

Heterogeneous Polymerization of Ethene with Metallocene Catalysts. A Comparison of Poly(organosiloxane) Microgels and Silica as Support Materials for MAO-Type Cocatalysts

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Received 15 November 1999; accepted 6 July 2000

ABSTRACT: Zirconocene dichloride and bis(*n*-butylcyclopentadienyl)zirconium dichloride are used as catalyst precursors for the heterogeneous polymerization of ethene. A methyl-substituted microgel as support material for heterogeneous cocatalysts on the basis of MAO is compared with different commercially available silica-supported cocatalysts. The catalyst performances and the properties of the obtained polyethenes show considerable differences. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 613–617, 2001

Key words: poly(organosiloxane) microgels; heterogeneous catalysis; metallocene catalysts; olefin polymerization; polyethene

INTRODUCTION

Metallocene complexes with group four metals are very attractive catalysts for olefin polymerization due to their ability to produce new polymers with interesting properties (refs. 1–5, and references therein). In combination with an excess of methylalumoxane (MAO), most of them show high productivities under homogeneous polymerization conditions. Unfortunately, problems are caused in the technical application just because of these conditions. To avoid the so-called “reactor-fouling,” the sticking of the formed polymer on the reactor walls, the catalyst must be heterogeneous. Industrial scale production of polyolefins is accomplished only with heterogenized catalysts. Different silicas can be used as suitable support

materials for the cocatalyst on the basis of MAO. Recently, a new support material, the “microgels,” have been developed,^{6–8} which could substitute silica. But first they must prove their suitability due to the fact that the support material influences the productivity of the catalysts as well as the property of the polymers.^{9–13}

RESULTS AND DISCUSSION

In this work we describe the comparison between a methyl substituted microgel as support material for MAO-like cocatalysts and commercially available silica-based cocatalysts in combination with the standard metallocene dichloride complexes Cp_2ZrCl_2 and $(\text{C}_5\text{H}_4\text{Bu})_2\text{ZrCl}_2$.

The heterogenized silica-based cocatalysts were either purchased from Akzo Nobel Chemicals, The Netherlands, (SMAO), or were obtained from Witco GmbH, Germany, (HL/PQ and HL/04). In addition, a heterogenized metallocene cat-

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Contract grant sponsors: Bayerischen Forschungsverbund Katalyse (FORKAT) and Wacker-Chemie GmbH.

Journal of Applied Polymer Science, Vol. 80, 613–617 (2001)
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alyst precursor, $(C_5H_4Bu)_2ZrCl_2$, on a silica-based cocatalyst was available (Witco).

Methyl-functionalized microgel was chosen as support material because it has proven the best properties in heterogeneous olefin polymerization catalysis.⁸

Comparison of the Productivity of Different Supported Catalysts with Cp_2ZrCl_2 as Catalyst Precursor

The content of aluminum in the silica-supported catalysts has been determined by elemental analysis (Witco HL/04: 23.1%; HL/PQ: 24.6%; Akzo SMAO: 13.9%). The polymerizations were conducted at 60°C and 10 bar ethene pressure in 500 mL pentane as slurry polymerizations.

Zirconocene dichloride was immobilized on the different available cocatalysts. In Figure 1 the productivities of the various catalysts for ethene polymerization are compared. The differences in productivity are considerable. The lowest productivity was found for the silica-supported catalyst from Witco (HL/PQ) followed by the SMAO supported catalyst from Akzo Nobel. Within the tolerances only the silica supported catalyst from Witco (HL/04) and the catalyst supported on methyl functionalized microgel are comparable.

The differences in productivities can be explained by the different nature of the surface of the support materials.

Dependence of the Aluminum/Zirconium Ratio on the Productivity of Different Supported Catalysts

An important criterion for a metallocene catalyst is the ratio of aluminum to zirconium. Under homogeneous polymerization conditions metallocene complexes require a high excess of MAO for

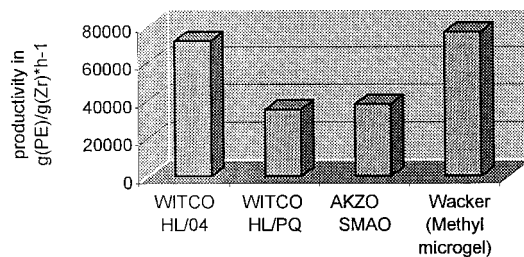


Figure 1 Productivity of Cp_2ZrCl_2 depending on the support material of the cocatalyst. Polymerization conditions: 10 bar ethene pressure; 70°C; in 500 mL *n*-pentane; 60 min.

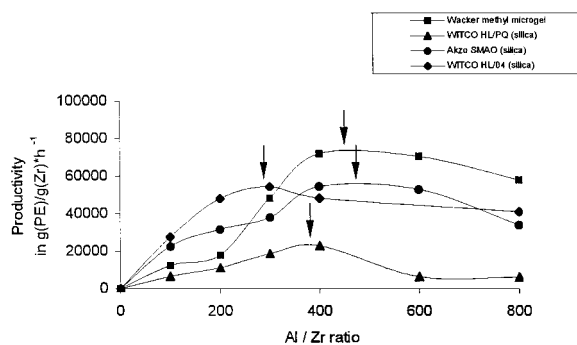


Figure 2 Influence of the Al/Zr ratio on the productivity of Cp_2ZrCl_2 fixed on various cocatalysts. Polymerization conditions: 10 bar ethene pressure; 70°C; in 500 mL *n*-pentane; 60 min.

an acceptable productivity. The major advantages of heterogenized catalysts are a low Al/Zr ratio and the prevention of reactor fouling. The available cocatalysts were used with different amounts of the catalyst precursor to investigate the influence of different Al/Zr ratios (Fig. 2).

All systems show their maximum productivity at different Al/Zr ratios. The Witco HL/04 supported catalyst reaches its best performance at a ratio of about 280 : 1; the Witco HL/PQ supported catalyst at about 390 : 1, but at a considerably lower level. The SMAO-supported catalyst from Akzo Nobel reveals a productivity plateau between 420 and 500 : 1. The methyl-functionalized microgel-supported catalyst shows its top productivity at about 430 : 1.

Comparison of the Productivities of Different Supported Catalysts with $(C_5H_4Bu)_2ZrCl_2$ as Catalyst Precursor

Zirconocene dichloride is cheap, easy to handle, and best suitable for different tests, but in homogeneous solution it is not as active as bis(*n*-butylcyclopentadienyl) zirconium dichloride, $(C_5H_4Bu)_2ZrCl_2$. Witco GmbH supplied us with activated and heterogenized $(C_5H_4Bu)_2ZrCl_2$ on a silica-supported cocatalyst with an Al/Zr ratio of 62 : 1. For comparison, $(C_5H_4Bu)_2ZrCl_2$ was activated with the silica-supported cocatalyst SMAO and the methyl functionalized microgel-supported cocatalyst with the same Al/Zr ratio (Fig. 3).

The Akzo SMAO-supported catalyst showed the highest productivity. The microgel-supported catalyst and the Witco catalyst system are comparable in their productivities. However, because the applied heterogeneous catalyst Cp_2ZrCl_2 had

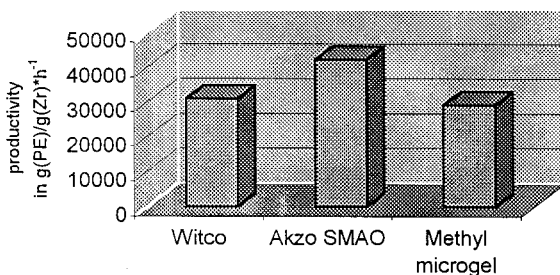


Figure 3 Productivities of various heterogeneous $(C_5H_4Bu)_2ZrCl_2/MAO$ catalysts. Polymerization conditions: 10 bar ethene pressure; 70°C; in 500 mL *n*-pentane; 60 min.

a better productivity than $(C_5H_4Bu)_2ZrCl_2$, this must be attributed to the higher MAO ratios.

Characterization of the Polyethenes

Densities of the Produced Polyethenes

The polymer properties of the produced polyethenes were investigated. The polymer densities were compared with the density of the polyethene, which was obtained under homogeneous polymerization conditions (Table I).

The polymer densities of those polyethenes obtained with heterogenized catalysts are slightly lower than the polymers produced under homogeneous polymerization conditions. Referring to the polymer densities, all polyethenes belong to the class of MDPEs (middle density polyethenes).¹⁴

Regarding the data from DSC measurements of the produced polyethenes, no significant differences were evident. Therefore, rheological measurements were performed.

Rheological Measurements with the Produced Polyethenes

A microstructural analysis of polyethene is relatively difficult due to its bad solubility. Practical methods like high temperature ¹³C-NMR spectroscopy can only be applied with technical difficulties. To obtain more information, rheological measurements are helpful. Information on the investigated systems can be collected due to the fact that small changes in the material properties cause large changes in the parameters being measured. Thus, statements on the polymer structure can be obtained, although the microstructure of the polymer sample is unknown.

Four polyethenes were examined rheologically. The polyethene produced under homogeneous po-

lymerization conditions with $(C_5H_4Bu)_2ZrCl_2$ was compared with the three polymers obtained with the comparable heterogenized catalysts. A defined frequency ν was applied to polymer test bodies while heating them constantly. The damping $\tan \delta$ dependent on the temperature was measured. Figure 4 shows $\tan \delta$ in the melting area of the polymer samples.

It becomes obvious that the homopolymerized polyethene and the polyethene produced with the methyl-functionalized microgel-supported catalyst show almost no difference concerning melting behavior, whereas those polymers produced with silica-supported catalysts differ significantly.

EXPERIMENTAL

All preparations were performed under inert gas using the standard Schlenk technique to prevent traces of air or moisture. As inert gas purified and dried argon was used (BTS catalyst, molecular sieves). All solvents were purchased in technical grade, and purified by distillation over Na/K alloy under argon atmosphere.

Differential Scanning Calorimetry

The thermal properties of the polymer samples were measured on a NETZSCH DSC 200 instrument. Polymer (4–6 mg) was dried *in vacuo* and fused in standard aluminum pans (\varnothing 5 mm). The following temperature program was used: (1) heating phase: 70–200°C, heating rate 20 K min⁻¹, isothermic phase: 3 min; cooling phase down to 70°C, cooling rate 20 K min⁻¹. (2) heating phase: 70–200°C, heating rate 20 K min⁻¹, isothermic phase: 3 min; cooling phase 20 K min⁻¹. The temperature linearly corrected relative to indium ($\Delta H_m = 28.45$ J g⁻¹) was used for calibration. The degree of crystallinity (α) was calculated

Table I Polymer Densities from Polyethenes Produced with Different Supported Catalysts

Polyethene from Cp_2ZrCl_2 and	ρ [g/cm ³]
SMAO	0.938
Witco	0.934
Methyl microgel/MAO	0.936
Homopolymer/MAO	0.943

Density data: average from six measurements (in methanol/water).

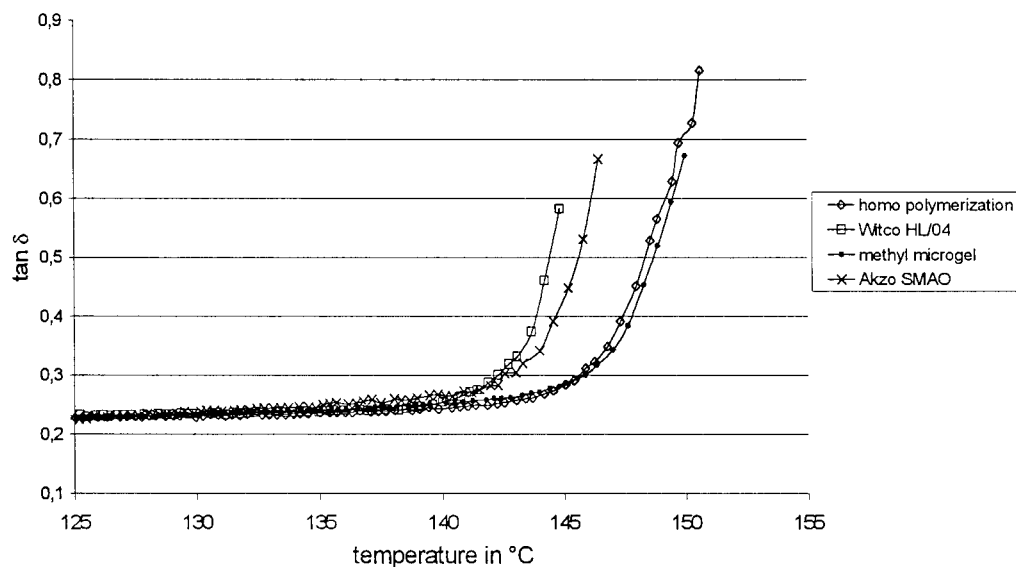


Figure 4 Rheological investigation of differently produced polyethenes. Catalyst precursor: $(C_5H_4Bu)_2ZrCl_2$.

from the equation $a = \Delta H_m / \Delta H^0$. The parameter ΔH_m and the melting points were derived from the second course of the DSC. The fusion enthalpy ΔH^0 was estimated for a 100% crystalline polyethylene to $292.9 \text{ J} \cdot \text{g}^{-1}$.¹⁴

Rheological Measurements

Rheological measurements were performed on a Dynamic Thermal Analyzer (DMTA) Mark IV of Rheometric Geometries company. A temperature range between -150°C to 500°C with a heating rate $0.1^\circ\text{C}/\text{min}$ up to $40^\circ\text{C}/\text{min}$ could be used; during the cooling phase the cooling ratio was between 0.1 – $20^\circ\text{C}/\text{min}$. The frequency range could be chosen between $1.6 \cdot 10^{-6}$ to 200 Hz . In the dynamic mode the total deflection was ± 0.5 to $\pm 128 \mu\text{m}$ (in the static mode 30 mm). Maximum performance was 15 N . The range of the moduli was between 10^3 to 10^{12} Pa by a sensitivity of 10^{-4} . Measurements could be conducted either horizontally or vertically.

Polymerization of Ethene

Polymerization of ethene was conducted in a 1 l Büchi steel reactor equipped with a mechanical stirrer at 60°C and 10 bar ethene pressure for 1 h in *n*-pentane. MAO was used as a 30% solution in toluene from Witco, Germany. The polymerization was stopped by venting excess ethene. The

obtained polymer was adequately washed with HCl/methanol and dried *in vacuo*.

Synthesis of the Microgel-Supported Catalysts

One gram of the methyl-functionalized microgel was dispersed in 100 mL toluene. To the dispersion 30 mL of a 1.76 M TMA solution in toluene were added. After stirring for 1 h , the flask with the dispersion was connected to a second one in which 0.75 mL of distilled water were vaporized. Dry argon was passed through both flasks so that the water steam saturated argon hydrolyzed the TMA. After the partial hydrolysis of the TMA the catalyst precursors Cp_2ZrCl_2 or $(C_5H_4Bu)_2ZrCl_2$ were added in the desired ratio. The mixture was stirred for additional 30 min until a color change from white to yellow indicated the activation of the catalyst precursor. The mixture was filtered over a frit (P1 filter). After filtration, the obtained solid was washed twice with *n*-pentane and dried *in vacuo* until the weight had stabilized. Yield: 85–95%.

Synthesis of Silica-Supported Catalysts

The immobilized silica-supported cocatalysts were used as received unless the fully heterogenized catalyst was used.

After suspending 2.0 g of the cocatalyst in 50 mL toluene, the catalyst precursor was added. After stirring for 1 h the activated catalyst was

filtered, washed twice with *n*-pentane, and dried *in vacuo*. Yield: 85–90%.

We thank the Bayerischen Forschungsverbund Katalyse (FORKAT) and Wacker-Chemie GmbH for their financial support. Furthermore, we like to thank Akzo Nobel Chemicals, The Netherlands, and Witco GmbH, Germany, for their donation of heterogenized cocatalysts and catalysts.

REFERENCES

1. Kaminsky, W. *J Chem Soc Dalton Trans* 1998, 1413.
2. Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew Chem Int Ed Engl* 1995, 34, 1143.
3. Alt, H. G. *J Chem Soc Dalton Trans* 1999, 1703.
4. Aulbach, M.; Küber, F. *Chemie Unserer Zeit* 1994, 26, 197.
5. Benedikt, G. M.; Goodall, B. L. *Metallocene Catalysed Polymers*; *Plastics Design Library*: Norwich, NY, 1998.
6. Baumann, F.; Deubzer, B.; Geck, M.; Dauth, J.; Sheiko, S.; Schmidt, M. *Adv Mater* 1997, 9, 955.
7. Köppl, A.; Alt, H. G.; Schmidt, R. *J Organomet Chem* 1999, 577, 351.
8. Schmidt, R.; Alt, H. G.; Ebenhoch, J. *J Appl Polym Sci*, in press.
9. Alt, H. G.; Baumann, F.; Weis, J.; Köppl, A. Wacker-Chemie GmbH, Ger. Offen. Pat. DE 197,41,201, A1 1999.
10. Soga, K.; Kaminaka, M. *Makromol Chem Rapid Commun* 1992, 13, 221.
11. Soga, K.; Kaminaka, M. *Makromol Chem* 1993, 194, 1745.
12. Soga, K.; Arai, T.; Nozawa, H.; Uozomi, T. *Macromol Symp* 1995, 97, 53.
13. Goretzki, R.; Fink, G.; Tesche, B.; Steinmetz, B.; Rieger, R.; Uzick, W. *J Polym Sci Part A Polym Chem* 1999, 37, 677.
14. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; J. Wiley & Sons: New York, 1989, Vol. 15, 3rd ed.