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Heterogenization of Metallocene Catalysts for Alkene Polymerization[**]

Hendrikus C. L. Abbenhuis[*]

Metallocenes, when used in combination with suitable activating agents, are extremely active catalysts for alkene polymerization.[1] At present, research in this area has reached such a level of sophistication that new metallocenes and activating agents can be more or less designed in a rational way. Current work focuses on controlling the stereoselectivity of alkene polymerization and, increasingly, minimizing competing insertion and chain-transfer reactions as well as determining the mechanisms that account for catalyst deactivation.

In developing large-scale industrial processes for gas-phase and slurry polymerization of alkenes it is extremely important to heterogenize the essentially homogeneous metallocene/activator catalyst systems. Without heterogenization of metallocenes many new polyolefins could not be produced at all on an industrial scale! The reason is that although homogeneous polymerization catalysts form at best finely divided polymer powders, a heterogeneous catalyst can control the morphology of the polymer formed. As a result the formed polymer beads are enlarged duplicates of the catalyst particles (Figure 1).[2]

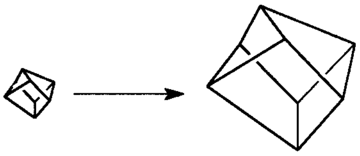

Figure 1.

Due to the complexity of the systems, catalyst immobilization is difficult to approach at the molecular level. Common supports, such as high-surface-area silica and alumina have received the most attention and have proved to be very successful for the commercial-scale production of polyolefins.[3] Yet despite their apparent simplicity, these supports have undesirable or ill-exploited properties that can lead to multiple active sites, catalyst deactivation, and leaching. Clearly, support characteristics such as microstructure, surface functionalities, and polarity must be further investigated, and catalyst-anchoring techniques including, for instance, grafting, tethering, physisorption, and electrostatic immobilization must be devised. This highlight describes some approaches to developing new catalyst supports and the corresponding methods to best exploit valuable metallocene catalysts.

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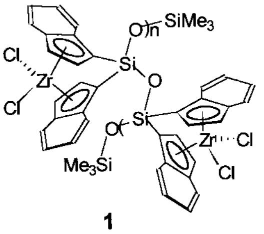
Table 1. Selected data on alkene polymerization by (supported) metallocenes.

Entry	Support	Metallocene[a]	Al:M	Alkene	Activity[b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [d]	Ref.
1	MCM-41	$[C_2H_4(1\text{-ind})_2Zr(CH_3)_2]$	40:1	ethene/propene	3.88	1.28	1.94	[7]
2	SiO_2-SiMe_3	$[Cp_2ZrMe_2]$	0	ethene	0.046	–	–	[8]
3	poly(siloxane)	**1**	5000:1	ethene	7.80	290	1.9	[9]
4	poly(siloxane)	**1**	5000:1	propene	3.40	20[e]	3.3	[9]
5	poly(siloxane)	**2a**	5000:1	ethene	2.20	120	3.2	[9]
6	poly(siloxane)	**2b**	5000:1	ethene	2.90	120	1.7	[9]
7	–	**3**	250:1	ethene	12.0	900	–	[10a]
8	–	**3**	10000:1	propene	22.0	78	1.7	[10b]
9	polystyrene derivative	**4**	–	ethene/1-hexene	0.422	99.6	2.9	[11]
10	polystyrene derivative	**5**	1000:1	ethene	0.041	–	–	[12]

[a] Abbreviations: ind = indenyl; Cp = cyclopentadienyl. [b] In units of 10^6 g of polymer per mole of Zr per atmosphere per hour. [c] Weight-average molecular weight. [d] Ratio of weight- to number-average molecular weight. [e] Ratio of the fraction soluble to that insoluble in boiling pentane is 33.5:66.5.

When the common activator methyl aluminoxane (MAO) is used in homogeneous metallocene catalysis, the required ratio of activator to metallocene can be on the order of 1000:1 or even higher![4] With the new heterogenization methods the amount of activator can be reduced considerably, and MAO:metallocene ratios as low as 40:1 have been used successfully in specific cases.[5] In one interesting approach to in situ heterogenization aluminoxane-coated silica is prepared: the adsorbed water on silica gel reacts directly with a trimethylaluminum solution to form an aluminoxane-coated silica.[6] Treatment of the resulting support with a metallocene precursor results in the desired immobilized catalyst with a high catalytic activity. This methodology was recently applied to prepare mesoporous MCM-41 type silicates used as supports for $[\{C_2H_4(1\text{-indenyl})_2\}Zr(CH_3)_2]$. This immobilized catalyst was found to be active for the cooligomerization of ethene and propene, and a low Al:Zr ratio (40:1 to 360:1) was also possible.[7] Representative polymerization data for the catalysts described here are given in Table 1. A noteworthy finding was that the molecular weight of the copolymer formed increases with the decreasing pore radius of the MCM-41 support. Since the copolymers were either oils (m.p. −20 °C) or waxes (m.p. −8 °C), the relation between catalyst and polymer morphologies could not be investigated. This should be a topic for further research because the uniform hexagonal structure of MCM-41 is clearly different from that of the commonly employed amorphous silica. Finally, silylated silicas were recently reported to be suitable supports for $[Cp_2Zr(CH_3)_2]$. This system enables morphology control in ethene polymerization even without activation by aluminoxane.[8] The catalytic activity, however, was low [46 kg PE (mol Zr h bar)$^{-1}$].

Other current research is aimed at linking metallocenes to organic supports having a more defined structure. This work may eventually result in heterogenous catalysts in which the spacing of the active sites over the support can be controlled. For instance, the new poly(siloxane)-supported zirconocene precatalysts **1** and **2** can be activated with methylaluminoxane in the conventional way, in other words, with high Al:Zr ratios (5000:1 to 10000:1).[9]



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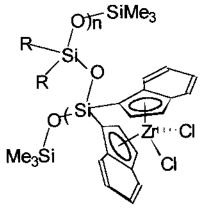
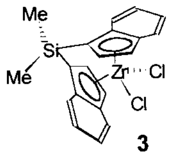


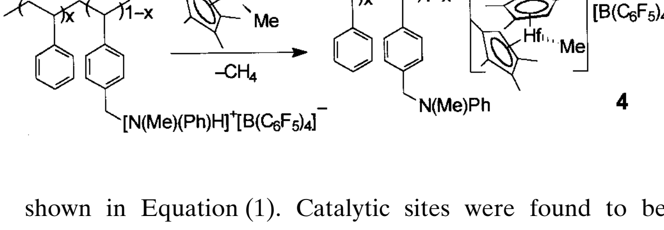
2a (R = Me)
2b (R = Ph)



3

The zirconocene catalysts supported on poly(bisindenylsiloxane) and poly(bisfluorenylsiloxane) gave high activities for ethene polymerization [up to 10300 kg PE (mol Zr h bar)$^{-1}$] and moderate activities for propene polymerization [up to 5900 kg PP (mol Zr h bar)$^{-1}$]. For comparison, the activity of the closely related complex $[\{Me_2Si(1\text{-indenyl})_2\}ZrCl_2]$ (**3**) in homogeneous catalysis is also given in Table 1.[10] The molecular mass distributions of the polymers were rather broad (ca. 1.7 to 9.1), and during propene polymerization large amounts of atactic polymer formed. Both observations might be related to the way the supported metallocenes were generated, which likely provided mixtures of *rac* and *meso* isomers.

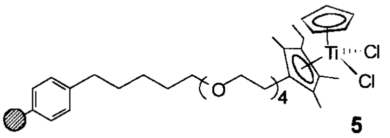
Modified polystyrene beads have been examined as interesting catalyst supports and have led to several new immobilization techniques. One of these is the phase immobilization of active cationic metallocene sites on noninteracting polystyrene.[11] Supported catalysts were prepared by treating lightly cross-linked, chloromethylated polystyrene beads successively with a secondary amine, an ammonium salt of a weakly coordinating anion (the actual activating agent), and finally a neutral dialkylmetallocene. The last step of this sequence generating the active heterogeneous catalyst **4** is shown in Equation (1). Catalytic sites were found to be distributed homogeneously throughout the support particle. In contrast to reactions with surface-supported metallocene catalysts, the polymerization occurs within the catalyst



(1)

particle, which swells during the process. The supported catalysts displayed good activity for the slurry-phase copolymerization of ethene/1-hexene, and the spherical morphology of the catalyst was accurately replicated during polymer formation. One of the drawbacks of this technique, which must be overcome for practical application, is the leaching of homogeneous catalyst out of the support at higher reaction temperatures ($>40\,^{\circ}\mathrm{C}$). This was evident from the poor polymer morphology that resulted from higher temperature polymerizations.

Undesired leaching of a metallocene catalyst from polystyrene beads could be avoided in a recent application in which a peralkylated titanocene complex was covalently bonded to the support.[12] The precatalyst **5**, the product of a ten-step synthesis, displayed, upon activation with MAO, low activity for ethene polymerization [41 kg PE (mol Ti h bar)$^{-1}$]. This poor activity, together with poor noodlelike polymer morphology might be related to the use of a catalyst support that did not adequately swell during polymerization.



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German version: *Angew. Chem.* **1999**, *111*, 1125–1127

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