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Silica gel supported zirconocene dichloride/methylalumoxane catalysts for ethylene polymerization: Effects of heterogenation on activity, polymer microstructure and product morphology

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SUMMARY:

The system zirconocene dichloride/methylalumoxane was supported on silica in order to provide ethylene polymerization catalysts for suspension or gas phase processes. Highest activity was found for a sandwich-like, three layer anchoring of the zirconium centers on the support surface. The new catalyst systems show a decrease of activity compared to polymerization experiments in homogeneous phase. However, the molecular weights are increased and the weight distributions remain narrow by immobilization of the active catalyst sites. Those supported metallocene catalysts could find application for the synthesis of polyethylene materials with controlled rheology.

ZUSAMMENFASSUNG:

Das Katalysatorsystem Zirkonocendichlorid/Methylalumoxan wurde auf Siliciumdioxid aufgebracht, um Katalysatoren für die Suspensions- oder Gasphasenpolymerisation von Ethylen herzustellen. Die höchste Aktivität wurde für eine sandwichartige, dreilagige Verankerung von Zirkonzentren auf der Trägeroberfläche gefunden. Die neuen Katalysatorsysteme besitzen eine im Vergleich zu den entsprechenden homogenen Katalysatoren geringere Aktivität. Die Immobilisierung der aktiven Katalysatorzentren führt zu einer deutlichen Erhöhung der Polymermolmassen. Dabei bleibt die enge Molekulargewichtsverteilung der Polymerprodukte nahezu erhalten. Solche auf Träger aufgebrachte Metallocen-Katalysatoren könnten für die Herstellung von Polyethylenen mit kontrollierter Rheologie Anwendung finden.

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1. Introduction

Homogeneous metallocene/alumoxane catalysts for the polymerization of olefins are subject of an intense research competition in the academic as well as in the industrial sector (see for example¹). This new catalyst generation offers a number of advantages when compared to conventional Ziegler-Natta catalysts. The metallocene/alumoxane systems combine high activity with the possibility to tailor polymer properties such as molecular weight, molecular weight distribution, comonomer insertion and -distribution, as well as the stereoregularity of α -olefin polymers through the ligand design at the transition metal center (see for example²⁻⁴).

With a few exceptions⁵⁻⁷, the properties of these new catalysts have only been studied in homogeneous solution. For modern gas phase and slurry polymerization processes, however, heterogeneous catalyst systems are required, with silica gel being exclusively used as a support material for the active titanium (III) centers in conventional Ziegler-Natta catalysts. Silica gel allows a controlled fragmentation during the polymerization reaction, thus leading to the formation of uniform polymer particles with a narrow particle size distribution and a high bulk density⁸.

This work deals with the support of zirconocene dichloride/methylalumoxane ($\text{Cp}_2\text{ZrCl}_2/\text{MAO}$) systems on silica gel and with the properties of the resulting heterogeneous catalysts in comparison to polymerizations in the homogeneous phase.

2. Experimental

All experiments were carried out under argon with standard Schlenk techniques. The silica gels used (Grace 532 spheroidal, surface area 320 m^2/g , pore volume 1.65 ml/g , particle size 30–100 μm ; Grace Al-Cogel 8, surface area 526 m^2/g , pore volume 1.41 ml/g , particle size 30–100 μm) were obtained from Grace GmbH (Worms, Germany) and dried 5 h at 180 °C in vacuum prior to use. Methylalumoxane (MAO) was purchased from Schering AG (now Witco, Bergkamen, Germany) as a 10% (m/m) toluene solution (1.6 M; M_w ca. 1100 g/mol). Ethylene (BASF AG, Ludwigshafen) was polymerization grade and used without further purification. Toluene was refluxed over and distilled from sodium metal under inert gas. Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC, Waters 150 Chromatograph, 140 °C, in 1,2,4-trichlorobenzene). Melting points (T_m) as well as melting enthalpies were measured by differential calorimetry (Perkin-Elmer DSC 4). Zirconium and aluminium analyses were carried out with atomic absorption spectroscopy (AAS).

2.1 Charging the silica with the zirconocene/alumoxane component

13.0 g of silica gel were suspended in 85 ml of toluene followed by addition of 40 ml of methylalumoxane solution and stirring for 2 h at 50 °C. Upon cooling, the clear supernatant toluene solution was decanted from the silica gel, which was washed twice with 20 ml of toluene, and was resuspended in 40 ml of toluene. 40 ml of a saturated bis(cyclopentadienyl)zirconium dichloride solution in toluene were added dropwise to the well stirred silica gel slurry. When the addition was complete, stirring was continued for another 2 to 4 h and the mixture allowed to stand overnight, during which time the silica gel became yellow. The clear toluene solution was again decanted, the residue washed with 40 ml of toluene, resuspended in 50 ml of decane and mixed with 50 ml of methylalumoxane solution. After stirring briefly for 15–30 min, the solvents were slowly distilled off at 100–110 °C in vacuum to leave a yellow, well-flowing powder. Heptane extracts of these supported catalysts did not contain a polymerization-active material, even after the addition of MAO.

2.2 Polymerization reactions

In solution: 300 ml of toluene were thermostatted in a 11-Büchi glas autoclave to the selected polymerization temperature, mixed with the necessary amount of MAO-solution and saturated with ethylene at the pressure chosen. The polymerization reaction was started through the addition of a zirconocene-toluene solution via a pressure burette. The autoclave temperature was kept constant within ± 1 °C, the ethylene pressure within ± 50 mbar. The reaction was terminated through injection of 5 ml of HCl-acidic methanol. The polymer product was precipitated with methanol, washed and dried at 70 °C overnight.

Heterogeneous: The experimental set-up used was the same as described above for the solution reaction. To avoid leaching of polymerization-active particles from the silica gel, the polymerization was carried out in 400 ml of heptane to which 0.1 to 0.5 g of the catalyst were added before pressurizing with ethylene. No aluminium alkyls were added. After the polymerization run was finished, the product slurry was drained, the heptane was removed with steam distillation and the product dried at 70 °C overnight.

3. Results and discussion

3.1 Catalyst preparation and activity

Deposition of zirconocene dichloride and methylalumoxane (MAO) in a “sandwich” layer arrangement (1. MAO, 2. zirconocene dichloride, 3. MAO) onto silica gel gave catalyst systems with a high activity at low Al: Zr-ratios.

In the first step of preparation the MAO molecules were anchored through reactions with the OH-groups on the silica surface. Into this MAO cover, the Cp_2ZrCl_2 units could be embedded under methylation and most likely formation of a cation/anion couple⁹. A direct deposition of the zirconium component onto the support surface led to a considerable reduction in activity, probably through reaction of the active centers with surface-active OH-groups (cf. Tab. 1, entry 4). In a second production step, another amorphous MAO layer was then precipitated onto the catalyst particles. Without this MAO envelope, the catalyst activity drops drastically (cf. Tab. 1, entry 5).

A comparison of the polymerization results in Tab. 1 shows that the catalyst activity, when based on the zirconium concentration, increases with the Al: Zr-ratio. Based on the technically interesting total mass of the catalyst ($\text{SiO}_2 + \text{MAO} + \text{Cp}_2\text{ZrCl}_2$) the activity depends on the absolute amount of zirconium deposited and on the respective Al: Zr-ratio (Tab. 1, entries 1–3).

The usage of an aluminium-containing silica gel (Al-Cogel, Tab. 1, entries 6–9) did not enhance the activity of the catalysts. Rather, the activity decreased significantly at an almost constant Al: Zr-ratio and comparative zirconium content (Tab. 1, entry 1 and 7), while the molecular weight and distribution of the polymer products remained essentially unaltered in comparison to a catalyst based on the 532-spheroidal silica gel. The polymer parameters also did not change with an increase in the Al: Zr-ratio through an enhancement of the MAO load (Tab. 1, entry 6). A noteworthy broadening of the molecular weight distributions at low Al: Zr-ratios may indicate a larger dispersion in zirconium activation (see below).

3.2 Comparison of polymerization properties of the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system in solution and supported on silica gel

In solution, the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system belongs to the most active of the hitherto known ethylene polymerization catalysts. The molecular weights of the polymer products can be controlled by the use of various metallocene dichlorides¹⁰ or by addition of aluminium alkyls^{11,12}. The special feature of the structurally well-defined metallocene catalysts lies in the uniformity of the polymerization-active centers, which is reflected in the narrow molecular weight distributions. These uniform polymer products could be used for a targeted control of the polymer rheology, for example, through combination of different metallocene dichlorides. Since supported catalysts are exclusively used in commercial processes, it seemed important to us to compare the

Tab. 1. Results of polymerizations with supported zirconocene/MAO-catalyst systems.

Cat.	Support	Zr-Cont. (wt.-%)	Al/Zr	A/g cat.	Activity ^a A/mol Zr	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	M_w/M_n
1	SiO ₂	0.84	64	163	1 770	209	66	3.15
2		0.12	197	62	4 716	156	34	4.54
3		1.1	37	57	474	256	64	3.99
4 ^b		0.65	25	12		n. d. ^d	n. d.	n. d.
5 ^c		0.72	12	5	26	n. d.	n. d.	n. d.
6	Al-Cogel	0.51	123	52	931	206	65	3.17
7		0.89	58	86	885	205	60	3.43
8		1.9	32	59	283	188	24	7.74
9		1.5	41	53	319	193	26	7.37

^a A/g cat: g PE (g cat · h)⁻¹; A/mol Zr: 10³ g PE (mol Zr · h)⁻¹; polymerization temperature = 80 °C; C₂-pressure = 10 bar; 1 h polymerization time.

^b Without inner MAO-Layer.

^c Without outer MAO-layer.

^d Not determined.

polymerization properties of a soluble, homogeneous with a supported, heterogeneous metallocene system, using $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ as an example.

Tab. 2 comprises the important results from the polymerization experiments. All experiments in the homogeneous phase were done at constant zirconium concentration and an Al: Zr-ratio of 2000:1 (Tab. 2, entries 1–6). For a supported catalyst, the one with the highest activity was used (Tab. 1, entry 1). Toluene served as a polymerization medium in the homogeneous phase, heptane was used for the heterogeneous polymerization runs. A control experiment (Tab. 2, entry 6), where a zirconocene/MAO/toluene solution was calibrated in hexane, gave almost constant activity at otherwise comparable conditions.

The supported metallocene system proved to be much less active in comparison to the solution polymerization. A plot of activity versus polymerization temperature in Fig. 1 illustrates that the activity of the supported system rises linearly with temperature. For the homogeneous case, a tendency for a non-linear progression appears, as was also found for chiral propylene polymerization catalysts^{15,16}.

Two possible explanations can be offered for this drastic difference in activity. If we formulate the activation reaction between Cp_2ZrCl_2 and MAO according to the equilibrium



then only a fraction of all available Zr centers will be activated at the low Al:Zr ratios, as they were set on the silica support. A further explanation follows from the product morphology: If the polymerization takes place on the support surface without concurrent fragmentation of the support material, then the polymer cover hampers the ethylene diffusion and subsequently decreases the activity. This will be discussed below in more detail.

Interestingly, the molecular weight of all heterogeneously produced polymer products is increased significantly. The average molecular weight of the long chain (M_w) is increased 1.6- to 2.7-fold compared to the solution experiments. Most likely this finding is due to a lowered chain transfer rate between the immobilized zirconium and aluminium centers. The molecular weight distributions with values between 3.3 and 4.5 are only slightly broader in comparison to the solution polymerizations.

Tab. 2. Comparison of ethylene (C_2) polymerization behavior of supported Cp_2ZrCl_2/MAO and in homogeneous solution.

Run	T_p (°C)	Zr ^a (mg)	C_2 -pressure (bar)	$[C_2]^b$ (mol/l)	Yield (g)	Activity (10^3 g PE (g cat · h · $[C_2]^{-1}$))	$M_w \cdot 10^{-3}$	M_w/M_n
1 ^c	30	0.046	6.0	0.73	7.0	221.4	506	2.20
2	60	0.046	6.0	0.48	4.4	623.9	285	2.55
3	80	0.046	6.0	0.39	6.2	1 321.1	105	2.40
4	60	0.046	2.5	0.18	1.8	236.3	202	2.53
5	60	0.046	4.0	0.30	5.9	450.0	187	2.15
6	60	0.056	6.0	0.54	7.7	648.4	157	4.17
7	30	5.3	6.0	0.81	3.8	1.0	1 374	4.52
8	60	5.2	6.0	0.54	5.8	2.3	474	3.55
9	80	5.7	6.0	0.44	7.4	3.5	234	3.30
10	60	5.4	2.5	0.21	1.9	1.7	427	3.62
11	60	4.5	4.0	0.38	3.7	2.0	478	3.25

^a Zr-content.

^b The C_2 concentrations have been calculated according to the Lee-Kessler equation of state (cf.¹³). The parameters were taken from¹⁴.

^c Runs 1–6 Cp_2ZrCl_2/MAO , run 7–11 supported system; run 1–5 in toluene solution, run 6–11 in heptane slurry.

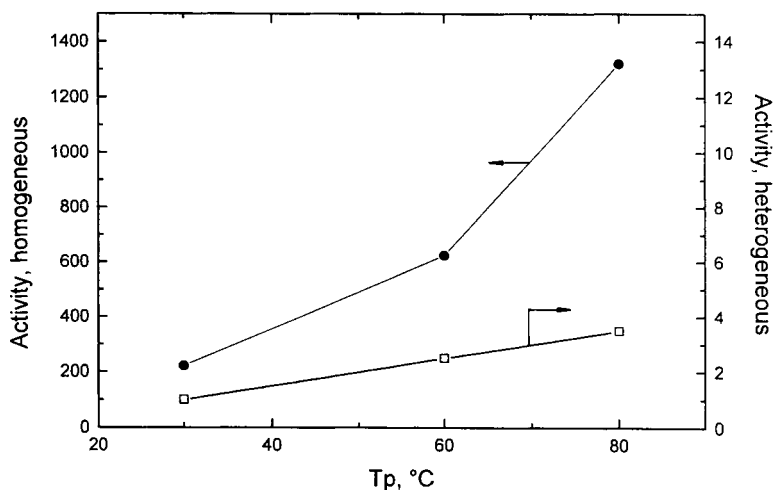


Fig. 1. Activity (in 10^3 g PE (mol Zr · h) $^{-1}$) of catalysts versus polymerization temperature ; (●) homogeneous, (□) heterogeneous.

3.3 Catalyst- and product morphology

The heterogeneous metallocene catalysts give polymer products with a rather uniform particle size. The particle size distribution has been determined for the case of a polymerization at 80 °C (Tab. 2, entry 9). Changes in the polymerization conditions did not have significant effects on the product homogeneity. Tab. 3 lists the particle size distribution together with the polymer molecular weights and the melting points of the fractions.

Tab. 3. Particle size distribution and polymer properties^a.

Particle diameter (mm)	Fraction (wt.-%)	$M_w \cdot 10^{-3}$	M_w/M_n	T_m (°C)	Enthalpy ^{fusion} (J/g)
> 1 (< 2)	7.5	228	3.0	126	134
> 0.5	70.0	233	3.3	126	122
> 0.25	19.9	235	3.6	126	129
> 0.125	2.5	238	3.9	128	124

^a $T_p = 80$ °C; bulk density = 430 g/l.

The polymer properties of all fractions indicate very uniform products concerning the polymer microstructure. The molecular weights show a weak trend to higher values for smaller particle sizes, however, the values differ too little for a safe interpretation.

Scanning electron microscopy studies on polymer particles obtained at low monomer concentrations (2.5 bar ethylene, cf. Tab. 2, entry 10) present the formed polymer as resembling a cracked shell around the silica support (Fig. 2). In a larger magnification one recognizes a two-dimensional network of polymer threads holding together massive fragments of the polymer particles. The unchanged silica matrix is clearly visible in the background. A fragmentation of the silica matrix combined with the exposition of new, polymerization active centers does not take place, in contrary to the behavior of classical Ziegler-Natta catalyst systems.

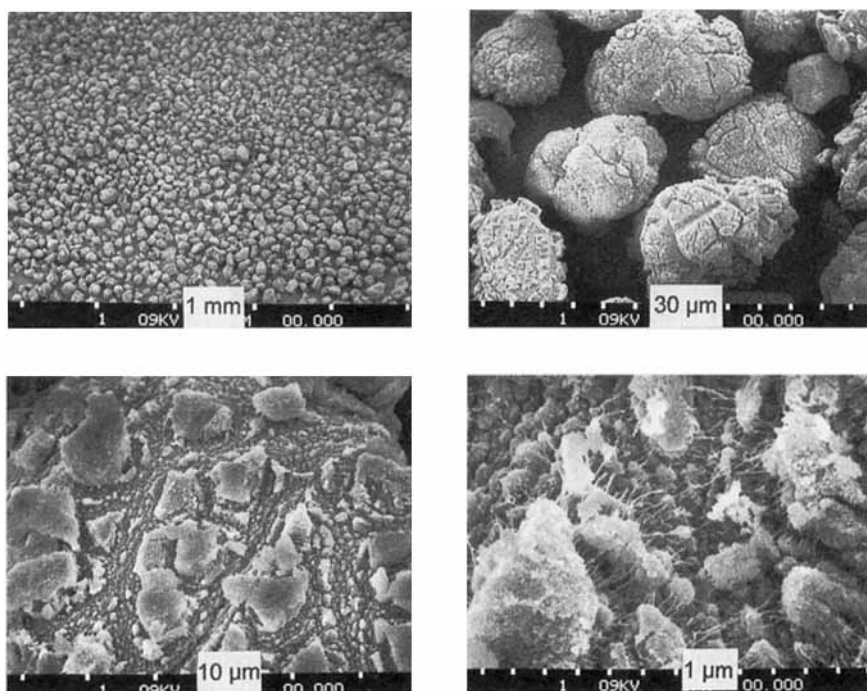


Fig. 2. Scanning electron microscopy study of catalyst particles after low ethylene consumption.

At higher monomer concentrations (6 bar ethylene, cf. Tab. 2, entry 7) a sponge-like, low-density polymer coating with worm-like outgrowths forms around the carrier grain because of the increased insertion rate (Fig. 3).

These findings show that supporting the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system according to the method presented here, leads to an anchoring of the zirconium species only on the outer surface of the support material. This restricts the number of polymerization-active centers which can be brought onto a given mass of the carrier, and thus limits the technically relevant productivity of catalyst per mass unit.

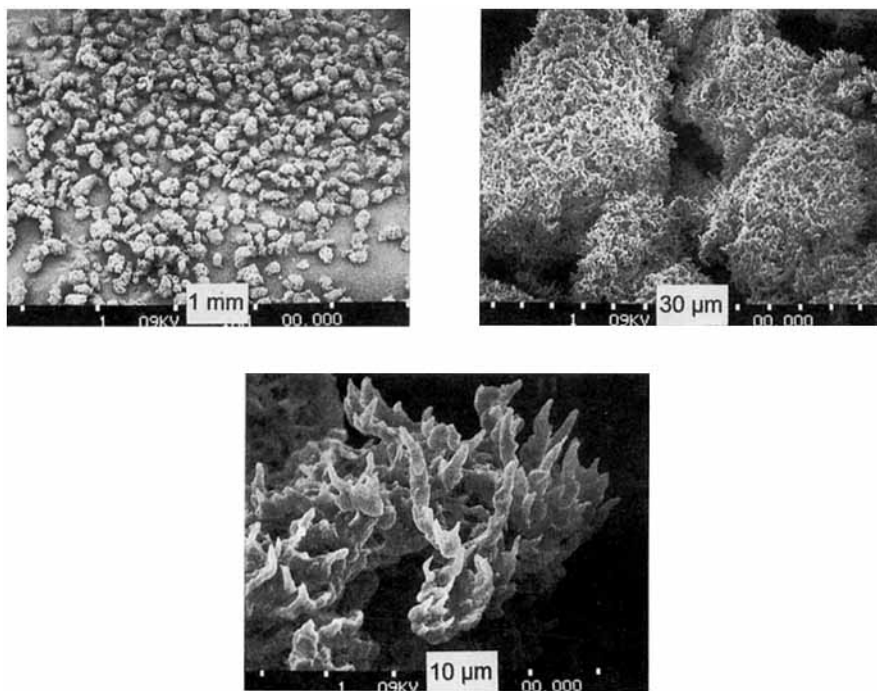


Fig. 3. Scanning electron microscopy study of catalyst particles after high ethylene consumption.

It is important to note, however, that the molecular weight distributions of polymers obtained from supported metallocene catalysts remain narrow, according to our results, so that a decisive tool for the tailoring of material properties is not adversely affected. Therefore, supported polymerization

catalysts should be accessible where the material- and process-determined properties of the polymers obtained can be designed through the use of different immobilized metallocene dihalides. Our subsequent studies aim at optimizing the productivity of these solid catalyst through improved charging methods for the support or through the use of novel carrier materials¹⁷.

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- ¹ J. Okuda, *Nachr. Chem. Tech. Lab.* **41** (1993) 8
- ² W. Kaminsky, *Angew. Makromol. Chem.* **145/146** (1986) 149
- ³ J. C. W. Chien, D. W. He, *J. Polym. Sci., Part A: Polym. Chem.* **29** (1991) 1585
- ⁴ T. Uozumi, K. Soga, *Makromol. Chem.* **193** (1992) 823
- ⁵ J. C. W. Chien, D. W. He, *J. Polym. Sci., Part A: Polym. Chem.* **29** (1991) 1603
- ⁶ M. Kaminaka, K. Soga, *Makromol. Chem., Rapid Commun.* **12** (1991) 367
- ⁷ W. Kaminsky, F. Renner, *Makromol. Chem., Rapid Commun.* **14** (1993) 239
- ⁸ R. J. L. Graff, G. Kortleve, C. G. Vonk, *Polym. Lett.* **8** (1970) 735
- ⁹ R. F. Jordan, *Adv. Organomet. Chem.* **32** (1992) 325
- ¹⁰ D. T. Mallin, M. D. Rausch, J. C. W. Chien, *Polym. Bull. (Berlin)* **20** (1988) 421
- ¹¹ J. C. W. Chien, B.-P. Wang, *J. Polym. Sci., Part A: Polym. Chem.* **26** (1988) 3098
- ¹² B. Rieger, C. Janiak, *Angew. Makromol. Chem.* **215** (1994) 35
- ¹³ U. Plöcker, H. Knapp, J. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.* **17** (1978) 324
- ¹⁴ L. Kay, *Ind. Eng. Chem.* **40** (1948) 1459
- ¹⁵ B. Rieger, X. Mu, D. T. Mallin, M. D. Rausch, J. C. W. Chien, *Macromolecules* **23** (1990) 3559
- ¹⁶ B. Rieger, *J. Organomet. Chem.* **428** (1992) C33
- ¹⁷ C. Janiak, B. Rieger, R. Völkel, H. G. Braun, *J. Polym. Sci., Part. A: Polym. Chem.* **31** (1993) 2959