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A New Type of Polymer-Supported Metallocene Catalyst for Ethylene Polymerization

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Abstract: A new polymer-supported metallocene catalyst has been prepared. The polymer-supported metallocene displayed considerably high activity in ethylene polymerization, the highest being 3.62×10^7gPE/molZr•h, the molecular weight of the polyethylene produced was Mn = 1.29×10^5, about 3-4 times those of corresponding homogeneous zirconocenes. The polymer-supported metallocene keeps the characteristics of homogeneous metallocene catalysts, and offers some features,such as adaptable to gas phase and slurry processes; easy to prepare in low cost; relatively high activity and lower MAO/Zr ratio; lower inorganic residues in the polyolefins as compared to cases of SiO_2, Al_2O_3 or $MgCl_2$; unitary active structure, no complex surface as with SiO_2; good control of morphology of the resulting polymer.

Keywords: Polymer-support, metallocene, catalyst, ethylene polymerization.

Although homogeneous metallocene catalysts show some specific characteristics, such as single site, extremely high catalytic activity, high ability to incorporate monomers, narrow molecular weight and comonomer distribution, and excellent control of stereoregularity, but they also suffer some drawbacks, a very large amount of MAO requirement, inability to be used in slurry or gas phase processes, and poor control of polymer morphology. Therefore, it is necessary to modify the catalysts for the practical applications. One of the methods available in the literatures[1-12] to overcome the shortcomings is to immobilize the metallocenes on inorganic supports, for example, silica, alumuna or magnesium chloride. Only a few of report[13-20] are related to polymer supported metallocene catalysts.

Recently, polymer-supported metallocene has been developed in our group in order to enhance their value for commercial applications.

The polymer-supported metallocene is a new type of metallocene catalyst, prepared according to the scheme: the polymer acts as both a support and a ligand.

Polymer–supported metallocene features

easy to prepare in low cost

Substituted metallocenes and bridged metallocenes are likely to be priced at up to ten times the cost of their closest nonbridged analogs. The polymer–supported metallocene was prepared by using Cp_2ZrCl_2 and commercial products as the starting materials. It is close to the typical supported Z–N catalyst cost, much less than those of substituted metallocenes and bridged metallocenes (**Table 1).**

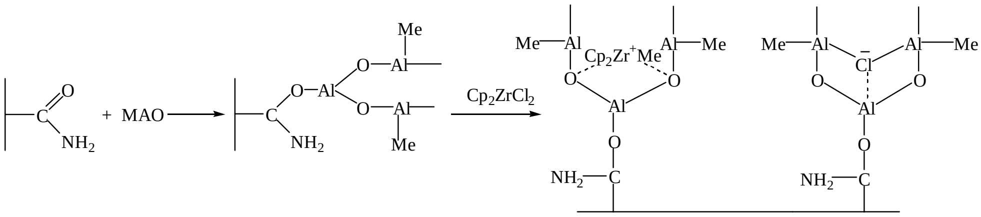

Table 1 Tentative prices for metallocenes

Meallocene	Laboratory Supplier Basis		Possible Semi-Commercial	
	($/b)	(¥/b)	($/b)	(¥/b)
Cp_2ZrCl_2	570.00	4200.00	150.00 230.00	1300.00 1900.00
$[C_5(CH_3)_5]_2TiCl_2$	17300.00	143200.00	1140.00 1820.00	9500.00 15100.00
″Constrained-Geometry″ Metallocenes e.g $[Me_4CpSi(Me)_2N(t\text{-}Bu)]TiCH_2[O\text{-}PhN(Me_2)]$	N/A	N/A	1500.00 2270.00	12500.00 18900.00
3rd/4th generation Z-N PP Catalyst	N/A	N/A	140.00 210.00	1200.00 1700.00
Polymer-Supported Metallocene Catalyst	250.00	2075.00		

adaptable to gas phase and slurry processes

The catalyst showed higher activities in lower MAO/Zr ratio in both slurry and gas phase processes, and the bulk density of the polyethylene was at the levels from 0.35 to 0.43 g/cm^3(**Table 2,3**)

Table 2 Ethylene polymerization with olymer–supported metallocene catalyst in gas phase process

Zr (μmol)	Al/Zr (molar ratio)	Temperature (℃)	Butene-1 %	Activity (10^7g/mol Zr)	Bulk Density (g/cm^3)
17	300	60	12.5	0.11	0.43
15	500	80	0	0.83	0.41
17	500	90	0	0.84	0.40
14	600	90	0	1.15	0.41

keeping the features of homogeneous metallocenes

Single site, narrow molecular weight distribution, but higher molecular weight(**Table 4)**.

Table 3 Ethylene polymerization with PSAm • Zr/MAO in slurry process

Zr (μ mol)	Al/Zr (molar ratio)	Temperature (℃)	Pressure (Mpa)	Activity (10^7g/mol• Zr)
5	300	50	0.10	0.10
5	500	50	0.10	0.15
15	600	70	0.14	0.30
13	600	70	0.70	3.51
16	500	80	1.00	3.62

Table 4 Molecular weight and molecular weight distribution of polyethylene reduced by PSAm • Zr/MAO

Polyethylene	Mw (10^5)	Mn (10^5)	Mw/Mn
PE–2 A	3.24	1.19	2.7
PE–2 B	3.11	1.12	2.8
PE–2 C	3.38	1.24	2.7
PE–2 D	3.38	1.29	2.6

Polymerization conditions: Al/Zr(molar ratio)=500, ethylene pressure = 0.7Mpa, 50°C, 1h.

lower inorganic residues in the polyolefins as compared to cases of SiO_2*,* Al_2O_3 *or* $MgCl_2$

The ash of the polymer–supported metallocene is much less than those of some supported Z–N systems, which can give ash up to 1000 ppm, with most of this ash being comprised of the SiO_2 or magnesium chloride catalyst support. Ash of 300 ppm for metallocenes is a acceptable level. The ash of polymer–supported metallocene in the product is below the ash limit **(Table 5)**

Table 5 The ash in polyolefin by different catalysts

Catalyst	Ash in Polyolefin (ppm)
Ziegler–Natta	1000
Metallocene	300 (ash limit)
Polymer–supported metallocene	40–70

good control of morphology of the resulting polymer **(Figure 1)**

Figure 1 Micrograph of polymer-supported metallocene particle (a) and granule of polyethylene(b) produced

a b

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