industrially relevant, or both if needed. Since these catalysts are used industrially, and since faster, longer lifetime, and more selective catalysts are always of interest, there is an incentive for additional studies, along with a host of the necessary control experiments—for example, comparing the best or other's catalysts to one's own catalyst, all under identical conditions.

When one considers the obstacles to understanding the effects of all possible variables in Ziegler-type catalyst preparation, it becomes easier to understand why this class of industrial catalysts has not been exhaustively investigated, and why contradictory data exist. Isolation of any single variable for study is difficult because of how many variables there are (*at least* 11), the possibility that additional, still-unidentified variables exist, and the indication [58,70] that many variables may be correlated with one another. A modern systematic and/or combinatorial study holds the potential of identifying superior industrial catalysts, for example.

Furthermore, accurate evaluation of catalyst activity, the indicator most often used for the effect on the catalyst, may be hindered by an H_2 gas-to-solution mass-transfer limitation (MTL) [85–88].[6] The presence of an H_2 gas-to-solution MTL in hydrogenations using Ziegler-type catalysts is especially likely because of their high catalytic activities—indeed, we have routinely run into such MTL issues in our own studies [55,56]. Additionally, when polymers are the substrate, adequate mixing is difficult to achieve in the viscous polymer solutions thereby increasing the chances that kinetics will be dominated by MTL. Despite this, *few studies discussed herein mentioned efforts to avoid MTL kinetics* [41,57,69,75]. It is possible that many of the kinetic results reported for Ziegler-type hydrogenation catalysts are questionable because their studies have fallen victim to MTL effects. Unless specifically ruled out, undetected MTL should be suspected for instances where there is disagreement about whether or not a given variable had any effect on the catalyst properties of a given system. For these reasons, all research, both the patent literature assembled in Appendix C, Table C.1, and other published studies shown in Table 1, should, in our opinion, be viewed with a critical eye and with possible MTL effects in mind.

Importantly, the effects that synthesis variables have on the catalytic properties of Ziegler-type hydrogenation catalysts (e.g., activity), are likely to be closely related to the effects of those variables on the *homogeneous or heterogeneous nature of the catalysts*. When catalyst formation of a non-Ziegler-type hydrogenation catalyst is carried out in situ, "the lesson is that the nature of the true catalyst can change with the reaction conditions" [16]; this may be just as true for Ziegler-type hydrogenation catalysts pre-formed by the addition of AlR_3. Therefore, a way to look for answers as to

how catalyst synthesis variables affect catalytic activity would be to study the composition and structure (i.e., the homogeneous or heterogeneous nature) of the resulting catalysts. Connecting these aspects of Ziegler-type hydrogenation catalysts—namely synthesis variables, catalytic properties, and homogeneous or heterogeneous nature—remains a, if not *the*, significant challenge for the field.

2.2. The nature and mechanism of formation of Ziegler-type hydrogenation catalysts

Because of the desire to make rationally-directed improvements to Ziegler-type hydrogenation catalysts, important topics include: the reaction between the precatalyst and the cocatalyst; the true nature of the active catalyst; and the identity of the cocatalyst species in the resulting catalyst solution. Specifically of interest are the homogeneous or heterogeneous nature of the true catalyst(s), the oxidation state of the transition metal, and the resultant form and role of the initially added, for example AlR_3, cocatalyst species. A detailed mechanism of the reaction between catalyst precursor components is also desired, one that includes the compositions and structures of all intermediate species and the kinetics of constituent elementary steps [89]. However, this level of detail is still unrealized with Ziegler-type hydrogenation catalysts.

As noted above, a main question about Ziegler-type hydrogenation catalysts is whether they are homogeneous (e.g., single metal organometallics) or heterogeneous (e.g., nanoclusters). The patent literature (Appendix C, Table C.1) has given only cursory attention to the topic; uncertainty and disagreement exist [60,77,78]. This is understandable since determining the true nature of a catalyst is a classic, non-trivial problem [16,90]. A generalized methodology for addressing this problem does exist [12,13,15–18], and has been successful at distinguishing between heterogeneous and homogeneous catalysts; it has identified catalysts of both types, even in a system where slight differences in conditions were a deciding factor [17]. One of the main ideas behind this approach is (i) to first address the question of what species are present that could be catalysts—that is, what are the main, resting forms of the (pre)catalyst, and then (ii) to *determine which species contribute to catalysis primarily via kinetic and quantitative poisoning experiments* [12,13,15–18]. In studying Ziegler-type hydrogenation catalyst systems, nearly all workers have struggled to answer the difficult question of what species are present (i.e., what are the products and the catalyst formation reaction stoichiometry?). The needed kinetic and poisoning experiments are only rarely present [57,58]; without definitive kinetic evidence, species identified in the following papers may or may not be related to the actual catalyst(s) [91].[7] In many cases they might be "catalyst reservoir" species that actually are not in the catalytic cycle and therefore, may even detract from the overall rate. The classic example of this is the "catalyst reservoir" of five observable species identified in Halpern's studies of Wilkinson's hydrogenation (pre)catalyst; only the spectroscopically invisible, 16-electron $RhClL_2$(solvent) and subsequent species contribute to the observed hydrogenation catalysis [10].

2.2.1. The "Ziegler-type catalysts are homogeneous" hypothesis
2.2.1.1. *Systems investigated by Wilke and co-workers [4]: Ni(acac)$_2$ plus AlMe$_3$, AlEt$_3$, or Al(i-Bu)$_3$.* When Karl Ziegler and co-workers first discovered the "Ni effect" in 1953, it was assumed that the Ni in

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[6] See the references listed [85–88] for a more in-depth discussion of MTL effects and its consequences. MTL should be a concern for one attempting to measure the kinetics of any solution phase reaction where one of the reactants (H_2 in this case) is supplied as a gas. If the hydrogenation reaction of interest is fast relative to the mass transfer of H_2 gas into solution, then the overall reaction kinetics will be dominated by the slower mass-transfer step. In certain cases where there may be competing reactions, such as isomerization or olefin oligomerization [58] with Ziegler-type hydrogenation catalysts, the presence of significant MTL effects can also alter product ratios.

[7] This point is based on two basic principles in catalysis. The first is that the majority, or even all, of the observed catalysis could be due to a minority, but highly active species [10]. The second is Bergman's formulation, somewhat tongue-in-cheek, of "Halpern's Rules" for catalysis, which state, "if you can isolate it, it is probably not the catalyst; if it is metastable and you can detect it, it *could* be the catalyst; and if it is highly unstable and undetectable, then it probably *is* the catalyst!" [91].

the complexes took the form of a metal colloid which, in attempted ethylene *polymerizations*, was responsible for chain cleavage after each insertion step [1–5]. Wilke and co-workers [4] have written that this assumption was based, at least in part, on the lack of knowledge at the time about metal π-complexes. Consequently, the work of Wilke and co-workers [4,92–96] was carried out with the different hypothesis that the Ni species responsible may be π-complexes, and *not* colloidal Ni. Wilke and co-workers [4] analyzed catalyst formation in two stages: (i) the reduction of the precatalyst by AlR$_3$, and (ii) the subsequent reactions between the zero-valent transition metal, AlR$_3$, and olefin.

The reduction of Ni(acac)$_2$ by AlMe$_3$, which resulted in the formation of Ni(0), AlMe$_2$(acac), and methane and ethane gases, was thought to proceed by "homolysis of the Ni–C bond of an intermediate dimethylnickel species" [4]. The presence of intermediate dimethylnickel species was based on the isolation of crystalline [(α,α′-bipyridyl)NiMe$_2$] complex from a model system [4,94]. Methane and ethane formation were rationalized by homolysis of the Ni–C bond of the proposed NiMe$_2$ complexes, followed by either H-abstraction from AlMe$_3$ (disproportionation) or radical combination [4]. The reduction of Ni(acac)$_2$ by AlEt$_3$ or Al(i-Bu)$_3$ was described as "homolysis giving alkyl radicals, which abstract H atoms, and the dimerization of alkyl groups, are accompanied by β–H elimination to give a Ni–H species and an olefin," Scheme 2 [4]. Evidence for [(acac)Ni–H] was provided by the addition of 1,5-COD, then isolation and X-ray crystal structure determination of the 4-cyclooctenyl(acac)nickel formed [4].

The second stage of catalyst formation consisted of the subsequent reactions of Ni(0) with AlR$_3$ and olefin. By analogy to reactions investigated in a variety of model systems, Wilke and co-workers suggested the formation of Ni–olefin π-complexes similar to Ni(0)(ethylene)$_3$ [4,97]. This and other complexes, such as allyl–Ni species, similar to the Ni–olefin π-complexes, have been referred to as "bare" Ni atoms [93]. The π-complexes were thought to interact with AlR$_3$ via multicenter bonds comprised of Ni(0) plus Al and a bridging C atom. In Fig. 1, from the work of Wilke and co-workers [4], one can see how the close proximity of the AlR$_3$ β–H atom to the olefinic double bond could permit an electrocyclic reorganization to give the proposed active catalyst species. A prominent feature of Wilke's proposed catalyst is the absence of Ni–H. Ni–olefin π-complexes were proposed as the active catalyst species in alkyl-olefin exchange reactions between Grignard reagents (RMgBr) and olefins by Marko and co-workers [98,99], in which H migration within the organonickel complex was suggested *without* formation of a definite Ni–H bond. However, others have studied similar Ni plus AlR$_3$ systems and their results do impli-
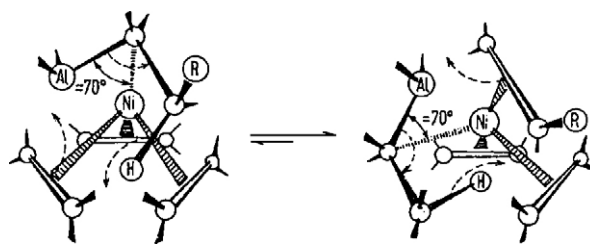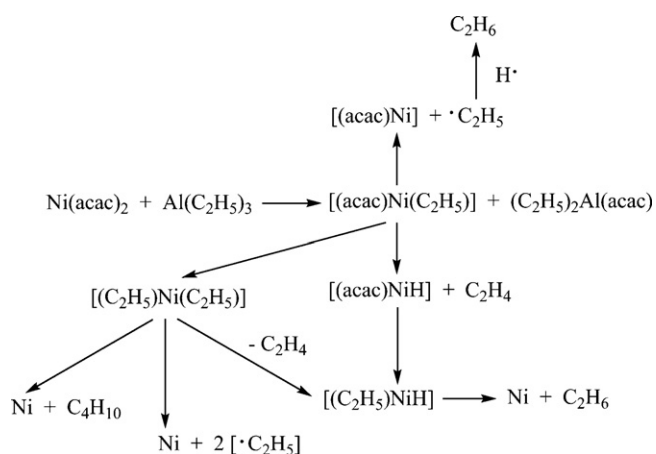

Fig. 1. Ni(0)–olefin π-complexes proposed by Wilke and co-workers [4]. Interaction with AlR$_3$ is depicted as occuring through Ni–C–Al multicenter bonds. H migration is shown in a reorganization involving the AlR$_3$ β–H atom, and without forming a definite Ni–H species. Reproduced with permission.

cate Ni–H species as responsible for catalysis in olefin dimerization or oligomerization reactions [41,100]. It is important to emphasize that Wilke and co-workers were *not* investigating catalysts for hydrogenation reactions [4]. Hence, their postulation of an alkyl-olefin exchange reaction without formation of Ni–H would seem to have little bearing on a mechanism of *hydrogenation* with similar systems.

Lardicci et al. [101] studied the effect of the transition metal precatalyst on the nature of the resulting catalyst. Their observation of a difference in catalytic activity using two different precatalysts, Ni(acac)$_2$ and Ni(N-alkylsalicylaldimino)$_2$ (plus AlR$_3$), lead them to the conclusion that the catalyst species formed are different in nature, thus ostensibly ruling out the "bare" Ni atoms concept [93]—that is, if the same "bare" Ni atoms were the catalyst in both systems, then the catalytic activity would have been the same, not different as observed. However, the expectation that the same catalyst would form when two different precursors are used seems flawed because the anion of the Ni precatalyst is expected to affect the catalysis as discussed previously in Section 2.1.1 of this review.

Wilke and co-workers concluded that their true catalyst was likely a Ni(0) complex, although they did note that the colloidal catalyst hypothesis was impossible to disprove via their studies [4,102]. One of the important observations in the work of Wilke and co-workers [4] was that, "the extent to which a reaction follows a particular direction is dependent upon a number of external factors (purity of Ni(acac)$_2$, hydride content of the Al(C$_2$H$_5$)$_3$, solvent, temperature, presence of ligands)." For that reason, confirmation of reactions, products, and intermediates, under exact reaction conditions—and without the use of trapping agents or non-Ziegler-type model systems [103][8]—although difficult, would contribute considerably to our understanding of Ziegler-type hydrogenation catalyst formation and the nature of the true catalyst.

2.2.1.2. Systems investigated by Sloan et al. [57]: M(acac)$_n$ plus AlEt$_3$, Al(i-Bu)$_3$, or AlH(i-Bu)$_2$; M = Fe(III), Co(II and III), Ni(II), Ru(III), or Pd(II). Sloan et al. [57] tested a wide variety of systems for potential catalytic hydrogenation activity, and observed similarities between the catalytic behavior of these soluble catalysts and their insoluble, heterogeneous counterparts such as Raney Ni. For example, Sloan et al. [57] reported kinetic experiments that indicated the reaction was first order in [H$_{2,gas}$]^1 and zero-order in [olefin]^0, which "is the same rate behavior observed in many heterogeneous hydrogenations." As mentioned in the previous section, they also found that, like the effects observed in heterogeneous catalysts such as Raney Ni, greater degrees of substitution on olefinic carbons generally led to slower hydrogenation. The research was conducted, in part,

Scheme 2. A reconstruction of a reaction scheme for Ni(acac)$_2$ plus AlEt$_3$ proposed by Wilke and co-workers [4]. Redrawn with permission.
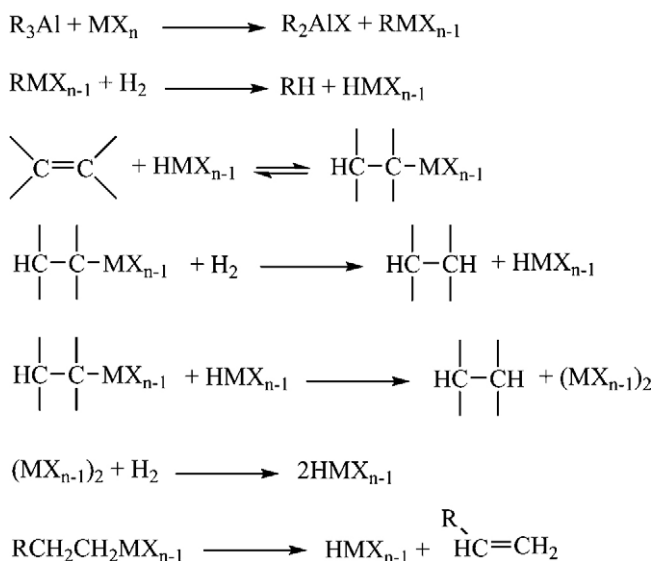
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[8] In the final analysis, the use of a model system that is available for study over another system rigorously only yields information about the model (as one would logically expect). Another noteworthy general comment on models is that "all models are wrong, but some are useful," a quote attributed to George E. P. Box [103].

with the goal of being able to use soluble Ziegler-type and related hydrogenation catalysts as mechanistic models for heterogeneous hydrogenation by bulk or supported metal catalysts despite the author's belief that the true catalysts are homogeneous [104].

In an effort to rule out either the homogeneous or heterogeneous catalyst hypothesis, the authors performed catalyst poisoning experiments—an important type of kinetics-based experiment. They observed that the addition of ethanol or acetone to the catalyst systems under investigation killed the catalytic activity. They concluded that colloidal metal must therefore be absent and the catalysts must be homogeneous. However, another interpretation of this result is plausible, namely that the observed catalyst poisoning could be due to reaction of ethanol or acetone with the AlR_3-derived components of the (heterogeneous) catalyst. Furthermore the result itself has been contradicted (albeit with other systems): Kroll [75], using a $Co(acac)_2$ plus $Al(i\text{-}Bu)_3$–p-dioxane catalyst, found that the catalyst activity was decreased, but *not* killed by the addition of even a >200 fold excess of butyl alcohol over the Al present. Shmidt and co-workers [114], studying a $Pd(acac)_2$ plus $AlEt_3$ system (discussed below), found that the addition of ethanol either enhanced or decreased the catalyst activity depending on the specific Al/Pd and EtOH/Al ratios used. Therefore, the Sloan et al. poisoning experiment alone cannot discern whether Ziegler-type hydrogenation catalysts are homogeneous or heterogeneous—they probably are reporting more on the AlR_3-component of the catalyst than on the $(metal)_n$ nuclearity (n value) of the catalyst(s).

Sloan et al. proposed a generalized mechanistic scheme, shown below in Scheme 3, starting with the precursor components, showing both catalyst formation and hydrogenation of olefins. It was based on the concept that any such hydrogenation mechanism should be analogous to that of heterogeneous hydrogenation. This mechanistic scheme was noted by the authors as speculative and deliberately oversimplified, "since the structures of the various catalysts are largely uninvestigated" [57].

In the generalized mechanistic scheme, the transition metal precatalyst is first alkylated by the organoaluminum cocatalyst. Hydrogenolysis of the newly formed metal alkyl bond gives a metal hydride and an alkane. The authors mentioned elimination from

the metal alkyl as an alternative way to generate the transition metal hydride. The reduction of transition metal and the formation of transition-metal–Al and/or transition-metal–olefin complexes were given as other possibilities [38].[9] The addition of the olefin substrate was shown as a single-step insertion into the Ni–H bond leading to a new metal alkyl, but it was mentioned that it is probably preceded by complex formation with the olefin π-bonded to the metal.[10] Note that this equilibrium step (or steps) must lie to the far right in order to explain the observed zero-order olefin kinetics. The catalytic cycle is completed in this mechanism by hydrogenolysis of the M–R bond, either by molecular H_2 or by another molecule containing hydride followed by reduction, to give the saturated olefin and regenerate the M–H catalyst species.

The simple alternative explanation here is that the catalysts used by Sloan et al. are heterogeneous. Evidence for this alternative hypothesis are the similarities in catalytic behavior to known heterogeneous catalysts and the likely alternative interpretation of their poisoning experiment given above (i.e., that additions of ethanol or acetone react with the AlR_3-derived component). In short, while an important and early effort, one that included kinetic and poisoning experiments, the homogeneous versus heterogeneous nature of the true catalysts is uncertain despite these early studies.

2.2.1.3. Systems investigated by Lapporte [58]: M(2-ethylhexanoate)$_2$ plus m AlEt$_3$, M = Ni or Co, m = 3–4. Similar to the work of Sloan et al. [57], Lapporte [58] had observed that the rate behavior of his soluble catalysts bore similarity to heterogeneous catalysts.[11] Lapporte pointed out that the diminished hydrogenation activity when $NiCl_2$ was used as the Ziegler-type precatalyst was analogous to the diminished rate of hydrogenation when Cl^- was present using a Raney Ni catalyst. Also like Sloan et al., Lapporte was motivated by the prospect of using soluble Ziegler-type and related hydrogenation catalysts as models of heterogeneously catalyzed hydrogenation [104]. Therefore, it is no surprise that Lapporte gave a simplified mechanistic scheme (see Equations 6 and 9–11 detailed elsewhere [58]) that is quite similar to the scheme by Sloan et al.

One minor difference between the Sloan et al. and Lapporte schemes is that in the Lapporte scheme, reduction of the Ni(II) precatalyst with $AlEt_3$ to Ni(0) was shown proceeding via the formation of Ni–Et. Magnetic susceptibility measurements of the Al/Ni = 4 catalyst solutions at variable temperatures were interpreted as containing diamagnetic $3d^{10}$ Ni species, although binuclear Ni(I) species could not be ruled out. Another difference is that Ni–H was shown as generated by elimination from the metal alkyl, and metal–olefin π-complex formation was depicted before insertion into the Ni–H bond. Like Sloan et al., Lapporte observed substrate isomerization and carried out a deuterium labeling experiment. It was noted that the observation of 1,2-dideuteroethylene and HD are consistent with Ni–ethylene π-complex and Ni–H intermediates, and reversible addition of the Ni–H species to the olefin double bond. Further, more direct evidence for the presence of Ni–ethylene π-complex and Ni–H species was obtained from low temperature

Scheme 3. A reconstruction of a reaction scheme postulated by Sloan et al. [57]. The first step in this mechanism is alkylation of the transition metal precatalyst MX_n by the aluminum alkyl. Hydrogenolysis forming a metal hydride and olefin coordination follow. Elimination from the M–alkyl is shown as an alternative path to M–H formation (last line). Hydrogenolysis to give saturated olefin is shown as possibly involving either H_2 or another molecule of metal–hydride. Redrawn with permission.

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[9] The timing of steps in a case like this is a standard mechanistic ambiguity; whether the addition of olefin occurs before or after H_2 enters and the formation of the metal hydride is possible, but often difficult, to ascertain [38].

[10] To test part of the proposed scheme, a solution of a $Cr(acac)_3$ plus $Al(i\text{-}Bu)_3$ catalyst with 2-methyl-2-butene as substrate was treated with D_2 gas. Analysis of the reaction products by MS showed mono-, di-, and trideuterated species, explained by reversible olefin migratory insertion to a M–D(H).
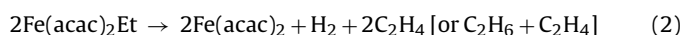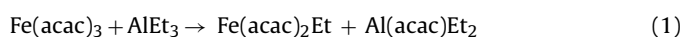
[11] One exception, however, was that nitrobenzene, which is easily hydrogenated using non-AlR_3 containing heterogeneous Ni_n catalysts, showed only sparing conversion with the Ni Ziegler-type hydrogenation catalyst studied by Lapporte [58]. It is now known that nitrobenzene reduction is not a reliable indicator of heterogeneous catalysis [16].

^{1}H NMR spectra [58]. However, it was found that these signals irreversibly disappeared upon warming of the catalyst solutions to room temperature. The reasons and implications for this were not discussed, and it is not clear if the observed species are on, or off, the catalytically productive pathway. Lapporte's NMR observations are, however, a great lead for someone to pursue to see if the observed species do (or do not) show the kinetics of a catalytically competent intermediate.

Lapporte also interpreted his observations in terms of the knowledge available at the time, that is, that the true catalyst was homogeneous. Lapporte cited the "bare" Ni atoms idea of Wilke and co-workers [93] in proposing the catalysts could be mononuclear Ni(0) species solubilized by labile –H, –R, solvent, or $Al(Et)_2$(2-ethylhexanoate) ligands that could be easily displaced by the unsaturated substrate. Additionally, Lapporte observed that gas evolution, apparently the products of reduction of the Ni(II) pre-catalyst by $AlEt_3$, was greatest at the same Al/Ni giving optimal catalytic activity, ostensibly suggesting a Ni(0) catalyst. However, like the work of Sloan et al., none of the results can be taken to rule out either homogenous or heterogeneous catalysts as the active species—indeed, we can be pretty sure now that it was pretty much impossible to solve the homogeneous versus heterogeneous catalysis question for these complex catalysts at that time [16]. The formation of a dark color upon hydrogenation of ketones to the corresponding alcohol was interpreted as "decomposition of at least some Ni to metal, albeit very finely dispersed" [58]. The black reaction mixture, though inseparable by ultracentrifugation, is consistent with M_n nanocluster formation [16], nanoparticles which are expected to be a potent hydrogenation catalyst in the presence of moderate amounts of AlR_3 and in hydrocarbon solvents under H_2.

2.2.1.4. System investigated by Klinedinst and Boudart [105]: $Fe(acac)_3$ plus 6 $AlEt_3$.

Klinedinst and Boudart sought to determine the nature of Ziegler-type hydrogenation catalysts of especially Fe using IR and Mössbauer spectroscopy. An IR spectrum of the catalyst solution was similar to the superposition of spectra of $AlEt_3$ and $AlEt_2$(acac) obtained separately for the sake of comparison. This qualitatively indicated that the catalyst formation reaction between precursor components involved the transfer of acac from $Fe(acac)_3$ to the cocatalyst. However, exchange of ethyl from Al to Fe could not be detected by IR because the band region characteristic of the C–H stretch in "$FeEt_2$" was obscured by the same C–H stretch in $AlEt_3$.

The authors hoped that Mössbauer spectroscopy of the catalyst solutions would confirm the presence of metallic particles too small to be detected by X-ray diffraction. Catalyst samples were prepared for Mössbauer spectroscopy in toluene at 190 K and then rapidly quenched to 77 K. The spectra obtained indicated that high spin Fe(II) were the only Fe species present. A possible explanation offered was that the reaction of $Fe(acac)_3$ with $AlEt_3$ may be limited to a one electron reduction at these temperatures. This is depicted in Equations (1) and (2) below, reproduced from the original publication [105]. However, evidence for the gaseous products H_2, ethane and/or ethylene was not provided as part of this study and would be useful for anyone interested in reinvestigating this $Fe(acac)_2$ plus $AlEt_3$ system.

$$Fe(acac)_3 + AlEt_3 \rightarrow Fe(acac)_2Et + Al(acac)Et_2 \tag{1}$$

$$2Fe(acac)_2Et \rightarrow 2Fe(acac)_2 + H_2 + 2C_2H_4 \text{ [or } C_2H_6 + C_2H_4] \tag{2}$$

When the catalyst sample was warmed to room temperature and then re-quenched to 77 K, it gave a Mössbauer spectrum identical to those of active catalyst samples prepared at room temperature. These Mössbauer spectra of activated catalysts showed that further reaction of the high spin Fe(II) had taken place. The most significant finding was that no metallic iron particles ≥ 1.7 nm were detected,
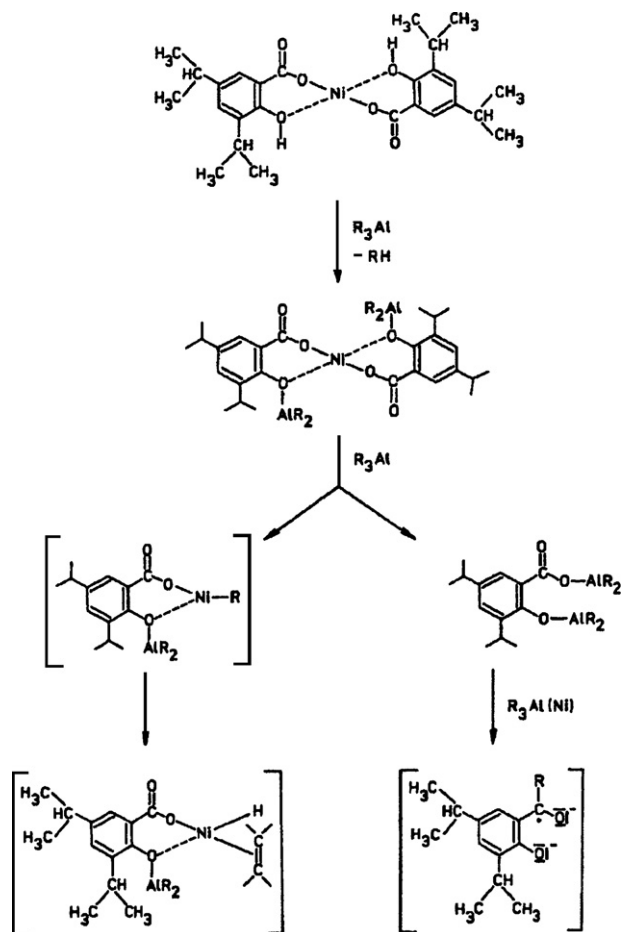
which was taken to be consistent with a homogeneous catalyst hypothesis. The obvious alternative hypothesis is that the catalyst is heterogeneous, but consists entirely of particles smaller than 1.7 nm. Another possibility is that the catalysts are heterogeneous, but do not display the hyperfine pattern in Mössbauer spectra characteristic of metallic iron because they are amorphous [106,107], or are amorphous until exposed to high pressure H_2 [108] (these samples were not exposed to H_2). However, while it provides (negative) evidence against a crystalline heterogeneous Fe_n, catalyst of diameter ≥ 1.7 nm (which corresponds to $Fe_{\geq 218}$ if it were close-packed Fe(0), [50]),[12] even this clever study by Klinedinst and Boudart was unable to answer the difficult homogeneous versus heterogeneous catalysis question.

2.2.1.5. System investigated by Alvanipour and Kispert [67]: $Co(stearate)_2$ plus 2 $AlEt_3$.

Alvanipour and Kispert [67] concluded that Ziegler-type hydrogenation catalysts are most likely homogeneous metal hydride or π-complexes. Their basis for this conclusion is their own finding that "high speed" centrifugation was unable to induce a separation in a solution of the catalyst in their $Co(stearate)_2$ plus 2 $AlEt_3$ system, and the absence of other evidence of metallic particles. In addition, they cited the results of others that suggested Ziegler-type hydrogenation catalysts are homogeneous: Wilke's isolated $[(P(Ph)_3)_2Ni(C_2H_4)]$ complex [92], the diamagnetic $3d^{10}$ Ni(0) catalyst species proposed by Lapporte [58], and the Mössbauer spectroscopy results of Klinedinst and Boudart [105]. However, their work did not include the kinetic studies required to identify the true catalyst(s).

2.2.1.6. Systems investigated by Reguli and Staško [70]: NiL_2 plus AlR_3 or BuLi (L = 3,5-diisopropylsalicylate, acac, stearate, or benzohydroxamate; R = Et or i-Bu).

The study by Reguli and Staško is noteworthy for its detailed examination of a range of variables in search of the optimum synthesis conditions for their Ziegler-type hydrogenation catalysts [70]. The authors also considered the nature of the catalyst preparation reaction and the resulting catalyst. In aliphatic solvent, EPR spectra indicated two paramagnetic species, interpreted as Ni(I), and ketylradicals ($ArCO^{\bullet-}R$), which were thought to form during the last stage of reaction between the precursors. The (unquantitated) concentrations of these species increased with Al/Ni to a maximum at Al/Ni = 8–10, yet the catalytic activity was optimal at Al/Ni in the 2–4 range, providing an important disconnect between the EPR signals and the (kinetic) catalysis. Based on this observation, the active catalyst species were thought to be diamagnetic species of Ni(II) formed by alkylation of the precatalyst, although these results do not necessarily mean the catalyst must be a homogeneous Ni(II) complex, only that the catalyst is not likely a Ni(I) species. A scheme depicting formation of the active catalyst species was proposed and is reproduced, Scheme 4.

2.2.1.7. System investigated by Barrault et al. [37]: $Co(acac)_2$ plus $AlEt_3$.

Studies by Barrault et al. investigated the catalyst formation reactions in a $Co(acac)_2$ plus $AlEt_3$ system using IR spectroscopy of the reaction solutions and GC analysis of the gas products. IR spectra at 25 min and 18 h indicated that the timescale of reaction at room temperature was rapid, and GC showed completion of gas production after only three min of mixing. IR spectra were obtained at Al/Co = 0.5, 1.0, and 1.5. At lower Al/Co ratios they showed formation of $Al(acac)_3$. At Al/Co = 1.5, formation of $Al(Et)_2$(acac) and complete

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[12] The number (N) of atoms in a metal nanocluster of diameter (D) can be estimated according to the equation: $N = (N_0\rho(4/3)\pi(D/2)^3)/M$, where $N_0 = 6.022 \times 10^{23}$ mol^{-1}, ρ = the room temperature density of the pure bulk metal, and M = atomic mass [50]. For Fe: ρ = 7.87 g/cm^3 and M = 55.845 g/mol [83].

Scheme 4. A speculative reaction scheme and structures proposed by Reguli and Staško for Ni(diisopropylsalicylate)$_2$ plus AlR$_3$ [70]. Reproduced with permission.
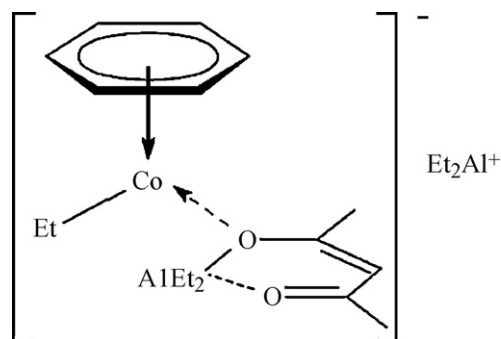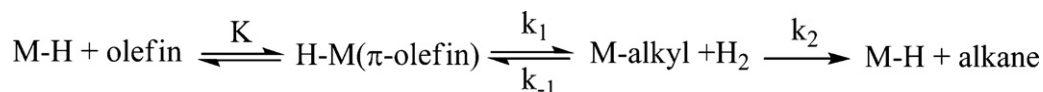

Fig. 2. A Co(0) complex suggested as a possible active Ziegler-type hydrogenation catalyst species by Shmidt and co-workers [109–111]. In later work and based on additional evidence (vide infra), this species, whose presence was identified spectroscopically, was reinterpreted as the *precursor* for the Co(0)$_n$ Ziegler nanoclusters now proposed as the active catalyst [113]. Reprinted with permission.

interpreted as evidence of such soluble mononuclear species. However, the authors were correct to conclude that, despite the fact that the carbonylation experiments showed the *presence* of complexed Co(0) species, neither these nor Co(0)$_n$ metal particles could be ruled out as the sole active catalyst.

2.2.1.8. Systems investigated by Shmidt and co-workers: AlEt$_3$ plus Co(acac)$_2$ [109], Co(acac)$_3$ [110,111], Ni(acac)$_2$ [42,111], Fe(acac)$_3$, or Pd(acac)$_2$ [111]. The reactions of AlEt$_3$ with the above-listed metals and precursors were monitored using UV–vis and IR spectroscopies. Transfer of acac ligands from the transition metal to Al was observed with the consequent formation of a mixture of Al(acac)$_3$ and AlEt$_2$(acac) for M = Fe, Co or Ni, and only AlEt$_2$(acac) at various Al/M ratios for M = Pd. Analysis of aromatic hydrocarbon solutions of the Co catalyst with EPR spectroscopy led the authors to propose a paramagnetic Co(0) complex as the active catalyst [109], which is shown in Fig. 2; AlEt$_2$(acac) is proposed as a ligand of the Co(0) complex along with a molecule of the arene solvent, and AlR$_3$ bound through a carbon atom. It is understood, however, that "Et$_2$Al$^+$" cations such as that in Fig. 2 are normally stabilized through coordination by a Lewis base [112].

Magnetic measurements of the catalyst solutions appeared to confirm the reduction of transition metals to the zero-valent state. However, as clearly mentioned by the authors, the presence of low spin Co(II) or Ni(II) complexes exhibiting the same μ_{eff} as Co(0) and Ni(0), could not be ruled out [111]. Furthermore, quantitative analysis of these magnetic susceptibility studies showed that *3–8% of the Co in the sample exists in Co(0)$_n$ particles of up to 100 Å.* Without further information, especially the necessary kinetic studies, it is entirely plausible that the observed Co(0)$_n$ particles are responsible for some or all of the observed catalysis.

Shmidt and co-workers [42] proposed a simple mechanistic scheme for the hydrogenation of olefins using Ziegler-type catalysts. This scheme was very similar to the Sloan et al. [57] and Lapporte [58] schemes, and is shown in Scheme 5. The true catalyst was assumed to be a complex metal hydride. The idea of initial reversible olefin π-complex addition was supported by the observation that these catalysts cause olefin isomerization. The final step producing saturated hydrocarbon and regenerating the M–H catalyst was shown as hydrogenolysis of the metal–carbon bond as it was in the previous schemes [57,58]. It is shown in Scheme 5 as

transfer of the acac ligands from the Co(acac)$_2$ precatalyst was observed. GC showing the production of ethane was interpreted as suggesting the disproportionation shown, Equation (3).

$$2C_2H_5 \rightarrow C_2H_6 + C_2H_4 \tag{3}$$

However, the observed ethane fraction was >96% of the gas composition, whereas according to Equation (3) the reduction of Co(II) to Co(0) is expected to produce *equal amounts* of ethane and *ethylene*. Therefore, Barrault et al. postulated that either the disproportionation was not taking place, or that some of the ethylene was involved in π-binding interactions with soluble Co(0) complexes. The IR spectra obtained are at least consistent with such π-bonded Co(0)–ethylene complexes.

Carbonylation experiments were also carried out in which Al/Co = 1 catalyst samples were bubbled with a mixture of CO and H$_2$ gases, and monitored by IR spectroscopy. The highest ν(CO) frequency observed indicated CO binding to Co(0) centers that were more electron-donating to the $2\pi^*$ orbital of CO than what had been previously observed for CO surface-bound to Co(0) particles. Mononuclear Co(0) species complexed by such ligands as π-bound CH$_2$=CH$_2$ were expected to be more electron rich than exposed Co(0) on the surface of metal particles. Therefore, this result was

$$M\text{-}H + olefin \underset{}{\overset{K}{\rightleftharpoons}} H\text{-}M(\pi\text{-}olefin) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M\text{-}alkyl + H_2 \overset{k_2}{\longrightarrow} M\text{-}H + alkane$$

Scheme 5. A reproduction of the scheme for catalytic olefin hydrogenation using a Ziegler-type hydrogenation catalyst from Shmidt and co-workers' 1970 paper [42]. Used here with permission.

involving a molecule of H_2, which was a common depiction at the time [38], a mechanism consistent with the kinetic observations that olefin isomerization occurred at a slower rate with increasing H_2 pressure, and that the reaction is first order in H_2 pressure (by both their and other's data) [42,57,70].

However, it is now understood that such a hydrogenolysis is unlikely as an elementary mechanistic step, at least with late metal homogeneous catalysts. Moreover, such a step is probably better depicted by reductive elimination involving M–H formed by a prior oxidative addition of H_2 to the metal [10,89].

2.2.2. The "Ziegler-type catalysts are heterogeneous" hypothesis

2.2.2.1. Systems investigated by Shmidt and co-workers: $Co(acac)_{2,3}$ [19,113], or $Pd(acac)_2$ [81,114] plus $AlEt_3$.

In 2005 and 2006, Shmidt and co-workers replaced their earlier conclusion of a Co(0) complex catalyst [109–111] with a postulate of catalysis by $Co(0)_n$ nanoclusters [19,113]. The presence of nanoclusters is consistent with the observation that dark brown solutions formed in both Co and Pd systems upon combination of the precursor components [16]. TEM images of Co samples demonstrated the presence of these clusters, and a particle size histogram displayed two maxima at 2.6 and 5.0 nm. Larger particles of 10–50 nm were thought to be agglomerates of the smaller particles. In the catalyst system prepared from $Pd(acac)_2$, TEM images exhibited the presence of 4.2 nm particles when Al/Pd = 4. Increasing the Al/Pd ratio to ≥8 decreased the particle size to 1–2 nm [81,114].

The Co clusters were shown to be amorphous by XRD, but formed 10 nm crystalline particles after calcination at 450 °C for 4 h. The Co(0) complex previously proposed as the catalyst, and based on earlier UV–vis and EPR spectroscopic results, Fig. 2 [109–111] (vide supra), was reinterpreted as being the *precursor* for the $Co(0)_n$ nanoclusters, something fully consistent with Halpern's Rules (really guidelines) for catalysis [91].[7] The finely dispersed component observed in the earlier studies was reinterpreted as the 10–50 nm agglomerates of the smaller $Co(0)_n$ nanoparticles [19,113].

Catalyst formation and the role of $AlEt_3$ were studied using IR spectroscopy, and analysis of the gaseous and solid products. A reaction scheme based on the IR results was proposed, which showed the reaction of $Et_2Al(acac)$ with excess $AlEt_3$, Scheme 6. The amounts of these species, the stability of the nanoclusters (as judged by the amount and time until precipitate was formed), and their catalytic activity were all found to depend on the Al/M ratio. Activity and stability varied inversely to each other, again consistent with Halpern's Rules, or guidelines, for catalysis [91],[7] cited earlier.

Based on their observations, Shmidt and co-workers proposed that the various Al-containing species and arene solvent molecules act as the nanocluster catalyst stabilizers, Fig. 3. Their difference in binding strengths to the nanocluster surface could explain the ease with which they are replaced by the olefin substrate molecules, and
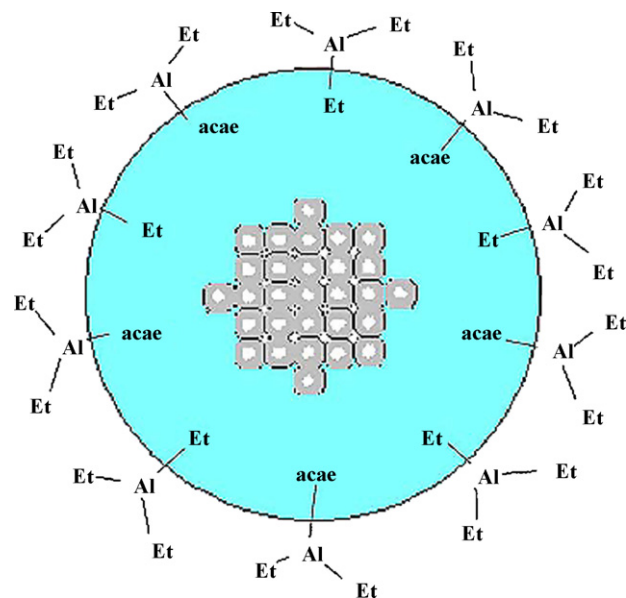
Fig. 3. A cobalt nanoparticle and the associated organoaluminum stabilizer layer suggested by Shmidt and co-workers [113]. The gray circles in the center are Co atoms in an apparent crystalline array. Reprinted with permission.

therefore the differences in catalyst stability and activity. $AlEt_3$ itself was thought to have the highest binding strength, which would explain the observation that increasing excesses of $AlEt_3$ resulted in increasingly stable, yet decreasingly active catalysts.

The higher catalytic activity and immediate black precipitate formation when precatalysts with crystal H_2O were used were explained by the formation of alumoxane ($R_2AlOAlR_2$) oligomers and their acac derivatives. This requires the assumption of *weaker coordination of alumoxane compounds to the nanocluster surface*, and therefore less stabilization compared to the other proposed stabilizers $AlEt_2(acac)$, $AlEt_3$, or their reaction products, a potentially important, more general conclusion. The results from IR and elemental analyses on samples of catalyst precipitates showed the remaining Al compounds were a mixture of species including oligomeric alumoxanes with characteristic Al–O–Al bonding. However, the catalyst precipitates had Al/Co ratios of 1.9–2.2 regardless of whether the initial Al/Co used in their preparation was 2, 4, or 8. The authors suggested that this result indicated that excess $AlEt_3$ and $AlEt_2(acac)$ not bound to the catalyst surface were washed away by hexane during sample preparation. However, it is not clear why the purported stronger binding $AlEt_3$ and $AlEt_2(acac)$ would wash away instead of the supposed weaker binding alumoxane. Not all aspects of the observed nanocluster and stabilizers from this important study are fully explained [113].
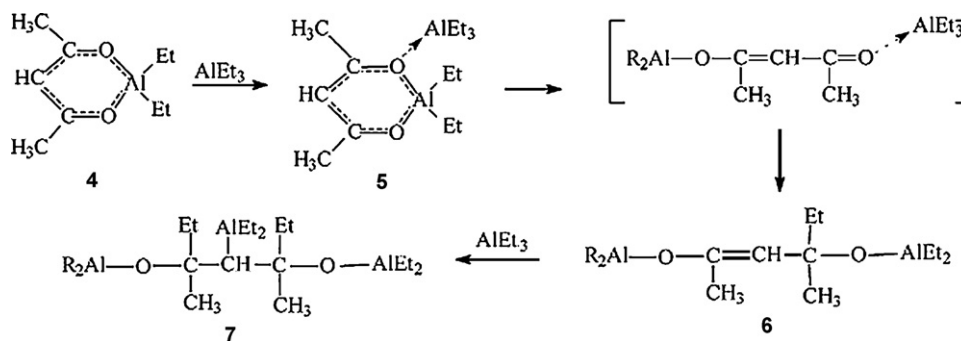
Scheme 6. A scheme proposed for the reaction of $Et_2Al(acac)$ with excess $AlEt_3$ based on the results of IR spectroscopy by Shmidt and co-workers [113]. Reprinted with permission.

Gas analysis, deuterium labeling, and radical trapping experiments were carried out, the interested reader is referred to the details of those experiments elsewhere [19,113]. The general process of catalyst formation in these studies can be summarized as follows: (i) the anions of the transition metal precatalyst are replaced by R groups from AlR$_3$, (ii) the M–alkyl intermediate decomposes during the reduction of M, specifically for Co, the Co(0) nanocluster precursor complex forms (i.e., the complex previously thought of as the catalyst), and (iii) M(0)$_n$ nanoclusters then form from that Co(0) precursor complex, and are stabilized by Al-containing compounds, the details and identities of which depend on the initial Al/M.

This description still lacks a mechanism for formation of nanoclusters from M(0) complex intermediates. Additionally, and importantly, *in the absence of kinetic evidence, the simple observation of the presence of nanoclusters does not itself necessitate that they are the active catalysts*—although it certainly opens up that hypothesis as a dominant one to try to disprove. Schmidt and co-workers [113] observed Co concentration-dependent turnover frequencies (TOF = moles of product/(moles of catalyst × unit time) [115]), specifically *lower Co concentrations giving higher TOFs*. Since the TOF would be [Co]-independent for a mononuclear homogeneous catalyst, this indicates that either a Co(0)$_n$L$_x$ + mL $\rightleftharpoons$ nCo(0)L$_{(x/n+m)}$ or related equilibrium is present (see p. 334 elsewhere [16]), that the catalysts are heterogeneous, or possibly some other explanation such as a competing, bimolecular catalyst deactivation pathway. However, the explanation that catalyst solutions with lower [Co] make less-agglomerated catalysts, with higher TOF's directly contradicts the observation [19,113] that catalyst solutions with *more* agglomeration give higher catalytic rates. These studies do, however, identify kinetics as a function of metal/AlR$_3$ concentrations as key experiments for future studies. Such studies with a model Ir catalyst have recently been done [52–54], as will be briefly described (vide infra).

2.2.2.2. System investigated by Pasynkiewicz et al. [71]: Co(acac)$_3$ plus 1 AlMe$_3$ in benzene.

The 1974 paper by Pasynkiewicz et al. investigated the possible reaction pathways and products of the catalyst formation reaction by IR spectroscopy of the reaction mixtures and MS analysis of the gas products. They suggested the following reaction stoichiometry, Equation (4).

$$3Co(acac)_3 + 3(CH_3)_3Al$$
$$\rightarrow 3Co(0) + 3Al(acac)_3 + [CH_4 + C_2H_6 + C_2H_4] \qquad (4)$$
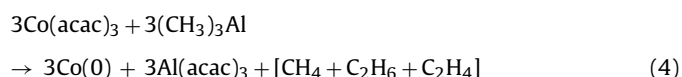
The identity of Al(acac)$_3$ was confirmed by IR, NMR, and elemental analysis. The amount of each of the gaseous products was measured. The yields of the gaseous products were 60–70% based on the number of methyl groups, yet hydrolysis of the products did not result in further gas evolution, which was taken to mean that all the hydrolysable methyl groups had reacted. This leaves 30–40% of methyl groups unaccounted for by the proposed stoichiometry, so that finding the rest of the organic products is a difficult but needed part of understanding Ziegler-type hydrogenation catalyst formation.

Analysis of the solvent after the reaction led to the detection of small amounts of toluene. When benzene-d$_6$ was used as the solvent 10% of the gas product was CH$_3$D by MS. These observations suggested that multiple reactions are probably present (and that not all reactions are on the path to catalyst formation). A mechanistic scheme was proposed containing the following steps: (i) migration of a CH$_3$ group from Al to Co and simultaneous formation of Al(CH$_3$)$_2$(acac) and Co(acac)$_2$CH$_3$, (ii) complex formation between the Co(acac)$_2$CH$_3$ intermediate and another molecule of AlMe$_3$, leading to (iii) nucleophilic substitution at hydrogen, carbon, or Co atoms, and (iv) further reaction of the intermediates,

ultimately resulting in metallic Co(0)$_n$ thought to be the true catalyst.

The evidence supporting the notion that metallic Co(0)$_n$ was the true catalyst consisted of: (i) the color of the reaction solution changed to black, (ii) the catalyst residue obtained from solvent evaporation reacted violently with air, methanol, or water, and (iii) reaction of this residue with HCl gave CoCl$_2$ and H$_2$. The problem with this conclusion is that while these results suggest the presence of metallic Co(0) in the residue, they in no way definitively rule out homogeneous catalysis in solution. The kinetic studies necessary to support or refute the Co(0)$_n$ catalyst hypothesis remain to be done for this system as well.

2.2.2.3. Systems investigated by Goulon and co-workers: M(2-ethylhexanoate)$_2$ plus AlEt$_3$ (M = Co or Ni) [40,116], or Ni(acac)$_2$ or Fe(acac)$_3$ plus AlEt$_3$ [40].

Goulon and co-workers studied Ziegler-type hydrogenation catalysts and their precursors using EXAFS spectroscopy. In their important 1984 paper, they had greater success using the Ni precatalyst than Co because spectra of the Co catalyst solutions were overly affected by their preparation and aging [116]. EXAFS spectra of the Ni catalyst solution obtained at a series of Al/Ni ratios demonstrated Ni–Ni first-neighbors at distances equal to, or slightly larger than, those found in Ni foil. Signals were also detected for Ni–X at shorter distances, where X is C or O. The relative strength of these two signals varied with Al/M, but also with mode of preparation and aging, making truly definitive conclusions difficult. The Ni–Ni signals expected for the higher metal shells were not observed, arguing, according to one interpretation, against the presence of (extensive amounts of) Ni(0)$_n$.

These results were interpreted by Goulon and co-workers [116] as consistent with amorphous clusters, but could also have been explained by small Ni(0)$_n$ clusters, $n \approx 4$–10, based on their reported Ni–Ni first shell coordination of 3.8 ± 1 [117,118].[13] The detection of Ni–X signals by Goulon and co-workers [116] suggests the presence of ligands that may stabilize any small clusters present and is also consistent with the samples showing Ni–Ni distances slightly larger than those found in Ni foil [119,120].[14]

A shift observed in the absorption edge supported the hypothesis that Ni species were zero-valent, but incomplete reduction could not be ruled out by EXAFS. The authors pointed out that earlier magnetic susceptibility data, interpreted as ruling out the presence of metal clusters [116], may have been misleading. In light of the definitive EXAFS evidence for the existence of close M–M interactions, the earlier lack of detected ferromagnetism expected for metal clusters could be explained if "carbonaceous 'screens'...prevent magnetic coupling" [116].

In their subsequent study, Goulon and co-workers [40] used other catalyst precursors in an attempt to avoid the variability problems of the initial study. They again observed EXAFS signals dominated by Ni–Ni first neighbors suggesting the presence of metal clusters. The model of molecular "[Ni,Al]" complexes or clusters was ruled out by the similarity of spectra using GaEt$_3$ as the cocatalyst, and by Ga K-edge spectra. Interestingly, EXAFS spectra

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[13] See the references cited [117,118] for an explanation on how the conversion between average coordination number and number of atoms in a cluster is carried out, which is closely related to the method used for estimating number of atoms in a metal cluster of a given diameter [50].

[14] Goulon and co-workers tentatively discounted the data as indicative of small clusters because of the expectation that Ni–Ni distances would be shorter for metal clusters of less than about 10 atoms. However, in a recent study of Rh clusters [119], contraction of M–M distances was expected for metal nanoclusters *without* ligands according to an approximate $n^{-1/3}$ relationship (where n = the number of atoms) [120], whereas in experimentally observed clusters *with* ligands, *larger* Rh–Rh distances were observed. This observation was explained by donation of M–M valence electrons to M–ligand bonds, thereby lengthening the M–M distance.

of the Fe(acac)$_3$ plus 6 AlEt$_3$ catalyst system were interpreted as ruling out the presence of small Fe metal particles, but were similar to the EXAFS spectra of amorphous iron carbide. When the amorphous metal carbide model was used to fit the Ni sample spectra, the initial results were promising, but not definitive. Formation of clusters in these systems is undeniable, but whether they are small ~4–10 atom clusters, amorphous M or M–carbide clusters, or some combination is still unclear. Furthermore, the question of which species is the predominant catalyst remains open, kinetic studies being required to answer that question.

2.2.2.4. Systems investigated by Bönnemann and co-workers: Ni(acac)$_2$ plus 3 Al(i-Bu)$_3$ [121], Pt(acac)$_2$ plus 4 AlMe$_3$ [121,122–125], or [(COD)Pt(CH$_3$)$_2$] plus 10 AlEt$_3$, or Al(C$_8$H$_{17}$)$_3$ [126]. Bönnemann and co-workers have studied the reaction between Ziegler-type precursors and have worked on characterizing the products. They observed that solutions turned brown or black upon precursor combination in the Ni(acac)$_2$ plus 3 Al(i-Bu)$_3$ and Pt(acac)$_2$ plus 4 AlMe$_3$ systems, which is consistent with the formation of nanoclusters [16].[15] In addition, TEM images of these systems revealed the presence of 3.2 ± 0.8 nm and 2.5 nm Ni and Pt nanoclusters, respectively. TEM images alone, however, can be misleading as (i) the technique has been shown to be sensitive to sample preparation, especially with samples of Ziegler-type systems [9], and also (ii) can *cause* particle formation and/or crystallization under the electron beam, especially for the lighter first and second row metals [17,127]. Unlike Shmidt and co-workers who used a minimal beam current and compared images from repeated beam exposures [113], Bönnemann and co-workers [121–124,126] reported no attempt to rule out these potential TEM artifacts.

Bönnemann and co-workers focused several of their subsequent studies on the Pt(acac)$_2$ plus 4 AlMe$_3$ system. A fit of the EXAFS spectrum taken of the isolated dried colloid gave a Pt–Pt interaction with an average coordination number of 5.0 ± 0.5, and a lack of longer range Pt–Pt shells. These two observations could be explained by the predominance of clusters with ~8–13 atoms, nanoclusters with an amorphous structure, or a combination of the two. High resolution TEM images and corresponding optical diffractograms showed 1.2 nm amorphous particles. Analysis of the samples by anomalous small-angle X-ray scattering (ASAXS) spectroscopy confirmed the presence of 1.2 nm amorphous nanoclusters. The different sizes of nanoclusters observed in the Pt(acac)$_2$ plus 4 AlMe$_3$ system (2.5 nm by TEM vs. 1.2 nm by HRTEM and ASAXS) may be a result of the different methods used, differences in sample preparation, or a combination of the two.

Formation of nanoclusters was monitored as a function of time with in situ ASAXS, Fig. 4 [124,125]. The clusters of final 1.2 nm diameter were observed within 1 hour of the start of the reaction, and stayed constant for at least 1000 hours. The constant final size of the nanoclusters, and a fit of the data by an empirical [128], exponential model, Fig. 4 (bottom), were interpreted as evidence for continuous "nucleation" or "agglomeration" of reduced Pt(0) atoms into 1.2 nm diameter, Pt(0)$_{~55}$ nanoclusters,[16] without any observable
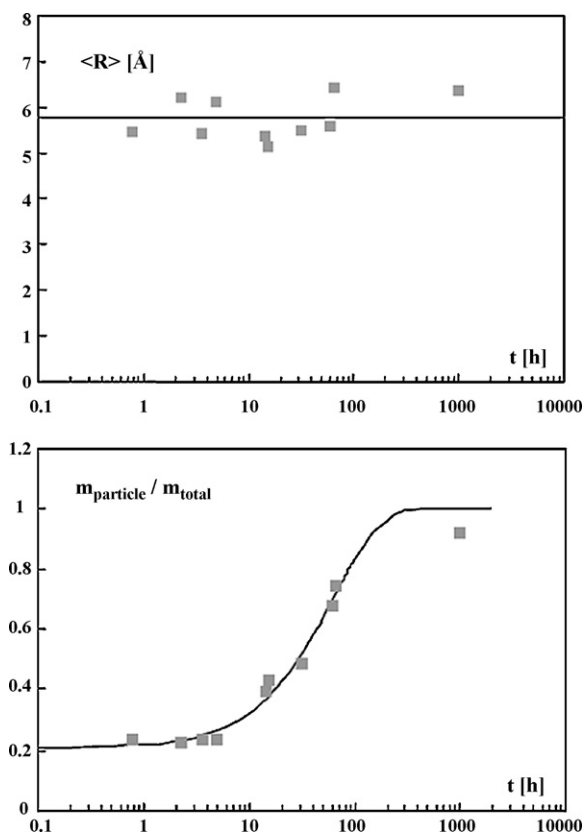

Fig. 4. The results of in situ ASAXS to monitor the formation of Pt(0) nanoparticles by Bönnemann and co-workers [124]. The mean particle radius (top) remained essentially constant from the time particles were first detected, and up to 1000 h attesting to particle stability (mean particle diameter = 1.2 nm). The mass fraction ($m_{particle}/m_{total}$) of Pt atoms in nanoparticles as a function of time (bottom) fit with an empirical exponential model. Reprinted with permission.

contribution from nanocluster "growth" [124]. The identity of the clusters as Pt(0)$_{~55}$ is significant because 55 is the second of the "magic number" series of atoms for icosahedra with a full/closed outer shell, and thus more stable than non-magic number clusters [129]. To the best of our knowledge, Bönnemann and co-workers' study is the first that has successfully monitored the in situ formation of nanoclusters from Ziegler-type precursors, an important contribution.

Some confusion may be created by the terminology used by Bönnemann and co-workers for nanocluster formation [124], which is different than the terminology commonly used in the nucleation and growth literature [49,130–132]. In a range of systems, and according to a well-precedented nanocluster formation mechanistic model (nucleation A → B (rate constant k_1), and autocatalytic growth A + B → 2B (rate constant k_2) [130], the term "nucleation" refers only to the k_1 step, which is typically followed by (autocatalytic surface) "growth", the step with rate constant k_2. Subsequent increases in size could then proceed by either continued "growth" or by, mechanistically now precedented, particle "agglomeration" (the combination of nanoparticles to form larger agglomerates) [131]. However, in the work by Bönnemann and co-workers [124], "nucleation" is used to describe the formation of the final-sized 1.2 nm nanoparticles, "agglomeration" is used to describe a part of the "nucleation" process (the joining of single zero-valent Pt atoms, the other part of the "nucleation" process being the initial precursor decomposition), and "growth" is used to describe an increase in size of the 1.2 nm nanoparticles after "nucleation" has taken place (presumably occurring via continued "agglomeration"). In short, the mechanistic nomenclature used elsewhere [124] is incon-

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[15] Bönnemann and co-workers use the terms "colloidal nanometals," "transition metal nanocolloids," and "nanosized organosols" interchangeably for what we define herein as "Ziegler nanoclusters" (and only for cases where an AlR$_3$ component is present).

[16] Bönnemann and co-workers discuss the clusters as being comprised of 53 Pt atoms based on an ideal icosahedral structural model and their experimentally determined 1.2 nm diameter. This is actually an approximation since the techniques used show the clusters are amorphous (i.e., not ideally icosahedral) and that a distribution of cluster sizes exists. The clusters have been written here as Pt(0)$_{~55}$ to emphasize these facts according to a convention established in the literature for representing the approximate number of atoms in such (non-monodisperse) nanoclusters [50].
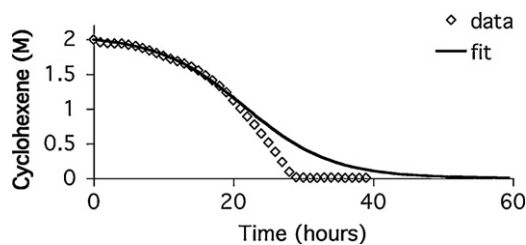
Fig. 5. A representative reaction of $Pt(acac)_2$ plus 4 $AlEt_3$ followed by the cyclohexene hydrogenation reporter reaction method [50,130,133] ([Pt] = 1.2 mM, solvent = toluene, temperature = 22.0 °C, initially 40.0 psig H_2, stirring = 1000 rpm), and attempted fit of the data using the now well-established A → B (rate constant k_1), A + B → 2B (rate constant k_2) mechanistic model for nanocluster nucleation and autocatalytic growth [130]. The resulting rate constant values taken from 5 such runs are $k_1 = 0.004 \pm 0.002$, and $k_2 = 0.09 \pm 0.03$. All the fits obtained were similarly poor in the last part of the curve, with a range of R^2 values of 0.9491–0.9954.

sistent with the existing literature [49,130–132], and therefore confusing. However, despite the above nomenclature issues, the relatively slow nanoparticle development observed for this system makes it promising—if catalytically competent for hydrogenation, as is expected—for further studies aimed at determining the true nature of the catalyst and the catalyst formation mechanism. In addition, Bönnemann and co-workers studies along with Goulon's and co-workers' efforts nearly 20 years earlier [40], promise to be important classic studies in identifying what we term "Ziegler nanoclusters".

A similar system, $Pt(acac)_2$ plus 4 $AlEt_3$ ([Pt] = 1.2 mM, solvent = toluene, temperature = 22.0 °C, initially 40.0 psig H_2, stirring = 1000 rpm.), has been tested for its ability to catalytically hydrogenate cyclohexene. The results of following the formation of a Ziegler-type hydrogenation catalyst from this system by the cyclohexene hydrogenation reporter reaction method [50,130,133] are shown here for the first time, Fig. 5 (for complete experimental details see Supporting Information).[17] The hydrogenation curves show the production of active Ziegler-type hydrogenation catalysts after an induction period, but the curves end abruptly upon total consumption of cyclohexene, and do not have a truly sigmoidal shape. The same, now well precedented nanocluster formation mechanistic model discussed above (nucleation A → B (rate constant k_1), and autocatalytic growth A + B → 2B (rate constant k_2) [130]) was employed, but failed to produce good fits in the latter portions of the curves. A representative hydrogenation curve is shown, and the fitting results are given, Fig. 5. The different systems and conditions used prohibit direct comparison between these experiments and the findings of Bönnemann and co-workers. However, the use of slow-forming catalysts, even if such model systems are not what are desired industrially, appears to be one important way in which new insights could be gained. Hence, the $Pt(acac)_2$ plus AlR_3 system is one of interest for further studies.

Bönnemann and co-workers reported the presence of a binuclear Pt complex $Me_4Pt(\mu\text{-}AlMe)_2PtMe_4$ as an intermediate in the formation of Pt nanoparticles [122–124]. Its existence and structure were investigated using ^1H and ^{13}C NMR, MS, XPS and EXAFS studies. Decomposition of the binuclear platinum intermediate lead to "nucleation" of the 1.2 nm, $Pt_{\sim 55}$ nanoparticles. From the in situ ASAXS experiments, the rate of "nucleation" was found to be linearly proportional to the concentration of the binuclear intermediates. Bönnemann and co-workers concluded, therefore, that the
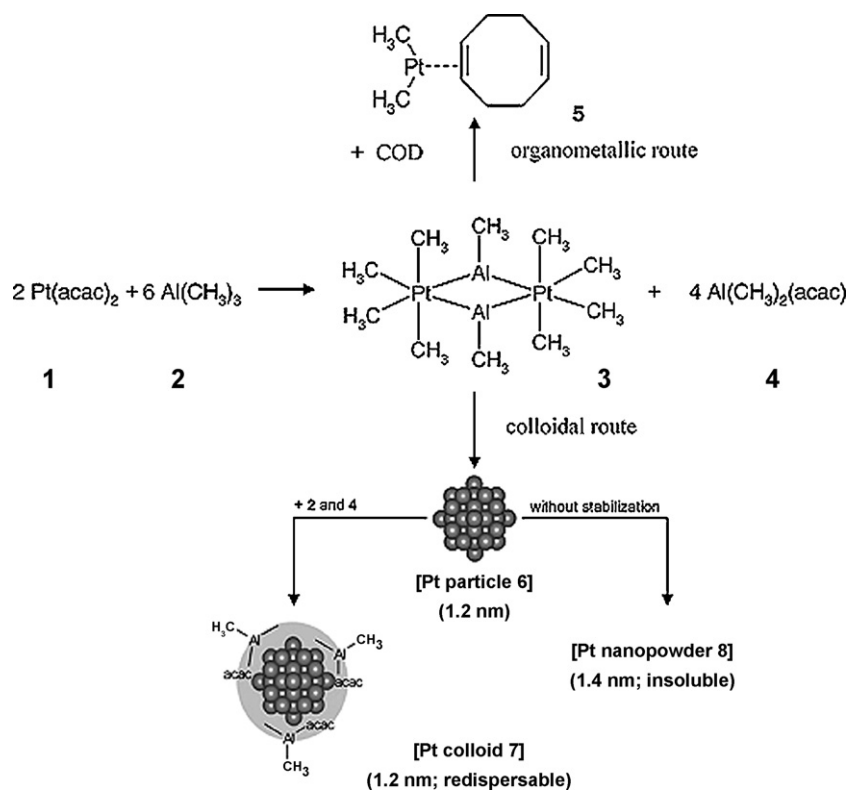
rate-determining step in nanocluster formation is the decomposition of the binuclear intermediate. A word and picture mechanism of colloid formation from the work of Bönnemann and co-workers [124] is reproduced below, Scheme 7. In the absence of excess $AlMe_3$ or $AlMe_2(acac)$, an insoluble "Pt nanopowder" was observed made of 1.4 nm diameter clusters [123].

In the soluble, stabilized nanoclusters, the stabilizer layer has been referred to by Bönnemann and co-workers as an "organo-aluminum protecting shell" [121]. In situ ^1H NMR studies confirmed an exchange reaction between the methyl groups of $AlMe_3$ and the acac ligands from $Pt(acac)_2$, resulting in the appearance of $AlMe_2(acac)$ peaks [122,124]. Protonolysis of a sample of the dry colloid allowed the calculation that 6 active Al–C bonds per Pt atom exist in the stabilizer of Pt nanoclusters. The representation of the resulting stabilized cluster is shown, Scheme 7.

Bönnemann and co-workers also analyzed the products formed upon the reaction of $[(1,5\text{-}COD)Pt(CH_3)_2]$ plus 10 $AlEt_3$ or $Al(C_8H_{17})_3$ [126]. As with other systems studied, the solution became a brown/black color upon the addition of AlR_3. The presence of $Pt(0)_{13}$ nanoclusters was observed in TEM images showing 0.7 nm clusters. This finding was supported by comparison of experimental XANES spectrum with theoretical model spectra of 1-shell and 2-shell clusters. The zero-valent state of Pt in the $Pt(0)_{13}$ nanoclusters was confirmed by both XPS and XANES. Increasing the temperature during formation of the nanoclusters from room temperature to 60 °C resulted in a slight increase in size from 0.7 nm to 0.82 ± 0.19 nm, which was interpreted as a contribution from Pt_{55} nanoclusters in addition to the major constituent, Pt_{13} clusters. Such an interpretation could be supported by a distinct bimodal size distribution obtained from TEM images. However, this was not provided; the reported size and dispersity do not correlate well with truly monodisperse, precise 13 and 55 Pt atom particles as reported. Truly monodisperse nanoparticle samples are rare: single crystals of thiol-protected Au_{102} nanoparticles are, for example, one case of a *truly* monodisperse nanoparticle sample [134].

The timescale of the reaction varied between 1 h to more than one month depending on the temperature and whether $Al(C_8H_{17})_3$ or $AlEt_3$ was used. No color change was observed using $AlMe_3$, implying the absence of nanoclusters in the resulting solution. However, the authors did not mention the temperature or time allowed for observation, so that observation does not rule out possible nanocluster formation with $AlMe_3$ as the cocatalyst. Bönnemann and co-workers [126] believed that β–H elimination was rate-determining in nanocluster formation, yet that explanation is not necessarily consistent with the observation of cluster formation in their own $Pt(acac)_2$ plus $AlMe_3$ system [121–125], or with catalyst formation using $AlMe_3$ in other systems [4,71]. Furthermore, if β–H elimination is rate-determining, one might have expected faster cluster formation with $AlEt_3$ than with $Al(C_8H_{17})_3$, since the former has 50% more β–H's (and if one assumes an equal amount of Al-alkyl is present in each case at the rate determining step). Moreover, β–H elimination is typically very facile in organometallic chemistry and rarely a rate-determining step to our knowledge [10]. Clearly, there are many aspects of the mechanism of formation of Ziegler nanoclusters that require further explanation.

Bönnemann and co-workers have several other, valuable publications dealing with interesting topics that are related to Ziegler-type hydrogenation catalysts. Other research on the $Pt(acac)_2$ plus 4 $AlMe_3$ system was focused on the characterization of networks formed by the nanoclusters [135,136]. Syntheses starting with $Ni(COD)_2$ and $AlEt_3$, and using high temperatures, resulted in the formation of $NiAl_x$ materials [137,138]. Another system gave ~ 10 nm $Co(0)_n$ nanoclusters by the combination of $Co_2(CO)_8$ and AlR_3 [139]. These studies, however, are beyond the scope of this review; the interested reader is referred to those original publications [135–139].

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[17] Other systems surveyed for use as model Ziegler-type hydrogenation catalysts are [(1,5-COD)Ir(acac)], [(1,5-COD)Rh(acac)], Rh(acac)$_3$, Co(acac)$_2$. The results of these previously unpublished hydrogenation survey experiments are also given in Supporting Information for the interested reader.

Scheme 7. A depiction of Pt particle and colloid formation from the Pt(acac)$_2$ plus 6 AlMe$_3$ system proposed by Bönnemann and co-workers [124]. Decomposition of the dimeric, Al-bridged Pt intermediate is thought to be the rate determining step. Reproduced with permission.

It is still unclear why *cluster* formation is relatively slow in both the Pt(acac)$_2$ plus 4 AlEt$_3$ and [(COD)Pt(CH$_3$)$_2$] plus 10 AlEt$_3$, or Al(C$_8$H$_{17}$)$_3$ systems investigated by Bönnemann and co-workers, when *catalyst* formation is rapid in virtually all other systems explored [37]. One possible explanation of this is that the heterogeneous component observed in some systems is the product of catalyst deactivation, as has been observed in a Ni(diisopropylsalicylate)$_2$ plus AlR$_3$ system with aromatic solvents [70]. Another conceivable explanation, in light of the studies of Shmidt and co-workers [19,81,113,114] (who showed the presence of nanoclusters in systems of active hydrogenation catalysts) and the results in Fig. 5, vide supra, showing an induction period prior to the catalytic hydrogenation of cyclohexene using a similar Pt(acac)$_2$ plus 4 AlEt$_3$ system, is that the slow cluster formation reaction is inherent to the use of these particular precursors, conditions, or both. These studies serve to again illustrate the importance of kinetic experiments in studies attempting to determine the true catalyst. Notable here is that the slow formation of these systems could be exploited in the pursuit of a more detailed investigation into the kinetics and mechanism of Ziegler–nanocluster formation, a key goal in the field of Ziegler-type hydrogenation catalysts.

2.2.2.5. Systems investigated by Alley, Hamdemir, Wang, Frenkel, Li, Yang, Menard, Nuzzo, Özkar, Johnson, and Finke: [(1,5-COD)Ir(μ-O$_2$C$_8$H$_{15}$)]$_2$ plus AlEt$_3$ [52–54], Co(neodecanoate)$_2$ plus AlEt$_3$ [55], and Ni(2-ethylhexanoate)$_2$ [56] plus AlEt$_3$. Model and industrial Ziegler-type hydrogenation catalyst systems that have recently been under investigation by the above-noted team include AlEt$_3$ plus [(1,5-COD)Ir(μ-O$_2$C$_8$H$_{15}$)]$_2$ [52–54], Co(neodecanoate)$_2$ [55], or Ni(2-ethylhexanoate)$_2$ [56]. Studies have been carried out using a variety of analytical methods including kinetic measurements,

TEM, MALDI MS, EXAFS, XPS, and NMR. Interestingly, the catalytic activity of the Ir model system varies inversely with Ir concentration, similar to the [Co]-dependent TOF results reported by Shmidt et al. using their Co(acac)$_{2,3}$ plus AlEt$_3$ system already discussed [113]. Some of the other key results thus far appear to be that the precatalyst plus cocatalyst reactions in these Ziegler-type catalyst systems produce a mixture of sub-nanometer *and* amorphous M(0)$_n$ nanoclusters, and that this result would have gone unrealized without using a combination of analytical methods. This review is one of the necessary first steps of the studies in progress, work currently in various stages of preparation for publication [53–56].

The above group has also briefly investigated the mechanism of cyclohexene hydrogenation using a Ziegler-type hydrogenation catalyst made from Co(neodecanoate)$_2$ plus AlEt$_3$, Al/Co = 3. A D$_2$ labeling experiment was used to determine the location of the rate-determining step with regard to the Shmidt mechanism shown back in Scheme 5. Based on those results, reported here for the first time, an updated mechanistic scheme is proposed, Scheme 8. A full description of the results and experimental details will be found by the interested reader in the Supporting Information. Briefly, the Co-based Ziegler-type hydrogenation catalyst was prepared in cyclohexane, cyclohexene substrate was added, and the vessel containing the solution was pressurized with D$_2$. The amount of deuterium incorporation into the resulting hydrogenation product cyclohexane was analyzed by gas chromatography mass spectrometry, Figs. S6 and S7, Supporting Information. The observation of a significant amount of cyclohexane containing >2 deuterium atoms supports the precedented hypothesis, in line with the accepted mechanism for heterogeneous transition metal catalyzed hydrogenations [140], that reductive elimination, as opposed to migratory insertion [42], is the rate determining step, with prior equilibria existing in the earlier step(s). In fact, this updated mech-
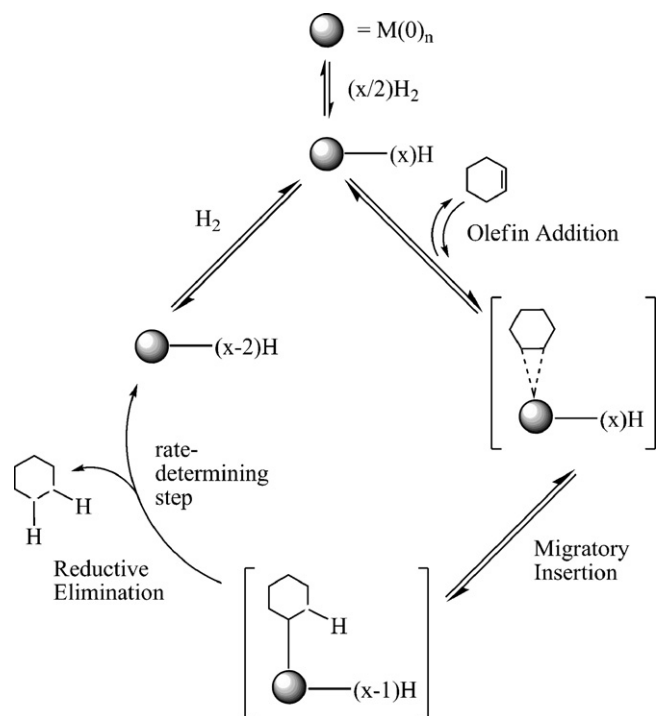
Scheme 8. A schematic catalytic olefin hydrogenation mechanism (shown here for cyclohexene for convenience) using Ziegler-type hydrogenation catalysts. The ball implies a transition metal nanocluster catalyst, but could also represent a monometallic catalyst. The postulated steps are oxidative addition of H_2, olefin addition, migratory insertion to form an alkyl hydride species, and irreversible, rate-determining reductive elimination yielding the saturated cyclohexane. Evidence for reductive elimination being rate limiting is our observation of multiply deuterated (>2 deuterium atoms) in the hydrogenation product of cyclohexene (the results and experimental details are given in Supporting Information for the interested reader). The actual timing of oxidative addition of H_2 versus olefin addition steps is a standard mechanistic ambiguity [38], so that the H_2 activation (first) pathway is shown only for the sake of illustration.

anism, Scheme 8, better explains the previous observation that the reaction becomes zero order in H_2 at pressures above 1.5 atm [42]. A caveat on these studies is that they are not complete as of this writing, so that their full findings and resultant insights remain to be completed.

2.2.2.6. Conclusions for the section on the nature and mechanism of formation of Ziegler-type hydrogenation catalysts. The following results appear to apply across different systems: (i) the exchange of ligands between AlR_3 and the precatalyst has been established by IR and ^1H NMR spectroscopy; (ii) for $M(L)_2$ precatalysts plus AlR_3, the resulting Al species present are $AlR_2(L)$, $AlR(L)_2$, $Al(L)_3$, or some combination of the three depending on the Al/M used, and the presence of additional impurities or additives such as H_2O; (iii) the formation of alumoxanes (i.e., Al–O–Al complexes) and their contribution to the stabilizer layer of observed nanoclusters also has some precedent, but could still use additional study; and (iv) the most recent studies favor the hypothesis of $M(0)_n$ nanocluster catalysts. In these cases AlR_3 is generally believed to reduce the higher valent transition metal from the precursor to the zero-valent state, and it or its reaction products are thought to ligate and stabilize the resulting $M(0)_n$ nanocluster catalyst. However, disagreement persists concerning the reaction forming Ziegler-type hydrogenation catalysts, and the nature of the catalysts themselves. Whether or not the catalysts are homogeneous or heterogeneous is still a central remaining issue, as is the composition of the active catalyst(s). In most cases, the kinetic studies required to answer

the homogeneous versus heterogeneous catalysis question are lacking.

Several factors conspire to make solving the homogeneous or heterogeneous catalysis question especially difficult for Ziegler-type catalyst systems. The high sensitivity of Ziegler-type hydrogenation catalyst systems to factors such as air and water complicates reproducible catalyst preparation, and has probably contributed to the occasional contradictory characterization results seen for otherwise ostensibly similar systems. There is also the possibility that some Ziegler-type catalyst systems are homogeneous and some are heterogeneous, especially when considering the identities of the catalyst precursor components in different systems. This sentiment was expressed by Breslow and Newburg back in 1959 [23], "It is our belief that there is not one, but a family of Ziegler-type catalysts." Even given identical systems, the variables of the synthesis procedure affect catalyst activity and may lead to modifications in the nature of the resulting catalyst. This was recognized by Barrault et al. [37], who noted that "the nature of these complexes is largely controlled by differences in preparation." In other words, despite the narrow definition used herein for Ziegler-type hydrogenation catalysts, the creation of fundamentally different catalysts from similar *or even identical* starting materials may occur because of differences in other variables in the catalyst preparation, or conditions employed during analysis [10,17]. This is a reflection of an insight of Halpern's from the mechanistic study of organometallic systems [141,142], which "underlines the danger of assuming the mechanisms. . . or of extrapolating from one system or set of conditions to another (even closely related) one" [141]. Hence, it is certainly possible that small changes may alter the state of the transition metal from single metal complexes to multimetallic nanoclusters, which are quite different species and catalysts.

Despite the conflicting reports that exist concerning the homogeneous or heterogeneous nature of Ziegler-type polymer hydrogenation catalysts, there is good reason to believe that, in many systems and under conditions commonly employed, there is at least a heterogeneous, nanocluster, or possibly sub-nanocluster component to the active catalysts [16]. That early researchers favored the conclusion that Ziegler-type hydrogenation catalysts are homogeneous makes perfect sense. The prior lack of examples of organic-solvent-soluble nanoclusters, and prior lack of knowledge of the kinetics and mechanism of formation of transition-metal nanoclusters, meant that it simply was not possible to routinely know when soluble nanocluster catalysts were both forming and then serving as the kinetically dominant catalyst [16].[18] The recent observation of Ziegler nanoclusters in some systems is a direct result of characterizations using modern methods such as TEM, XAFS, and ASAXS. The availability and improvement of other, advanced analytical methods may eventually assist in the disproof of the homogeneous or heterogeneous catalyst hypothesis for a given system and set of conditions. Another reasonable hypothesis warranting disproof is that of the simultaneous existence of both homogeneous *and* heterogeneous active catalysts in a single system. Additionally, results from studies under well-documented conditions using *well defined precursor materials* (i.e., and in comparison to the common, but somewhat ill-defined, industrially used Ni and Co precursors) promises to allow generalization of any important findings [52]. Ideally, such studies would simultaneously be able to detect the effects of catalyst preparation variables on both catalyst properties *and* catalyst composition and structure (vide infra).

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[18] Ziegler-type $M(O_2CR)_2/AlR_3$ catalysts were listed in our 2003 review [16] on the "is it homogeneous versus heterogeneous catalysis?" question as systems where heterogeneous catalysis is strongly suspected, but where studies confirming or refuting this suspicion are needed.
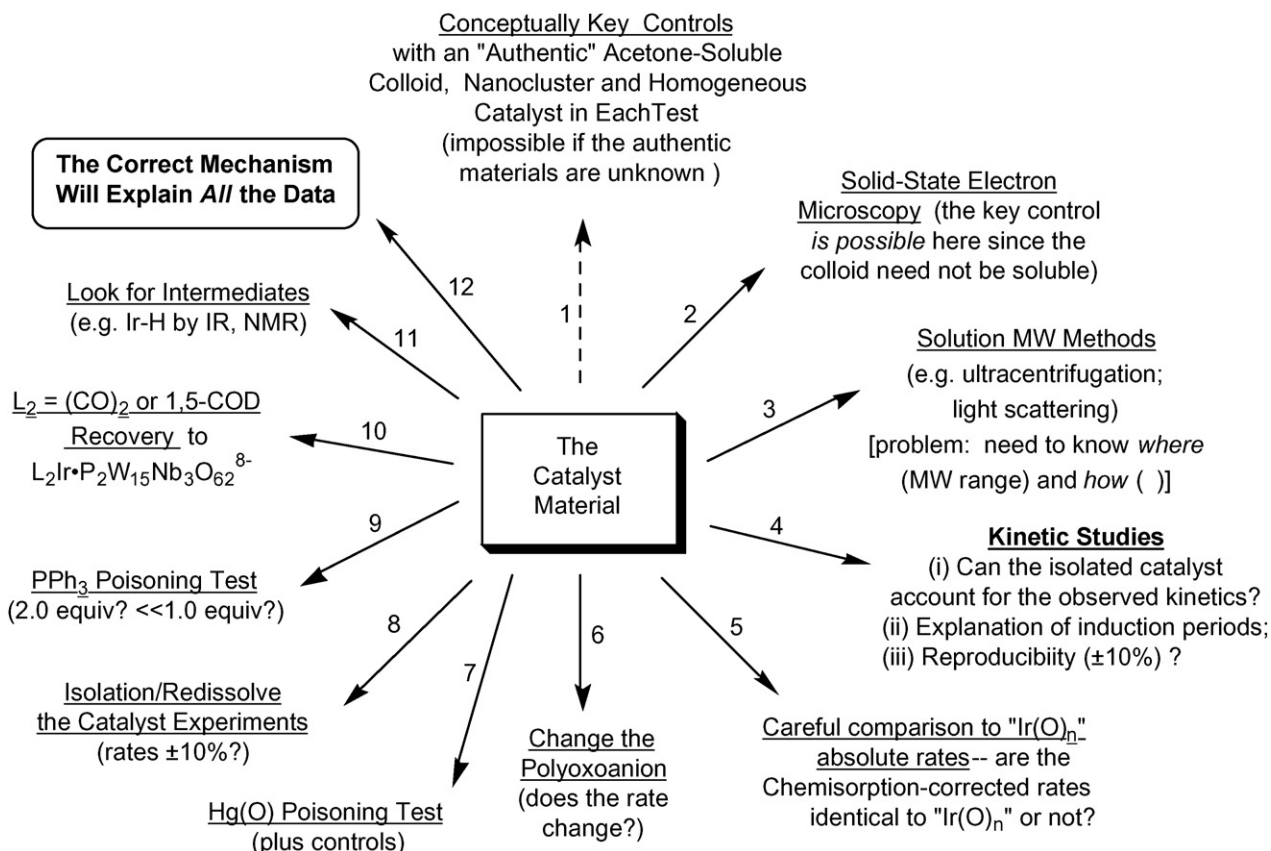
Fig. 6. The multi-step approach developed for distinguishing homogeneous from heterogeneous catalysis in acetone-soluble $Ir(0)_n$ nanocluster systems formed from a $[(1,5\text{-COD})Ir^I \cdot P_2W_{15}Nb_3O_{62}]^{8-}$ catalyst precursor under H_2 in acetone and in the presence of cyclohexene at room temperature [12]. Reprinted with permission.

2.3. A closer look at the more general homogeneous versus heterogeneous catalysis question

2.3.1. The 1994 four-prong methodology

Since it is central to the main unanswered question of industrial Ziegler-type hydrogenation catalysts, namely are they "homogeneous" or "heterogeneous" (or both), we conclude with a last section before the summary on the current methods and approaches to this historically challenging, if not perplexing, research question. In 1994, a *multi-pronged* approach with kinetic studies at its heart[19] was published [12]. That approach emphasizes using multiple analytical techniques and the requirement that any proposed explanation of the catalyst must satisfy *all* the data [13,16]. The approach has been shown to be successful in addressing the homogeneous versus heterogeneous catalysis question on at least four occasions [12,15,17,18]. The approach was the outgrowth of a painstaking, 5-year study that eventually identified novel, highly stabilized, as well as highly catalytically active $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion-stabilized $Ir(0)_{\sim 300}$ nanoclusters as the true catalyst in hydrogenation systems beginning with $[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]^{8-}$ as precatalyst under H_2 and in the presence of cyclohexene, Fig. 6.

A more general solution to the homogeneous versus heterogeneous catalysis problem, diagrammed in a simplified form, Fig. 7, resulted from that work because the polyoxoanion-stabilized nanoclusters turned out to be the most highly anionically stabilized nanocluster known at the time, and thus very "homogeneous-like" [12]. This extreme-case-developed methodology has since proven able to identify nanoparticle catalysts in at least 3 of 4 systems previously believed to be homogeneous catalysis [12,15,17,18]. The methodology even detected both homogeneous and nanocluster heterogeneous catalysis derived from a $[Rh(C_5Me_5)Cl_2]_2$ system, in which the nature of the catalyst changed depending on the conditions used [17]. Note that the goal is not to try the impossibility of "proving" that Ziegler-type hydrogenation catalysts are nanoclusters, but rather to have a way to rule out—that is to falsify, to disprove—all but one of the competing hypotheses for the nature of the true catalyst in a given system and for a specific set of conditions [143], leading to a set of data consistent with, and strongly supportive of, ideally one remaining hypothesis regarding the true catalyst(s). Fig. 8 provides the most current, "6-prong approach" to the "is it homogeneous or heterogeneous catalysis?" question.

Because this methodology ideally involves the use of all relevant techniques with the realization that a proposed answer must explain all the data for a given system, any interpretation of the data is open to continued testing by use of new or improved analytical techniques. Re-interpretation would be necessary if new data is acquired that is inconsistent with the existing explanation for the nature of the catalyst. There is an example of such an occurrence in the recent literature for researchers explicitly using the approach shown here [127,144], and a reexamination of the system using a different analytical technique, in this case XAFS [119,145]. This example serves to illustrate the importance of using all relevant, plus also kinetic studies, and understanding that any viable explanation must account for *all* the data on a given system.

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[19] Support for the central importance of kinetic experiments in catalyst studies comes from, as Halpern put it, "the fact that catalysis is, by definition, purely a kinetic phenomenon" [89].
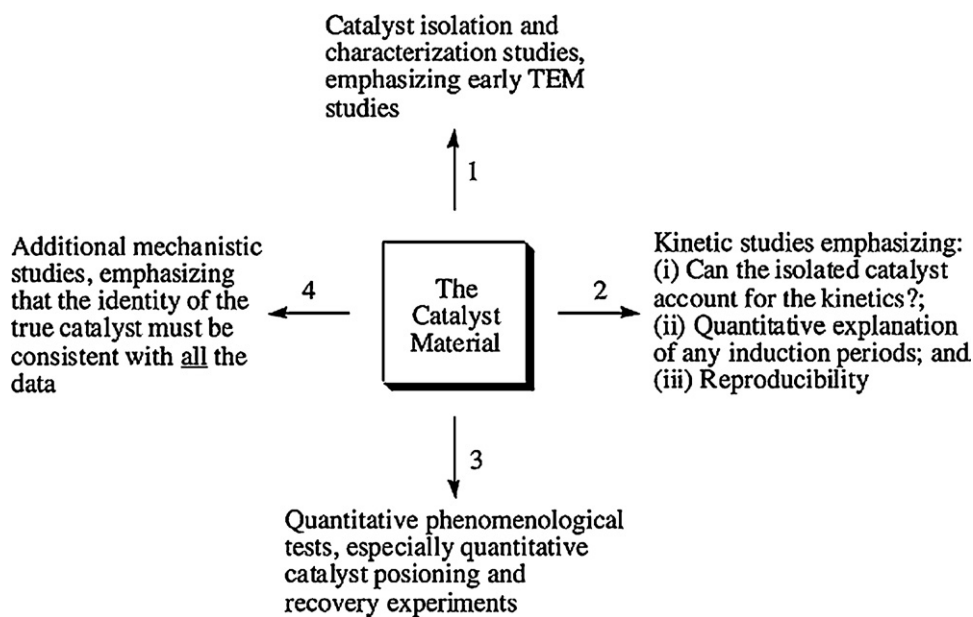
Catalyst isolation and
characterization studies,
emphasizing early TEM
studies

↑
1

Additional mechanistic
studies, emphasizing
that the identity of the
true catalyst must be
consistent with <u>all</u> the
data

4 ←

**The
Catalyst
Material**

→ 2

Kinetic studies emphasizing:
(i) Can the isolated catalyst
account for the kinetics?;
(ii) Quantitative explanation
of any induction periods; and
(iii) Reproducibility

↓
3

Quantitative phenomenological
tests, especially quantitative
catalyst posioning and
recovery experiments

Fig. 7. The 1994 four-prong generalized method for distinguishing homogeneous from nanocluster heterogeneous catalysts [12]. This scheme is a simplified version of the 12-step intellectual process and scheme shown in Fig. 6 [12]. Reprinted with permission.

2.3.2. Special challenges with (first row, Ni, Co, Fe) Ziegler-type hydrogenation catalysts

There are special challenges to answering the homogeneous versus heterogeneous catalysis question for (especially the first row, Ni, Co, Fe) Ziegler-type hydrogenation catalysts. These exist because Ziegler-type hydrogenation catalysts are: (i) notoriously sensitive to both the variables in their preparation (see Section 2.1 above), and sensitive to conditions during characterization experiments; (ii) difficult to isolate for the needed kinetic studies; and (iii) prone to giving spurious results in poisoning experiments, especially since *selective* poisons for the AlR$_3$-derived component and, separately, for the transition-metal components are needed, but do not exist at present. Efforts to isolate Ziegler-type hydrogenation catalysts in their resting state have often met with failure
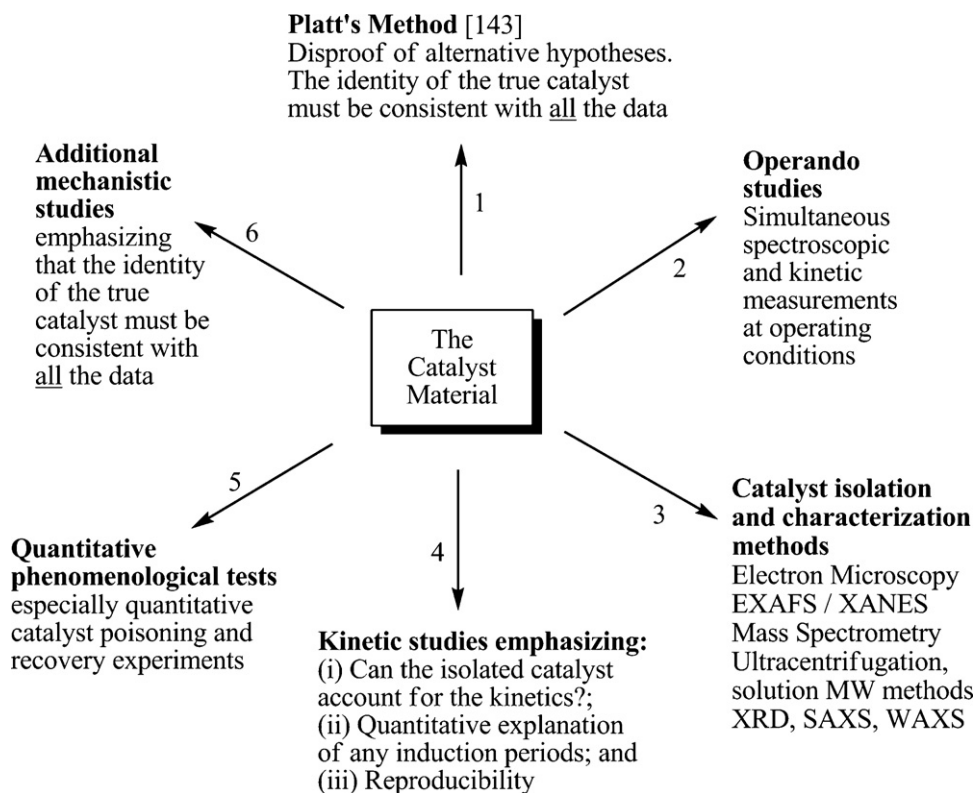
Platt's Method [143]
Disproof of alternative hypotheses.
The identity of the true catalyst
must be consistent with <u>all</u> the data

**Additional
mechanistic
studies**
emphasizing
that the identity
of the true
catalyst must be
consistent with
<u>all</u> the data

6

**Operando
studies**
Simultaneous
spectroscopic
and kinetic
measurements
at operating
conditions

1   2

**The
Catalyst
Material**

5   4   3

**Quantitative
phenomenological tests**
especially quantitative
catalyst poisoning and
recovery experiments

Kinetic studies emphasizing:
(i) Can the isolated catalyst
account for the kinetics?;
(ii) Quantitative explanation
of any induction periods; and
(iii) Reproducibility

**Catalyst isolation
and characterization
methods**
Electron Microscopy
EXAFS / XANES
Mass Spectrometry
Ultracentrifugation,
solution MW methods
XRD, SAXS, WAXS

Fig. 8. The updated "six-prong" approach for distinguishing homogeneous from heterogeneous catalysis, updated to include operando spectroscopy. The basic principles, however, remain the same: (i) find what form or forms the precursor materials take in a sample of the resting form(s) of the catalyst; (ii) perform kinetic studies from resting state(s) to determine which are the kinetically competent/dominant species; (iii) use all available/applicable techniques; and (iv) eliminate alternative hypotheses [143] to arrive at, ideally, a unique explanation that accounts for all the data.

(e.g., M(2-ethylhexanoate)$_2$ plus m AlEt$_3$, M = Ni or Co, m = 3–4, and Co(stearate)$_2$ plus 2 AlEt$_3$ systems) [58,67]. Early successful efforts required use of non-Ziegler-type catalyst models such as [(α,α'-bipyridyl)NiMe$_2$], [4] or experiments under atypical conditions such as low temperatures [4,58,105]. The 2005 and 2006 work of Shmidt and co-workers [19,81,113], and 1999–2005 work of Bönnemann and co-workers [121–124,126], reports successful isolation of the catalyst-related material, and nanocluster materials, respectively. However, the handling procedures required for isolation of these materials, which often involves removal of the solvent under vacuum, washing the residue with hexane, and drying, may influence the nature of the material, the characterization results, or both [146]. This is especially true for the use of TEM, which despite some recent success [19,81,113,121–124,126], has also given results that were highly dependent on the method of sample preparation in some Ziegler-type catalyst systems [9]. Furthermore, and as already mentioned, without checking for artifacts when using TEM (by control experiments and complementary characterization techniques), misleading change in, or damage to, the sample from the electron beam of the TEM may occur and go undetected [17,127]. *This is especially true for TEM of* Ziegler-type *catalyst samples of the relatively light elements of Ni and Co*, which are more susceptible to certain types of TEM-beam-induced damage in addition to poor contrast and image quality [147].

Normally, quantitative catalyst poisoning experiments using established poisons such as CS$_2$ have the potential to give definitive results [148]. Less than 1 equivalent of poison should be needed to completely kill catalyst activity if the catalyst is a particle with only a fraction of transition metal atoms on its surface. However, if a full equivalent of poison is needed it may indicate a molecular homogeneous catalyst [16]. The use of such poisons with Ziegler-type hydrogenation catalysts is problematic because the Lewis acidic AlR$_3$ component can be expected to compete with the transition metal for the poison—again, ideally two types of selective poisons are needed. Attempts to use alcohol in catalyst poisoning led to contradictory results, as has already been discussed [57,75,114]. Poisoning Ziegler-type hydrogenation catalysts with Hg(0)—a (non-definitive, but often useful) test of heterogeneous catalyst formation—suffers from the possibility that Hg(0) might also poison homogeneous complex catalysts or catalyst precursors [16]. Difficulties with the Hg(0) poisoning test have been discussed elsewhere [90]. Additionally, control experiments to illuminate or rule out these effects would need to take into account the fact that most Ziegler-type hydrogenation catalysts are rapidly pre-formed before use in hydrogenation.

Finally, the requirement that the correct explanation be consistent with all the data is an important, but tall order for Ziegler-type hydrogenation catalysts. A lot of conflicting data on what appears to be comparable systems exists. This requirement is, nevertheless, one that will have to be met before a systematic understanding of Ziegler-type hydrogenation catalyst systems is realized.

2.3.3. Conclusions for the section on the more general homogeneous versus heterogeneous catalysis question

Despite the success of the 1994 approach in Figs. 6 and 7, applying it toward determining the true nature of Ziegler-type hydrogenation catalysts is changing and upgrading that approach [53–56]. However, it must be remembered that the approach in Figs. 6 and 7 is nothing more than a guideline for one's own, creative thinking and approach for the specific, "true catalyst determination" problem and catalyst at hand. The central tenets of the methodology should still apply: (i) find what form or forms the precursor materials take in a sample of the resting state(s) of the catalyst; (ii) perform kinetic studies from resting state(s) to determine which are the kinetically competent/dominant species; (iii) use all available/applicable techniques;

and (iv) eliminate all reasonable alternative hypotheses to arrive at, ideally, a unique catalyst formulation that accounts for all the data.

The ideal goal in this updated approach to the "homogeneous versus heterogeneous catalysis" problem is the *simultaneous spectroscopic and kinetic analysis of a catalyst at the desired or normal operating conditions,* that is, via "operando" spectroscopy (the term "operando" is from the Latin for "working" or "operating") [149–152]. This combination overcomes weaknesses of using either kinetic [89,153] or spectroscopic analysis alone [152], especially if *multiple* spectroscopic techniques are simultaneously used [154]. However, the use of operando spectroscopy requires overcoming difficult challenges in experiment and reactor cell design [154]. Considerable challenges are likely to be encountered in any attempt to analyze Ziegler-type hydrogenation catalysts by operando spectroscopy. The use of an experimental setup, no matter how sophisticated, cannot supplant the importance of using Platt's method of disproof of all reasonable alternative hypotheses [143].

3. Summary

The key points from the introduction section are:

- Ziegler-type hydrogenation catalysts made of group 8–10 transition metal precatalysts, particularly first row metal chelates or carboxylates, and AlR$_3$ cocatalysts, are important for the industrial hydrogenation of a variety of unsaturated organic compounds, including diene polymers. Ziegler-type *hydrogenation* catalysts should *not* be confused with Ziegler–Natta *polymerization* catalysts, which were not a part of this review.
- Despite their relatively long history of industrial use, there is a need for an improved fundamental understanding of Ziegler-type hydrogenation catalysts. That improved understanding should, in turn, drive further *rationally-directed* synthetic, mechanistic, and industrial improvements.
- The key general areas investigated in the literature can be categorized as: (i) the variables important to catalyst synthesis and their effect on catalyst properties, particularly hydrogenation activity, (ii) the reaction between the transition metal precatalyst and cocatalyst components, (iii) the compositional and structural nature of the active catalyst species, and (iv) the mechanism of catalytic hydrogenation.

The main findings from the section on catalyst preparation variables are:

- The most important variables of catalyst preparation appear to be: (i) the identities of the transition metal precatalyst and the organometallic cocatalyst; (ii) the ratio of these two components and the role of impurities, particularly H$_2$O; (iii) the solvent; (iv) the identity of the substrate; (v) the details of component addition (such as order and rate, presence of substrate, atmosphere, and temperature); and (vi) the aging of prepared catalyst before use in hydrogenation reactions.
- Catalysts made from Ni or Co precursors are favored by industry. They tend to have the highest activities, and have an advantageous balance of desirable properties, low cost, and relative ease of preparation.
- The anions present are another important aspect of the identity of the precatalysts. Anions such as 2-ethylhexanoate and acac are the most popular for use and study. The activity of catalysts made with these precursors appears to be positively correlated to their solubility. Some precatalyst anions, especially halogens, reduce catalyst activity, likely by acting as poisons.

- Short chain AlR_3 cocatalysts, particularly $AlEt_3$, are most commonly used. The preferred cocatalyst varies with the particular system.
- One of the main variables appears to be the Al/M ratio. Most studies seem to agree that there is an optimum Al/M ratio for most systems. The optimum Al/M ratio has been reported to exist due to incomplete activation at too low Al/M and poisoning by excess AlR_3 at high Al/M. Water and other impurities have been reported to have both beneficial and detrimental effects, depending on the particulars of the system being studied, and appear to affect the optimum Al/M ratio. The optimum Al/M ratio is one of the areas where a greater fundamental understanding of the nature of the catalyst for each given system could help to make sense of the range of results observed in the literature.
- The other variables involved in catalyst preparation (the solvent, the substrate, the order and rate of component addition, the presence or absence of substrate, the atmosphere, the temperature, and catalyst aging before use) are not universally agreed to be important. However, in most cases, they have been reported as having an effect on the activity of the resulting catalyst, but generally less so than the identity of the catalyst precursors, the Al/M ratio, and the amount of H_2O present. Many variables are likely connected to each other in complicated ways, such as the Al/M ratio and the amount of H_2O, but these relationships are incompletely understood.
- Mass transfer limitations should be suspected in many studies for these active catalysts, and unless the control experiments designed to rule out MTL were specifically done and reported in detail. This is especially true for instances where reports claim that certain catalyst preparation variables were not important to catalytic activity, but other reports claim that they are.
- The ability to explain the effects of variables in the preparation of Ziegler-type hydrogenation catalysts is hampered by the fact that the effects themselves are often dissimilar for ostensibly similar, but in fact different systems. Answers as to *how* variables in catalyst synthesis affect catalytic activity are needed and are possible from studies of the ways in which each variable affects the mechanism of formation, composition, and resultant structure of the catalyst. Ultimately being able to connect the variables to catalyst activity, composition, structure and formation mechanism remains a significant challenge.

The main findings from the section on the nature and mechanism of formation of Ziegler-type hydrogenation catalysts are:

- The most important unknowns in Ziegler-type hydrogenation catalysis are the reaction between the catalyst precursors, whether the resulting catalysts are homogeneous or heterogeneous, and the details of the mechanism of catalytic hydrogenation? The most important of these questions is the nature of the true catalyst. Specific questions in this regard include: (i) how the catalyst is formed, (ii) how many transition metal atoms constitute the active catalyst species, (iii) what are their oxidation states, and (iv) what is the composition, structure, and role of the cocatalyst?
- Ziegler assumed early on that the catalyst of the Ni effect took the form of colloidal Ni. Early efforts by Wilke and co-workers attempted to disprove this, and to show that the catalyst could be a homogeneous allyl-complex. That classic work laid the groundwork for subsequent researchers of Ziegler-type *hydrogenation* catalysts to propose homogeneous catalysts for those systems. More recent research, with the aid of much improved instrumentation technology and improved precedent for hydrocarbon-soluble colloids, has generally obtained results that suggest the true catalysts are heterogeneous, what we have termed herein as "Ziegler nanoclusters."

- Definitive *kinetic* evidence remains to be reported for many Ziegler-type hydrogenation catalyst systems. Without that data, the homogeneous versus heterogeneous catalysis question cannot be answered.
- It may be that no single type of catalyst results for Ziegler-type hydrogenation catalyst systems. Small but important differences in outwardly similar systems may cause fundamental differences in the type(s) of catalyst(s) present. This, in turn, reveals the importance of using well-defined catalyst precursors, and carefully controlled conditions, in the needed studies attempting to identify the true catalyst(s). Additionally, some Ziegler-type hydrogenation catalyst systems may *simultaneously* contain catalytically active homogeneous *and* heterogeneous components. If so, it will take an extraordinarily careful, comprehensive, and detailed effort, all on the right/"best" system, to definitively support this particular hypothesis.

The key messages from the section taking a closer look at the more general homogeneous versus heterogeneous catalysis question are:

- A multi-pronged approach, demonstrated on multiple occasions to be successful, exists for distinguishing between homogeneous versus heterogeneous catalysis. Explicit application of that approach in addressing the homogeneous versus heterogeneous catalysis question for Ziegler-type hydrogenation catalysts, is proving useful in work underway [53–56].
- There are special challenges to answering the homogeneous versus heterogeneous catalysis question for Ziegler-type hydrogenation catalysts: (i) they are typically very sensitive to both the variables in their preparation, and conditions during characterization experiments; (ii) they have been difficult to isolate for the needed kinetic studies; and (iii) poisons selective for each of the metal and Al-based components do not currently exist.
- The multi-pronged approach to the homogeneous versus heterogeneous catalysis problem has been updated to include operando spectroscopy for catalyst characterization.

We would like to end by noting that, despite the many challenges summarized in this review, Ziegler-type hydrogenation catalysts hold considerable promise for other applications. Ziegler-type hydrogenation catalysts are, despite the homogeneous versus heterogeneous catalysis question, largely unrecognized as hydrocarbon soluble, readily self-assembled catalysts with neutral charge, high activity, and long lifetime, at least in many of the cases examined herein. Additional catalytic application, fundamental kinetic, spectroscopic, as well as other studies are strongly encouraged, regardless of whether Ziegler nanoclusters are the true catalysts in all, or even selected, cases.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.07.007.

Appendix B.

See Tables B.1–B.3 .

Table B.1
Patent literature.

Authors (year)	Catalyst systems	Other variables in catalyst synthesis	Ref.
Breslow and Matlack (1963)	Ti(i-Pr)$_4$, V(n-Bu)$_3$, Cr(acac)$_3$, MoO$_2$(acac)$_2$, Mn(acac)$_3$, Ru(acac)$_3$, Co(acac)$_3$, Fe(acac)$_3$, Ni(acac)$_2$, or Pd(acac)$_2$ + Al(i-Bu)$_3$	*Solvent:* n-heptane, or heptanes. *Hydrogenation substrate:* Cyclohexene, 1-octene, ethynylbenzene, polyisoprene rubber, 2-methylbutene-2, hexane-1, or tetramethylethylene. *Order of addition*: cocatalyst added to the precatalyst in both the presence and absence of substrate. *Synthesis atmosphere:* H$_2$ gas at 50 psi, 43 psi, 40 psig, 21 psig, or 35 psig. *Synthesis temp:* room temp, 40 °C, 50 °C, 30 °C.	[59]
Lapporte, S. (1965)	Ni(acac)$_2$, Fe(acac)$_2$, Ni(benzoate)$_2$, Ni(acac)$_2$, Cr(acac)$_2$, Co(acac)$_2$, or Cu(acac)$_2$ + 1–5, 8 or 30 AlEt$_3$ or BEt$_3$	*Solvent:* Benzene. *Hydrogenation substrate:* Benzene, o-xylene, 1,3-butadiene, 4-vinylcyclohexane, 1,5,9-cyclododecatriene, naphthalene, methyl ethyl ketone, maleic anhydride, cinnamic acid, benzoic acid, dimethyl terephthalate, benzaldehyde, dimethylphthalate, phenol, nitrocyclohexane, isophthalonitrile, pyridine, aniline, nitrobenzene, 3-hexyne. *Order of addition*: cocatalyst added to precatalyst in the presence of substrate. *Synthesis atmosphere:* N$_2$; *Synthesis temp:* −50 °C to 200 °C	[72]
Kroll (1968)	Co(acac)$_2$, Fe(acac)$_n$, Ni(acac)$_n$, Pt(acac)$_n$, Cr(acac)$_n$, V(acac)$_n$[a] + 4, 6, 8, 10 or 35 Al(i-Bu)$_3$, AlEt$_2$(n-BuO), AlMe$_2$(acac), AlEt$_3$, or AlH(i-Bu)$_2$, Al(i-Bu)$_3$-p-dioxane, AlEt$_2$Cl/AlEtCl$_2$	*Solvent:* Heptane, dimethoxyethane, triethylamine, benzene, decane, p-dioxane, p-xylene, pentane, ether, dimethoxyethane. *Hydrogenation substrate:* Cyclohexene, cis, trans,trans-cyclododecatriene, benzonitrile, quinoline, cyclopentadiene, benzophenone, 4-vinylcyclohexene, phenylacetylene, 1-hexene, n-methylmorpholine, anisole, diphenylether, cyclododecatriene, octyne-4, dicyclopentadiene, cyclooctadiene, 3-methyl-1-butene, 2-methyl-2-butene. *Order of addition:* Precatalyst + cocatalyst (substrate is not mentioned). *Synthesis atmosphere:* N$_2$. *Aging:* Overnight, or 5 min. Additional notes: "The stability and/or activity of Ziegler-type catalysts is markedly improved by the addition of a third component, i.e., Lewis base such as p-dioxane or SEt$_2$, weak organic acid such as n-butanol or t-butylalcohol, oxygen, to the catalyst system."	[64]
Yoshimoto et al. (1970)	Ni naphthenate, Co(acac)$_n$,[a] Fe napthenate, bis (salicylaldehyde)Ni, Ni cyclohexylcarboxylate, Co octanoate, or Co naphthenate + 3, 4, or 12 AlEt$_3$, MgEt$_2$, (n-Bu)Li, or LiAlH$_4$, Ni benzenesulphonate or Ni p-toluene sulfonate + AlEt$_3$	*Solvent:* Toluene, hexane, tetrahydrofuran, or n-hexane. *Hydrogenation substrate:* Butadiene units of styrene butadiene copolymer. *Order of addition:* Precatalyst and cocatalyst are mixed in the presence of olefinically unsaturated hydrocarbon which does not act as hydrogenation substrate. *Synthesis atmosphere:* N$_2$ or H$_2$. *Synthesis temp:* 30 °C, 29 °C, 28 °C, 80 °C, 50 °C, −78 °C. *Aging:* 5 min. Additional notes: An olefinically unsaturated hydrocarbon such as cyclohexene, 1-heptene, dicyclopentadiene, styrene or 1,7-octadiene, is added to the reaction medium to form the, so called, "three components catalyst." The use of olefinically-unsaturated hydrocarbon becomes increasingly important to the production of an effective and stable catalyst as temperatures are increased from 0 to 100 °C. Excess unsaturated hydrocarbon causes an, "undesirable induction period due to the auxiliary reaction in the catalyst formation."	[68]
Yoshimoto et al. (1970)	Ni naphthenate, Co naphthenate, bis(ethylacetoacetate) Ni, bis(acetylacetone) Ni, Fe naphthenate, Ni 2-ethylhexanoate, or Co 2-ethylhexanoate + 0.6, 1.3, 2.7, 4.0, or 6.7 (n-Bu)Li, or MgEt$_2$	*Solvent:* Toluene. *Hydrogenation substrate:* Styrene butadiene copolymer, or polybutadiene. *Order of addition:* Substrate + H$_2$ (gas) + precatalyst and cocatalyst (order of addition of precatalyst or cocatalyst is not given). *Synthesis atmosphere:* H$_2$. *Synthesis temp:* 30 °C. *Aging:* 5 min. Additional notes: Presence or absence of polymer to be hydrogenated is not an important factor in catalyst preparation.	[60]
Wald and Quam (1971)	Ni acac + 2 AlEt$_3$ or Al(i-Bu)$_3$	*Solvent:* Cyclohexane. *Hydrogenation substrate:* Polystyrene-polyisoprene-polystyrene block copolymer. *Synthesis temp:* 40 °C. *Aging:* >15 min. Additional notes: Selectively hydrogenates the diene portions of block copolymers without hydrogenating the vinyl aromatic portions thereby reducing oxygen sensitivity, and without "appreciable degradation" (chain scission).	[65]
Wald and Quam (1972)	Ni octoate, or Ni acac + 2, or 3 AlEt$_3$	*Solvent:* Cyclohexane. *Hydrogenation substrate:* Polystyrene-poly(styrene/isoprene) copolymer. *Order of addition:* Substrate + H$_2$ (gas) + pre-prepared catalyst (order of addition of precatalyst and cocatalyst is not given), or precatalyst + cocatalyst + substrate. *Synthesis temp:* 250 °C. *Aging:* 15 min. Additional notes: Provides selectively hydrogenated block copolymers with improved processability with minimum degradation of the polymers in the form of chain scission by the hydrogenation catalyst.	[66]
De La Mare (1973)	Ni(octoate)$_2$ or Co(2-ethylhexabunoate)$_2$ + 2.5 AlEt$_3$	*Solvent:* Isooctane/cyclohexane. *Hydrogenation substrate:* Butadiene-2-vinylpyridine copolymer. *Order of addition:* Substrate + solvent + pre-prepared catalyst (order of addition of precatalyst and cocatalyst is not given) + H$_2$ (gas); *Synthesis temp:* 25 °C, or 170 °C. Additional Notes: Treatment of copolymers containing blocks from polar monomers with 1–3 mol of a Lewis acid, preferably BF$_3$, per polar group facilitates hydrogenation. Without this treatment it is not possible to use these catalysts to hydrogenate polar copolymers.	[76]

Table B.1 (*Continued*)

Authors (year)	Catalyst systems	Other variables in catalyst synthesis	Ref.
Loveless et al. (1976)	Ni acac, Ni naphthenate, or Fe(acac)$_3$ + 0.8, 3.0, 3.3, 6.0 or 10.0 (*n*-Bu)Li	*Solvent:* *n*-heptane, or cyclohexane. *Hydrogenation substrate:* Polyisoprene, sulfur vulcanizable elastomers, or 1-octene. *Order of addition:* Precatalyst + substrate + H$_2$(gas) + cocatalyst. *Rate of addition:* Cocatalyst is slowly added (i.e., 250 mmol of (*n*-Bu)Li is added over 10 min). *Synthesis atmosphere:* H$_2$. *Synthesis temp:* room temp. *Aging:* 10 min. Additional Notes: A phenolic substance, such as p-nonyl phenol, is added to the precatalyst solution to produce soluble organometallic complex before the addition of other catalyst components. A claim is that this catalyst is superior to previous ones in, "degree and rapidity of hydrogenation which is possible." There is no upper limit to the amount of cocatalyst that can be used, but there is no benefit to using more than the amount prescribed. "The catalyst is not sensitive to small traces of impurities such as water."	[77]
Baumgartner and Balas (1976)	Ni(2-ethylhexanoate)$_2$ + 2.5 or 3.0 AlEt$_3$	*Solvent:* Cyclohexane. *Hydrogenation substrate:* Styrene-isoprene copolymer. *Synthesis temp:* 80 °C. Additional Notes: Excess AlEt$_3$ was added after the reduction of the substrate was completed to some extent. This addition interrupted the hydrogenation. The addition of 2-ethylhexanol after the interruption caused the hydrogenation to resume.	[82]
Ladenberger et al. (1980)	Ni(acac)$_2$ + Al(*i*-Bu)$_3$	*Solvent:* Toluene, hexane. *Hydrogenation substrate:* Butadiene-styrene copolymer. *Synthesis atmosphere*: H$_2$. *Synthesis temp:* 25–30 °C. Additional Notes: A more active catalyst is achieved through the addition of H$_2$O after reaction of the precatalyst, cocatalyst and the substrate. H$_2$ uptake frequently only starts after the H$_2$O addition. Aromatics are more readily hydrogenated if a high Al/M is used.	[78]
Durand et al. (1981)	Two metal chelate compounds: the first of Co or Ni, and the second of another metal Fe, Zn, Zr, Mn, Mo (all preferably acac or carboxylates), +1.5 to 6 AlEt$_3$, Al(*i*-Bu)$_3$ or LiBu	*Solvent:* Heptane, cyclohexanol, decahydronaphthalene, benzene, diisopropylether. *Hydrogenation substrate:* Bis phenol A, phenol, cyclododecatriene, benzene, propionitrile, oleonitrile, adiponitrile. *Order of addition:* Substrate + pre-prepared catalyst (order of addition of the precatalysts and the cocatalyst is not given), or Substrate + Catalyst 1 (precatalyst 1 + cocatalyst) + Catalyst 2 (precatalyst 2 + cocatalyst). *Synthesis temp:* 90 °C. Additional Notes: if the metal salts were reacted separately with the same cocatalyst, an inferior catalyst, or even non-active solution will result. The mode of catalyst preparation is not critical, but is preferably carried out in the absence of substrate in most cases.	[155]
Willis et al. (1990)	Ni 2-ethylhexanoate + 6 or 2.3 (s-Bu)Li or AlEt$_3$	*Solvent:* Cyclohexane, tetrahydrofuran. *Hydrogenation substrate:* Two different styrene butadiene block copolymers. *Order of addition:* Substrate + catalyst (order of addition of precatalyst and cocatalyst is not given). *Synthesis temp:* 47 °C, room temp. Additional Notes: Water should be present when the precatalyst and the cocatalyst are combined. Catalysts so prepared are suitable for hydrogenating polymers containing acidic functionality when certain other procedures are followed. Without said procedures (the focus of the patent), acidic functional groups interfere with the hydrogenation reaction by catalyst deactivation and/or gelling of the polymer solution.	[61]
Abraham et al. (1991)	Fe, Co or Ni halides, acetates, or acacs Co(neodecanoate)$_2$ or Pd(PPh$_3$)$_4$, Pt(PPh$_3$)$_4$, or Rh(PPh$_3$)$_3$ + 4 AlR$_3$ where each R = alkyl has 1–4 C atoms	*Solvent:* Toluene. *Hydrogenation substrate:* Butadiene-methyacrylate copolymer. *Order of addition:* Precatalyst + cocatalyst added over substrate. *Synthesis atmosphere:* N$_2$. *Synthesis temp:* room temp. *Aging:* 1 h. Additional Notes: The use of a complexing agent, such as phosphines (R$_3$P) or phosphites ((RO)$_3$P), is necessary in catalysis of hydrogenation of high MW nitrile-butadiene rubber (NBR) random copolymers. Without the complexing agent, gelation occurs due to complexation of the transition metal catalyst to the polar groups on the polymer chains.	[44]
Hoxmeier and Slaugh (1991)	Nickel 2-ethylhexanoate + 1, 2, 3, 4, 7, or 10 MAO (Methylalumoxane) or EAO (Ethylalumoxane), an equimolar blend of MAO/EAO, or AlEt$_3$	*Solvent:* Cyclohexane. *Hydrogenation substrate:* Polystyrene-polybutadiene-polystyrene tribock copolymer. *Order of addition:* Substrate + catalyst (order of addition of precatalyst and cocatalyst is not given). *Synthesis temp:* 25 °C. *Aging:* 30 min. Additional Notes: 0.5 equivalents of H$_2$O is present in the precatalyst solution. Catalysts made in this manner with MAO offer improved control over the extent of hydrogenation in polymers containing both ethylenic and aromatic unsaturation by an initially slower hydrogenation reaction, but compared to similar catalysts made with AlR$_3$, retain higher activities over longer time spans. However, the catalyst formed with longer alkyl chain alumoxanes (C$_2$–C$_8$) are more active for hydrogenation at all times than similar catalysts made with AlR$_3$.	[62]

Table B.1 (*Continued*)

Authors (year)	Catalyst systems	Other variables in catalyst synthesis	Ref.
Coolbaugh et al. (1991)	Ni(octoate)$_2$ or Ti(n-Bu)$_4$ + 3.6, 2.5, or 6.0 AlEt$_3$	*Solvent:* Cyclohexane. *Hydrogenation substrate:* Isoprene-Butadiene-isoprene triblock copolymer. *Order and rate of addition:* Precatalyst + cocatalyst, 20.80 mL of cocatalyst is added as quickly as possible (i.e., in 15 s); or solvent + precatalyst and cocatalyst simultaneously added over 25 min. The catalyst solutions prepared as above are added over substrate. *Synthesis atmosphere:* N$_2$. *Aging:* 10 min. Additional Notes: The molar ratio of the transition metal compound to the cocatalyst should be kept essentially constant by either simultaneous addition of solutions of the two, or by as rapid addition of the cocatalyst as possible. If added over the course of more than about 15 min a less selective catalyst results, which may also ppt. from solution. The reversal of the addition sequence is likewise detrimental. "Extreme care must be used to exclude air, moisture and other impurities capable of interfering with the delicate chemical balance involved in the synthesis of the catalyst."	[63]
Gooodwin and Willis (1992)	Ni(2-ethylhexanoate)$_2$ + 2.6 AlEt$_3$	*Solvent:* Cyclohexane. *Hydrogenation Substrate:* Polyisoprene, or polybutadiene. Additional Notes: Complete hydrogenation of olefinic unsaturation in low molecular weight diene polymers, particularly those having terminal hydroxyl groups, is achieved (previously not possible using these catalyst systems) by removing fine particles of ionic Li residues such as LiOR and LiOH through filtering or decanting the polymer solutions prior to hydrogenation.	[73]
Hergenrother et al. (1994)	Ni octoate + 3, 6, 7 Al(i-Bu)$_3$, or AlEt$_3$	*Solvent:* Hexane, toluene. *Hydrogenation Substrate:* Polybutadiene. *Order of addition:* Precatalyst + cocatalyst. The catalyst solution added over the substrate. *Synthesis atmosphere*: H$_2$. *Synthesis temp:* −25 °C, or 66 °C. *Aging:* 1 h. Additional notes: Cyclohexene is added to precatalyst solution before cocatalyst addition to stabilize the catalyst prior to hydrogenation. Hydrogenation saturation controlled by treating polymers with an arylphosphine in the presence of the hydrogenation catalyst. The order of reagent addition is unimportant with either the precatalyst or the cocatalyst added incrementally throughout the hydrogenation reaction.	[45]
Handlin et al. (1995)	Ni 2-ethylhexanoate + 2.6 AlEt$_3$	*Solvent:* Cyclohexane. *Hydrogenation substrate:* Polybutadiene. Additional Notes: the catalyst is used to hydrogenate butadiene polymers having terminal functional groups to give low viscosity polymers.	[74]
Johnson et al. (2002)	Co neodecanoate, or Ni octoate + 2.0, 2.2, or 1.3 AlEt$_3$	*Solvent:* Cyclohexane, diethylether. *Hydrogenation substrate:* Linear triblock copolymer of styrene and ethylene/butadiene, polystyrene-polybutadiene-polystyrene triblock copolymer, or linear polystyrene-polyisoprene-polystyrene-polyisoprene block copolymer. *Order and rate of addition*: The catalyst is prepared by slowly adding cocatalyst over the precatalyst in the absence of substrate.	[46]

^a The "*n*" values of the precatalyst components are not given; they may be the same or different in different transition metal precatalyst compounds.

Table B.2
Nature and mechanism of formation of the catalyst—the "*Ziegler-type Catalysts are Homogeneous*" hypothesis.

Authors (year)	Catalyst systems	Results	Ref.
Wilke and co-workers (1973)	Ni(acac)$_2$ + AlMe$_3$, AlEt$_3$ or Al(i-Bu)$_3$	A homogeneous Ni(0) complex formed as a result of the reaction of Ni–olefin π–complex with Al cocatalyst. The resulting complex is proposed to contain multicenter bonds including C, Ni(0), and Al atoms.	[4]
Sloan *et. al.* (1963)	Fe(acac)$_3$, Co(acac)$_2$, Co(acac)$_3$, Ni(acac)$_2$, Ru(acac)$_3$, or Pd(acac)$_2$ + AlEt$_3$, Al(i-Bu)$_3$, or AlH(i-Bu)$_2$	M–H species, given as MHX$_{n-1}$, are claimed as the active catalyst. The M–H species are proposed to form by alkylation and then hydrogenolysis of the precatalyst.	[57]
Lapporte (1969)	Ni(2-ethylhexanoate)$_2$, or Co(2-ethylhexanoate)$_2$ + 3–4 AlEt$_3$	Mononuclear H–M(0) –L species, L = labile –H, –R, solvent, olefin, or AlEt$_2$(2-ethylhexanoate), is proposed as the catalyst. However, binuclear M(I) is not ruled out.	[58]
Klinedinst and Boudart (1973)	Fe(acac)$_3$ + 6 AlEt$_3$	Mössbauer spectroscopy shows that high spin Fe(II) are the only Fe species present at low temp. Rules out catalysis by (crystalline) metallic Fe particles ≥1.7 nm in diameter.	[105]
Alvanipour and Kispert (1988)	Co(stearate)$_2$ + 2 AlEt$_3$	Homogeneous M(0) species are proposed to form via unstable ethyl–Ni (L$_3$Ni–Et) and/or Ni–H (L$_2$Ni–H–C≡C) where L: solvent, CH$_2$=CH$_2$ or RCO$_2$AlEt$_2$.	[67]
Reguli and Stasko (1987)	Ni(3,5-diisopropylsalicylate)$_2$, Ni(acac)$_2$, Ni(stearate)$_2$, or Ni(benzohydraxamate)$_2$ + AlEt$_3$, Al(i-Bu)$_3$, or BuLi	Homogeneous diamagnetic Ni(II) formed by alkylation of the transition metal precatalyst is suggested as the active catalyst species. Ni colloid formation is observed in the presence of aromatic compounds.	[70]
Barrault et al. (1994)	Co(acac)$_2$ + AlEt$_3$	Co(0) clusters, and Co(0) complexes are simultaneously present, neither of which can be ruled out as active catalyst species.	[37]
Shmidt and co-workers (1970, 1979, 1983)	Co(acac)$_2$, Co(acac)$_3$, Ni(acac)$_2$, Fe(acac)$_3$ or Pd(acac)$_2$ + AlEt$_3$, AlMe$_3$, n-BuLi, n-PrMgBr or i-PrMgBr	A paramagnetic homogeneous Co(0) complex, stabilized by arene solvent, R of AlR$_3$ and acac from the Co precatalyst is thought to be the active catalyst. Presence of low spin M(II) is not ruled out. In addition, ≤100 Å M(0) particles are observed.	[42,109–111]

Table B.3
Nature and mechanism of formation of the catalyst—the "*Ziegler-type Catalysts are Heterogeneous*" hypothesis.

Authors (year)	Catalyst systems	Results	Ref.
Shmidt and co-workers (2005, 2006)	$Co(acac)_2$, $Co(acac)_3$, or $Pd(acac)_2 + AlEt_3$	Observe ferromagnetic β-$Co(0)_n$ or $Pd(0)_n$ nanoparticles 1–5 nm) apparently stabilized by $AlEt_3$, and/or acetylacetone derivatives of $AlEt_3$ including $AlEt_2(acac)$ or alumoxanes. The $Co(0)$ complex proposed previously as the active catalyst is reinterpreted as the precursor to $Co(0)_n$ nanoclusters.	[19,113,81,114]
Pasynkiewicz et al. (1974)	$Co(acac)_3 + 1$ $AlMe_3$	A mixture of Co(II), Co(I) complexes and metallic Co(0) are reported. Suggest the true catalyst is metallic Co(0). The other reaction products proposed: $[Co(acac)_2CH_3]$, $(CH_3)_2Al(acac)$, $[(acac)Co{=}CH_2]$, $[Co(acac)]$, $[(acac)Co(CH_3)_2]$.	[71]
Goulon and co-workers (1984, 1986)	$Ni(acac)_2$, $Ni(2$-ethylhexanoate$)_2$, $Co(2$-ethylhexanoate$)_2$, or $Fe(acac)_3 + AlEt_3$	$M(0)_n$ clusters are proposed as catalysts. However, whether they are small ~4–10 atom clusters, amorphous M or M-carbide clusters, or some combination is unclear.	[40,116]
Bonnemann and co-workers (1999–2005)	$Ni(acac)_2 + 3$ $Al(i$-$Bu)_3$, $Pt(acac)_2, + 4$ $AlMe_3$, $[(1,5$-$COD)Pt(CH_3)_2] + 10$ $AlEt_3$ or $Al(C_8H_{17})_3$, and a variety of other systems	$M(0)_n$ amorphous nanoclusters stabilized by an organoaluminum multilayer are observed. Catalytic activities are not tested.	[121–126]

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